LABORATORY INVESTIGATIONS OF STRATOSPHERIC HALOGEN CHEMISTRY

A Final Report for the Period 01/01/87-12/31/96

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INTRODUCTION

This is the final report for NASA Grant No. NAGW-1001 (Georgia Tech project A-4698) covering the period of 1/1/87 to 12/31/96. A discussion of work which has not yet been published is given in the first section following this introduction. All subsequent chapters contain reprints of published papers that acknowledge support from this grant.
PROGRESS REPORT

In recent years, our NASA-supported efforts have focused on three areas of research: (1) kinetic, mechanistic, and thermochemical studies of reactions which produce weakly bound chemical species of atmospheric interest, (2) development of flash photolysis schemes for studying radical-radical reaction kinetics and implementation of these schemes for studying radical-radical reactions of stratospheric interest, and (3) photochemistry studies of interest for understanding stratospheric chemistry. Progress on the above research tracks is summarized below. Reference numbers in brackets refer to the respective numbers for the subsequent chapters of this report.

Reactions Producing Weakly Bound Species of Atmospheric Interest

We have investigated the formation-dissociation kinetics of a number of weakly bound adducts of halogen atoms with atmospheric trace gases. These studies provide information about the rate coefficient for addition of the halogen atom to the atmospheric trace gas, the lifetime of the adduct toward unimolecular decomposition, and the bond dissociation energy of the adduct. Studies of the following reactions have been completed and written up for publication [21, 22, 15, 14, 2]:

\[
\begin{align*}
\text{Cl} + \text{O}_2 + \text{O}_2 & \rightleftharpoons \text{ClOO} + \text{O}_2 \\
\text{Cl} + \text{CO} + \text{N}_2 & \rightleftharpoons \text{CICO} + \text{N}_2 \\
\text{Cl} + \text{CS}_2 + \text{M} & \rightleftharpoons \text{CS}_2\text{Cl} + \text{M}, \text{M} = \text{N}_2, \text{O}_2 \\
\text{Br} + \text{NO}_2 + \text{N}_2 & \rightleftharpoons \text{BrNO}_2 + \text{N}_2 \\
\text{Cl} + \text{C}_2\text{Cl}_4 + \text{N}_2 & \rightleftharpoons \text{C}_2\text{Cl}_5 + \text{N}_2
\end{align*}
\]

(R1) (R2) (R3) (R4) (R5)

A paper describing our study of R5 appeared in a January 1996 issue of the Journal of Physical Chemistry [2]. Our interest in R5 was stimulated by the use of C\textsubscript{2}Cl\textsubscript{4} as a tracer for assessing the importance of chlorine atoms as a tropospheric oxidant [Rudolph et al., 1995; Singh et al., 1996]. While it is known that C\textsubscript{2}Cl\textsubscript{4} reacts several hundred times more rapidly with Cl than with OH at T = 298 K and P = 750 Torr air, the temperature and pressure dependences of the Cl + C\textsubscript{2}Cl\textsubscript{4} rate coefficient had not been systematically investigated. The results presented in chapter 2 firmly
establish the temperature and pressure dependences of $k_5$ and the dissociation energy of the Cl-CCl$_2$CCl$_2$ bond.

Recently, we have focused attention on formation of weakly bound adducts in reactions of chlorine atoms with haloalkanes. In the atmospheric literature these reactions are assumed to occur via hydrogen atom transfer or, in a few thermochemically favorable cases (such as Cl reactions with CF$_3$I and CH$_2$CII), by halogen atom transfer. At relatively high temperatures, the expected behavior is, indeed, observed. We have characterized the "high-temperature" kinetics of Cl reactions with CH$_3$F and CH$_3$Br with sufficient precision and over sufficiently wide temperature ranges to clearly demonstrate non-Arrhenius behavior. Also, we have carried out the first temperature dependent kinetics studies of Cl reactions with CH$_3$I, CF$_3$I, CH$_2$CII, CH$_2$CIBr, C$_2$H$_5$I, and C$_2$D$_5$I. Our "high temperature" results for the above reactions are summarized in Table I. For Cl reactions with CH$_3$Br, CF$_3$I, CH$_2$CII, and CH$_2$CIBr, our results agree well with those reported from other laboratories, although our experiments cover a considerably wider temperature range. The results in Table I represent the first reported kinetic data for Cl reactions with CH$_3$I, C$_2$H$_5$I, C$_2$D$_5$I, and CF$_3$CH$_3$I.

At sufficiently high pressure and low temperatures (ranging from $\sim 310$ K for CH$_3$I, C$_2$H$_5$I, and C$_2$D$_5$I to $\sim 180$ K for CH$_3$Br) observed kinetic behavior suggests that formation of weakly bound adducts becomes the dominant pathway for Cl reactions with CH$_3$I, CH$_3$Br, C$_2$H$_5$I, C$_2$D$_5$I, CF$_3$I, and CF$_3$CH$_3$I. Through direct observation of association-dissociation kinetics, adduct bond strengths (at 298K) have been evaluated (see Figure 1). Ab-initio calculations employing density functional theory have been carried out by our collaborator, Mike McKee of Auburn University; the calculations reproduce experimental bond strengths reasonably well and predict structures where the C-X-Cl bond angles are close to 90 degrees (X = I or Br). As can be seen by examination of Figure 1, an excellent inverse correlation exists between observed adduct bond strengths and the haloalkane ionization potential. The potential importance of Cl and OH adducts with haloalkanes in atmospheric chemistry cannot be readily assessed without further experimentation. However, it is worth noting that Wallington and co-workers [private communication] have observed complex kinetic behavior and product distributions in the Cl reaction with CH$_3$I at atmospheric pressure and $T = 298K$; their observations can only be explained if an adduct is postulated which undergoes chemical transformations other than dissociation back to reactants.
<table>
<thead>
<tr>
<th>haloalkane</th>
<th>Range of T(K)</th>
<th>$C_{a,b}$</th>
<th>$n_{a,b}$</th>
<th>$A_{a,b}$</th>
<th>$D_{a,b}$</th>
<th>$E_{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$F</td>
<td>200-699</td>
<td>$3.09 \times 10^{-18}$</td>
<td>2.25</td>
<td>$1.08 \times 10^{-11}$</td>
<td>2.62</td>
<td>8.20</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>187-697</td>
<td>$3.19 \times 10^{-15}$</td>
<td>1.26</td>
<td>$1.47 \times 10^{-11}$</td>
<td>5.56</td>
<td>8.55</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>364-694</td>
<td>$5.50 \times 10^{-11}$</td>
<td>-10.48</td>
<td>-1.63</td>
<td>-1.63</td>
<td>13.05</td>
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<tr>
<td>CF$_3$I</td>
<td>220-418</td>
<td>$8.14 \times 10^{-11}$</td>
<td>-1.63</td>
<td>-1.63</td>
<td>-1.63</td>
<td>13.05</td>
</tr>
<tr>
<td>CH$_2$ClBr</td>
<td>222-400</td>
<td>$7.79 \times 10^{-12}$</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>CH$_2$ClI</td>
<td>206-432</td>
<td>$4.33 \times 10^{-11}$</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>CH$_3$CH$_2$I</td>
<td>350-434</td>
<td>$6.34 \times 10^{-11}$</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>CD$_3$CD$_2$I</td>
<td>350-434</td>
<td>$2.67 \times 10^{-11}$</td>
<td>3.31</td>
<td>3.31</td>
<td>3.31</td>
<td>3.31</td>
</tr>
<tr>
<td>CF$_3$CH$_2$I</td>
<td>274-434</td>
<td>$4.50 \times 10^{-12}$</td>
<td>2.21</td>
<td>2.21</td>
<td>2.21</td>
<td>2.21</td>
</tr>
</tbody>
</table>

a. $k = Ct^b \exp(-D/RT) = A^{Ea/Rt}$, $A = Ct^b e^b$ and $E_a = D + nRT$

b. Units of C and A are cm$^3$ molecule$^{-1}$s$^{-1}$; units of D and $E_a$ are kJ mol$^{-1}$. 

Table I. Rate constants for non-adduct-forming channels in Cl + haloalkane reactions.
Dependence of the Cl -- haloalkane bond strength on the ionization potential of the haloalkane.
Radical-Radical Reactions

We invested considerable effort into a detailed study of the reaction

$$O + BrO \rightarrow Br + O_2$$ \hspace{1cm} (R6)

A novel dual laser flash photolysis-long path absorption-resonance fluorescence technique was employed to study the kinetics of R6 as a function of temperature (231-328K) and pressure (25-150 Torr) in N₂ buffer gas. The experimental approach preserves the principal advantages of the flash photolysis method, i.e., complete absence of surface reactions and a wide range of accessible pressures, but also employs techniques which are characteristic of the discharge flow method, i.e., chemical titration as a means for deducing the absolute concentration of a radical reactant and use of multiple detection axes. Our results demonstrate that $k_6$ is independent of pressure, and that the temperature dependence of $k_6$ is adequately described by the Arrhenius expression $k(T)_6 = 1.91 \times 10^{-11} \exp(230/T)$ cm³molecule⁻¹s⁻¹; the absolute accuracy of measured values for $k_6$ is estimated to vary from ±20% at T ~ 230 K (a typical middle stratospheric temperature) to ±30% at T ~ 330 K. Our results demonstrate that, at mid-stratospheric temperatures, the O + BrO rate coefficient is about a factor of 1.7 faster than previous “guesstimates” suggested. The catalytic cycle with reaction (6) as its rate-limiting step appears to be the dominant BrO₅ odd-oxygen destruction cycle at altitudes above 24 km. A paper describing our study of R6 appeared in a March 1995 issue of the Journal of Chemical Physics [4].

Our most recent efforts in the area of radical-radical reaction kinetics have focused on the very important stratospheric reaction

$$HO_2 + BrO \rightarrow HOBr + O_2$$ \hspace{1cm} (R7a)
$$\rightarrow HBr + O_3$$ \hspace{1cm} (R7b)

Both $k_7(T)$ and the branching ratio $k_{7a}/k_7$ must be known quantitatively in order to assess the role of reaction (7) in stratospheric chemistry. While there is a growing consensus based on both laboratory and field observations that $k_{7a}/k_7$ is very small, some differences have arisen concerning the value of $k_7(298K)$. Two recent studies report $k_7(298K) > 3 \times 10^{-11}$ cm³molecule⁻¹s⁻¹ [Bridier et al., 1993;
Larichev et al., 1995] while two other studies report values about a factor of two slower [Elrod et al., 1996; Li, et al., 1995]. There is agreement between Larichev et al., Elrod et al., and Li et al. that R7 has a significant negative activation energy, although one study (Li et al.) reports non-Arrhenius behavior while the other two do not.

Our initial studies of R7 employed 193 nm laser flash photolysis of $\text{H}_2\text{O}_2/\text{O}_3/\text{Br}_2/\text{N}_2$ mixtures, with simultaneous time-resolved detection of BrO (by UV absorption spectroscopy at 338.3 nm) and HO$_2$ (by infrared diode laser absorption spectroscopy at 1372 cm$^{-1}$). Typical experimental conditions were $[\text{H}_2\text{O}_2] = (1-2) \times 10^{16}$ per cm$^3$, $[\text{O}_3] = (2-5) \times 10^{15}$ per cm$^3$, $[\text{Br}_2] = (5-10) \times 10^{13}$ per cm$^3$, $P = 10-100$ Torr N$_2$, and laser fluence $\sim 50$ millijoules per cm$^2$. In the above scheme, BrO is generated from photolytically produced oxygen atoms via the $\text{O} + \text{Br}_2$ and $\text{Br} + \text{O}_3$ reactions while HO$_2$ is generated from photolytically produced OH radicals via their reaction with H$_2$O$_2$. Interpretation of observed temporal profiles requires simulations which employ a mechanism consisting of 29 reactions; however, significant time windows exist where BrO removal is dominated by reaction with HO$_2$, and where HO$_2$ removal is dominated by the HO$_2$ + HO$_2$ and HO$_2$ + BrO reactions. The data we have obtained to date support relatively slow values for $k_7$, i.e., values in the range $(1-1.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$. However, the above scheme has two major problems. First, the requirement for high concentrations of H$_2$O$_2$ makes the scheme unviable at sub-ambient temperatures. Secondly, we have had problems with reproducibility which we believe result from heterogeneous loss of Br$_2$ on reactor surfaces; these reactions probably involve H$_2$O$_2$ and/or HO impurity in the H$_2$O$_2$.

As a solution to the problems mentioned above, we have adopted a new photochemical scheme which involves 351 nm laser flash photolysis of Cl$_2$/CH$_3$OH/O$_2$/Br$_2$/NO$_2$ mixtures. Studies involving this scheme will carry into the next funding cycle, so details are described in a later section of the proposal.

**Photochemistry**

Carbonyl sulfide (OCS) is thought to be an important photolytic precursor for the background (i.e., non-volcanic in origin) lower stratospheric sulfate aerosol layer [Crutzen, 1976]. We employed time-resolved detection of carbon monoxide (CO) by tunable diode laser absorption spectroscopy to measure the quantum yield for CO production from 248 nm photodissociation of OCS relative to the well-established quantum yield for CO production from 248 nm photolysis of
phosgene (Cl\textsubscript{2}CO). The temporal resolution of the experiments was sufficient to distinguish CO formed directly by photodissociation from that formed by subsequent S(3P) reaction with OCS. Under the experimental conditions employed, CO formation via the fast S(1D) + OCS reaction was minimal. Measurements at 297 K and total pressures from 4 to 100 Torr N\textsubscript{2} + N\textsubscript{2}O show the CO yield to be greater than 0.95 and most likely unity. This result suggests that the contribution of OCS as a precursor to lower stratospheric sulfate aerosol is somewhat larger than previously thought. A paper describing our study of OCS photochemistry appeared in a March, 1995 issue of Geophysical Research Letters [5].

Recently, we have focused attention on the photochemistry of the halogen nitrates. Recent work at JPL suggests that ClONO\textsubscript{2} photochemistry is much more complicated than previously thought [Nickolaisen et al., 1996]. Both the total photodissociation quantum yield and the fraction of photodissociation events which lead to production of Cl + NO\textsubscript{2} versus ClO + NO\textsubscript{2} now appear to depend on wavelength and pressure in a rather complex way. Our initial studies of ClONO\textsubscript{2} photochemistry involved detection of the atomic chlorine photoproduct following photolysis at both 266 nm and 355 nm at pressures in the range 5-200 Torr. Phosgene and molecular chlorine (Cl\textsubscript{2}) were used as \( \Phi(\text{Cl}) = 2.0 \) calibrations at 266 nm and 355 nm, respectively. For reasons which will require further experimentation to sort out, we had considerable difficulty obtaining reproducible Cl atom yields. However, some useful results were obtained from these experiments. First, by monitoring the pseudo-first order chlorine atom decay rate as a function of the ClONO\textsubscript{2} concentration, a value of 1.1x10\textsuperscript{-11}cm\textsuperscript{3}molecule\textsuperscript{-1}s\textsuperscript{-1} was obtained for the Cl + ClONO\textsubscript{2} rate coefficient at 298K; this result agrees well with other values reported in the literature [Margitan, 1983; Kurylo, et al., 1983; Yokelson et al., 1995]. Another interesting result is summarized by the data shown in Figure 2, i.e., at very short times after the photolysis flash a fast component in the decay of the resonance fluorescence signal is observed. The fast component is more pronounced in 10 Torr N\textsubscript{2} than in 100 Torr N\textsubscript{2} (compare traces (a) and (c) in Figure 2). Our interpretation of the above observations is that ClONO\textsubscript{2} photolysis produces Cl\((^2\text{P}_{1/2})\) in considerable excess over the fraction expected to be present in thermal equilibrium with Cl\((^2\text{P}_{3/2})\). The resonance fluorescence technique simultaneously detects both spin-orbit states, but is more sensitive to the excited state, Cl\((^2\text{P}_{1/2})\); hence, as the excited state rapidly relaxes, a fast component in the resonance fluorescence temporal profile is observed. When CO\textsubscript{2}, an excellent quencher for Cl\((^2\text{P}_{1/2})\), is added to the reaction mixture,
Figure 2.

\[ \text{Cl}(^{2}P_{3}) \text{ decay profiles in the presence of ClONO}_{2} \text{, showing the effect of added CO}_{2} \text{ on the Cl signal at short times. Experimental conditions: 298K; N}_{2} \text{ buffer gas} - (a) 100 \text{ torr}, (b) 100 \text{ torr}, (c) 10 \text{ torr; [ClONO}_{3} \text{] (10}^{14} \text{ molecules cm}^{-3}) - (a) 3.11, (b) 3.11, (c) 2.18; [CO}_{2} \text{] (10}^{16} \text{ molecules cm}^{-3}) - (a) 0, (b) 2.95, (c) 0. \]
the fast component in the fluorescence temporal profile disappears (see trace (b) in Figure 2); this confirms the above interpretation. Shortly after carrying out the above experiments, we became aware that the NCAR kinetics group had made similar observations and had, in fact, followed up on their observations to carry out an excellent study of the kinetics of Cl(P,12) deactivation by a number of collision partners [Tyndall et al., 1995]. Given the excellent work on ClONO₂ photochemistry being done at JPL and NCAR, we decided to shift our attention to the photochemistry of BrONO₂ (see below).

Our initial studies of BrONO₂ photochemistry have involved detection of ground state atomic bromine, Br(P,32), following laser flash photolysis at 266 nm. CF₂Br₂ has been employed as a $\Phi$(Br) = 1.0 calibration, and CO₂ has been added to the photolysis mixtures to insure rapid relaxation of any photolytically generated Br(P,12). Some experiments have been carried out with NO added to the photolysis mixtures in order to rapidly convert photolytically generated BrO to Br; hence, quantum yield information for both Br and BrO has been obtained. In addition, by measuring the pseudo-first order loss rate of Br(P,32) as a function of the bromine nitrate concentration, kinetic data for the Br + BrONO₂ reaction have been obtained. The experimental set-up allows BrONO₂ to be monitored (by UV photometry) in the slow flow system both upstream and downstream from the photolysis/reaction cell. We find that some BrONO₂ is lost upon traversal from the upstream absorption cell to the downstream absorption cell, with the largest differences occurring when the photolysis/reaction cell is cold. Loss of BrONO₂ can be kept very small (~5%) if (a) care is taken to eliminate all leaks from the flow system and (b) the system is treated with N₂O₅ before a set of BrONO₂ photochemistry/kinetics experiments are undertaken; surface reaction of BrONO₂ with H₂O is the probable BrONO₂ loss mechanism. Over the temperature range 228-352 K, our Br + BrONO₂ kinetic data are well described by the Arrhenius expression (units are cm³ molecule⁻¹s⁻¹):

$$k = (2.00 \pm 0.08) \times 10^{-11} \exp \left[\frac{(329 \pm 28)}{T}\right]$$

Uncertainties in the above Arrhenius expression are 2σ and represent precision only. The results of quantum yield measurements for Br and BrO are summarized in Table II. We find that the quantum yields for Br and BrO production are similar in magnitude and sum to a value which is unity within experimental uncertainty. Our studies of BrONO₂ photochemistry will extend into the next funding
Table II. Quantum yields ($\Phi$) for Br and BrO from 266 nm photodissociation of BrONO₂.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>P(Torr)</th>
<th>$\Phi$(Br)</th>
<th>$\Phi$(Br)/$\Phi$(BrO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>50</td>
<td>0.52±0.04</td>
<td>1.11±0.10</td>
</tr>
<tr>
<td>298</td>
<td>10</td>
<td>0.57±0.010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.52±0.06</td>
<td>1.12±0.16</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.51±0.06</td>
<td>1.20±0.20</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.55±0.06</td>
<td>1.24±0.26</td>
</tr>
</tbody>
</table>

a. Uncertainties are 2σ
cycle and will include pressure and temperature dependent studies at two additional photolysis wavelengths (308 nm and 355 nm); in addition, direct observation of two additional possible photoproducts (NO₃ and O) will be carried out.

References

Kinetics and Thermochemistry of the Cl(2P_J) + C2Cl4 Association Reaction

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A laser flash photolysis—resonance fluorescence technique has been employed to study the kinetics of the Cl(2P_J) + C2Cl4 association reaction as a function of temperature (231–390 K) and pressure (3–700 Torr) in nitrogen buffer gas. The reaction is found to be in the falloff regime between third and second order over the range of conditions investigated, although the second-order limit is approached at the highest pressures and lowest temperatures. At temperatures below 300 K, the association reaction is found to be irreversible on the experimental time scale of ~20 ms. The kinetic data at T < 300 K have been employed to obtain falloff parameters in a convenient format for atmospheric modeling. At temperatures above 330 K, reversible addition is observed, thus allowing equilibrium constants for C2Cl5 formation and dissociation to be determined. Second- and third-law analyses of the equilibrium data lead to the following thermochemical parameters for the association reaction: \( \Delta H^{\circ}_{298} = -18.1 \pm 1.3 \) kcal mol\(^{-1} \), \( \Delta H^0 = -17.6 \pm 1.3 \) kcal mol\(^{-1} \), and \( \Delta S^{\circ}_{298} = -27.7 \pm 3.0 \) cal mol\(^{-1} \) K\(^{-1} \). In conjunction with the well-known heats of formation of Cl(2P_J) and C2Cl4, the above \( \Delta H \) values lead to the following heats of formation for C2Cl5 at 298 and 0 K: \( \Delta H^{\circ}_{298} = 8.0 \pm 1.3 \) kcal mol\(^{-1} \) and \( \Delta H^0 = 8.1 \pm 1.5 \) kcal mol\(^{-1} \). The kinetic and thermochemical parameters reported above are compared with other reported values, and the significance of reported association rate coefficients for understanding tropospheric chlorine chemistry is discussed.

Introduction

Tetrachloroethylene (C2Cl4) is used widely for dry cleaning, for metal degreasing, and as an industrial solvent.\(^1,2\) Global production of C2Cl4 over the decade from the early 1980s to the early 1990s averaged around 600 ktons yr\(^{-1} \), and a majority of this production has found its way into the atmosphere.\(^3\) Field observations of the global distribution of atmospheric C2Cl4 have been employed in conjunction with spatially resolved emissions data to deduce an average tropospheric lifetime of about 0.4 yr.\(^1,3,4\) This lifetime is consistent with the notion that C2Cl4 removal from the troposphere is dominated by reaction with the OH radical, although uncertainties in the OH + C2Cl4 rate coefficient and in tropospheric OH concentrations are such that the lifetime for C2Cl4 toward reaction with OH could be anywhere in the range 0.20–0.65 yr.\(^2\)

Comparison of available kinetic data for the OH + C2Cl4 reaction\(^5,6\) with available data for the Cl(2P_J) + C2Cl4 reaction\(^7–16\) suggests that the Cl(2P_J) + C2Cl4 rate coefficient is several hundred times faster than the OH + C2Cl4 rate coefficient at tropospheric temperatures and pressures. Until recently, it has been thought that chlorine atom levels in the troposphere were so low that Cl(2P_J) could not be an important tropospheric reactant. However, evidence is now mounting which suggests that chlorine atom levels in the marine boundary layer may be as much as one-tenth as high as OH levels,\(^12,18\) with the chlorine atom source probably being photochemically labile chlorine species such as Cl2 and ClNO2 produced via heterogeneous reactions on the surfaces of moist sea salt particles.\(^19\) Hence, it appears that in certain regions of the troposphere reaction with Cl(2P_J) is an important removal mechanism for C2Cl4.

Reaction 1 must proceed via an addition mechanism, i.e., for N2 buffer gas,

\[
\text{Cl}(2P_J) + C_2Cl_4 + N_2 \rightarrow C_2Cl_5 + N_2
\]  

(1)

The current state of knowledge concerning the atmospheric oxidation mechanism for C2Cl4 has recently been reviewed by Franklin.\(^2\) Phosgene (Cl2CO) is the major end product, but significant yields of carbon tetrachloride, a compound with a large ozone depletion potential, have been reported.\(^20\) While CCl4 can be produced via the gas phase photolysis of the intermediate photooxidation product CCl3CLO, it is now thought that most CCl4 observed in laboratory photooxidation studies is formed by heterogeneous photochemical processes.\(^2\) Hence, yields of CCl4 observed in laboratory "smog chamber" studies may be larger than those which would actually be produced in the atmosphere.

While numerous kinetics studies of reaction 1 have been reported,\(^7–16\) the temperature and pressure dependences of the rate coefficient have not been systematically investigated. In this paper we report the results of experiments where laser flash photolysis of Cl2/C2Cl4/N2 mixtures has been coupled with Cl(2P_J) detection by time-resolved atomic resonance fluorescence spectroscopy to investigate the kinetics of reaction 1 over the temperature range 231–298 K and the pressure range 3–700 Torr.
Kinetics of the Cl(2Pj) + C2Cl4 Association Reaction

Torr; over this range of experimental conditions the reaction is found to be in the falloff regime between third and second order, although the high-pressure second-order limit is approached at the low-temperature and high-pressure limits of the range of conditions investigated. We also report experiments at higher temperatures (332–390 K) where Cl(2Pj) regeneration is observed on the experimental time scale (10^{-2}–10^{-3} s), thus indicating the occurrence of the reverse dissociation reaction:

\[ \text{C}_2\text{Cl}_3 + \text{N}_2 \rightarrow \text{Cl}(2p_j) + \text{C}_2\text{Cl}_4 + \text{N}_2 \]  

(-1)

Analysis of equilibration kinetics as a function of temperature provides information about the thermochemistry of reaction 1.

**Experimental Technique**

The laser flash photolysis—resonance fluorescence apparatus employed in this study was similar to those employed in our laboratory in several previous studies of chlorine atom kinetics. \(^{21,22}\) Important features of the apparatus and experimental techniques which are specific to this study are described below.

Chlorine atoms were produced by 355 nm laser flash photolysis of Cl2. Third harmonic radiation from a Quanta Ray Model DCR-2 Nd:YAG laser provided the photolytic light source. The photolysis laser could deliver up to 1 x 10^14 photons per pulse at a repetition rate of up to 10 Hz; the pulse width was 6 ns. Fluences employed in this study ranged from 5 to 50 mJ cm^{-2} pulse^{-1}.

In order to avoid accumulation of photochemically generated reactive species, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was typically 3 cm s^{-1} while the laser repetition rate was varied over the range 2–10 Hz. (It was 2 Hz in most experiments at T < 300 K and 10 Hz in most experiments at T > 300 K.) Since the direction of flow was perpendicular to the photolysis laser beam, no volume element of the reaction mixture was subjected to more than a few laser shots. Molecular chlorine (Cl2) and C2Cl4 were flowed into the reaction cell from 12 L Pyrex bulbs containing dilute mixtures in nitrogen buffer gas, while N2 flowed directly from its high-pressure storage tank. The Cl2:N2 mixture, C2Cl4:N2 mixture, and additional N2 were premixed before entering the reaction cell. Concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The C2Cl4 concentration was also measured in situ in the slow flow system by UV photometry at 228.8 nm using a cadmium penray lamp as the light source. The C2Cl4 absorption cross section at 228.8 nm was measured during the course of this study and was found to be 8.36 x 10^{-18} cm^2. Kinetics results were found to be independent of whether the 60.3–201 cm long absorption cell was positioned upstream or downstream from the reaction cell. In the lowest pressure experiments a small correction was required for the pressure differential between the absorption cell and the reaction cell; the pressure differential never exceeded 1%. In all photometric measurements (including the absorption cross section measurements) the absorption cell temperature was 297 ± 3 K.

The gases used in this study had the following stated minimum purities: N2, 99.999%; Cl2, 99.9%. \(^{23}\) Nitrogen was used as supplied while Cl2 was degassed at 77 K before being used to prepare mixtures with N2. The liquid C2Cl4 sample had a stated purity of 99%. It was transferred under nitrogen atmosphere into a vial fitted with a high vacuum stopcock and then degassed repeatedly at 77 K before being used to prepare mixtures with N2.

**Results and Discussion**

In all experiments, chlorine atoms were generated by laser flash photolysis of Cl2:

\[ \text{Cl}_2 + h\nu (355 \text{ nm}) \rightarrow n\text{Cl}(2p_{3/2}) + (2 - n)\text{Cl}(2p_{1/2}) \]  

(2)

The fraction of chlorine atoms generated in the excited spin-orbit state, Cl(2p_{3/2}), is thought to be very small, i.e., less than 0.01. \(^{24,25}\) Recently, it has been reported that the rate coefficient for Cl(2p_{3/2}) quenching by N2 is considerably slower than previously thought, i.e., 5.0 x 10^{-15} cm^3 molecule^{-1} s^{-1}. \(^{26}\) However, on the basis of reported rate coefficients for Cl(2p_{3/2}) deactivation by saturated halocarbons (all gas kinetic except, possibly, CF4), \(^{26-29}\) we expect that the rate coefficient for Cl(2p_{3/2}) deactivation by C2Cl4 is very fast, i.e., \((2 ± 1) x 10^{-10}\) cm^3 molecule^{-1} s^{-1}. Hence, it seems safe to assume that all Cl2 + C2Cl4 kinetic data are representative of an equilibrium mixture of Cl(2p_{3/2}) and Cl(2p_{3/2}). As a further check on the assumption of spin state equilibration, the rate coefficient at T = 297 K and P = 26 Torr was measured with and without CF2Cl2, a very efficient Cl(2p_{3/2}) quencher, \(^{26,28,29}\) added to the reaction mixture; as expected, this variation in experimental conditions had no effect on the observed reaction rate (see Table 1).

The equilibrium fraction of chlorine atoms in the 2p_{3/2} state ranges from 0.0021 at 231 K to 0.019 at 390 K. It is worth noting that, given the small fraction of chlorine atoms in the 2p_{1/2} state and the fast values for k1, which are measured (Tables 1 and 2), it must be the case that observed reactivity is dominated by chlorine atoms in the 2p_{3/2} state.

All experiments were carried out under pseudo-first-order conditions with C2Cl4 in large excess over Cl(2p). Hence, in the absence of side reactions that remove or produce chlorine atoms, the Cl(2p) temporal profile following the laser flash would be described by the relationship

\[ \ln \left[ \frac{\text{Cl}(2p)}{\text{Cl}(2p)_{\text{expt}}} \right] = (k_1 + k_4) t = k't \]  

(1)

**TABLE 1: Summary of Kinetic Data for the Reaction**

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<tr>
<th>T (K)</th>
<th>P (Torr)</th>
<th>[Cl2]</th>
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<th>[C2Cl4]_expt</th>
<th>k1 ± 2σ</th>
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* Units: T (K); P (Torr); concentrations (10^{10} molecules cm^{-3}); k_{1,10^{-12}} cm^3 molecule^{-1} s^{-1}. Expt = determination of one pseudo-first-order decay rate. Errors represent precision only. \(1.0 \times 10^{13} \text{CF}_2\text{Cl}_2\) per cm added to reaction mixture.
where $k_3$ is the rate coefficient for the process

$$\text{Cl} \rightarrow \text{Cl}^*$$

first-order loss by diffusion from the detector field of view and/or reaction with background impurities (3)

The bimolecular rate coefficients of interest, $k_i([N_2], T)$, are determined from the slopes of $k'$ versus $[C_2Cl_4]$ plots for data obtained at constant $[N_2]$ and $T$ and under conditions where $N_2$ is the dominant third body collider with the energized $C_2Cl_4$ complex. Observation of Cl$(^2P_J)$ temporal profiles that are exponential, i.e., obey eq I, a linear dependence of $k'$ on $[C_2Cl_4]$, and invariance of $k'$ to variation in laser photon fluence and photolyte concentration strongly suggests that reactions 1 and 3 are, indeed, the only processes that significantly affect the Cl$(^2P_J)$ time history.

Kinetics at $T < 300$ K. For all experiments carried out at temperatures below 300 K, well-behaved pseudo-first-order kinetics were observed; i.e., Cl$(^2P_J)$ temporal profiles obeyed eq I, and $k'$ increased linearly with increasing $[C_2Cl_4]$ but was independent of laser photon fluence and photolyte concentration. Typical data are shown in Figures 1–3. Measured bimolecular rate coefficients, $k_i([N_2], T)$ are summarized in Table 1. As expected for an association reaction in the non-high-pressure-limit regime, $k_i([N_2], T)$ is found to increase with increasing pressure and with decreasing temperature.

Parametrization of $k_i([N_2], T)$ for Atmospheric Modeling.

For purposes of atmospheric modeling, it is convenient to generate a mathematical expression that can be used to compute $k_i([N_2], T)$ over the range of relevant temperatures and pressures. (The efficiency of $O_2$ as a third body collider is generally very similar to that of $N_2$.) The expression generally used for this purpose is

$$k_i([N_2], T) = \{A/[1 + (A/B)]\} F_c^{[1 + (\log A/B)]^{-1}} \quad \text{(II)}$$

where

$$A = k_{1,0}(T)[N_2] = k_{1,0}(300 \text{ K})(T/300)^{-4}[N_2] \quad \text{(III)}$$

$$B = k_{1,\infty}(T) = k_{1,\infty}(300 \text{ K})(T/300)^{-6} \quad \text{(IV)}$$

$$F_c = 0.6 \quad \text{(V)}$$

In the above expression, $k_{1,0}$ and $k_{1,\infty}$ are approximations to the low- and high-pressure limit rate coefficients for reaction 1, and $F_c$ is the "broadening parameter". The value $F_c = 0.6$ is found to fit data for a wide variety of atmospheric reactions reasonably.
well, although in principle $F_r$ may vary with temperature and may be different for different reactions. Fitting our measured values for $k_1([N_2], T)$ to eq II gives the following parameters:

$$k_{1,0}(T) = 1.40 \times 10^{-28}(T/300)^{-8.5} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_{1,0}(T) = 3.97 \times 10^{-11}(T/300)^{-1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Experimental falloff data are compared with curves calculated using the above parameters in Figure 4. The parametrization represents the experimental data reasonably well. Variation of the parameter $F_r$ does not significantly improve the quality of the fits.

**Kinetics at $T > 330$ K.** At temperatures above 330 K, chlorine atom regeneration via a secondary reaction became evident. Under these experimental conditions, observed Cl($^{2P_J}$) temporal profiles were independent of laser fluence and Cl$_2$ concentration but varied as a function of [Cl$_2$]$_4$, pressure, and temperature in the manner expected if unimolecular decomposition of Cl$_2$Cl$_2$ was the source of regenerated Cl($^{2P_J}$). Assuming that Cl$_2$Cl$_2$ decomposition is the source of regenerated Cl($^{2P_J}$), the relevant kinetic scheme controlling the Cl($^{2P_J}$) temporal profile includes not only reactions 1 and 3 but also reactions $-1$ and 4:

$$\text{Cl}_2\text{Cl}_2\rightarrow \text{first-order loss by processes}$$

that do not regenerate Cl($^{2P_J}$) (4)

Assuming that all processes affecting the temporal evolution of Cl($^{2P_J}$) and Cl$_2$Cl$_2$ are first-order or pseudo-first-order, the rate equations for reactions 1, $-1$, 3, and 4 can be solved analytically:

$$S/S_0 = \{(Q + \lambda_1) \exp(\lambda_1 t) - (Q + \lambda_2) \times \exp(\lambda_2 t)\}/(\lambda_1 - \lambda_2) \quad (VI)$$

where $S$ and $S_0$ are the resonance fluorescence signal levels at times $t$ and 0, and

$$Q = k_{-1} + k_4 \quad (VII)$$

$$Q + k_3 + k_1[C_2\text{Cl}_4] = -(\lambda_1 + \lambda_2) \quad (VIII)$$

$$k_3Q + k_4k_1[C_2\text{Cl}_4] = \lambda_1\lambda_2 \quad (IX)$$

Typical Cl($^{2P_J}$) temporal profiles observed in the high-temperature experiments are shown in Figure 5 along with best fits of each temporal profile to eq VI. The results for all high-temperature experiments are summarized in Table 2. It is worth noting that values for $k_1([N_2], T)$ obtained from analysis of the high-temperature data are consistent with those expected based on extrapolation of the results from $T < 300$ K. We believe that reported values for $k_1$, even at high temperature where Cl($^{2P_J}$) regeneration is fast, are accurate to within ±20%. Absolute uncertainties in reported values for $k_{-1}$ are somewhat more difficult to assess. Inspection of Table 2 shows the precision of multiple determinations of $k_{-1}$ at a particular temperature and pressure (for varying [Cl$_2$Cl$_2$]) is quite good. An inherent assumption in our analysis is that the only significant Cl$_2$Cl$_2$ loss process that results in chlorine atom production is reaction $-1$; as long as this assumption is correct (it almost certainly is), we believe the relative accuracy of our reported $k_{-1}$ values is ±30% over the full range of temperature and pressure investigated.

**Possible Secondary Chemistry Complications.** The photochemical system used to study the kinetics of reactions 1 and $-1$ appears to be relatively free of complications from unwanted side reactions. The only potential secondary reactions we are aware of which could destroy or regenerate chlorine atoms (other...
The concentrations of photochemically generated radicals employed in this study, i.e., $\leq 3\times 10^{11}$ molecules cm$^{-3}$, were sufficiently small that a radical–radical interaction such as reaction 5 could not be an important Cl($^3P_J$) removal process even if the rate coefficient were gas kinetic. Experimentally, the fact that observed kinetics were unaffected by significant variations in [Cl$_2$] confirms that reaction 5 did not contribute significantly to Cl($^3P_J$) removal. The only kinetics studies of reaction 6 reported in the literature involved competitive chlorination studies where kinetic information was derived by fitting observed product distributions to a complex chemical mechanism; these studies, while indirect, suggest that $k_4$ is much too slow for reaction 6 to be a significant interference. Experimentally, we found that observed kinetics were unaffected by significant variations in [Cl$_2$].

\[ \text{Cl($^3P_J$)} + C_2Cl_3 \rightarrow \text{Cl}_2 + C_2Cl_4 \]  
(5a)

\[ M \rightarrow C_2Cl_6 \]  
(5b)

\[ C_2Cl_5 + \text{Cl}_2 \rightarrow C_2Cl_4 + \text{Cl($^3P_J$)} \]  
(6)

The observed kinetics were unaffected by significant variations in [Cl$_2$].
by significant variations in Cl₂ concentration, thus confirming that reaction 6 played no role in controlling observed Cl(2P₃/2) temporal profiles.

**C₂Cl₃ Thermochernistry: Second-Law Analysis.** The equilibrium constants, \( K_p \), given in Table 2 are computed from the relationship

\[
K_p = k/k_{-1}RT = K_p/RT \quad (XIII)
\]

Use of eq XIII involves making the assumption that reaction \(-1\) is truly the reverse of reaction 1, i.e., that the products of reaction \(-1\) do not contain substantial internal excitation. If, for example, reaction \(-1\) resulted in production of predominantly Cl(2P₃/2), it would be inappropriate to use the ratio \( k/ k_{-1} \) as a basis for evaluating the thermochemistry of reaction 1. While it seems reasonable to assume that energy is distributed statistically in the translational and internal degrees of freedom of the C₂Cl₃ and Cl(2P₃/2) products of reaction \(-1\), it should be kept in mind that there presently exists no experimental verification that this assumption is correct.

Assuming that \( K_p \) can be computed from the ratio of measured values for \( k \) and \( k_{-1} \), a van’t Hoff plot, i.e., a plot of \(
\ln K_p = (\Delta S/\mathbf{R}) - (\Delta H/RT)
\)

the enthalpy change associated with reaction 1 is obtained from the slope of the van’t Hoff plot while the entropy change is obtained from the intercept. At 360 K, the midpoint of the experimental \( T^{-1} \) range, this "second-law analysis" gives the results \( \Delta H = -17.5 \pm 0.6 \text{ kcal mol}^{-1} \) and \( \Delta S = -26.1 \pm 1.8 \text{ cal mol}^{-1} \text{ K}^{-1} \), where the errors are 2σ and represent precision only.

**C₂Cl₃ Thermochernistry: Third-Law Analysis.** In addition to the second-law analysis described above, we have also carried out a third-law analysis, where the experimental value of \( K_p \) at 360 K (79 800 ± 8000 atm⁻¹) has been employed in conjunction with a calculated entropy change to determine \( \Delta H \).

Since experimental data concerning the structure of C₂Cl₃ are not available, \textit{ab initio} calculations have been carried out for this species. The calculations employed density functional theory\(^{25-31}\) as implemented in the GAUSSIAN 92/DFT program system. With an appropriate choice of gradient correction and a modest basis set, DFT has been shown to frequently give results of near chemical quality.\(^{39-44}\) In addition, spin contamination does not seem to be as serious for DFT compared to Hartree–Fock (HF) theory.\(^{45}\) Becke3LYP, which seems to be a good choice of exchange and correlation functional, has been used with the 6-31+G(d) basis set to optimize geometries for C₂Cl₃. Vibrational frequencies have been calculated with the same method. The results for C₂Cl₃ can be compared with experiment to lend credibility to the approach while the results for C₂Cl₄ can be employed to compute its absolute entropy as well as heat capacity corrections. As a check on the DFT results, MP2/6-31+G(d) optimizations were also carried out for C₂Cl₄ and C₂Cl₅. Only small differences in the geometries were noted. Since the DFT results were closer to experiment for C₂Cl₃, the DFT geometries and frequencies for C₂Cl₄ were used in the third-law analysis.

Two distinctly different Cl(2P₃/2)–C₂Cl₃ adducts are possible. A chlorine atom could add symmetrically to Cl₃CCl₂ to form a π-complex or a three-membered ring with unpaired spin density on chlorine. Alternatively, a chlorine atom could add unsymmetrically to form a σ-complex with unpaired spin density on the β-carbon. Our calculations predict that the most stable form for C₂Cl₃ is the haloalkyl radical CCl₃C(π)Cl, i.e., the σ-complex. Calculated structures for C₂Cl₃ and C₂Cl₄ are shown in Figure 7. For comparison, experimental bond lengths and bond angles for C₂Cl₄,\(^{46}\) are also shown in Figure 7; the calculated structure of C₂Cl₃ is in good agreement with experiment.

To carry out the third-law analysis, absolute entropies as a function of temperature were obtained from the JANAF tables,\(^{46}\) for Cl(2P₃/2), calculated using vibrational frequencies and moments of inertia taken from the JANAF tables for C₂Cl₄,\(^{47}\) and calculated using the moments of inertia and vibrational frequencies in Table 3 for C₂Cl₃. The moments of inertia in Table 3 were computed using the C₂Cl₃ structure shown in Figure 7. The vibrational frequencies in Table 3 were calculated using the approach described above. Because calculated vibrational frequencies for C₂Cl₄ are very close to those given in the JANAF tables,\(^{46}\) no scaling of the C₂Cl₃ frequencies is deemed necessary. At 360 K, the third-law analysis gives the results \( \Delta H = -18.6 \pm 0.5 \text{ kcal mol}^{-1} \) and \( \Delta S = -29.3 \pm 1.0 \text{ cal mol}^{-1} \text{ K}^{-1} \).
Absolute Entropies and Heat Capacity Corrections

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*Δs as assumed energy splitting between lowest two electronic states. C₂Cl₂ has no low-lying excited electronic states, and C₂Cl₄ is assumed to have none.

**TABLE 4: Thermochromical Parameters for the Reaction**

\( \text{Cl}_2(P_2) + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_2\text{Cl}_3 \)

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \Delta H ) (kcal mol⁻¹)</th>
<th>( \Delta S ) (cal mol⁻¹ K⁻¹)</th>
<th>( \Delta H^{0\text{r}}(\text{C}_2\text{Cl}_3) ) (kcal mol⁻¹)</th>
</tr>
</thead>
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<tr>
<td>360</td>
<td>17.5 ± 0.6</td>
<td>26.1 ± 1.8</td>
<td>8.1 ± 1.5</td>
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<td>3rd law</td>
<td>16.8 ± 0.5</td>
<td>29.3 ± 1.0</td>
<td>7.8 ± 0.5</td>
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<td>298</td>
<td>17.5 ± 0.7</td>
<td>26.2 ± 1.9</td>
<td>8.5 ± 0.8</td>
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<td>3rd law</td>
<td>18.7 ± 0.6</td>
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<td>7.4 ± 0.7</td>
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<td>17.1 ± 0.8</td>
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<tr>
<td>3rd law</td>
<td>18.2 ± 0.7</td>
<td>29.4 ± 1.0</td>
<td>7.5 ± 0.8</td>
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</tbody>
</table>

* Units: \( T \) (K); \( \Delta H \), \( \Delta H^{0\text{r}} \) (kcal mol⁻¹); \( \Delta S \) (cal mol⁻¹ K⁻¹).

* Calculated using values for \( \Delta H^{0\text{r}}(\text{Cl}) \) and \( \Delta H^{0\text{r}}(\text{C}_2\text{Cl}_4) \) taken from ref 46.

Comparison with Previous Research. Although this study represents the first systematic investigation of the temperature and pressure dependence of \( k \), there are several published measurements with which our results can be compared. Davis et al. in one of the pioneering applications of the flash photolysis–resonance fluorescence technique, measured \( k_1 \) at 298 K in helium buffer gas; they reported rate coefficients of \( 4.8 \times 10^{-12} \) and \( 6.10 \times 10^{-12} \) cm⁻³ molecule⁻¹ s⁻¹ at pressures of 15 and 100 Torr, respectively. The magnitude of Davis et al.'s rate coefficients seems a little low compared to values one might expect based on our measurements in \( N_2 \) buffer gas, and the ratio \( k_1 \) (100 Torr of \( He/1.12 \) obtained by Davis et al. is smaller than one would predict based on the 297 K falloff curve we have obtained using \( N_2 \) as the buffer gas (Figure 4).

Franklin et al. have employed a discharge flow system with an EPR detector to study the kinetics of the \( O(2P) + \text{C}_2\text{Cl}_4 \) reaction at 298 K and 0.3 Torr total pressure in \( O_2 \) buffer gas. They observed that \( \text{Cl}^- (2P) \) was produced as a reaction product and, by following the temporal evolution of both \( O(2P) \) and \( \text{Cl}^- (2P) \), extracted a value of \( 3 \times 10^{-13} \) cm⁻³ molecule⁻¹ s⁻¹ for \( k_1 \); this value is slower than one would predict from extrapolation of our 297 K falloff curve down to \( P = 0.3 \) Torr under the assumption that \( N_2 \) and \( O_2 \) are equally efficient as third body colliders. In addition to the two "direct" studies discussed above, there have been a number of competitive kinetics studies of reaction 1, 9-13,16 two of which 13,16 report results where meaningful comparisons can be made with our results. Franklin et al. employed CW photolysis of \( \text{Cl}_2 \) in conjunction with gas chromatographic detection of \( \text{C}_2\text{Cl}_4 \); they employed the reference reactants \( \text{C}_2\text{H}_6 \) and \( \text{CH}_2\text{Cl}_2 \) to measure the ratio \( k_5/k_1 = 0.0295 \) at 310 K and \( k_8/k_1 = 1.66 \) at 348 K.

\( \text{Cl}(^2P) + \text{CH}_2\text{Cl}_2 \rightarrow \text{HCl} + \text{CHCl}_2\text{Cl} \) (7)

\( \text{Cl}(^2P) + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5 \) (8)

Assuming \( k_5(310 \text{ K}) = 1.7 \times 10^{-12} \) cm⁻³ molecule⁻¹ s⁻¹ 46 and \( k_8(348 \text{ K}) = 5.9 \times 10^{-12} \) cm⁻³ molecule⁻¹ s⁻¹, Franklin et al.'s data give \( k(310 \text{ K}) = 5.8 \times 10^{-11} \) cm⁻³ molecule⁻¹ s⁻¹ and \( k(348 \text{ K}) = 3.6 \times 10^{-11} \) cm⁻³ molecule⁻¹ s⁻¹; these rate coefficients are not quantitatively consistent with each other but are in approximate agreement with the values expected based on our measurements in \( N_2 \) at pressures of 15 and 100 Torr, respectively. In light of their work, the underestimation of the \( \text{Cl}^- \text{C} \) bond energy by DFT is not unexpected.
this is slightly faster than the value we report but in agreement within combined experimental uncertainties.

Franklin et al.,\textsuperscript{13} in their competitive kinetics studies (described above) derived the following relationship from their data: \( k(T) = 4.90 - 10650/4.576T \) mol\(^{-1}\) L\(^2\) s\(^{-1}\). They used their determinations of \( k(T) \) in conjunction with the measurements of \( k(273) \) reported by Dusdeim et al.,\textsuperscript{34} to obtain values for \( k(T) \). Franklin et al.,\textsuperscript{35} values, when corrected for updated information about \( k(T) \) and \( k(T) \), give rates for \( k(T) \) which are somewhat faster than the values we report. A more quantitative comparison does not appear to be worthwhile because (a) the Arrhenius expression for \( k(T) \) is highly uncertain,\textsuperscript{10,34} (b) Franklin et al. report \( k(T) \) to be pressure independent while we find \( k(T) \) to be pressure dependent (Table 2), and (c) as mentioned above, Franklin et al. employed more efficient third-body colliders (\( \text{C}_2\text{Cl}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}_2 \)) in their study than we did in ours (\( \text{C}_2\text{H}_4 \)). From their evaluations of \( k(T) \) and \( k(T) \) at two temperatures, Franklin et al. derived \( \Delta H = -16.9 \pm 1.0 \) kcal mol\(^{-1}\), i.e., somewhat higher than the value we report but in agreement within combined experimental uncertainties. (We believe the uncertainty in the Franklin et al. determination of \( \Delta H \) is actually considerably larger than their published estimate \( \pm 1.0 \) kcal mol\(^{-1}\).)

The best fit value for the parameter \( n \) (describing the temperature dependence of \( k_0 \), obtained in this study, i.e., \( n = 8.5 \), is larger than is typically found for association reactions of atmospheric interest.\textsuperscript{30} Recommended values of \( n \) for 62 atmospheric association reactions range from 0.0 to 6.7, with the largest values found for the \( \text{CF}_2\text{ClO}_2 + \text{NO} \) and \( \text{CCI}_3 + \text{O}_2 \) reactions.\textsuperscript{30} Interestingly, both \( \text{CF}_2\text{ClO}_2 \text{NO}_2 \) and \( \text{CCI}_3 \text{O}_2 \) are relatively weakly bound species, with bond strengths only a few kcal mol\(^{-1}\) stronger\textsuperscript{51,52} than that of \( \text{Cl}_2\text{Cl}_5 \). While the results reported in this paper clearly demonstrate that \( k(T) \) increases significantly with decreasing temperature, the value of \( n \) is rather uncertain because no data were obtained at pressures anywhere near the low-pressure limit. As a result, extrapolation of our results outside of the experimental temperature regime should be carried out with caution.

The 298 K falloff curves for \( \text{Cl}(^{2P}_j) \) reactions with \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{Cl}_4 \) over the pressure range 1-10 000 Torr of \( \text{N}_2 \) are compared in Figure 8. The \( \text{C}_2\text{Cl}_4 \) curve is based on the falloff parameters determined in this study while the \( \text{C}_2\text{H}_4 \) curve is calculated from the falloff parameters recommended by the NASA panel for chemical kinetics and photochemical data evaluation,\textsuperscript{30} which are based on the experimental data of Wallington et al.,\textsuperscript{53} over the pressure range 10-3000 Torr.

Interestingly, \( \text{Cl}(^{2P}_j) \) reacts much more rapidly with \( \text{C}_2\text{Cl}_4 \) than with \( \text{C}_2\text{H}_4 \) in the low-pressure limit, but much more rapidly with \( \text{C}_2\text{H}_4 \) than with \( \text{C}_2\text{Cl}_4 \) in the high-pressure limit. This interesting reactivity pattern can be rationalized in terms of the simple Lindemann-Hinshelwood mechanism,\textsuperscript{34,35} where reaction 1, for example, proceeds via the following three-step process:

\[
\text{Cl}(^{2P}_j) + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_2\text{Cl}_5^* \quad (a)
\]

\[
\text{C}_2\text{Cl}_5^* \rightarrow \text{Cl}(^{2P}_j) + \text{C}_2\text{Cl}_4 \quad (b)
\]

\[
\text{C}_2\text{Cl}_5^* + \text{M} \rightarrow \text{C}_2\text{Cl}_4 + \text{M} \quad (c)
\]

If one makes the steady state approximation for the energized adduct, \( \text{C}_2\text{Cl}_5^* \), the low- and high-pressure limit rate coefficients are obtained as \( k_{1.0} = k_1k_{1.0}/k_{1.0} \) and \( k_{1.0} = k_1 \). The fact that \( k_{1.0} > k_{1.0} \) implies that \( \text{Cl}(^{2P}_j) \) adds more rapidly to \( \text{C}_2\text{H}_4 \) than to \( \text{C}_2\text{Cl}_4 \) to form the energized species \( \text{C}_2\text{H}_5\text{Cl}^* \); this seems reasonable since the four chlorine atoms in \( \text{C}_2\text{Cl}_4 \) will be expected to sterically hinder approach of \( \text{Cl}(^{2P}_j) \) to a carbon atom. The fact that \( k_{1.0} < k_{1.0} \) also seems reasonable since collisional deactivation of \( \text{C}_2\text{H}_5\text{Cl}^* \) would be expected to be more efficient for \( \text{C}_2\text{Cl}_5^* \) than for \( \text{C}_2\text{H}_5\text{Cl}^* \) due to the much higher density of states in \( \text{C}_2\text{Cl}_5^* \).

Implications for Atmospheric Chemistry. The results reported in this paper confirm that \( \text{C}_2\text{Cl}_4 \) reacts with \( \text{Cl}(^{2P}_j) \) several hundred times faster than with \( \text{OH} \) under atmospheric conditions. Hence, in selected atmospheric environments such as the marine boundary layer, where \( \text{Cl}(^{2P}_j) \) levels appear to be particularly high,\textsuperscript{17-19} reaction with \( \text{Cl}(^{2P}_j) \) will be the dominant atmospheric removal mechanism for \( \text{C}_2\text{Cl}_4 \). In addition, \( \text{C}_2\text{Cl}_4 \) is being employed as a "tracer" for analyzing the potential importance of chlorine atoms as an oxidant in the free troposphere;\textsuperscript{56} the temperature- and pressure-dependent values for \( k(T,P) \) reported in this study are useful for making such an analysis as quantitative as possible.

Acknowledgment. The experimental component of this research was supported by the National Aeronautics and Space Administration, Upper Atmosphere Research Program, through Grant NAGW-1001 to Georgia Institute of Technology. Computer time for this study was made available by the Alabama Supercomputer Network and the NSF-supported Pittsburgh Supercomputer Center. We thank C. A. Piety for helping with some of the experiments.

References and Notes


(23) Stated minimum purity of liquid phase in high-pressure cylinder.


(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Frurip, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92/DFT (Rev. G. 2); Gaussian, Inc.: Pittsburgh, PA, 1993.


(47) We believe that the C2Cl4 absolute entropies as a function of temperature tabulated in ref 64 are incorrect.

(48) (a) Wong, M. W.; Radom, L. J. Phys. Chem. 1995, 99, 8582. (b) For example, the reaction enthalpy for addition of tert-butyl radical to C2H6 is too positive by DFT by 9.8 kcal/mol compared to QCISD.


(50) In their 310 K experiments, Franklin et al (ref 13) employed gas mixtures containing 80 Torr of O2 or SF6. In their 348 K experiments, the gas mixtures contained 100 Torr of C2Cl4, 20 Torr of C2H6, and 50–400 Torr of Cl2. No systematic dependence on λ1 on total pressure was reported.


(56) Singh, H. B. Private communication.
Kinetics of the Reaction of $O(^3P)$ with CF$_3$NO

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Abstract

A laser flash photolysis-resonance fluorescence technique has been employed to study the kinetics of the reaction of $O(^3P)$ with CF$_3$NO ($k_2$) as a function of temperature. Our results are described by the Arrhenius expression $k_2(T) = (4.54 \pm 0.70) \times 10^{-12} \exp\left[-560 \pm 46/T\right]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (243 K $\leq T \leq 424$ K); errors are 2σ and represent precision only. The $O(^3P)$ + CF$_3$NO reaction is sufficiently rapid that CF$_3$NO cannot be employed as a selective quencher for $O(^3P)$ in laboratory systems where $O(^3P)$ and $O_2(a^1\Delta_g)$ coexist, and where $O(^3P)$ kinetics are being investigated. © 1995 John Wiley & Sons, Inc.

Introduction

The first excited state of molecular oxygen, $O_2(a^1\Delta_g)$ ($\epsilon = 0.977$ eV), has a long radiative lifetime of 3900 s and typically is quenched inefficiently by closed-shell molecules [1]. Specifically, the rate coefficient for quenching of $O_2(a^1\Delta_g)$ by N$_2$ is less than $10^{-20}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [2] which results in a long $O_2(a^1\Delta_g)$ lifetime in N$_2$ even at pressures of hundreds of torr. Although rate coefficients for quenching of $O_2(a^1\Delta_g)$ by about 50 small molecules have been reported [1,3,4], only trifluorornitrosomethane, CF$_3$NO, has been found to have a large quenching rate coefficient at 300 K, i.e., $3.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [3].

In a recent study of the kinetics of the $O(^3P) + BrO$ reaction [5] we employed UV laser flash photolysis of $O_3$ as a source for generating large concentrations of $O(^3P)$. Ozone photolysis at 248 nm (KrF excimer laser) and at 266 nm (fourth harmonic of the Nd:YAG laser) produces primarily electronically excited “singlet” atomic and molecular oxygen, $O(^1D)$ and $O_2(a^1\Delta_g)$ [6,7]. $O(^1D)$ is rapidly quenched to the ground state, $O(^3P)$, by N$_2$ on a submicrosecond time scale at pressures greater than 1 torr [8]; hence, further $O(^1D)$ reactions can be neglected in kinetic experiments performed at higher pressures of N$_2$. However, $O_2(a^1\Delta_g)$ is long lived and in $O(^3P)$ kinetics experiments with high $O_3$ concentrations used as the photolyte, the reaction of $O_2(a^1\Delta_g)$ with $O_3$ can generate $O(^3P)$:

$$O_2(a^1\Delta_g) + O_3 \rightarrow O(^3P) + 2 O_2$$

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In such experiments it is desirable to employ an $O_2(a^1\Delta_g)$ quenching agent such as CF$_3$NO so that $O(3P)$ regeneration is minimized.

A stringent criterion for the use of CF$_3$NO as an $O_2(a^1\Delta_g)$ quenching agent in $O(3P)$ kinetics experiments is that it has a slow rate coefficient for reaction with $O(3P)$.

(2) \[ O(3P) + CF_3NO \rightarrow \text{products} \]

In this article we report a kinetics study of reaction of $O(3P)$ with CF$_3$NO. Reaction (2) was studied at pressures of 25, 100, and 400 torr N$_2$ and over the temperature range 243–424 K. There are no previous kinetic data reported for reaction (2).

Experimental Technique

A laser flash photolysis-resonance fluorescence technique was employed to study the kinetics of reaction (2). $O(3P)$ was generated by $266$ nm laser flash photolysis of $O_3$ in the presence of 25, 100, or 400 torr of N$_2$:

(3a) \[ O_3 + h\nu(266 \text{ nm}) \rightarrow O(^1D) + O_2(a^1\Delta_g) \]

(3b) \[ \rightarrow O(3P) + O_2(X^3\Sigma_g^-) \]

(4) \[ O(^1D) + N_2 \rightarrow O(3P) + N_2 \]

About 88\% of the photolytically produced O atoms are in the $^1D$ electronically excited state [7]. Experimental conditions were such that $O(^1D)$ was always quenched by N$_2$ on a time scale much faster than that for occurrence of reaction (2), i.e., $k_4[N_2] \gg k_2[CF_3NO]$ ($k_4 = 2.6 \times 10^{-11}$ cm$^3$molecule$^{-1}$s$^{-1}$ [8–10]). Pseudo-first-order conditions were employed with $[CF_3NO] \gg [O(3P)]$. The photolytic light source for O atom production was fourth harmonic radiation from a Nd:YAG laser (Quanta-Ray Model DCR-2). The laser could deliver up to $3 \times 10^{16}$ photons per pulse at a repetition rate of up to 10 Hz; the laser pulse width was 5 ns.

The laser flash photolysis-resonance fluorescence apparatus used in this study was similar to one which we have previously employed to study a number of O atom reactions with stable molecules [6,8,11–16]. A schematic of the experimental apparatus has appeared previously [6], and the important features of the apparatus are described below.

All experiments employed a pyrex, jacketed reaction cell with an internal volume of 150 cm$^3$ and a cross-sectional area of 12.5 cm$^2$; a schematic diagram of the reaction cell is given elsewhere [17]. The cell was maintained at a constant temperature by circulating ethylene glycol or methanol from a thermostated bath through the outer jacket. Between experiments, a copper-constantan thermocouple with a stainless steel jacket was inserted into the reaction zone through a vacuum seal. Thus, the gas temperature was measured under the precise pressure and flow rate conditions of the experiment.

An $O(3P)$ resonance lamp was situated perpendicular to the photolysis laser beam. The vacuum UV output radiation of this resonance lamp excited $O(3P)$ resonance fluorescence in the photolytically produced O atoms. The resonance lamp consisted of an electrodeless microwave discharge through about one torr of a flowing mixture containing a trace of O$_2$ in He. The flow of a 0.1\% O$_2$ in He mixture and pure He into the lamp were controlled by separate needle valves, thus allowing the total pressure and O$_2$ concentration to be adjusted for optimum signal-to-noise. Radiation was coupled out of the lamp through a MgF$_2$ window and into the reaction cell through
REACTION OF O(3P) WITH CF3NO

a MgF2 lens. Dry N2 was used as a purge gas in the volume between the lamp window and the cell lens to exclude room air and thus allow transmission of vacuum-UV radiation.

Fluorescence from excited O(3P) atoms within the reaction zone was collected by a MgF2 lens on an axis orthogonal to both the photolysis laser beam and the resonance lamp beam and imaged onto the photocathode of a solar blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with dry N2 and contained a CaF2 window to prevent detection of Lyman-α emission from the resonance lamp. The fluorescence signals were processed using photon counting techniques in conjunction with multichannel scaling. For each O(3P) atom decay rate measured, signals from a large number of laser shots (500 to 15,000) were averaged to obtain a well-defined temporal profile over (typically) three 1/e lifetimes of decay. The multichannel analyzer sweep was triggered approximately 3.2 ms prior to the photolysis laser in order to allow a fluorescence background baseline to be obtained immediately before the laser flash.

All experiments were carried out under "slow flow" conditions so as to avoid accumulation of photolysis or reaction products. The linear flow rate through the reactor was typically around 2 cm s⁻¹ and the laser repetition rate was 10 Hz. Hence, no volume element of the reaction mixture was subjected to more than two or three laser shots. The reactant CF3NO was flowed from 12 L bulbs containing dilute mixtures in N2 buffer gas into an absorption cell, which was used for in situ CF3NO concentration determination as described below. N2 buffer gas was mixed into the reactant flow before the absorption cell. The flow from a 12 L bulb containing O3 diluted with N2 was injected into the reaction cell through a 1/8 inch o.d. Teflon tube positioned such that the O3 mixed with other components about 1 to 5 cm upstream from the reaction zone.

The concentration of CF3NO was measured in situ by UV photometry at 202.6 nm using an absorption cell with a 200.3 cm path length and a zinc hollow cathode lamp light source (which emitted the 202.6 nm Zn⁺ line). Because the output of the zinc lamp includes several other strong lines in the same wavelength region, it was necessary to isolate the 202.6 nm line with a 0.25 m monochromator (Jarrell-Ash) positioned at the exit from the absorption cell. A side-on photomultiplier connected directly to the exit aperture of the monochromator provided the signal detection and a 4½ place digital picoammeter provided the signal readout. A CF3NO absorption cross section of (6.08 ± 0.10) x 10⁻¹⁹ cm² at 202.6 nm (error is 2σ, precision only) was determined with a separate 10.0 cm path length absorption cell and was the value used for all CF3NO in situ and bulb concentration determinations.

In addition the photometric measurements, the CF3NO concentration in the reaction mixture was also determined from measurements of the flow rate of the CF3NO/N2 mixture, the total flow rate, the cell pressure, and the known CF3NO/N2 bulb concentration. There was good agreement between the CF3NO concentration measured in situ and the values calculated from the flow rate measurements. However, the reported k2 values are based upon the CF3NO concentrations determined from the in situ photometry measurements; the flow rate based measurements averaged 7.4% less.

One experiment was performed using in situ visible photometry at 632.8 nm to determine the CF3NO concentration. The same 200.3 cm length absorption cell was used, but a HeNe laser replaced the zinc hollow cathode lamp as the radiation source. A diffuser was placed in front of the monochromator entrance slit to attenuate the
probes beam and prevent saturation of the photomultiplier. A CF$_3$NO absorption cross section of $(4.26 \pm 0.28) \times 10^{-20}$ cm$^2$ was determined with a separate 10.0 cm path length absorption cell and was the value used for all CF$_3$NO concentration determinations at 632.8 nm. The $k_2$ value determined with visible photometry was in good agreement with the experiments which used 202.6 nm as the wavelength for CF$_3$NO monitoring.

The concentration of O$_3$ in the reaction mixture was determined from measurements of the appropriate mass flow rates, the total pressure, and the known O$_3$ bulb concentration. The determination of the O$_3$ concentration in the O$_3$/N$_2$ bulb used the in situ UV photometry apparatus described above. At 202.6 nm the O$_3$ absorption cross section is $3.2 \times 10^{-19}$ cm$^2$ [2].

The He and N$_2$ gases used in this study had stated minimum purities of 99.999% and were used as supplied. Ozone was prepared in a commercial ozonator using UHP oxygen (99.99%). It was collected and stored on silica gel at 195 K, and degassed at 77 K before use. The CF$_3$NO (95% minimum purity) was obtained from PCR, Inc. and was degassed twice at 77 K before each use. The IR spectrum of the degrassed CF$_3$NO agreed with that reported in the literature [18]. The CF$_3$NO was also analyzed for the presence of the dimer, (CF$_3$)$_2$NONO, and NO$_2$ by UV-Visible absorption spectroscopy. (CF$_3$)$_2$NONO was monitored at 372 nm, where the absorption cross section is $6.38 \times 10^{-20}$ cm$^2$ [19]; the CF$_3$NO absorption cross section at 372 nm is a factor of 640 lower [20]. The upper limit mole fraction of dimer present was determined to be 0.05%. No NO$_2$ absorption features were observed in the visible region. The CF$_3$NO gas was used without further purification.

**Results and Discussion**

All experiments were carried out under pseudo-first-order conditions with CF$_3$NO in large excess over O($^3$P). Thus, in the absence of secondary reactions which enhance or deplete the O($^3$P) atom concentration, the O($^3$P) atom temporal profile is dominated by the reactions

\begin{equation}
O(^3P) + CF_3NO \longrightarrow \text{products}
\end{equation}

\begin{equation}
O(^3P) \longrightarrow \text{loss by diffusion from the detector field of view and/or reaction with background impurities.}
\end{equation}

The background O($^3$P) loss rate, $k_5$, was typically 35–45 s$^{-1}$ for $P = 100$ torr. The reaction of O($^3$P) with O$_3$ can be neglected as an O($^3$P) atom loss mechanism since the rate coefficient is small [2] and O$_3$ concentrations were relatively low (Table I). Similarly, generation of O($^3$P) by reaction (1) can be neglected. Integration of the rate equations for the above scheme yields the following simple relationship:

\begin{equation}
\ln\left(S_0/S_t\right) = (k_2[CF_3NO] + k_5)t = k_2't
\end{equation}

In eq. (I), $S_0$ is the O($^3$P) fluorescence signal at a time shortly after the laser fires and $S_t$ is the O($^3$P) fluorescence signal at time $t$. The bimolecular rate coefficient, $k_2$, is determined from the slope of a $k_2$ vs. [CF$_3$NO] plot.

For the O($^3$P) + CF$_3$NO reaction, the O($^3$P) temporal profiles were found to be exponential and the O($^3$P) decay rates were found to increase linearly with increasing CF$_3$NO concentration, i.e., the kinetic observations are consistent with eq. (I). The observed pseudo-first-order decay rates were found to be independent of laser photon fluence and O$_3$ concentration. This set of observations, coupled with the photometric
The reaction of $\text{O}^{(3P)}$ with $\text{CF}_3\text{NO}$

TABLE I. Kinetic data for the reaction of $\text{O}^{(3P)}$ with $\text{CF}_3\text{NO}$.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Press. (torr)</th>
<th>Concentrations$^a$</th>
<th>Laser Fluence (mJ/cm$^2$)</th>
<th>Number of Expts.$^c$</th>
<th>$k_2^{max}$ (s$^{-1}$)</th>
<th>$10^{13} k_2^d$ (cm$^3$ molecule$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>243</td>
<td>100</td>
<td>22. 0.29 $523-5150$</td>
<td>1.0</td>
<td>5</td>
<td>1550</td>
<td>$4.75 \pm 0.17$</td>
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<tr>
<td>264</td>
<td>100</td>
<td>20. 0.24 $376-2700$</td>
<td>0.9</td>
<td>5</td>
<td>1540</td>
<td>$5.43 \pm 0.25$</td>
</tr>
<tr>
<td>296</td>
<td>25</td>
<td>10. 1.4 $195-1130$</td>
<td>11.</td>
<td>5</td>
<td>914</td>
<td>$7.13 \pm 0.10$</td>
</tr>
<tr>
<td>297</td>
<td>100</td>
<td>7.1 0.27 $227-1176$</td>
<td>3.0</td>
<td>7</td>
<td>896</td>
<td>$7.14 \pm 0.05$</td>
</tr>
<tr>
<td>298</td>
<td>100</td>
<td>7.1 0.27 $4560-156000$</td>
<td>1.1</td>
<td>5</td>
<td>10570</td>
<td>$6.69 \pm 0.80$</td>
</tr>
<tr>
<td>299</td>
<td>100</td>
<td>7.1 0.27 $583-2270$</td>
<td>0.3</td>
<td>4</td>
<td>1720</td>
<td>$7.24 \pm 0.44$</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>7.1 0.27 $575-2410$</td>
<td>4.4</td>
<td>4</td>
<td>1710</td>
<td>$6.93 \pm 0.62$</td>
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<tr>
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<td>100</td>
<td>7.1 0.27 $532-2180$</td>
<td>1.7</td>
<td>5</td>
<td>1560</td>
<td>$6.84 \pm 0.35$</td>
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<tr>
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<td>100</td>
<td>7.1 0.27 $256-759$</td>
<td>10.0</td>
<td>5</td>
<td>759</td>
<td>$6.42 \pm 0.44$</td>
</tr>
<tr>
<td>316</td>
<td>100</td>
<td>7.1 0.27 $510-1840$</td>
<td>1.4</td>
<td>5</td>
<td>938</td>
<td>$8.91 \pm 0.27$</td>
</tr>
<tr>
<td>324</td>
<td>100</td>
<td>7.1 0.27 $122-1210$</td>
<td>1.6</td>
<td>6</td>
<td>1620</td>
<td>$12.6 \pm 0.93$</td>
</tr>
</tbody>
</table>

$^a$Concentration units are $10^{12}$ molecules cm$^{-3}$.

$^b$CF$_3$NO concentration based on in situ UV photometry at 202.6 nm.

$^c$Experiment = measurement of one $\text{O}^{(3P)}$ temporal profile.

$^d$Errors are 2σ and represent precision only.

$^e$CF$_3$NO concentration based on in situ visible photometry at 633 nm.

Impurity analyses described above, strongly supports the contention that reactions (2), (4), and (5) are the only processes which affected the post-laser-flash $\text{O}^{(3P)}$ time history in these experiments.

Results from our study of reaction (2) are summarized in Table I. Experiments at room temperature (296-301 K) were performed with variations in laser fluence (0.3-11 mJ cm$^{-2}$), O$_3$ concentration (4.4-56 x 10$^{12}$ molecule cm$^{-3}$), initial O$^{(3P)}$ concentration (0.17-1.4 x 10$^{12}$ atoms cm$^{-3}$), and N$_2$ pressure (25, 100, and 400 torr). The rate coefficient, $k_2$, is found to be independent of pressure over the range 25-400 torr and at 298 K has the value $k_2(298\text{ K}) = (6.98 \pm 0.39) \times 10^{-13}$ cm$^3$ molecule$^{-1}$s$^{-1}$ (errors are 2σ, precision only). $k_2$ was found to increase with increasing temperature over the range 243-424 K. Typical O$^{(3P)}$ temporal profiles are shown in Figure 1 while $k_2$ vs. [CF$_3$NO] plots for data taken at 264 K, 299 K, and 424 K and P = 100 torr are shown in Figure 2.

An Arrhenius plot for reaction (2) is shown in Figure 3. A linear least-squares analysis of the ln $k_2$ vs. 1/T data gives the Arrhenius expression

$$k_2(T) = (4.54 \pm 0.70) \times 10^{-12} \exp\left((-560 \pm 46)/T\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$  

Errors in the above expression are 2σ and represent precision only. The estimated absolute uncertainty (2σ) in $k_2(T)$ at any temperature within the range of this study is ±20%. To our knowledge, there have been no previous kinetics studies of the O$^{(3P)}$ + CF$_3$NO reaction with which to compare our results.

Possible sources of systematic error in this study include secondary reactions arising from the 266 nm photolysis of CF$_3$NO

$$\text{CF}_3\text{NO} + h\nu(266\text{ nm}) \rightarrow \text{CF}_3 + \text{NO}.$$  

Both photolysis products, CF$_3$ and NO, consume O$^{(3P)}$.
Figure 1. Typical $\text{O}_3^3\text{P}$ temporal profiles. Experimental conditions: $T = 299$ K; $P = 100$ torr $N_2$; $[\text{O}_3] = 5.6 \times 10^{13}$ molecules cm$^{-3}$; $[\text{O}(^3\text{P})] = 2.2 \times 10^{11}$ atoms cm$^{-3}$; $[\text{CF}_3\text{NO}]$ in units of $10^{15}$ molecules cm$^{-3}$ = (a) 0.0, (b) 5.93, and (c) 22.7; number of laser shots averaged = (a) 2000, (b) 1500, and (c) 4000. Solid lines are obtained from least-squares analyses and give the following pseudo-first-order decay rates in units of s$^{-1}$: (a) 44, (b) 489, and (c) 1720.

Figure 2. Plots of $k'_2$ vs. $[\text{CF}_3\text{NO}]$ for data obtained at $T = 424$ K, 299 K, and 264 K and $P = 100$ torr. Solid lines are obtained from linear least-squares analyses and give the following rate coefficients in units of $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$: 5.43 ± 0.25 at 264 K, 7.24 ± 0.44 at 299 K, and 12.6 ± 0.93 at 424 K; errors are 2σ, precision only.
Figure 3. Arrhenius plot for the $\text{O}(^3\text{P}) + \text{CF}_3\text{NO}$ reaction. Solid line is obtained from a least-squares analysis of all data. Circles are data obtained at $P = 100$ torr. The triangle and square are data obtained at $P = 25$ and 400 torr, respectively. The diamond is data obtained at 100 torr with [CF$_3$NO] determined in situ by visible photometry at 632.8 nm. Error bars are $2\sigma$ and represent precision only.

However, at 298 K and 400 torr total pressure, reaction (7) is approximately 30 times faster than reaction (8) (with $k_7 = 3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ [20] and $k_8(400\text{ torr}) = 9.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ [2]). Even at the highest laser fluence and CF$_3$NO concentrations used (11 mJ/cm$^2$ and $1.13 \times 10^{12}$ molecule cm$^{-3}$), the initial CF$_3$ concentration is only $1.2 \times 10^{11}$ molecule cm$^{-3}$ because of a low CF$_3$NO absorption cross section at 266 nm ($1.34 \times 10^{-21}$ cm$^2$ [21]). Thus, the pseudo-first-order decays do not require correction for reactions (7) and (8).

Another possible source of systematic error is $\text{O}(^3\text{P})$ consumption from impurities present in the CF$_3$NO sample. In particular, exposure of CF$_3$NO to light results in production of (CF$_3$)$_2$NONO ($\text{O}$-nitrosobis(trifluoromethyl)hydroxylamine). The rate coefficient for reaction (9) is unknown.

\begin{equation}
\text{O}(^3\text{P}) + (\text{CF}_3)_2\text{NONO} \rightarrow \text{products}
\end{equation}

To assess the potential role of reaction (9) as a kinetic interference in our study of reaction (2), a crude measurement of $k_9$ was carried out. A sample of CF$_3$NO in a 1-liter pyrex bulb was irradiated for 90 h with a tungsten-halogen lamp; a glass cut-off filter prevented radiation at wavelengths shorter than 580 nm from entering the bulb, thus minimizing secondary photolysis of CF$_3$NO photo-products. UV-visible spectral analysis of the sample after irradiation (and degassing at 77K) showed that (CF$_3$)$_2$NONO and NO$_2$ were present at approximately a 20:1 concentration ratio, and that about 85% of the CF$_3$NO was converted to (CF$_3$)$_2$NONO. Mason [22] has reported observation of CF$_3$NO$_2$, CF$_3$NF, (CF$_3$)$_2$NO, NO$_2$, NO, N$_2$O, CO$_2$, and SiF$_4$ as minor products of the photochemical degradation of CF$_3$NO. When the laser flash photolysis-resonance fluorescence technique was employed to study the kinetics of the reaction of $\text{O}(^3\text{P})$ with the irradiated mixture, an apparent rate coefficient
of $2.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$ was obtained; this rate coefficient was found to be independent of pressure (25–100 torr) and temperature (298–369 K). Considering that the O($^3P$) + NO$_2$ rate coefficient is approximately $1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$ over the temperature range of this study [2], these observations suggest that $k_9 < 3 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$. Therefore, in our studies it was always the case that $k_2/k_9 \geq 0.016$ (see Table I). Since the spectrophotometric analyses discussed above demonstrated that the mole fraction of (CF$_3$)$_2$NONO in the CF$_3$NO sample was $\leq 0.0005$, we conclude that reaction (9) could contribute no more than a few percent to observed reactivity in the low temperature studies of reaction (2) and even less at higher temperatures.

Excited state chemistry also represents a potential source of systematic error. The quenching of O$_2$(a$^1\Delta_g$) by CF$_3$NO is believed to occur via an excitation transfer mechanism which forms a low-energy CF$_3$NO* triplet state [3]. Reaction of O$_3$ with CF$_3$NO* could yield O($^3P$) (10)

$$\text{CF}_3\text{NO}^* + \text{O}_3 \rightarrow \text{O}^{(3P)} + \text{O}_2 + \text{CF}_3\text{NO}$$

It is, however, very unlikely that reaction (10) occurs. It is not energetically favored; the O–O$_2$ bond dissociation energy in O$_3$ is 25.5 kcal mol$^{-1}$ which is 3.0 kcal mol$^{-1}$ higher than the electronic energy possessed by O$_2$(a$^1\Delta_g$). Furthermore, vibrational relaxation of CF$_3$NO would be expected to compete favorably with the CF$_3$NO* + O$_3$ reaction under the conditions of our experiments, i.e., [N$_2$]/[O$_3$] $> 10^5$.

Using a $\Delta H^\circ$ value for CF$_3$NO of $-132.2$ kcal mol$^{-1}$ (obtained from a shock tube study of the thermal dissociation of CF$_3$NO [23]), there appear to be four energetically accessible product channels for reaction (2):

$$\begin{align*}
(2a) & \quad \text{O}^{(3P)} + \text{CF}_3\text{NO} \rightarrow \text{CF}_3 + \text{NO}_2 \quad \Delta H = -31.5 \text{ kcal mol}^{-1} \\
(2b) & \quad \quad \quad \quad \quad \quad \quad \rightarrow \text{CF}_2\text{O} + \text{FNO} \quad \Delta H = -96.4 \text{ kcal mol}^{-1} \\
(2c) & \quad \quad \quad \quad \quad \quad \quad \rightarrow \text{CO}_2 + \text{NF}_3 \quad \Delta H = -52.9 \text{ kcal mol}^{-1} \\
(2d) & \quad \quad \quad \quad \quad \quad \quad \rightarrow \text{CF}_3\text{NO}_2 \quad \Delta H \neq ?
\end{align*}$$

The results reported in this study do not provide information concerning the product branching ratio, although reactions (2a) and/or (2b) would appear to be the most likely reaction channel(s). The observed independence of $k_2$ to significant variations in pressure argues against the occurrence of reaction (2d) while the large number of (very strong) chemical bonds which must be broken and formed argues against the occurrence of channel (2c). Further studies aimed at quantitative detection of reaction products would be of interest.

**Summary**

The laser flash photolysis-resonance fluorescence technique has been employed to study the temperature dependence of the thermal rate coefficient for reaction (2); this represents the first kinetics study of the O($^3P$) + CF$_3$NO reaction. The temperature dependence of $k_2$ is adequately described by the following Arrhenius expression:

$$k_2 = (4.54 \pm 0.70) \times 10^{-12} \exp[-(-560 \pm 46)/T] \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$ 

The absolute uncertainty in the measured rate coefficient at any temperature within the range studied is estimated to be $\pm 20\%$. Reaction (2) is sufficiently fast to preclude use of CF$_3$NO as a selective quencher for O$_3$(a$^1\Delta_g$) in laboratory systems where O($^3P$) kinetics are being investigated.
REACTION OF O(3P) WITH CF3NO

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Laser flash photolysis studies of radical–radical reaction kinetics: The O\(^{(3P)}\) + BrO reaction

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A novel dual laser flash photolysis-long path absorption-resonance fluorescence technique has been employed to study the kinetics of the important stratospheric reaction \(\text{O}^{(3P)} + \text{BrO} \rightarrow \text{Br}^{(2P)} + \text{O}_2\) as a function of temperature (231-328 K) and pressure (25-150 Torr) in N\(_2\) buffer gas. The experimental approach preserves the principal advantages of the flash photolysis method, i.e., complete absence of surface reactions and a wide range of accessible pressures, but also employs techniques which are characteristic of the discharge flow method, namely chemical titration as a means for deducing the absolute concentration of a radical reactant and use of multiple detection axes. We find that \(k_1\) is independent of pressure, and that the temperature dependence of \(k_1\) is adequately described by the Arrhenius expression

\[
k_1(T) = 1.91 \times 10^{-11} \exp(230/T) \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1};
\]

the absolute accuracy of measured values for \(k_1\) is estimated to vary from \(\pm 20\%\) at \(T=230\) K to \(\pm 30\%\) at \(T=330\) K. Our results demonstrate that the \(\text{O}^{(3P)} + \text{BrO}\) rate coefficient is significantly faster than previously "guesstimated," and suggest that the catalytic cycle with the \(\text{O}^{(3P)} + \text{BrO}\) reaction as its rate-limiting step is the dominant stratospheric BrO₃ odd-oxygen destruction cycle at altitudes above 24 km.

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I. INTRODUCTION

The reaction of ground state oxygen atoms, \(\text{O}^{(3P)}\), with BrO radicals is the rate determining step in a catalytic cycle via which bromine destroys odd oxygen in the middle stratosphere:\(^1-3\)

\[
\begin{align*}
\text{O}^{(3P)} + \text{BrO} & \rightarrow \text{Br}^{(2P)} + \text{O}_2 & (1) \\
\text{Br}^{(2P)} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 & (2)
\end{align*}
\]

Net: \(\text{O}^{(3P)} + \text{O}_3 \rightarrow 2\text{O}_2\).

Reactive BrO radicals are produced in the stratosphere primarily by photodissociation of methyl bromide (CH\(_3\)Br) and the halons CF\(_3\)Br, CF\(_2\)ClBr, and CF\(_2\)BrCF\(_2\)Br.\(^4\)

No direct measurements of \(k_1\) have been reported, although Clyne et al. obtained the estimate \(k_1(298\text{ K}) = 2.5 \times 10^{-11} \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}\) (factor of 2 reported uncertainty) based on observation of secondary \(\text{O}^{(3P)}\) consumption and \(\text{Br}^{(2P)}\) production in a study of \(\text{O}^{(3P)} + \text{Br}_2\) kinetics.\(^5\) High quality kinetic data for reaction (1) are needed to facilitate quantitative understanding of the role of the above catalytic cycle in stratospheric chemistry. Furthermore, reaction (1) is a likely side reaction in laboratory studies of the Br\(_2\)–O\(_2\) photochemical system, so knowledge of \(k_1(T)\) would assist interpretation of experiments designed to study other important BrO₃ reactions. Finally, comparison of kinetic data for reaction (1) with available data for other \(\text{O}^{(3P)} + \text{XO}\) reactions (X = Cl, O\(_3\), H\(_2\)O, ... )\(^6\) could prove useful for refining theoretical procedures for calculating radical–radical reaction rates.

In this paper we report the results of a direct kinetics study of reaction (1) as a function of temperature (231-328 K) and pressure (25-150 Torr). A dual laser flash photolysis-long path absorption-resonance fluorescence technique (DLFP-LPA-RF) has been employed in our study. This novel experimental approach, which features simultaneous time-resolved detection of BrO (by long path absorption) and \(\text{O}^{(3P)}\) (by atomic resonance fluorescence) has evolved from our earlier studies of \(\text{O}^{(3P)} + \text{H}_2\text{O}\) (Refs. 7 and 8) and \(\text{O}^{(3P)} + \text{ClO}\) (Ref. 9) reaction kinetics. We find that, under midstratospheric conditions, reaction (1) is considerably faster than previously thought; the implications of this result for stratospheric BrO₃ chemistry are discussed.

II. EXPERIMENTAL TECHNIQUE AND KINETIC SCHEME

The DLFP-LPA-RF technique preserves the principal advantages of the flash photolysis method, i.e., the complete absence of side reactions catalyzed by wall surfaces and a wide range of accessible pressures, while also incorporating some advantages normally associated with the discharge
flow method, namely chemical titration as a means for deducing the absolute concentration of a radical reactant and employment of multiple detection axes. Although the two free radical reactants cannot be generated in spatially separated regions (as they can in the discharge flow method), some chemistry complications can be avoided by controlling the time delay between generation of the two reactants. Because the experimental approach is to some extent dictated by the nature of secondary chemistry complications, the experimental technique and the kinetic scheme are best presented in a single section of the paper.

Consider a mixture of $N_2$, $O_3$, and $Br_2$ with $[N_2] >> [O_3] >> [Br_2]$. When this mixture is subjected to flash photolysis at 248.4 nm (KrF laser), the only species which undergoes significant photodissociation is $O_3$:

$$O_3 + h\nu(248.4 \text{ nm}) \rightarrow O(1^2D_2) + O_2(a^1\Delta_g)$$  \hspace{1cm} (3a)

$$\rightarrow O(3P_f) + O_2(X^1\Sigma_g^-)$$  \hspace{1cm} (3b)

The yields of singlet and triplet photoproducts are 0.91 and 0.09, respectively. Since $N_2$ is present in large excess over $O_3$ and $Br_2$, essentially all $O(1^2D_2)$ generated by the photoflash is rapidly quenched by $N_2$:

$$O(1^2D_2) + N_2 \rightarrow O(3P_f) + N_2.$$  \hspace{1cm} (4)

The rate coefficient for the quenching reaction at 298 K is $k_q = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with little or no temperature variation. Suppose that the concentration of oxygen atoms created by the photoflash is greater than the concentration of $Br_2$ initially present in the reaction mixture, then $Br_2$ can be titrated to $BrO$ via the following reactions:

$$O(3P_f) + Br_2 \rightarrow BrO + Br(2P_{\frac{1}{2}})$$  \hspace{1cm} (5)

Br$(2P_{\frac{3}{2}}) + O_3 \rightarrow BrO + O_2.$  \hspace{1cm} (2)

Reaction (5) is sufficiently exothermic to generate atomic bromine in the spin–orbit excited electronic state $Br(2P_{\frac{3}{2}})$. However, if experimental conditions are maintained where $[N_2] >> [O_3]$, then relaxation of $Br(2P_{\frac{3}{2}})$ to $Br(2P_{\frac{1}{2}})$ via collisions with $N_2$ is rapid compared to the time scale for $Br(2P_{\frac{3}{2}})$ reaction. Any excess $O(3P_f)$ remaining after consumption of all $Br_2$ would be expected to react with $O_3$ directly via reaction (6) or (primarily) via the catalytic cycle composed of reactions (1) and (2):

$$O(3P_f) + O_3 \rightarrow 2O_2.$$  \hspace{1cm} (6)

If the chemistry in the $O_3$–$Br_2$–$N_2$ photolysis system were completely described by reactions (1)–(6), and if experimental conditions could be adjusted such that the rate of $O(3P_f)$ consumption by the slow reaction (6) was negligible compared to its rate of consumption by $Br_2$ and $BrO$, then $k_1$ could be evaluated based on measurements of the $O(3P_f)$ decay rate at long times after the laser flash when $Br_2$ had been quantitatively converted to $BrO$; under such conditions the decay of $O(3P_f)$ would be essentially pseudo-first-order since $BrO$ lost by reaction with $O(3P_f)$ would be regenerated via reaction (2). Unfortunately, the following side reactions complicate the measurement of $k_1$:

$$BrO + BrO \rightarrow 2Br(2P_f) + O_2.$$  \hspace{1cm} (7a)

$$O_2(a^1\Delta_g) + O_3 \rightarrow O(3P_f) + 2O_2.$$  \hspace{1cm} (7b)

Reaction (7) is moderately fast [$k_7(298 \text{ K}) = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]; both the absolute rate coefficient and the branching ratio for reaction (7) are well established over the range of temperature employed in this study. Fortunately, regeneration of $Br_2$ via reaction (7) is relatively slow because reaction (7b) is the minor channel. Although it is quite slow [$k_7(298 \text{ K}) = 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $E_a = 5.65 \text{ kcal mol}^{-1}$], reaction (8) has a profound effect on observed $O_3(P_f)$ temporal profiles. Instead of decaying rapidly to zero concentration via reactions (1) and (5), the $O_3(P_f)$ concentration reaches a near-steady-state level at long times after the laser flash where loss via reactions (1) and (5) is counterbalanced by production via reaction (8). The occurrence of reaction (8) severely complicates the evaluation of $k_1$, from observations of $O_3(P_f)$ kinetics.

One approach for circumventing the kinetic complications caused by the occurrence of reaction (8) is to identify a quencher which efficiently converts $O_2(a^1\Delta_g)$ to $O_2(X^1\Sigma_g^-)$ but does not otherwise interfere with the chemistry under investigation. Rate coefficients for quenching of $O_2(a^1\Delta_g)$ by small molecules are typically very slow ($10^{-16} - 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for many quenching reactions which have been studied). One exception is $CF_3NO$, which quenches $O_2(a^1\Delta_g)$ very efficiently [$k(298 \text{ K}) = 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]. We find that $CF_3NO$ also reacts rapidly with $O_3(P_f)$ [$k(298 \text{ K}) = 6.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]. Hence, a suitable $O_2(a^1\Delta_g)$ quencher for use in our kinetics experiments could not be identified.

A second more successful approach for circumventing the kinetic complications caused by the occurrence of reaction (8) involves the use of a second photolysis laser. Once the concentration of $O_3(P_f)$ has reached its near-steady-state level (typically 10–50 ms after the KrF laser fires) a second pulsed laser operating at 532 nm (second harmonic, Nd: YAG laser) photolyzes a small fraction of the remaining ozone:

$$O_3 + h\nu(532 \text{ nm}) \rightarrow O(3P_f) + O_2.$$  \hspace{1cm} (9)

Computer simulations employing typical experimental conditions strongly suggest that the decay of the additional $O_3(P_f)$ produced by the 532 nm laser back to the near-steady-state level is dominated by reaction (1). A schematic diagram of the DLFP-LPA-RF apparatus is shown in Fig. 1, and important experimental details are discussed below. A jacketed borosilicate glass reaction cell was used in all experiments. Thermostated liquids (ethylene glycol–water mixture or methanol) were circulated through the jacket to control the reaction cell temperature (for the sake of clarity, the jacket is not shown in Fig. 1). Measurement of the temperature in the reaction zone under the precise pressure and flow conditions of the experiment was accomplished as described previously. The main body of the reaction cell was a 29.5 cm by 21.5 cm cross which was 4.0 cm in diameter. The longer axis was used for $BrO$ detection while the pho...
tolysis lasers counterpropagated along the shorter axis. At the center of the cell were three additional 1.5-cm-i.d. sidearms. Radiation from an atomic resonance lamp entered the cell through the upper sidearm and exited through the lower sidearm. The resonance fluorescence signal was collected through the third sidearm, which was in the same plane as the BrO and photolysis axes.

The KrF laser (248.4 nm) could deliver up to $1 \times 10^{18}$ photons per pulse at a repetition rate of $\leq 10$ Hz; the pulse width was 25 ns. The laser beam was passed through a beam expanding telescope, then reflected off a segmented aperture optical integrator (SAOI) and an aluminum mirror into the reaction cell. A 1-cm-wide aperture selected only the central, most spatially uniform section of the beam. The use of the SAI to obtain spatially uniform photolysis laser beams is discussed in earlier publications from our laboratory.7 The fluence of the 248.4 nm laser beam was measured using a photodiode-based radiometer which was capable of measuring individual pulses. Immediately before and after acquisition of each temporal profile, 20 laser shots were averaged to obtain a statistically meaningful laser fluence. For this measurement, the aluminum mirror was moved out of the beam path and the radiometer was positioned the same distance from the mirror as was the center of the reaction cell. The fluence at the center of the reaction cell was taken to be the fluence measured by the radiometer corrected for losses upon reflection off the aluminum mirror, transmission through the reaction cell entrance window, and reflection off the reaction cell exit window. Calibration of the radiometer was achieved using an ozone actinometry technique which is described in detail elsewhere.1

The second harmonic Nd:YAG laser (532 nm) could deliver up to $3 \times 10^{17}$ photons per pulse at repetition rates of $10/n$ Hz ($n = 1, 2, 3, ...$); the pulse width was approximately 7 ns. The 532 nm beam was much smaller than the optically integrated 248.4 nm beam. It propagated through the middle of the region irradiated by the 248.4 nm beam.

The triggering scheme used for synchronizing the firing of the excimer laser, the Nd:YAG laser, and the signal acquisition electronics was somewhat more complex than suggested schematically in Fig. 1. The design of the triggering scheme was based on the requirements that (1) the Nd:YAG laser flash lamps must flash at a rate of 10 Hz while chemistry considerations (see below) require a much lower repetition rate for the two-laser sequence passing through the reactor and (2) the Nd:YAG laser must be Q-switched approximately 3.2 ms after triggering of the Nd:YAG laser firing sequence, but only for the small fraction of flash lamp firings when second-harmonic radiation is desired. A schematic diagram containing details of the triggering scheme, which requires a pulse generator, two digital delay generators, and a divider network, is shown elsewhere.21

The concentration of BrO was monitored using multipass UV absorption at 338.3 nm, the peak of the strong 7-0 band of the $A^2\Pi \rightarrow X^2\Sigma$ system. Details of the technique and its application to BrO detection are discussed elsewhere.22 To minimize photolysis of O$_3$ by the xenon arc lamp probe light source, a Pyrex filter was inserted between the arc lamp and the multipass optics. Reflective losses in the multipass system were minimized by using White cell mirrors coated for high reflectivity around 338 nm and reaction cell windows coated for maximum transmission around 338 nm. In preliminary experiments, absorption of multipass radiation by molecular chlorine at 330, 338, and 346 nm was employed to test the effective multipass absorption path length. At all three wavelengths, the path length calculated from the Cl$_2$
absorption measurements was equal within a few percent to the path length estimated by multiplying the measured length of the reaction cell by the number of passes (evaluated by counting the UV spots impinging on a piece of fluorescent paper moved across the White cell mirrors). Typically, the White cell was adjusted for 30 passes. As discussed above, a mask limited the width of the 248.4 nm photolysis beam to 1.0 cm, thus giving an absorption path length for BrO detection of 30 cm. One other modification from our earlier approach\(^2\) was the installation of masks with a 1.9 cm height aperture at both reaction cell windows along the BrO detection axis; this ensured complete spatial overlap of the BrO detection volume and the 248.4 nm photolysis region. The slits on the 0.22 m monochromator which isolated 338.3 nm radiation were each set at widths of 100 \(\mu\)m, giving a resolution of 0.36 nm; this monochromator resolution is very close to the 0.4 nm resolution employed to obtain the best available measurements of BrO absorption cross sections.\(^{24}\)

Since we find that the observed BrO absorption cross section at 338.3 nm is independent of resolution within the range 0.25–0.50 nm, the BrO absorption cross section values at 338.3 nm of 1.55 \(\times 10^{-17}\) \(\text{cm}^2\) at 298 K and 1.95 \(\times 10^{-17}\) \(\text{cm}^2\) at 223 K which were reported by Wahner et al.\(^24\) can be used to convert the measured BrO absorbance to a concentration (as long as the absorption path length is accurately known).

Radiation exiting the monochromator was detected by a photomultiplier, the time-dependent output from which was monitored on channel A of a dual channel signal averager with 1.5 \(\mu\)s time resolution and 10 bit voltage resolution.

Time-resolved detection of \(O(3\,P_J)\) was accomplished using the resonance fluorescence technique.\(^7\)–\(^9\),\(^11\),\(^18\) An atomic resonance lamp, mounted above the reaction cell and perpendicular to both the photolysis and BrO detection axes, excited resonance fluorescence in photolytically generated \(O(3\,P_J)\) atoms. The resonance lamp consisted of an electrodeless microwave discharge through about 1 Torr of a flowing mixture containing a trace of \(O_2\) in He. The vacuum-UV resonance radiation (at about 130 nm) was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. The region between the lamp window and the cell lens was purged with dry \(N_2\). Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to the resonance lamp beam and imaged onto the photocathode of a solar blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with dry \(N_2\); in addition, a calcium fluoride window was inserted into this region to prevent detection of Lyman-\(a\) emission from hydrogen impurity in the lamp discharge. Signals were processed using photon counting techniques in conjunction with multichannel scaling. Channel B of the dual channel signal averager could be operated in the multichannel scaling mode (for \(O(3\,P_J)\) detection) while, simultaneously, channel A was operated in the analog mode (for BrO detection).

Typically, 256–1024 pairs of flashes were averaged to obtain \(O(3\,P_J)\) and BrO temporal profiles with sufficient signal to noise to allow quantitative kinetic analysis. The shot-to-shot stability of the 248.4 nm laser was about \(\pm 10\%\). Because BrO was produced under conditions where \([O(3\,P_J)] > [Br_2]_0\), i.e., under conditions where \(Br_2\) was titrated to BrO, 10% fluctuations in 248.4 nm laser power result in very small shot-to-shot variations in the BrO concentration temporal profile.

In order to avoid accumulation of reaction or photolysis products, all experiments were carried out under "slow flow" conditions. To promote spatial uniformity of concentrations and minimize regions of flow stagnation, each of the four ends of the reaction cell had a port. The gas mixture entered the reaction cell through the two ports on the BrO probe beam axis and exited through the two ports on the laser photolysis axis. This flow pattern exhausted the long-lived BrO radicals from the BrO detection volume more rapidly than if the reaction mixture had exited along the BrO detection axis. The linear flow rate through the reaction cell was (typically) \(3.5\) cm s\(^{-1}\). The repetition rate of the two laser sequence varied from 1/8 Hz at \(P = 25\) Torr to 1/5 Hz at \(P > 100\) Torr. These rates were determined by observing the time required for the BrO signal to return to the pretrigger baseline value under typical experimental conditions.

As shown in Fig. 1, the \(O_3\), \(Br_2\), and \(N_2\) gases were premixed before entering the reaction cell. The concentrations of \(Br_2\) and \(N_2\) in the reaction mixture were determined through measurement of the appropriate mass flow rates and the total pressure. The fraction of \(Br_2\) in the \(Br_2-N_2\) mixture, which was prepared manometrically in a 12 \(\ell\) bulb, was measured by photometry at 404.7 nm as described previously.\(^{22}\) Ozone was flowed from a U-tube containing \(O_3\) adsorbed on silica gel and maintained at dry ice temperature (195 K); nitrogen was passed through the U-tube to obtain a stable \(O_3-N_2\) flow. The ozone concentration was measured in \(situ\) in the slow flow system by UV photometry at 253.7 nm using an Hg pen-ray lamp as the light source and a 30.2 cm absorption cell positioned between the mixing cell and the reaction cell; interference from absorption of 253.7 nm radiation by \(Br_2\) was negligible for the reaction mixtures employed \(([O_3] = [Br_2])\). Conversion of measured ozone absorbances to concentrations employed an \(O_3\) absorption cross section of 1.145 \(\times 10^{-17}\) \(\text{cm}^2\) at 253.7 nm.\(^{25}\)

The gases used in this study had the following stated minimum purities: \(N_2\), 99.999%; and \(O_2\), 99.99%; they were used as supplied. Ozone was prepared by passing \(O_2\) through a commercial ozonator. It was collected and stored on refrigeration grade silica gel maintained at a temperature of 195 K. The \(Br_2\) used in this study had a stated minimum purity of 99.94%. It was transferred under nitrogen atmosphere into a glass vial fitted with a high vacuum stopcock, and then was degassed repeatedly at 77 K before being used to prepare \(Br_2-N_2\) mixtures.

**III. RESULTS**

Observed \(O(3\,P_J)\) fluorescence and BrO absorbance temporal profiles for a typical experiment are shown in Fig. 2; in this typical experiment, the time delay between the two lasers was 25 ms. At short times, i.e., \(t < 5\) ms for the data shown in Fig. 2, the \(O(3\,P_J)\) concentration is very high, causing the fluorescence signal to be influenced by radiation trapping effects. Thus, the fluorescence signal is proportional to the \(O(3\,P_J)\) concentration only after the signal has decayed...
significantly from its peak value. The approach to a near-steady-state \(O(3P_j)\) fluorescence level clearly occurs at \(t > 10\) ms. Firing of the 532 nm laser at \(t = 25\) ms results in only a modest increase in the \(O(3P_j)\) fluorescence signal because the ozone absorption cross section at 532 nm is quite low (2.8 \(\times 10^{-21}\) cm\(^2\)). The data in Fig. 2 show that during the first several ms after the 248.4 nm laser fires, BrO appearance "tracks" \(O(3P_j)\) disappearance. Disappearance of BrO at \(t = 8\) ms is presumably due to the occurrence of reaction (7b).

The \(O(3P_j)\) fluorescence signal (same data as in Fig. 2) immediately before and after firing of the 532 nm laser is shown in expanded form in Fig. 3. The solid "baseline" in Fig. 3 is obtained by fitting the data in the \(-10\) to \(-0.1\) ms and \(7-14\) ms time intervals to a double exponential function:

\[
\ln\left(\frac{S_t - S_{BL,0}}{S_t - S_{BL,1}}\right) = (k_4[BrO] + k_5[Br_2] + k_6[O_3])t = k't, 
\]

where \(t = 0\) is defined to be the time at which the 532 nm laser fired. The solid baseline was obtained from a double exponential fit to the data points in the intervals \(-10\) to \(-0.1\) ms and \(7-14\) ms where \(t = 0\) is the time the 532 nm laser fired.

Assuming that all processes contributing to \(O(3P_j)\) relaxation are first order or pseudo-first-order, the temporal behavior of the relaxation fluorescence signal should be described by the following relationship:

\[
\ln\left(\frac{S_t - S_{BL,0}}{S_t - S_{BL,1}}\right) = (k_4[BrO] + k_5[Br_2] + k_6[O_3])t = k't, 
\]

where \(t = 0\) is defined to be the time at which the 532 nm laser fires. \(S_0\) and \(S_t\) are the total signals at times 0 and \(t\), \(S_{BL,0}\) and \(S_{BL,1}\) are the baseline signals at times 0 and \(t\), and \(k_4\) is the rate coefficient for the following process:

\[
O(3P_j) \rightarrow \text{loss by diffusion and transport from the detection volume and by reaction with background impurities.}
\]

Equation (I) assumes that the concentrations of BrO, Br_2, and O_3 are constant over the time interval required for
TABLE 1. Assumed mechanism for simulation of \(O(P_a)\), BrO, \(Br(P_a)\), Br\(_2\), and 0\(_3\) temporal profiles.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction No.</th>
<th>(k)</th>
<th>(E/R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O(P_a) + BrO \rightarrow Br(P_a) + O)</td>
<td>(1)</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>(Br(P_a) + O \rightarrow BrO + O)</td>
<td>(2)</td>
<td>17</td>
<td>800</td>
</tr>
<tr>
<td>(O(P_a) + Br \rightarrow Br(P_a) + O)</td>
<td>(5)</td>
<td>17.6</td>
<td>-40</td>
</tr>
<tr>
<td>(O(P_a) + O_3 \rightarrow 2O)</td>
<td>(6)</td>
<td>8.0</td>
<td>2060</td>
</tr>
<tr>
<td>(Br + BrO \rightarrow 2Br(P_a) + O)</td>
<td>(7a)</td>
<td>1.4</td>
<td>-150</td>
</tr>
<tr>
<td>(Br_2 + BrO \rightarrow Br + Br(P_a) + O)</td>
<td>(7b)</td>
<td>0.9</td>
<td>-660</td>
</tr>
<tr>
<td>(O_3 + Br \rightarrow O + O(P_a) + 2O)</td>
<td>(8)</td>
<td>52.5</td>
<td>2840</td>
</tr>
<tr>
<td>(O(P_a) \rightarrow \text{bgnd. loss})</td>
<td>(10)</td>
<td>-10-40</td>
<td>0</td>
</tr>
</tbody>
</table>

*aArrhenius parameters are taken from Ref. 6 except where otherwise indicated.
*bUnits are 10\(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) except for reaction (10).
*cUnits are degrees Kelvin.
*dDetermined from experimental data using an iterative procedure (see the text).
*eFrom Ref. 29.
*fUnits are s\(^{-1}\); rate increases with decreasing pressure; values determined experimentally.

\[ [O(P_a)] \text{ relaxation: this is a good approximation, since the concentrations of all three species change by only a few percent over the time interval of interest. Since [O(P_a)] relaxation data were typically analyzed over 2–3 e-folding times of decay, we take the (measured or simulated) concentrations of BrO, Br\(_2\), and O\(_3\) at } t = t = 1/k \text{ to be the appropriate values for application of Eq. (1). Rate coefficients for reactions (5) and (6) are well established.}^{27,28} \text{ Values of } k_{10}(P,T) \text{ were determined experimentally by monitoring the decay of } O(P_a) \text{ following 532 nm laser flash photolysis of O}_3/\text{N}_2 \text{ mixtures; very low } O_3 \text{ levels were employed in these experiments in order to establish conditions where } k_{10}[O_3] < k_{10}. \text{ Measured values for } k_{10} \text{ ranged from 10 to 40 s}^{-1}; \text{ very little temperature dependence was observed, but } k_{10} \text{ increased with decreasing pressure.}

The bimolecular rate coefficients of interest, \(k_1(P,T)\), were evaluated from the slopes of \(k_{10}\) vs [BrO] plots where \(k_{10}\) is the measured pseudo-first-order decay rate corrected for contributions from Br\(_2\) and O\(_3\):

\[
k_{10} = k_1[Br_2] - k_6[O_3] = k_1[BrO] + k_{10}. \tag{II}
\]

Under the experimental conditions employed in this study, differences between \(k_1\) and \(k_{10}\) were dominated by reaction (5), i.e., reaction (6) made a negligible contribution to \([O(P_a)]\) relaxation. Values for \([BrO]\), \([Br_2]\), and \([O_3]\) as a function of time were determined using the ACUCHEM program\(^{29}\) to numerically integrate the rate equations (BrO) was, of course, also measured by time-resolved UV absorption). The mechanism assumed for the numerical simulations consisted of reactions (1), (2), (5), (6), (7a), (7b), (8), and (10). Literature values for the temperature-dependent rate coefficients used in the simulations are summarized in Table I. With the exception of \(k_1\), all other rate coefficients used in the simulations appear to be well established. Because \(k_1\) is highly uncertain, we employed an initial temperature-independent "guessimate" of \(3.0 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) in the simulations.\(^6\) Concentrations of Br\(_2\), Br\(_3\), and O\(_3\) were then calculated and used to obtain a new value for \(k_1\); subsequent iterations had no effect on the derived value for \(k_1\), i.e., convergence was obtained after a single iteration. Initial concentrations of \(O(P_a)\) and \(Br(P_a)\) for use in the simulations were computed from the measured 248.4 nm laser fluence, the measured O\(_3\) and Br\(_2\) concentration, and well-known O\(_3\) and Br\(_2\) absorption cross sections at 248.4 nm; the O\(_3\) absorption cross section was taken to be \(1.05 \times 10^{-17}\) cm\(^2\) independent of temperature\(^{30}\) while the Br\(_2\) absorption cross section was taken to be \(1.9 \times 10^{-20}\) cm\(^2\) (Ref. 31) (assumed to be independent of temperature). Compared to the amount of Br\(_2(P_a)\) generated from reactions (1) and (5), the amount generated from Br\(_2\) flash photolysis was very small, ranging from \(3 \times 10^9\) to \(2 \times 10^{10}\) atoms cm\(^{-3}\). Shown in Fig. 5 are simulated temporal profiles for Br\(_2\), Br\(_2(P_a)\), BrO, O\(_3\), and \(O(P_a)\) for the conditions employed to obtain the experimental data shown in Figs. 2 and 3.

FIG. 5. Simulated temporal profiles for Br\(_2\), Br\(_2(P_a)\), BrO, O\(_3\), and \(O(P_a)\) for the conditions employed to obtain the experimental data shown in Figs. 2 and 3. The simulations employ the mechanism and rate coefficients given in Table I. Assume \(t = 0\) is the time that the 248.4 nm laser fires, and ignore concentration changes induced by firing of the 532 nm laser.
FIG. 6. Typical plots of $k'$ and $k'_{\text{corr}}$ vs $[\text{BrO}]$, where $t' = t$ is defined as in Fig. 4 and $[\text{BrO}]$ is the average of concentrations deduced by computer simulations and by time-resolved UV absorption measurements. $T = 233$ K and $P = 50$ Torr. Open circles are uncorrected for $O(^{3}P_{J})$ reactions with Br and O, while solid squares are corrected for these reactions. Solid lines are obtained from linear least-squares analyses; their slopes give the rate coefficients shown in the figure in units of cm$^3$ molecule$^{-1}$ s$^{-1}$.

measurements are reported for only six of the twelve $P, T$ combinations for which data are reported. This is because a wavelength calibration error was discovered after some of the experiments were completed; hence, in some of the experiments, BrO was monitored in a wavelength interval which was slightly shifted off the peak of the 7.0 band. Rate coefficients based on UV absorption measurements of $[\text{BrO}]$

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$T$ (K) & $P$ (Torr) & $[O(^{3}P)]_L$ & $k'_{\text{corr}}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) \\
\hline
231 & 25 & 712-1140 & 3.97-24.0 \\
233 & 50 & 98-1150 & 7.56-32.8 \\
237 & 100 & 944-1160 & 5.05-21.9 \\
251 & 50 & 852-1070 & 8.02-35.4 \\
268 & 50 & 670-1210 & 8.94-37.2 \\
272 & 50 & 997-1310 & 6.39-24.8 \\
298 & 25 & 664-1250 & 7.01-25.2 \\
298 & 50 & 745-1050 & 7.60-24.8 \\
298 & 100 & 818-1030 & 4.94-18.1 \\
298 & 150 & 436-1050 & 6.23-25.5 \\
326 & 50 & 843-1020 & 8.40-25.6 \\
328 & 50 & 737-967 & 4.82-19.6 \\
\hline
\end{tabular}
\caption{Summary of experimental conditions in the $O(^{3}P_J)+\text{BrO}$ kinetics experiments.}
\end{table}

\begin{table}[h]
\centering
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\hline
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298 & 100 & 818-1030 & 4.94-18.1 \\
298 & 150 & 436-1050 & 6.23-25.5 \\
326 & 50 & 843-1020 & 8.40-25.6 \\
328 & 50 & 737-967 & 4.82-19.6 \\
\hline
\end{tabular}
\caption{Rate coefficients for the reaction $O(^{3}P_J)+\text{BrO} \rightarrow \text{Br}(^{2}P_J)+O_2$.}
\end{table}

Errors are $2\sigma$ and represent precision only. 
\*A: $[\text{BrO}]$ obtained from computer simulations using the mechanism in Table I. 
\*B: $[\text{BrO}]$ obtained from transient UV absorption measurements.

Examination of Table III shows that, within experimental uncertainty, $k_1(298 \text{ K})$ is independent of pressure over the range 25-150 Torr. Arrhenius plots of the $O(^{3}P_J)+\text{BrO}$ kinetic data are shown in Fig. 7. Separate plots are shown for rate coefficients obtained using (a) BrO concentrations obtained from Acuchem simulations, (b) BrO concentrations obtained from UV absorption measurements, and (c) BrO concentrations obtained from the average of the simulations and the UV absorption measurements. The lines in Fig. 7 are obtained from linear least-squares analyses of the $\ln k_1$ vs
nately, available laser powers and detection sensitivities as such as laser fluences and species concentrations. Unfortunately, available laser powers and detection sensitivities as well as constraints dictated by system chemistry limited the range over which important parameters could be varied. Nonetheless a series of experiments were carried out at $P=50$ Torr and $T=269$ K which verified that, for the same initial concentrations of $O(^3P)$ and $Br_2$, $k_{corr}$ was independent of a factor of 5 variation in $[O_3]$ (6-30x10$^4$ molecules cm$^{-3}$), a factor of 2 variation in 248.4 nm laser fluence (5-10 mJ cm$^{-2}$), and a factor of 1.5 variation in 532 nm laser fluence (130-195 mJ cm$^{-2}$). The range of 248.4 nm fluences was limited at the high end by the available laser power and at the low end by the need to generate enough $O(^3P)$ to rapidly titrate $Br_2$ to BrO, thus minimizing interference from the $O(^3P)+Br_2$ reaction. The range of 532 nm fluences was also limited at the high end by the available laser power. The lower limit 532 nm fluence was dictated by the requirement that $[O(^3P)]$ relaxation temporal profiles be obtained with signal-to-noise ratio suitable for quantitative kinetic analysis, even though the low repetition rate dictated by system chemistry prohibited extensive signal averaging.

Comparison of simulated (Fig. 5) and measured (Fig. 2) $O(^3P)$ and BrO temporal profiles shows qualitative but not quantitative agreement. The simulated $O(^3P)$ decay to the near-steady-state level is a little faster than observed experimentally while the simulated BrO appearance rate is a little slower than observed experimentally. Also, once near-steady-state conditions are established, the observed $O(^3P)$ fluorescence signal continues to decay slowly whereas the simulation predicts that $[O(^3P)]$ remains constant or even increases slightly as a function of time; one possible explanation for this difference between observation and simulation would be the existence of a significant (unidentified) $O_2(a^1Delta)$ destruction mechanism other than reaction with $O_3$; an additional first-order $O_2(a^1Delta)$ loss rate of about 90 s$^{-1}$ would yield the best agreement between simulation and experiment. While quantitative differences between simulated and observed $O(^3P)$ and BrO temporal profiles do exist, it is important to recognize that (a) the overall agreement is rather good considering the high radical concentrations employed and (b) the accuracy and integrity of this kinetics study is not necessarily dependent upon quantitative agreement between these temporal profiles (although the differences suggest some potential systematic errors which need to be examined). As discussed above, the validity of our determinations of $k_1(P,T)$ is supported by the facts that (a) $k_{corr}$ values scale linearly as a function of [BrO], (b) $k_{corr}$ values are independent of the 248.4 and 532 nm laser fluences (at constant [BrO]), and (c) $[O(^3P)]$ relaxation temporal profiles after the firing of the 532 nm laser are exponential and, according to both observation and simulation, are dominated by reaction (1).

With the exception of the $O(^3P)+BrO$ reaction, accurate kinetic data appear to be available for all reactions used in the simulations (Table I). However, additional simulations were carried out where selected rate coefficients were either increased or decreased to see if better agreement between simulation and observation could be obtained. Improved agreement could not be obtained by varying any of the rate coefficients in Table I by factors of 2 or less. Hence, our observations should not be considered evidence that one or

\[ k_1(P,T) = (2.48 \pm 0.67) \exp\left(\frac{181 \pm 74}{T}\right). \]

\[ k_1(T) = (1.11 \pm 0.64) \exp\left(\frac{344 \pm 149}{T}\right). \]

\[ k_1(T) = (1.91 \pm 0.56) \exp\left(\frac{230 \pm 76}{T}\right). \]

The magnitude of the activation energy one would derive from our data depends somewhat on which method for evaluation of the BrO concentration one prefers (see below), our data clearly support a small negative activation energy for reaction (1), i.e., the rate coefficient increases with decreasing temperature.

**IV. DISCUSSION**

**A. Potential systematic errors in $k_1(P,T)$ values**

One approach which is commonly employed to validate a kinetics study involves demonstration that the results are independent of wide variations in experimental parameters such as laser fluences and species concentrations. Unfortunately, available laser powers and detection sensitivities as well as constraints dictated by system chemistry limited the range over which important parameters could be varied. Nonetheless a series of experiments were carried out at $P=50$ Torr and $T=269$ K which verified that, for the same initial concentrations of $O(^3P)$ and $Br_2$, $k_{corr}$ was independent of a factor of 5 variation in $[O_3]$ (6-30x10$^4$ molecules cm$^{-3}$), a factor of 2 variation in 248.4 nm laser fluence (5-10 mJ cm$^{-2}$), and a factor of 1.5 variation in 532 nm laser fluence (130-195 mJ cm$^{-2}$). The range of 248.4 nm fluences was limited at the high end by the available laser power and at the low end by the need to generate enough $O(^3P)$ to rapidly titrate $Br_2$ to BrO, thus minimizing interference from the $O(^3P)+Br_2$ reaction. The range of 532 nm fluences was also limited at the high end by the available laser power. The lower limit 532 nm fluence was dictated by the requirement that $[O(^3P)]$ relaxation temporal profiles be obtained with signal-to-noise ratio suitable for quantitative kinetic analysis, even though the low repetition rate dictated by system chemistry prohibited extensive signal averaging.

Comparison of simulated (Fig. 5) and measured (Fig. 2) $O(^3P)$ and BrO temporal profiles shows qualitative but not quantitative agreement. The simulated $O(^3P)$ decay to the near-steady-state level is a little faster than observed experimentally while the simulated BrO appearance rate is a little slower than observed experimentally. Also, once near-steady-state conditions are established, the observed $O(^3P)$ fluorescence signal continues to decay slowly whereas the simulation predicts that $[O(^3P)]$ remains constant or even increases slightly as a function of time; one possible explanation for this difference between observation and simulation would be the existence of a significant (unidentified) $O_2(a^1Delta)$ destruction mechanism other than reaction with $O_3$; an additional first-order $O_2(a^1Delta)$ loss rate of about 90 s$^{-1}$ would yield the best agreement between simulation and experiment. While quantitative differences between simulated and observed $O(^3P)$ and BrO temporal profiles do exist, it is important to recognize that (a) the overall agreement is rather good considering the high radical concentrations employed and (b) the accuracy and integrity of this kinetics study is not necessarily dependent upon quantitative agreement between these temporal profiles (although the differences suggest some potential systematic errors which need to be examined). As discussed above, the validity of our determinations of $k_1(P,T)$ is supported by the facts that (a) $k_{corr}$ values scale linearly as a function of [BrO], (b) $k_{corr}$ values are independent of the 248.4 and 532 nm laser fluences (at constant [BrO]), and (c) $[O(^3P)]$ relaxation temporal profiles after the firing of the 532 nm laser are exponential and, according to both observation and simulation, are dominated by reaction (1).

With the exception of the $O(^3P)+BrO$ reaction, accurate kinetic data appear to be available for all reactions used in the simulations (Table I). However, additional simulations were carried out where selected rate coefficients were either increased or decreased to see if better agreement between simulation and observation could be obtained. Improved agreement could not be obtained by varying any of the rate coefficients in Table I by factors of 2 or less. Hence, our observations should not be considered evidence that one or
more of the Arrhenius parameters in Table I are incorrect.

We have considered in some detail the possibility that the mechanism summarized in Table I is incomplete. This exercise has not led to identification of additional thermal reactions involving species in their ground electronic states which could be important in controlling the temporal behavior of BrO or O(\(^3P_J\)). However, reaction (1) is sufficiently exothermic (62.9 kcal mol\(^{-1}\)) that the O\(_2\) product can be formed with considerable vibrational excitation and/or in any one of three electronic states (X \(^3Σ_g^+\), a \(^1Δ_g\), b \(^1Σ_g^+\)). The production of "hot" O\(_2\) is not only a potential source of the discrepancy between observed and simulated BrO and O(\(^3P_J\)) temporal profiles before the firing of the 532 nm laser, it is also a potential kinetic interference in our measurements of \(k_1\); this is because O(\(^3P_J\)) can be regenerated via the following reactions:

\[
O_{2}(X \ ^3Σ_g^+) + O_3 \rightarrow O(\ ^3P_J) + 2O_2,
\]

\[
O_2(a \ ^1Δ_g) + O_3 \rightarrow O(\ ^3P_J) + 2O_2,
\]

\[
O_2(b \ ^1Σ_g^+) + O_3 \rightarrow O(\ ^3P_J) + 2O_2.
\]

Under the experimental conditions employed to monitor relaxation of [O(\(^3P_J\))] (generated by the 532 nm laser) back to steady state, the rate of production of O(\(^3P_J\)) via reaction (8) is several orders of magnitude too slow for this process to represent a significant kinetic interference. It is, of course, possible that reaction (1) produces O\(_2(X \ ^3Σ_g^+)\) which is vibrationally hotter than the O\(_2(X \ ^3Σ_g^+)\) generated by 300 nm laser photolysis of O\(_3\) and that the rate of reaction (11) increases dramatically with increasing vibrational quantum number. However, Park and Slanger\(^{34}\) have recently shown that the rate of vibrational deactivation of O\(_2(X \ ^3Σ_g^+)\) by N\(_2\) increases with increasing vibrational quantum number up to \(v = 19\) (where a two-quantum \(v\rightarrow u\) transfer process is near resonant); hence, any increase in \(k_{11}\) as a function of vibrational quantum number would be counterbalanced by a faster competing rate of vibrational relaxation by N\(_2\) buffer gas, so the conclusion that reaction (11) does not contribute significantly to [O(\(^3P_J\))] relaxation should be valid for all energetically accessible vibrational levels of O\(_2(X \ ^3Σ_g^+)\).

Unlike reactions (8) and (11), reaction (12) is quite fast, i.e., \(k_{12} \approx 2.2 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Any O\(_2(b \ ^1Σ_g^+)\) which is generated as a product of reaction (1) would be converted to O(\(^3P_J\)) on a time scale which is fast compared to the time scale for [O(\(^3P_J\))] relaxation following the 532 nm laser flash. Hence, our approach for measurement of \(k_1\) is "blind" to a reaction channel which produces O\(_2(b \ ^1Σ_g^+)\), i.e., we have actually measured \(k_{1a} + k_{1b}\), not \(k_1 = k_{1a} + k_{1b} + k_{1c}\).

\[
O(\ ^3P_J) + BrO \rightarrow Br(\ ^2P_J) + O_2(X \ ^3Σ_g^+) + 2O_2,
\]

\[
Br(\ ^2P_J) + O_2(a \ ^1Δ_g) \rightarrow O_2(b \ ^1Σ_g^+)\]  

\[
Br(\ ^2P_J) + O_2(b \ ^1Σ_g^+) \rightarrow O_2(X \ ^3Σ_g^+) + 2O_2.
\]

Adiabatic correlation arguments suggest that the branching ratio for channel (1c) should be small, i.e., BrO(X \(^2Σ_g^+)\)+O(\(^3P_J\)) correlates with Br(\(^2P_J\))+O\(_2(X \ ^3Σ_g^+)\), a \(^1Δ_g\) but not with Br(\(^2P_J\))+O\(_2(b \ ^1Σ_g^+)\). Statistical arguments, which are based on the idea that the most probable products are those with the largest number of energetically accessible quantum states, suggest a negligible branching ratio for channel (1c). Also, Leu and Yung\(^{35}\) have shown that the yield of O\(_2(b \ ^1Σ_g^+)\) from the analogous O\(_2(b \ ^1Σ_g^+)\)+ClO reaction is very small, i.e., less than \(4.4 \times 10^{-4}\). Despite the above rationale for expecting a small O\(_2(b \ ^1Σ_g^+)\) yield from reaction (1), experimental verification would be reassuring. The rate coefficient for quenching of O\(_2(b \ ^1Σ_g^+)\) by N\(_2\) is known to be \(k_{13} = 2.1 \times 10^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Ref. 6)

\[
O_2(b \ ^1Σ_g^+) + N_2 \rightarrow O_2(\ ^1Δ_g + X \ ^3Σ_g^+) + N_2.
\]

Hence, over the range of N\(_2\) and O\(_3\) partial pressures employed in our study, the fraction of O\(_2(b \ ^1Σ_g^+)\) which reacts with O\(_3\), \(f\), spans a considerable range

\[
f = k_{12}[O_3]/(k_{12}[O_3] + k_{13}[N_2]).
\]

A plot of \(f\) vs (\([O_3] - k_{15}([BrO]) = k_{1}\)) is shown in Fig. 8. Even though reduction in O(\(^3P_J\)) detection sensitivity with increasing N\(_2\) pressure prohibited experimentation under conditions where \(f\) was very small, the data show no tendency for \(k_1\) to decrease with increasing \(f\) [as would be expected if the O\(_2(b \ ^1Σ_g^+)\) yield from reaction (1) was significant]. We are thus led to conclude that \(k_{1a} + k_{1b} = k_1\).

Reaction (2) is sufficiently exothermic that BrO can be generated in vibrational levels up to \(v = 16\) while reaction (5) can generate BrO in vibrational levels up to \(v = 5\). Vibrational relaxation of BrO following reaction (2) is very slow value \(k_{11} = 2.2 \times 10^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), suggesting that reaction (11) is also too slow to represent a significant kinetic interference. It is, of course, possible that reaction (1) produces O\(_2(X \ ^3Σ_g^+)\) which is vibrationally hotter than the O\(_2(X \ ^3Σ_g^+)\) generated by 300 nm laser photolysis of O\(_3\) and that the rate of reaction (11) increases dramatically with increasing vibrational quantum number. However, Park and Slanger\(^{34}\) have recently shown that the rate of vibrational deactivation of O\(_2(X \ ^3Σ_g^+)\) by N\(_2\) increases with increasing vibrational quantum number up to \(v = 19\) (where a two-quantum \(v\rightarrow u\) transfer process is near resonant); hence, any increase in \(k_{11}\) as a function of vibrational quantum number would be counterbalanced by a faster competing rate of vibrational relaxation by N\(_2\) buffer gas, so the conclusion that reaction (11) does not contribute significantly to [O(\(^3P_J\))] relaxation should be valid for all energetically accessible vibrational levels of O\(_2(X \ ^3Σ_g^+)\).
tionally excited BrO (symbolized by BrO*) could undergo the following transformations upon collision with other species present in the reaction mixture:

\[
\text{BrO}^* (v) + M \rightarrow \text{BrO}^* (v' < v) + M, \quad M = \text{N}_2, \text{O}_3, \text{Br}_3, \text{Br}, \tag{14}
\]

\[
\text{BrO}^* (v \geq 14) + \text{O}_3 \rightarrow \text{O}(^{3}P_J) + \text{BrO} + \text{O}_2, \tag{15}
\]

\[
\text{BrO}^* (v \geq 6) + \text{Br}(^{2}P_J) \rightarrow \text{Br}_2 + \text{O}(^{3}P_J). \tag{16}
\]

There are no kinetic data available in the literature for excited state reactions (14)–(16). Reaction (15) is probably not important in our experimental system because (a) very little BrO is expected to be generated in \( v \geq 14 \) and (b) vibrational relaxation of \( v \geq 14 \) by \( \text{N}_2 \) is almost certainly too fast to allow competition from reaction (15). The chlorine analog of reaction (16) is thought to be responsible for generation of the \( \text{O}(^{3}P_J) \) observed when \( \text{O}_3 \) reacts with an excess of chlorine atoms. The occurrence of reaction (16) in our experiment could result in increased levels of \( \text{O}(^{3}P_J) \) and \( \text{Br}_2 \) and decreased levels of BrO compared to levels predicted based on the mechanism given in Table I. To examine the potential role of reaction (16) in our study, computer simulations were performed where reactions (14) and (16) were added to the base mechanism (Table I) and values for \( k_{14} \) and \( k_{16} \) were adjusted over wide ranges. No improvement could be achieved in matching the shapes of the simulated and observed \( \text{O}(^{3}P_J) \) temporal profiles. As expected, the inclusion of reaction (16) in the mechanism can depress simulated BrO levels, but only if \( k_{14} \) is quite slow. If \( k_{14} = 10^{-14} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), i.e., if \( k_{14} \) is the same order of magnitude as observed for the analogous ClO* + \( \text{N}_2 \) relaxation process,\(^9\) then the dominant fate of BrO* is deactivation by \( \text{N}_2 \). Shown in Fig. 9 is a transient absorption spectrum in the wavelength region of the 7–0 band of the \( A^{1} \pi \rightarrow X^{3} \pi \) system of BrO; this spectrum, which is discussed in detail below, was obtained using a reaction mixture typical of those employed in the \( \text{O}(^{3}P_J) + \text{BrO} \) kinetics studies. The spectrum shows no evidence for the presence of BrO* at “nonthermal-equilibrium” levels; hence, direct experimental evidence supports the idea that vibrational relaxation of BrO* is rapid in the presence of 25–150 Torr of \( \text{N}_2 \).

As discussed briefly above, the most important source of systematic error in this study appears to be the evaluation of the absolute concentration of BrO appropriate for use in the kinetic analyses. Two independent methods have been employed to evaluate [BrO]. One method involves numerical integration of a set of rate equations which is based on the mechanism in Table I; experimental photometric, mass flow, and laser fluence measurements allow initial concentrations of \( \text{O}_3, \text{Br}_3, \text{Br}_2, \text{O}(^{3}P_J), \) and \( \text{Br}(^{2}P_J) \) to be evaluated and used as input to the numerical integration routine. The second method involves direct measurement of [BrO] by time-resolved UV absorption at 338.3 nm. Conversion of a measured absorbance at the appropriate time, i.e., one \( \text{e} \)-folding time for \( \text{[O}(^{3}P_J) \) relaxation after firing the 532 nm laser, employs an experimentally evaluated absorption path length and the best available literature values for the 338.3 nm BrO absorption cross section as a function of temperature;\(^24\) since the needed absorption cross sections have been measured at only two temperatures (223 and 298 K),\(^24\) the absorption cross section is assumed to depend linearly on temperature over the range of our study, i.e., 231–328 K. Differences between BrO concentrations obtained using the two different methods are largest for experiments with low \( \text{Br}_2 \) concentrations, and are larger at higher temperatures than at lower temperatures. According to the Arrhenius expressions given above, rate coefficients evaluated based on the two different approaches for determining [BrO] differ by a factor of 1.36 at \( T = 328 \) K and by a factor of 1.10 at \( T = 231 \) K. Fortunately, the low temperature regime where agreement is better represents the temperature in the middle stratosphere where reaction (1) is expected to be most important. In all cases, the slower rate coefficients are obtained using BrO concentrations derived from the time-resolved UV absorption measurements.

A potential systematic error in the UV absorption measurements could arise if BrO were not the only absorbing species at 338.3 nm. To investigate this possibility, experiments were carried out where the time-resolved absorption observed following 248.4 nm laser flash photolysis of \( \text{Br}_2, \text{BrO}, \text{N}_2 \) mixtures typical of those employed in the \( \text{O}(^{3}P_J) + \text{BrO} \) kinetics studies was mapped out over a wavelength range (330–347 nm) where the 6–0, 7–0, and 8–0 bands of the BrO \( A^{2} \pi \rightarrow X^{2} \pi \) system are observed. In particular, we focus on peak-to-valley absorbance ratios to see if there is evidence for continuum absorbance from a species other than BrO. The spectral resolution, 0.36 nm, was the same as employed in the kinetics experiments; it was slightly better than the resolution of 0.4 nm employed by Wahner et al.\(^24\) to carry out the best available measurements of BrO absorption cross sections as a function of wavelength.

![FIG 9. Transient absorption spectrum over the wavelength range 330–347 nm observed following 248.4 nm laser flash photolysis of an \( \text{O}_3, \text{Br}_2, \text{N}_2 \) mixture typical of those employed in the \( \text{O}(^{3}P_J) + \text{BrO} \) kinetics studies. T=298 K. P=50 Torr. Concentrations at \( t=0 \) (a time immediately after the 248.4 nm laser fires) are units of \( 10^{11} \) per cm\(^2\) and \([\text{O}_3]=64.5, [\text{Br}_2]=2.45, \) and \([\text{BrO}]=13.8 \). Laser fluence=13.1 mJ/cm\(^2\). Absorption path length=89 cm. Resolution=0.36 nm. Open squares and long dashed connecting line represent data obtained at the peak of the BrO temporal profile (at \( t=7 \) ms). Open circles and dotted connecting lines represent data obtained at \( t=3 \) ms. Open triangles and short dashed connecting line represent data obtained at \( t=20 \) ms. The solid curve represents the spectrum reported by Wahner et al. (Ref. 24) at a resolution of 0.4 nm.](image-url)
improve sensitivity in the spectral regions where absorbance was low, the 1 cm mask used in the kinetics studies was removed from the window where the 248.4 nm laser beam entered the reactor; this increased the absorption path length by approximately a factor of 3 at the cost of decreased spatial uniformity in the BrO concentration. Results of a typical experiment are shown in Fig. 9. Experiments employing relatively high and relatively low Br2 concentrations gave essentially identical results. We find that (1) the observed spectrum is independent of delay time after the 248.4 nm laser fires and (2) peak-to-valley ratios are larger than those reported by Wahner et al.24 (the solid line in Fig. 9 represents the spectrum reported by Wahner et al.). The low absorbance we observe in the spectral regions between bands could potentially be attributable to changes in the I0 light level due to depletion of Br2 and O3 after the laser flash. However, both Br2 and O3 have very low absorption cross sections in the 330–547 nm wavelength region; hence, time-dependent changes in the transmitted light level due to time-dependent changes in the O3 and Br2 concentrations are expected to be negligible. The spectroscopy experiments described above lead to two important conclusions. First, it appears that the time-resolved absorption technique employed to monitor BrO in our O(3Pj)+Br2 kinetics experiments is specific to BrO, i.e., there is no evidence for interfering absorptions from other chemical species (such as Br2O, BrOOB,19 or O2). Also, there are systematic differences in peak-to-valley BrO absorbance ratios obtained in our experiments compared to those reported by Wahner et al.24 These differences, which are potentially important for both laboratory and atmospheric field experiments where [BrO] is deduced from UV absorption measurements, cannot be readily explained at this time.

A number of potential systematic errors in our measurements of k1(P,T) are discussed above. We believe that errors resulting from excited state reactions or other unidentified side reactions are small. Despite our best efforts, the source of the differences between BrO concentrations evaluated from time-resolved UV absorption measurements and those evaluated from numerical integration of the appropriate rate equations is not clear. At this time, we feel that the best approach is to report k1(T) values which are based on the average of BrO concentrations obtained by the two methods, and to adjust error bars to span all reasonable possibilities. Based on this strategy, we report the following Arrhenius expression:

\[ k_1(T) = 1.91 \times 10^{-11} \exp(230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

The absolute uncertainty in k1(T) values is estimated to range from ±20% at the low temperature end of the experimental temperature range (T = 230 K) to ±30% at the high temperature end of the experimental temperature range (T = 330 K).

B. Comparison with previous research

In the only previous experimental observations relevant to establishing the absolute rate coefficients k1(P,T), Clyne et al.5 obtained the estimate k1(298 K) = 2.5 × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, with an uncertainty range of (1.0–5.0) × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; this estimate was obtained by observing secondary O(3Pj) consumption and Br2(P5) production in experiments whose primary objective was measurement of rate coefficients for the reactions of O(3Pj) with Br2 and BrCl. The experiments of Clyne et al. employed a discharge flow-resonance fluorescence technique; total pressures were about 0.5 Torr. For purposes of stratospheric modeling, the currently recommended Arrhenius expression is k1(T) = 3.0 × 10^{-11} \exp(0/7) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.6 The Arrhenius expression we report in this paper gives k1(298 K) = 4.13 × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, i.e., 38% faster than the currently recommended value. At 230 K, a temperature characteristic of the stratosphere at altitudes of 30–35 km, our results suggest k1(230 K) = 5.19 × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, i.e., 73% faster than the currently recommended value. Another discharge-flow study of the O(3Pj)+Br2 reaction has been reported by Butkovskaya et al.37 These authors observed OBrO as a product of secondary chemistry and suggested the wall-catalyzed O(3Pj)+Br2 reaction as a possible OBrO source. This result does not seem relevant for our study where all chemistry occurred in isolation from reactor surfaces.

Arrhenius parameters for O(3Pj)+XO→X+O2 reactions with X = H, OH, NO, NO2, Cl, and Br are compared in Table IV. All of these reactions are fast with k1(298 K) values ranging from 1.0 × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} for X = NO and NO2 to 6.0 × 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} for X = OH. Also, with the possible exception of O(3Pj)+NO3, all reactions are characterized by small negative activation energies, i.e., rate coefficients increase with decreasing temperature. The magnitudes and temperature dependencies observed for O(3Pj)+XO rate coefficients are characteristic of reactions which occur on potential energy surfaces with a minimum (corresponding to the XOO species) along the reaction coordinate. Long range attractive forces result in large cross sections for formation of the energized XOO species. Negative activation energies are reasonable because lower energy collisions at lower temperatures result in a longer lifetime for the energized complex lifetime.

The available temperature dependent data (Ref. 50) suggests that E/R is small, but is insufficient to define the sign of E/R.

### Table IV. Arrhenius parameters for O+XO→X+O2 radical–radical reactions.

<table>
<thead>
<tr>
<th>XO</th>
<th>A [cm^3 molecule^-1 s^-1]</th>
<th>E/R [kcal mol^-1]</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>22</td>
<td>-120</td>
<td>39–41</td>
</tr>
<tr>
<td>HO2</td>
<td>30</td>
<td>-200</td>
<td>7,8,42–44</td>
</tr>
<tr>
<td>NO2</td>
<td>6.5</td>
<td>-120</td>
<td>45–49</td>
</tr>
<tr>
<td>NO3</td>
<td>10</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>CO</td>
<td>30</td>
<td>-70</td>
<td>9.48,51–55</td>
</tr>
<tr>
<td>BrO</td>
<td>19</td>
<td>-230</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Units are 10^{-12} cm^3 molecule^-1 s^-1.

*Values for XO=OH, HO2, NO2, and CO are recommendations of the NASA panel (Ref. 6), which are based on the references given in the table.

*Units are degrees kelvin.

The available temperature dependent data (Ref. 50) suggests that E/R is small, but is insufficient to define the sign of E/R.
C. Implications for atmospheric chemistry

A one-dimensional photochemical modeling study of stratospheric bromine chemistry has recently been reported by Poulet et al. This study incorporates up-to-date kinetic information including a much faster rate coefficient for the BrO+HO2 reaction than had been employed in pre-1992 modeling studies. In Fig. 4 of the Poulet et al. paper, rates of odd oxygen destruction by the most important BrO cycles are plotted as a function of altitude and compared with the altitude dependence of the total odd-oxygen destruction rate. Bromine is most significant as a catalyst for odd-oxygen destruction in the lower stratosphere, the dominant BrO, odd-oxygen destruction pathway at all altitudes above 27 km. Incorporation of reaction (1) as the rate-limiting step becomes significant in the lower stratosphere above 25 km. As a result, the O(3P, T) into a model like that employed by Poulet et al. suggests that the catalytic cycle at altitudes above 27 km. Incorporation of reaction (1) as the rate limiting step becomes the dominant BrO, odd-oxygen destruction pathway at all altitudes above 24 km. At 25 km, about 1% of all odd-oxygen destruction occurs via the O(3P, T)+BrO catalytic cycle.

ACKNOWLEDGMENTS

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10. See, for example, B. J. Finlayson-Pitts and J. N. Pitts, Jr., Atmospheric Chemistry: Fundamentals and Experimental Techniques (Wiley, New York, 1986), Chap. 4-8.
Quantum yield for carbon monoxide production in the 248 nm photodissociation of carbonyl sulfide (OCS)

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Abstract. Tunable diode laser absorption spectroscopy has been coupled with excimer laser flash photolysis to measure the quantum yield for CO production from 248 nm photodissociation of carbonyl sulfide (OCS) relative to the well-known quantum yield for CO production from 248 nm photolysis of phosgene (Cl,CO). The temporal resolution of the experiments was sufficient to distinguish CO formed directly by photodissociation from that formed by subsequent S('P) reaction with OCS. Under the experimental conditions employed, CO formation via the fast S('D,)+OCS reaction was minimal. Measurements at 297K and total pressures from 4 to 100 Torr N2+N2O show the CO yield to be greater than 0.95 and most likely unity. This result suggests that the contribution of OCS as a precursor to the lower stratospheric sulfate aerosol layer is somewhat larger than previously thought.

Introduction

Stratospheric sulfate aerosols, first discovered over three decades ago [Junge and Manson, 1961], have been the subject of numerous investigations motivated by their potential influence on global climate and, more recently, their potential involvement in heterogeneous stratospheric chemistry. Diffusion of carbonyl sulfide (OCS) from the troposphere has been identified as a potentially significant source of stratospheric sulfur [Crutzen, 1976] and at least two studies have suggested that anthropogenic OCS emissions are causing a measurable increase in stratospheric sulfate aerosol levels [Sedlacek et al., 1983; Hofmann, 1990]. In the stratosphere OCS can be photolyzed by solar ultraviolet radiation

OCS + hv → CO + S

or oxidized by reactions with oxygen atoms or OH radicals to produce sulfur species which are readily converted to sulfate aerosol [Berresheim, et al., 1995]. Current estimates of the impact of photolysis reaction (1) are based on consistent measurements of OCS photodissociation cross sections (discussed below) and two somewhat disparate reports of the photodissociation quantum yield (which equals the quantum yield for CO production) [Sidhu et al., 1966; Rudolph and Inn, 1981]. Both of the quantum yield studies utilized low intensity, continuous light sources which irradiated the OCS sample for periods of several minutes or longer. Under these conditions, the sulfur atom formed in reaction (1) further reacted with OCS to produce a second CO:

OCS + S → CO + S2.

This second step was assumed to be 100% efficient; hence, the primary yield of CO from the photolysis step (Φ) was taken to be one half the measured CO divided by the number of photons absorbed. Sidhu et al. [1966], using the partial pressure of non-condensible (at 77K) gas as their CO measurement technique, reported the values Φ = 0.91 and 0.90 for the photolysis wavelengths 253.7 nm and 228.8 nm, respectively. While they did not quote uncertainty limits, they acknowledged that experimental error may have caused the observed yields to be less than unity. Rudolph and Inn [1981], using resonance fluorescence to detect CO after freezing out unreacted OCS at 77K, made measurements at five photolysis wavelengths from 214.0 to 253.7 nm and reported the value Φ = 0.72 ± 0.08 essentially independent of wavelength. These authors noted that structured absorption features in the OCS spectrum appear to account for 5-10% of the total oscillator strength while their yield result indicates a 28% bound state contribution. They suggested that perturbations between the 'A' and 'A'' components of the OCS excited electronic state may obscure some of the structure. However, as noted by Atkinson et al. [1992], there is currently no reported evidence for fluorescence from photoexcited OCS, and this fact, taken together with the observed wavelength independence of the CO quantum yield and the paucity of structure in the photoabsorption spectrum, suggests that dissociation may be the only significant loss channel for electronically excited OCS.

In this letter, we report measurements of the quantum yield for CO production from 248 nm photodissociation of OCS; our results suggest that this quantum yield is unity.

Experimental Technique

In the present work, tunable diode laser absorption was used to follow the concentration of CO after laser flash photolysis of flowing OCS/N2/N2O and Cl2CO/N2/N2O gas mixtures. A number of possible systematic errors were avoided by using 248 nm photolysis of phosgene (Cl2CO) as an in situ unit yield calibration standard [Stickel et al., 1993].

Cl2CO + hv(248 nm) → CO + 2 Cl('P).

The quantum yield for CO production from reaction (1) was determined by performing back-to-back experiments, one with OCS and one with Cl2CO as the photolyte, and taking the ratio of observed CO absorbances with corrections for small variations in photolysis energy and photolyte concentration. The apparatus is similar to that used for a number of previously published studies [e.g. Stickel et al., 1993]; hence, only a brief description is included here.

The photolytic light source was a KrF excimer laser (Lambda Physik EMG 200) which produced 248 nm pulses of approximately 25 ns duration with an intensity of up to 30

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ml cm\(^{-2}\) in the sample gas. The infrared probe beam was provided by a lead-salt diode laser (Laser Photonics/Analytics 5622) and detected by HgCdTe detectors cooled to 77K. A portion of the probe beam was diverted to a static CO reference cell. The probe wavelength was modulated (typically at 40 kHz) to give a first derivative reference signal which was used to stabilize the laser output on a CO rotational line near the peak of the P branch of the (1,0) vibrational transition (the P6 line at 2119.68 cm\(^{-1}\) and the P9 line at 2107.42 cm\(^{-1}\) were used). The photolysis and probe beams were merged by a dichroic optic and directed longitudinally through the sample cell, which consisted of a pyrex tube of 25 mm inside diameter and 118 cm length with calcium fluoride windows epoxied to the ends. A second dichroic separated the transmitted IR beam which was then passed through a 0.5 m monochromator for mode selection. The detected signal was digitized, summed over multiple flashes (typically 32) and stored for later second harmonic analysis. The linearity of the second harmonic signal was verified by CO standard addition.

In order to avoid accumulation of photolysis products, all experiments were carried out under "slow flow" conditions such that the contents of the cell were nearly completely replaced between flashes. Photolyte concentrations in the sample cell were determined in two ways: (1) using bulb partial pressures and flow mixing ratios, and (2) using in situ photometry at 228.8 nm. For reasons discussed below, the photometric determinations were used exclusively in the quantum yield analysis although the agreement between the photometric and flow measurements was typically 5% or better.

The gases used in this study were supplied with the following stated minimum purities: \(N_2\), 99.999%; \(N_2O\), 99.99%; OCS, 97.5%; \(Cl_2CO\), 99.0%. The \(N_2\) and \(N_2O\) were used as supplied. The \(Cl_2CO\) was degassed at 77K before use. Three different OCS preparations were used: (1) as supplied, (2) degassed at 77K, and (3) filtered through ascarite and trapped at 77K [Friedl, 1984]. Experimental results were found to be independent of OCS purification technique.

Results and Discussion

Typical data from a single quantum yield measurement are shown in Figure 1. Linear fits to both pre- and post-flash data were extrapolated to the instant of photolysis to give the amount of CO produced by the flash. As explained below, this signal includes CO from both photolysis and fast \(S(1D_2)\) chemistry. The resulting infrared CO absorption signal observed in an OCS experiment \((S)\) can be expressed as

\[
S = G \cdot Y \cdot \sigma(OCS, 248) \cdot E(OCS)
\]

(1)

and the corresponding expression for a \(Cl_2CO\) experiment is

\[
R = G \cdot \sigma(Cl_2CO, 248) \cdot E(Cl_2CO)
\]

(2)

In both cases \(G\) is the instrumental response, \(\sigma\) is the appropriate photoabsorption cross section for the excimer laser flash and \(E\) is the flash energy. If the concentrations of OCS and \(Cl_2CO\) are determined by 228.8 nm photometry in the same absorption cell, the observed CO yield \((Y)\) can be found from

\[
Y = \frac{\sigma(OCS, 229) \cdot \sigma(Cl_2CO, 248)}{\sigma(OCS, 248) \cdot \sigma(Cl_2CO, 229)}
\]

(3)

where \(L_1\) and \(L_2\) are the usual photometric intensities. Aside from the experimental results, i.e., \(S, R, L_1(Cl_2CO), L(Cl_2CO), L_2(OCS), L(OCS), E(Cl_2CO), E(OCS)\), the observed yield depends on absorption cross section ratios for the two photolyses (i.e., OCS and \(Cl_2CO\)) at the photolysis and photometric wavelengths. These ratios depend rather strongly on the exact wavelengths and, for OCS, on the gas temperature. The KrF laser spectrum was measured in the course of this study and found to have a single peak at 248.35 nm with a full width at half maximum of 0.4 nm. The ratio \(\sigma(OCS, 229)/\sigma(OCS, 248)\) was determined by interpolation from three published tables of absorption cross sections [Molina et al., 1981; Rutten and Inn, 1981; Locket et al., 1983]. The temperature dependence data of Lockett et al. were used to reduce all three results to the center of the experimental temperature range of 296.5 to 298.0 K. The mean and standard deviation of the three OCS absorption cross section ratios are 12.2 ± 0.2.
The branching ratio for reaction (4a), $r_4$, is 0.8. More recently Black (1986) observed $r_4 = 0.20 \pm 0.05$.

The rate constant for reaction (5) has been reported as 0.6 $k_4$ (Breckenridge and Taube, 1970), 0.4 $k_4$ (Donovan and Breckenridge, 1971) and as 1.6 $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Black and Jusinski, 1985). For reaction (6), Black and Jusinski (1985) measured a rate constant of 8.5 $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and McBane et al. (1992) reported $(7.1 \pm 1.0) 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In the present case the observed CO yield ($Y$) is given by

$$Y = \frac{A}{B \cdot r_4 \cdot k_4 \cdot I_{OCS}}$$

where $B$ is the fraction of sulfite atoms formed in the $1D_2$ state (assumed here to be unity). Because the error term depends linearly on the highly uncertain branching ratio $r_4$, we have chosen to adopt both "best estimate" and "maximum" corrections for the chemically generated CO signal. The rate constants and branching ratios for both cases are given in Table 1.

Quantum yield results are presented as a function of total gas pressure in Table 2. Averaged over the entire data set, the best estimate correction for secondary CO production reduced the observed yield by 2 percent while the corresponding maximum correction was 10 percent. The apparent pressure dependence of $\Phi$ values obtained using the maximum correction (see Table 2) suggests that the maximum

### Table 1. Kinetic data used for correcting observed quantum yields for the occurrence of $S(1D_2) + OCS$ reaction. The "Best Estimate" values are the result of a critical evaluation of the literature while the "Max. Corr." values were chosen to give the largest correction consistent with literature values for $k_4$, $r_4$, $k_5$, and $k_6$. Units of rate constants are $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

<table>
<thead>
<tr>
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<tr>
<td>$k_4$</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>$r_4$</td>
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<tr>
<td>$k_5$</td>
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</tr>
<tr>
<td>$k_6$</td>
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### Table 2. Summary of Experimental Results

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<th>[OCS]</th>
<th>[Cl$_2$CO]</th>
<th>[N$_2$O]</th>
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<th>$\Phi^c$</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>3.6 3</td>
<td>9.5 9.6</td>
<td>2.1 2.2</td>
<td>70 72</td>
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<td>4.2 4.3</td>
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<td>1.07</td>
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<td>6.4 26.9</td>
<td>1.3 6.5</td>
<td>48 310</td>
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<td>2.7 2.8</td>
<td>89 90</td>
<td>23.9 24.8</td>
<td>1.08</td>
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<tr>
<td>20 3</td>
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<td>2.8 2.9</td>
<td>90 91</td>
<td>23.3 24.8</td>
<td>1.05</td>
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<tr>
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<td>2.8 4.6</td>
<td>89 262</td>
<td>19.1 23.3</td>
<td>1.09</td>
</tr>
<tr>
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<td>302 315</td>
<td>23.0 24.6</td>
<td>1.06</td>
</tr>
<tr>
<td>89 6.4 44.1</td>
<td>1.3 10.5 48 315</td>
<td>7.6 26.3</td>
<td>1.06±0.04</td>
<td>1.04±0.04</td>
<td>0.96±0.05</td>
</tr>
</tbody>
</table>

(a) Units are P(Torr); Concentrations (10$^{15}$ molecules cm$^{-3}$); Fluence (mJ cm$^{-2}$).
(b) A: uncorrected yield; B: best estimate correction for secondary CO production; C: maximum possible correction for secondary CO production.
corrections are overly severe. The best estimate correction of two percent is smaller than the experimental uncertainty and suggests that the reaction \((4a)\) is not a significant source of CO in the present work. The yields and sample standard deviations at each of the pressures shown in Table 2 are all comparable to the overall results. This is a good indication that the measurement errors are uniformly random. The best estimate value for \(\Phi \pm 1\sigma\) of 1.04 ± 0.04 represents the weighted mean and standard deviation of the results at each pressure after application of the "best estimate" correction for secondary CO production; the weighting factors are the number of experiments at each pressure. Combining the 4% variability in the measured value for \(\Phi\) with an estimated 2% standard deviation in the product of absorption cross section ratios appearing in equation (III), leads to an overall 20% uncertainty of 9%, i.e., \(\Phi = 1.04 \pm 0.09\) at the 95% confidence level. Hence, we report \(\Phi > 0.95\) with a most probable value of unity. It should be remembered that the value of \(\Phi\) we report is actually the ratio of the CO yield from OCS photolysis to the CO yield from Cl-Cl photolysis. However, it seems virtually certain that the CO yield from Cl-Cl photolysis is unity.

The role of OCS as a source of stratospheric background (i.e., non-volcanic) sulfur aerosols has recently been analyzed by Chin and Davis [1994]. Using 0.85 as the OCS photodissociation quantum yield, i.e., the average of estimated maximum and minimum values, Chin and Davis conclude that photodissociation is the dominant stratospheric OCS destruction process and calculate a production rate of stratospheric background aerosol from OCS oxidation of 3.2 x 10\(^{10}\) g S yr\(^{-1}\), i.e., only 20–50% of the most recent estimates of the amount needed to maintain the background aerosol level [Servant, 1986; Hofmann, 1990]. Another interesting aspect of the Chin and Davis study is their finding that about 90% of OCS which is transported from the troposphere into the stratosphere is not photochemically destroyed, but instead is transported back to the troposphere where most of it is removed via uptake by vegetation. The OCS photodissociation quantum yield reported in this study will increase the calculated production rate of stratospheric background aerosol from OCS oxidation by about 15%, and will also slightly decrease the percentage of OCS which cycles from the stratosphere back to the troposphere without being photochemically destroyed.

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The fate of atmospheric phosgene and the stratospheric chlorine loadings of its parent compounds: CCl₄, C₂Cl₄, C₂HCl₃, CH₃CCl₃, and CHCl₃

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Abstract. A study of the tropospheric and stratospheric cycles of phosgene is carried out to determine its fate and ultimate role in controlling the ozone depletion potentials of its parent compounds (CCl₄, C₂Cl₄, CH₃CCl₃, CHCl₃, and C₂HCl₃). Tropospheric phosgene is produced from the OH-initiated oxidation of C₂Cl₄, CH₃CCl₃, CH₂Cl₂, and CH₃CCl₂. Simulations using a two-dimensional model indicate that these processes produce about 90 ppt/yr of tropospheric phosgene with an average concentration of about 18 pptv, in reasonable agreement with observations. We estimate a residence time of about 70 days for tropospheric phosgene, with the vast majority being removed by hydrolysis in cloudwater. Only about 0.4% of the phosgene produced in the troposphere avoids wet removal and is transported to the stratosphere, where its chlorine can be released to participate in the catalytic destruction of ozone. Stratospheric phosgene is produced from the photochemical degradation of CCl₄, C₂Cl₄, CH₂Cl₂, and CH₃CCl₂ and is removed by photolysis and downward transport to the troposphere. Model calculations, in good agreement with observations, indicate that these processes produce a peak stratospheric concentration of about 25-30 pptv at an altitude of about 25 km. In contrast to tropospheric phosgene, stratospheric phosgene is found to have a lifetime against photochemical removal of the order of years. As a result, we find that a significant portion of the phosgene that is produced in the stratosphere is ultimately returned to the troposphere, where it is rapidly removed by clouds. This phenomenon effectively decreases the amount of reactive chlorine injected into the stratosphere and available for ozone depletion from phosgene’s parent compounds; we estimate approximate decreases of 14, 3, 15, and 25% for the stratospheric chlorine loadings of CCl₄, CH₂Cl₂, C₂Cl₄, and CH₂CCl₂, respectively. A similar phenomenon due to the downward transport of stratospheric COCl₂ produced from CFC-11 is estimated to cause a 7% decrease in the amount of reactive chlorine injected into the stratosphere from this compound. Our results are potentially sensitive to a variety of parameters, most notably the rate of reaction of phosgene with sulfate aerosols. However, on the basis of the observed vertical distribution of COCl₂, we estimate that the reaction of COCl₂ with sulfate aerosol most likely has a γ < 5x10⁻³ and, as a result, has a negligible impact on the stratospheric chlorine loadings of the phosgene parent compounds.

1. Introduction

Phosgene (COCl₂) is produced in the Earth’s atmosphere from the degradation of a variety of chlorinated compounds including tetrachloroethylene (C₂Cl₄), trichloroethylene (C₃HCl₂), chloroform (CHCl₃), methylvchloroororm (CH₂Cl₂), and carbon tetrachloride (CCl₄) [e.g., Helas and Wilson, 1992]. These chlorinated compounds fall into two generic reactivity classes:

1. CCl₄, C₂Cl₄, CH₂Cl₂, and CH₃CCl₂, the four reactive phosgene parent compounds (referred to here as the RPP compounds) that are destroyed primarily in the troposphere by reaction with OH, and (2) CCl₄, which is unreactive in the troposphere and is destroyed primarily by photolysis in the stratosphere. Thus the degradation of the RPP compounds leads to the production of tropospheric COCl₂, while CCl₄ and to some extent also the RPP compounds lead to the production of stratospheric COCl₂.

Tropospheric COCl₂ is believed to be removed from the atmosphere by rainout and ocean deposition [Singh, 1976; Singh et al., 1977] with a residence time of the order of months [Helas and Wilson, 1992]. Observations suggest a fairly uniform distribution in the troposphere with an average concentration of about 15-20 pptv and a weak seasonal cycle of about 20% [Singh, 1976; Singh et al., 1977; Wilson et al., 1988]. Stratospheric COCl₂, on the other hand, is believed to be removed by UV-photolysis, and observations indicate a peak concentration of 25-30 pptv at about 25 km [Crutzen et al., 1978; Wilson et al., 1988].
While the subtypes of tropospheric and stratospheric COCl\textsubscript{2} have been studied previously [Cruz et al., 1978; Helas and Wilson, 1992], the interaction between these subtypes has not been studied and, yet, this interaction may potentially affect the ozone depletion potentials (ODPs) of phosgene's parent compounds. For instance, if instead of being removed in the troposphere, a small fraction of the COCl\textsubscript{2} produced in the troposphere from the RPP compounds is transported into the stratosphere and photochemically degraded there, the chlorine released in this degradation could contribute to the destruction of stratospheric ozone and thus cause an increase in the ODPs of the RPP compounds. On the other hand, if a fraction of the COCl\textsubscript{2} produced in the stratosphere were transported to the troposphere before degradation, the ODPs of the compounds producing stratospheric COCl\textsubscript{2} would be decreased.

To address this issue, we have developed a two-dimensional (2-D) model to simulate the tropospheric cycle of COCl\textsubscript{2} and thereby estimate the fraction of COCl\textsubscript{2} produced in the troposphere that is transported to the stratosphere. A one-dimensional (1-D) stratospheric model is then used to estimate the fraction of COCl\textsubscript{2} that is produced in the stratosphere and transported to the troposphere, where it is finally removed. In our discussion it will be convenient to distinguish two types of COCl\textsubscript{2}: (1) "tropospheric phosgene," that is, COCl\textsubscript{2} produced from the OH-initiated oxidation of the RPP compounds in the troposphere, and (2) "stratospheric phosgene," that is, COCl\textsubscript{2} produced from the photolysis of CCl\textsubscript{4} as well as the photolysis and OH-initiated oxidation of the RPP compounds in the stratosphere. By Dalton's law, the total COCl\textsubscript{2} cycle is then represented by the sum of these two independent subcycles. It is important to bear in mind that the terms "tropospheric" and "stratospheric" used in this context refer to the region of the atmosphere where the COCl\textsubscript{2} is produced, not necessarily to where it is found. Thus tropospheric COCl\textsubscript{2} can, in principle, be transported to and reside in the stratosphere, and stratospheric COCl\textsubscript{2} can be transported to and reside in the troposphere.

In the next sections we first describe the sources of atmospheric COCl\textsubscript{2} included in our calculations. We then discuss the basic components of our tropospheric and stratospheric models and the results of our model simulations for COCl\textsubscript{2} as well as phosgene's parent compounds. In the final sections we discuss the implications of our calculations for the ODPs of phosgene's parent compounds.

2. The Production of Phosgene

Atmospheric COCl\textsubscript{2} is produced from the oxidation of chlorinated ethenes and ethanes [Ohta and Mizoguchi, 1980; Nelson et al., 1984, 1990], and a review of the known source strengths of these compounds suggests that the major contributors to this production are C\textsubscript{2}Cl\textsubscript{4}, C\textsubscript{2}HCl\textsubscript{3}, CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, and CCl\textsubscript{4} [Singh, 1976; Wilson et al., 1988; Tuazon et al., 1988; Helas and Wilson, 1992]. As was noted earlier, these compounds fall into two generic classes: the RPP compounds, which react with OH and absorb in the UV and thus produce COCl\textsubscript{2} in both the troposphere and the stratosphere, and CCl\textsubscript{4}, which does not react with OH in the troposphere and thus produces COCl\textsubscript{2} only in the stratosphere.

Because the degradation mechanisms of both the RPP compounds and CCl\textsubscript{4} are not well defined, particularly in the case of the chloroethenes, the yield of COCl\textsubscript{2} from the oxidation of these compounds is uncertain. Nevertheless, reasonable estimates for these yields can be deduced on the basis of the molecular structures of the parent compounds along with recent laboratory experiments. In Table 1, we summarize the COCl\textsubscript{2} yields adopted in our calculations from the OH-initiated oxidation and photolysis of each of COCl\textsubscript{2}'s parent compounds. Note that as was described earlier, we divide the sources into two components: (1) production of tropospheric phosgene and (2) production of stratospheric phosgene.

3. Model Formulation for Tropospheric Phosgene and Its Parent Compounds

The basic framework for our tropospheric simulation is the 2-D model of Cunnold et al. [1983] and Cunnold et al. [1986]. The model, which was developed and validated using the Atmospheric Lifetime Experiment and Global Atmospheric Gases Experiment (ALEGAGE) data sets, distributes and transports atmospheric tracers in the vertical and latitudinal directions.

<table>
<thead>
<tr>
<th>Source</th>
<th>Yield</th>
<th>References and Notes</th>
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<tbody>
<tr>
<td>C\textsubscript{2}Cl\textsubscript{4} + OH</td>
<td>0.47 COCl\textsubscript{2}</td>
<td>Tuazon et al. [1988]</td>
</tr>
<tr>
<td>C\textsubscript{2}HCl\textsubscript{3} + OH</td>
<td>0.4 COCl\textsubscript{2}</td>
<td>Tuazon et al. [1988]</td>
</tr>
<tr>
<td>CH\textsubscript{2}ClCH\textsubscript{3} + OH</td>
<td>1 COCl\textsubscript{2}</td>
<td>upper-limit yield assumed on the basis of molecular structure of parent compound</td>
</tr>
<tr>
<td>CHCl\textsubscript{3} + OH</td>
<td>1 COCl\textsubscript{2}</td>
<td>upper-limit yield assumed on the basis of molecular structure of parent compound</td>
</tr>
</tbody>
</table>

| Stratospheric Phosgene Sources |
| C\textsubscript{4}H\textsubscript{2}Cl\textsubscript{2} + hv | 0 COCl\textsubscript{2} | upper-limit yield assumed on the basis of molecular structure of parent compound |
| C\textsubscript{3}HCl\textsubscript{3} + OH | 0.4 COCl\textsubscript{2} | Tuazon et al. [1988] |
| CHCl\textsubscript{3} + hv | 0 COCl\textsubscript{2} | Nelson et al. [1984] |
| CHCl\textsubscript{3} + OH | 1 COCl\textsubscript{2} | upper-limit yield assumed on the basis of molecular structure of parent compound |
This is accomplished by apportioning the atmosphere into 12 hydrostatic boxes as illustrated in Figure 1. The concentration, \( C(J) \), of species \( J \) in the \( n \)th box is determined in the model by integrating the time-dependent mass continuity equation

\[
\frac{\partial C(J)}{\partial t} = \frac{-C(J)}{\tau(J)} + S(J) + T(J)
\]

where \( \tau(J) \) is the lifetime for species \( J \) against photochemical loss and/or wet removal in box \( n \), \( S(J) \) represents the production of species \( J \) from photochemical processes (and emissions for the surface boxes) within box \( n \), and \( T(J) \) represents the net transport of \( J \) into box \( n \).

Transport between boxes in the 2-D model is simulated using zonally averaged meridional and vertical velocities and eddy diffusion coefficients. These parameters were taken from Newell et al. [1969] and appropriately modified to optimize the model's ability to reproduce the observed distribution of CFC-11 as described by Cunnold et al. [1986] and Prinn et al. [1987]. It should be noted that the model, which includes only transport between neighboring boxes and has transport coefficients inferred from the distribution of long-lived tracers (with lifetimes longer than a few years), is not ideally suited to the simulation of a compound like COCl\(_2\), whose atmospheric residence time is of the order of a month or two. On the other hand, observations suggest that COCl\(_2\) is relatively well-distributed in the troposphere without major spatial or temporal gradients [Singh et al., 1977, 1978, Wilson et al., 1988]. This is probably due to the fact that COCl\(_2\)'s sources and sink are disperse, its sources arising from the photochemical decomposition of its relatively long-lived parent compounds and its sink from slow hydrolysis in cloud water. (Calculations using the formulation of Chameides [1984] indicate that only about 3% of the available COCl\(_2\) within an air mass is removed by hydrolysis over the lifetime of a typical cloud. This estimate is not inconsistent with the observations of Singh [1977] who measured COCl\(_2\) concentrations in an air mass before and after a 2 to 3-day storm period and observed a decrease of only about 15-20%.) The absence of significant gradients in the distribution of COCl\(_2\) suggests that the simulations presented here should provide a reasonable estimate of its distribution and atmospheric budget. In fact, as we illustrate in section 9, a sensitivity model calculation in which we alter the transport code to allow for convective-like transport from the lower troposphere to the stratosphere yields essentially the same results as those from our standard model.

Three loss processes are considered in the determination of \( \tau(J) \) in our standard model; these are loss via reaction with tropospheric OH, loss in the troposphere by wet removal, and photochemical destruction in the stratosphere, so that

\[
\tau(J) = \frac{1}{\tau_{\text{OH}}(J)} + \frac{1}{\tau_{\text{wet}}(J)}
\]

where \( \tau_{\text{OH}}(J) \) is the rate constant for the reaction of species \( J \) with OH. The lifetime, \( \tau_{\text{wet}}(J) \), against loss due to wet removal is treated in the model using the parameterization described in section 4 and the lifetime, \( \tau_{\text{wet}}(J) \), against loss in the stratosphere is estimated using a one-dimensional eddy diffusion model, as described in section 5.

It should be noted that the tropospheric lifetimes defined by equation (2) only account for reactions of the RFP compounds with OH. However, it has been proposed that Cl-initiated oxidation in the marine boundary layer could be an important sink for organic compounds such as C\(_2\)Cl\(_4\) which react rapidly with Cl [Singh and Kasting, 1988, Keene et al., 1990]. On the other hand, the spectroscopic measurements of Harris et al. [1992] indicate an upper limit of 0.25 ppbv for HCl (compared to 1 ppbv adopted by Singh and Kasting, 1988) in the marine boundary layer suggest that the role of Cl may be more limited. In the calculations presented here Cl-initiated reactions have been neglected. In the case of C\(_2\)Cl\(_4\), however, which has an extremely large rate constant with Cl [Atkinson and Aschmann, 1987], a brief discussion of the possible effects of this reaction is presented in section 9.

4. Tropospheric Wet Removal

Kinetic and photochemical data suggest that COCl\(_2\) is essentially unreactive in the troposphere; its reaction with OH is endoergic [DeMore et al., 1992], it is unreactive toward H\(_2\)O vapor [Butler and Snelson, 1979] and its absorption cross section in the near UV and visible is quite small [Singh, 1976, Heydorn, 1991]. On the other hand, COCl\(_2\) is known to dissolve in water and hydrolyze [Manogue and Pigford, 1960] and as a result is most likely removed from the troposphere by cloudwater and by deposition onto the ocean and other wet surfaces [Singh, 1976, Wine and Chameides, 1989]. Thus a simulation of the COCl\(_2\) atmospheric cycle requires a quantitative treatment of its wet removal in clouds and to the ocean. (Treatment of deposition to the ocean is also needed in our calculations to accurately simulate the production of COCl\(_2\) from the oxidation of CH\(_3\)CCl\(_3\), since ocean deposition appears to represent a nonnegligible sink for this compound [Wine and Chameides, 1989, Butler et al., 1991]). To properly simulate these loss processes, we adopted a wet removal parameterization.
based on the formulations of Johnson [1981], Wine and Chameides [1989], and Butler et al. [1991]. This parameterization is described below.

4.1. Wet Removal Parameterization for Phosgene and Other Chlorinated Compounds

A schematic illustration of our wet removal parameterization is presented in Figure 2. We consider two removal pathways: one pathway involving removal by clouds, and the other involving removal by deposition to the ocean. The flux $\Phi_i(J)$ of species $J$ through pathway $i$ is represented by the ratio of the species' atmospheric concentration $C(J)$ and a parameter referred to as the pathway "resistance," $R$, which has units of second per centimeter [Danckwerts, 1970]. Thus

$$\Phi_i(J) = \frac{C(J)}{R_i}$$

The total flux, $\Phi_{wet}(J)$, through both pathways is then determined by adding the two resistances as if they formed a parallel circuit, so that

$$\Phi_{wet}(J) = \frac{C(J)}{R_{atm}} + \frac{C(J)}{R_{cloud}} = C(J) \left( \frac{1}{R_{ocean}} + \frac{1}{R_{cloud}} \right)$$

where $R_{ocean}$ and $R_{cloud}$ represent the resistances for loss to the ocean and to clouds and rain respectively.

As is illustrated in Figure 2, deposition to the ocean is assumed to be controlled by four processes: these are transport from the free troposphere to the marine boundary layer, transport through a thin "film" or stagnant layer between the atmosphere and the ocean surface, transport through a thin film on the ocean surface, and transport into and loss via hydrolysis in the ocean. In the case of the last process, we consider downward transport and hydrolysis in two ocean layers: the mixed layer and the so-called deep ocean below the thermocline.

Similar to the formulation adopted in equation (5) for the total pathway resistance, the flux or loss due to each of the four processes used to simulate ocean deposition can be represented in terms of a ratio between a concentration and a resistance specific to that process. Because these process-specific resistances act in series, it can be easily shown that

$$R_{ocean} = \left( R_{atm} + R_{air-film} + R_{ocean-film} + R_{ocean} \right)$$

where $R_{ocean}$ is the fraction of the surface covered by ocean and the $R$ are used to represent the resistances for each of the processes listed above. For our simple zeroth order calculations, $R_{ocean}$ is assumed to be 0.7, while for our 2-D model calculations it is allowed to appropriately vary with latitude. The process-specific resistances $r_i$ like the total pathway resistance $R$, have units of seconds per centimeter. In general, it can be shown by solving the one-dimensional diffusion equation (or Fick’s law), that $r$ is given by the thickness of the layer of transport (often referred to as the film thickness) divided by the appropriate diffusion coefficient [Danckwerts, 1970].

Loss in clouds is assumed to be controlled by three processes: these are transport from the ambient atmosphere to the interstitial air of a cloud, transport to and accommodation on the droplet surface, and transport into and hydrolysis within the droplet interior. As in the case of ocean deposition, the total resistance due to rainout can be represented as a sum of the regime-specific resistances so that

$$R_{cloud} = (r_{rain-cloud} + r_{accommodation} + r_{cloud})$$

where the $r$ are again used to represent the resistances through each of the transport regimes.

The expressions and values adopted here for each of the process-specific resistances are listed in Table 2. While the values can in general vary considerably depending on the specific species' thermodynamic properties and the assumed state of the atmosphere and ocean, a few generalizations can be made for the range of species considered here and for the conditions assumed for the atmosphere and ocean. We find, for instance, that the loss to the ocean in our calculations is always limited by the ocean film resistance ($r_{ocean-film}$) and/or the ocean resistance ($r_{ocean}$). The relative contributions of these two resistances largely depends on the species' hydrolysis rate, $k$. We find that resistance at the thin film generally controls the rate of ocean deposition for species with relatively large rates of hydrolysis (i.e., $k > 3.5 \times 10^{-5}$ s$^{-1}$). Ocean deposition for species with relatively small hydrolysis rates, on the other hand, is generally dominated by the ocean resistance. For all cases considered here, the resistances due to transport from the free troposphere to boundary layer ($r_{atm}$) and to the ocean surface ($r_{air-film}$) have a negligible impact; these resistances are important only for species with extremely high solubilities and/or hydrolysis rates, and such species are not considered in this work.

For removal by clouds we find that $r_{cloud}$, the resistance due to transport into and hydrolysis in the droplet, is generally the dominant term, with $r_{rain-cloud}$, the resistance due to transport from the atmosphere to the interstitial air of the cloud, making a non-negligible contribution only in the case of species with relatively large solubilities and/or hydrolysis rates. (In the case of the compounds specifically considered here, including COCl$_2$, $r_{rain-cloud}$ always makes a negligible contribution to the total wet-removal resistance.) Note that for our determination of $r_{accommodation}$, we have assumed that the accommodation coefficient $\alpha$ is always greater than $10^{-3}$; this assumption seems reasonable in light of several different laboratory experiments.

![Figure 2. Schematic illustration of the processes included in the wet removal parameterization.](image-url)
Table 2a. Resistances \( r \) Used to Determine Rate of Ocean Deposition for Wet Removal Parameterization

<table>
<thead>
<tr>
<th>Resistance, ( r )</th>
<th>Value or Expression Used</th>
<th>Comments and References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{\text{m}} )</td>
<td>3.5 s/cm</td>
<td>Resistance due to transport from the free troposphere to the boundary layer estimated from the inverse of the marine boundary layer entrainment velocity of 2-5 mm/s (Bandy et al., 1992). Note that this resistance does not have a significant impact on overall ocean deposition rate for the range of species considered here.</td>
</tr>
<tr>
<td>( r_{\text{air-film}} )</td>
<td>1.25 s/cm</td>
<td>Resistance due to transport through thin air film between the ocean and atmosphere adopted from Liss (1983). Note that this resistance does not have a significant impact on overall ocean deposition rate for the range of species considered here.</td>
</tr>
<tr>
<td>( r_{\text{ocean-film}} )</td>
<td>( \frac{R}{HRTN_A10^3} )</td>
<td>Resistance due to transport through thin ocean film between the ocean and atmosphere is based on formulation of Liss (1983).</td>
</tr>
<tr>
<td>( r_{\text{ocean}} )</td>
<td>( \left( \frac{H}{k_1D_1} \right) \left( \frac{S_0 - Q}{S_0 + Q} \right) )</td>
<td>Resistance due to transport through and hydrolysis in ocean is based on a two-layer ocean transport formulation similar to that of Butler et al. (1991). Diffusion coefficients ( D_1 ) and ( D_2 ) where adopted from Johnson (1981). Latitudinally dependent ocean temperatures for determining hydrolysis rates were taken from Reynolds (1982) for the mixed-layer and were assumed to be one-half of the mixed-layer temperature (in °C) for the thermocline following Butler et al. (1991). Latitudinally-dependent mixed layer thicknesses were adopted from Li et al. (1984).</td>
</tr>
</tbody>
</table>

Here, \( R = 170 \text{s/cm} \), \( R \) is gas constant, \( T \) is temperature, \( N_A \) is Avogadro’s number. \( H \) is species' solubility constant. \( S = (D_1 a_1 + D_2 a_2) / (2 D_1 a_1) \) \( e^{k_1 t} \); \( Q = (D_1 a_1 - D_2 a_2) / (2 D_1 a_1) \) \( e^{k_2 t} \); \( k_1 = \sqrt{k_1} / D_1 \), \( k_2 = \sqrt{k_2} / D_2 \). \( k_1 \) is pseudo first-order hydrolysis rate constant in ocean mixed layer, \( k_2 \) is pseudo first order hydrolysis rate constant below ocean thermocline, \( D_1 \) is diffusion coefficient in ocean mixed layer (= 40 cm²/s), \( D_2 \) is diffusion coefficient below ocean thermocline (= 1.7 cm²/s), and \( z_1 \) is thickness of ocean mixed layer.

which all yield accommodation coefficients significantly larger than \( 10^{-5} \) for a variety of species of varying solubilities (Mozurkewich et al.; 1987, Jayne et al., 1990, Van Doren et al., 1990). Given this assumption for \( c_{\text{a}} \), we find that \( r_{\text{a}} \) has a negligible impact on the overall rate of rainout for all species considered here. This latter result, which is equivalent to having thermodynamic equilibration of the species between the gas and aqueous phases of the cloud, is consistent with more detailed cloud chemistry calculations which yield gas/aqueous phase equilibration times for soluble species in clouds of only several seconds or less [Chameides, 1984, Schwartz, 1986].

4.2. Zeroth-Order Evaluation of Wet Removal Lifetimes

Before describing the application of the wet removal parameterization to our 2-D model, it is useful to use the parameterization in a zero-dimensional model to roughly estimate the range of wet removal lifetimes that we might expect to find for species as a function of their solubility and hydrolysis rate. To carry out this "zeroth-order evaluation" we first assume, for simplicity, that all species are distributed in the atmosphere with constant mixing ratios; we also neglect longitudinal and latitudinal variations. With these simplifications, the globally averaged lifetime, \( \tau_{\text{wet}}^{\text{avg}} (J) \), for a species "\( J \)" can be estimated by

\[
\tau_{\text{wet}}^{\text{avg}} (J) = \frac{H_A C(J)}{\Phi_{\text{Io}} - \frac{1}{R_{\text{ocean-Io}}} + \frac{1}{R_{\text{cloud-Io}}}}
\]

where \( H_A \) is the atmospheric scale height (taken here to be 8.4 km).

Wet removal lifetimes calculated from equation (9) using ocean and rainout resistances appropriate for globally averaged atmospheric and oceanic conditions (see Table 2) are plotted as a function of the species' solubility and mixed layer hydrolysis rate constants in Figure 3. Not surprisingly, we find that the total wet removal lifetime increases dramatically with decreasing solubility and decreasing hydrolysis rates. Note in Figure 3 that lifetimes of the order of 10 days are obtained for species with solubilities and hydrolysis rates greater than 1 (in units of molar per atmosphere and s⁻¹, respectively). On the other hand, lifetimes of 1000 years or longer are obtained for species with solubilities less than \( 10^{-4} \text{ M/atm} \) and hydrolysis rate constants less than \( 10^{-2} \text{ s}^{-1} \).

In Figure 4 we plot the ratio of \( R_{\text{ocean-Io}} \) to \( R_{\text{cloud-Io}} \). When this ratio is greater than one, removal via cloud deposition
Table 2b. Resistances r Used to Determine Rate of Loss in Clouds for Wet Removal Parameterization

<table>
<thead>
<tr>
<th>Resistance, r</th>
<th>Value or Expression Used</th>
<th>Comments and References</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_{atm-cloud}</td>
<td>1.0 \ s/cm</td>
<td>Resistance due to transport from the atmosphere to the interstitial air in a cloud assumed to be 1.0 \ s/cm. This value is adopted to ensure that the minimum lifetime for rainout of an infinitely soluble species is 10 days. Note that this resistance does only have a minor impact on overall rainout rate for the range of species considered here.</td>
</tr>
<tr>
<td>R_{accommodation}</td>
<td>\left(1 + \frac{4}{3} \alpha \right) \left(1 + \frac{8 \pi T}{8 R T}</td>
<td></td>
</tr>
</tbody>
</table><p>ight)^{-1} | Resistance due to transport to and accommodation on the droplet surfaces based on the formulation of Chameides [1984] and Schwartz [1986]. For our zeroth-order calculations, a value of 8.1 \times 10^5 \ \text{L/cm}^2 was adopted for the cloud liquid water column concentration [Greenwald et al., [1993]]. For our two-dimensional model calculations, a latitudinally-dependent cloud liquid water column concentration given by Greenwald et al. interpolated for every month of the year was used. It was further assumed that at each latitude, 75% of the liquid water column resided between 1000 and 500 mbar and the remaining 25% resided between 500 and 200 mbar. Note that as long as \alpha &gt; 10^5, this resistance does not have a significant impact on overall wet deposition rate for the range of species considered here. |
| R_{cloud} | \frac{1}{H k W_L R T N_A} \times 10^{-3} | Resistance due to transport into the cloud droplet and loss via hydrolysis is based on formulation of Chameides [1984] and Schwartz [1986]. Note that for the range of k adopted here, a dissolved species is always found to be well mixed within the droplet, and thus R_{cloud} is found to be independent of transport parameters such as the molecular diffusion coefficient. Here, (I) is mean free path (= 10^{-1} \ cm), (r) is droplet radius (= 10^{-1} \ cm), (\alpha) is accommodation coefficient, (m) is species' molecular weight, (R) is gas constant, (W_L) is total cloud liquid water column concentration in liters per square centimeter, (k) is first-order hydrolysis rate constant in cloud, (N_A) is Avogadro's number, (H) is species' solubility constant, (T) is droplet temperature for R_{accommodation} and cloud temperature for R_{cloud}. |</p>

The general results illustrated in Figure 4, we find in Table 3 that cloud removal is the dominant wet removal pathway for COCl_2, while deposition to the ocean dominates for CH_3CCl_3 and CHCl_3 (Note that our CH_3CCl_3 lifetime is essentially consistent with the estimate of Butler et al. \[1991\] and somewhat longer than that obtained by Wine and Chameides \[1989\].) As we will see later these lifetimes result in our finding that wet removal is a major sink for tropospheric COCl_2, a minor sink for CH_3CCl_3, and a negligibly small sink for CHCl_3.

4.3. Two-Dimensional Application of Wet Removal Parameterization

In order to apply the wet removal parameterization to the 2-D model, an ocean removal lifetime \(\tau_{ocean}^{\text{surf}}\) for the surface boxes (i.e., \(n = 1-4\)) and a cloud removal lifetime \(\tau_{cloud}^{\text{surf}}\) for all the tropospheric boxes (i.e., \(n = 1-8\)) must be specified. To do this, we assume that within each box, pressure and density are hydrostatically related. We also assume that the deposition flux to the ocean is proportional to \(C_o^J\) (J), the concentration of the species...
at the bottom of the box, while cloud removal is proportional to $C^n(J)$, the average concentration in the box. It then follows that

\[
\tau_{ocean-tot}^n(J) = \frac{\int_{-500}^{0} \exp(-z/H_A) dz}{C^n(J)/R_{ocean-tot}}
\]

0.5 \cdot H_A \cdot R_{ocean-tot}^n \quad n = 1 \text{ - } 4 \quad (10a)

\[
\tau_{cloud-tot}^n(J) = \frac{\int_{-500}^{0} \exp(-z/H_A) dz}{C^n(J)/R_{cloud-tot}}
\]

0.7 \cdot H_A \cdot R_{cloud-tot}^n \quad n = 1 \text{ - } 4 \quad (10b)

5. Stratospheric Model

We determine the stratospheric lifetimes by first estimating the vertical profiles of the species within the stratosphere using a 1-D eddy-diffusion model. These profiles are then used along with their rates of loss in the stratosphere as a function of altitude to calculate the lifetimes in the corresponding boxes of the 2-D model as a function of the solar zenith angle. The 1-D model divides the atmosphere from the tropopause (i.e., $z = 12$ km for global average conditions) to 49 km into 38 layers.

Figure 4. Ratio $R_{ocean-tot} / R_{cloud-tot}$ as a function of the hydrolysis rate constant and solubility constant.
Table 3. Zeroth-Order Estimation of $\tau_{\text{wet-ocean}}$, the Wet Removal Lifetime of Phosgene (COCl$_2$), Methylchloroform (CH$_3$CCl$_3$), and Chloroform (CHCl$_3$) Using Equation (5)

<table>
<thead>
<tr>
<th></th>
<th>COCl$_2$</th>
<th>CH$_3$CCl$_3$</th>
<th>CHCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ocean deposition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$, solubility constant, M/atm</td>
<td>0.2</td>
<td>0.08</td>
<td>0.00554</td>
</tr>
<tr>
<td>$k_1$, hydrolysis rate constant in mixed layer, s$^{-1}$</td>
<td>5</td>
<td>$1.3 \times 10^4$</td>
<td>$8.6 \times 10^{11}$</td>
</tr>
<tr>
<td>$k_2$, hydrolysis rate constant at thermocline, s$^{-1}$</td>
<td>5</td>
<td>$2.3 \times 10^6$</td>
<td>$1.5 \times 10^{11}$</td>
</tr>
<tr>
<td>$\tau_{\text{eq}}$, s/cm</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}$, s/cm</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}, s/cm$</td>
<td>35.37</td>
<td>88.44</td>
<td>1.28x10$^5$</td>
</tr>
<tr>
<td>$R_{\text{eq-cloud}}$, s/cm</td>
<td>$1.47 \times 10^2$</td>
<td>$3.37 \times 10^3$</td>
<td>$1.33 \times 10^6$</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}, years$</td>
<td>1.53</td>
<td>131.9</td>
<td>5.08x10$^6$</td>
</tr>
<tr>
<td><strong>Cloud deposition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H$, solubility constant, M/atm</td>
<td>0.2</td>
<td>0.08</td>
<td>0.00554</td>
</tr>
<tr>
<td>$k_1$, hydrolysis rate constant, s$^{-1}$</td>
<td>5</td>
<td>$7.57 \times 10^{11}$</td>
<td>$4.2 \times 10^3$</td>
</tr>
<tr>
<td>$\alpha$, accommodation coefficient</td>
<td>$&gt; 10^5$</td>
<td>$&gt; 10^5$</td>
<td>$&gt; 10^5$</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}$, s/cm</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}, s/cm$</td>
<td>$&lt; 0.69$</td>
<td>$&lt; 0.80$</td>
<td>$&lt; 0.76$</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}, s/cm$</td>
<td>5.68</td>
<td>$9.37 \times 10^{11}$</td>
<td>$2.46 \times 10^9$</td>
</tr>
<tr>
<td>$R_{\text{eq-cloud}}$, s/cm</td>
<td>6.68</td>
<td>$9.37 \times 10^{11}$</td>
<td>$2.46 \times 10^9$</td>
</tr>
<tr>
<td>$\tau_{\text{eq-cloud}}, years$</td>
<td>0.18</td>
<td>$2.5 \times 10^8$</td>
<td>$6.56 \times 10^8$</td>
</tr>
<tr>
<td><strong>Total wet removal</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_{\text{wet-ocean}}, years$</td>
<td>0.16</td>
<td>131.85</td>
<td>5.08x10$^4$</td>
</tr>
</tbody>
</table>

Calculations carried out assuming a global mean T of 293 K for the mixed layer and 283 K for the thermocline, a mixed layer depth of 75 m [Li et al., 1984], and T for clouds of 265 K. Solubility and hydrolysis rate constants for COCl$_2$, CH$_3$CCl$_3$, and CHCl$_3$ taken from D. Worsnop (private communication, 1993), Gerkens and Franklin [1989], and Jeffers et al. [1989], respectively. Note that the data for COCl$_2$ are uncertain [De Bruyn et al., 1992].

Each having a thickness of 1 km. A constant concentration $C_0$ is specified at the lower boundary (i.e., tropopause), and a flux of zero is assumed at the top boundary. The model then determines the species' concentration $C_z$ as a function of altitude $z$ by integrating the steady state continuity equation

$$0 = S_z(J) + L_z(J) = C_z = \frac{d}{dz} \left( K_z n_M \frac{dX_z(J)}{dz} \right)$$

where $S_z$ represents the source of the species (in units of molecules per cubic centimeter per second) as a function of altitude $z$, $L_z$ the loss of species (in units of reciprocal seconds), $K_z$ the eddy diffusion coefficient (adopted from Luther et al., [1979]), $n_M$ the atmospheric number density, and $X_z$ the species' mixing ratio (m/m).

In our standard model, the rate of stratospheric loss is determined from two photochemical processes: photolysis and reaction with OH. (Calculations indicate that reactions of the compounds considered here with O(1D) and with Cl atoms do not play a significant role.) Thus

$$L_z(J) = I_z(J) + k_{\text{O}(1D)} C_z(\text{O})$$

where $I_z(J)$ is the photolysis frequency for species $J$ (in units of reciprocal seconds) as a function of altitude $z$, and the other terms are all defined earlier. Concentrations for OH were adopted from Singh and Kasting [1988] and photolysis frequencies were calculated using the radiative transfer model of Stamnes et al. [1988] with cross sections and quantum yields taken from DeMore et al. [1992] and Berry [1974] for the RPP compounds and Heydorn [1991] for COCl$_2$.

In addition to the standard model calculations described above, we have carried out three sets of sensitivity model calculations: (1) calculations with $K_z$ increased and decreased by a factor of 2, (2) calculation with $C_z(\text{O})$ increased and decreased by a factor of 5, and (3) calculations which include an additional sink for stratospheric COCl$_2$ arising from reaction with sulfate aerosols. The results of these sensitivity calculations are discussed in section 9.

With the exception of the simulation of stratospheric COCl$_2$, model calculations are carried out with $S_z$ set equal to zero at all altitudes. As discussed in section 2 and outlined in the bottom section of Table 1, the source term for stratospheric COCl$_2$ is assumed to be given by
$S_1(COCl_2) = J_1(CCL_4) C_2(CCL_4) +$

$$k_{OH}(CH_3CCl_3) C_2(CH_3CCl_3) +$$

$J_1(CCL_4) C_2(CCL_4) + 0.47 k_{OH}(C_2Cl_4) C_2(C_2Cl_4) +$

$0.4 k_{OH}(C_2HCl_3) C_2(C_2HCl_3) +$

$$k_{OH}(CHCl_3) C_2(CHCl_3)$$

(13)

With the model parameters defined as described above, the stratospheric vertical profiles and loss rates for COCl$_2$ and its parent compounds are determined by the 1-D model as a function of the solar zenith angle $\theta$, with $\theta$ varying from 0° to 80°. An effective lifetime $\tau_{\text{eff}}(J)$ as a function of solar zenith angle is then given by

$$\tau_{\text{eff}}(J) = \frac{\int_{0}^{\infty} C(J) \, dz}{\int_{0}^{12 \, \text{km}} C(J) \, dz} \quad (14)$$

Note that a lower limit of 12 km is chosen for the integrals in equation (14) because this corresponds to the lower boundary of the stratospheric boxes of the 2-D model. Also note that because $C_t$ appears in both the numerator and denominator of equation (14) and $C_t$ is linearly dependent on the assumed lower boundary condition $C_0$, $\tau_{\text{eff}}$ is independent of this arbitrary model parameter. The seasonally dependent lifetimes for mid-latitudes (i.e., 50°) and tropical latitudes (i.e., 15°) are then used to represent the effective lifetimes for the appropriate stratospheric boxes in the 2-D model as a function of the day of the year.

The stratospheric lifetimes with a solar zenith angle of 60° (assumed to be a global average condition) are listed in Table 4. Note again that in keeping with our earlier discussions, we have calculated two sets of lifetimes for COCl$_2$: one for "tropospheric" COCl$_2$ (i.e., COCl$_2$ produced in the troposphere and transported into the stratosphere) and one for "stratospheric" COCl$_2$ (i.e., COCl$_2$ produced in the stratosphere). Because tropospheric COCl$_2$ enters the stratosphere at the tropopause and must first be transported to higher altitudes before it can be photolyzed, it has a longer stratospheric lifetime than that of stratospheric COCl$_2$, which is produced in the upper and middle stratosphere. In either case, it is also interesting to note that COCl$_2$'s stratospheric lifetime is of the order of years. This long lifetime is caused by the fact that COCl$_2$ is a weak absorber in the near and middle ultraviolet and does not react with OH. Because of this long lifetime, a significant fraction of the COCl$_2$ that is either produced in or transported to the stratosphere will tend to be cycled back to the troposphere before being photochemically destroyed.

### 6. Source Strengths of Tropospheric Phosgene

As summarized in the top part of Table 1, tropospheric COCl$_2$ is assumed to be produced from the OH-initiated oxidation of the four RPP compounds. The strength and distribution of each of these sources is determined by first simulating the cycle of each of the four RPP compounds in the 2-D model with the appropriate OH rate constant taken from DeMore et al. [1992] and the appropriate anthropogenic emission rate taken from the literature. With the exception of CHCl$_3$, the emission rate is assumed to be constant in time and to vary latitudinally in the manner described for CH$_3$CCl$_3$ by Mudgley [1989]. In the case of CHCl$_3$, in addition to the anthropogenic source distribution, an oceanic source has also been considered which varies latitudinally according to Khalil et al. [1983]. In the case of CH$_3$CCl$_3$, we include loss via wet deposition as described in section 4 as well as loss via OH oxidation. The results of these simulations are briefly outlined below and summarized in Table 5.

#### 6.1. Methylchloroform

The annual mean CH$_3$CCl$_3$ concentration calculated for the 1987 emission rate of 617 kt/yr [Mudgley, 1989] is plotted as a function of latitude and altitude in Figure 5. Also shown in Figure 5 are the average concentrations measured in 1989 from the ALE/GAGE surface network [Prinn et al., 1992]. We find good agreement between the calculated and observed concentrations; however this is not surprising since the model was originally tuned to reproduce the CH$_3$CCl$_3$ ALE/GAGE data.

Our calculations yield a globally averaged concentration of 154 pptv and an average atmospheric residence time of 5.6 years. About 83.5% of the CH$_3$CCl$_3$ released at the surface is estimated to be destroyed in the troposphere by OH, 4.1% is lost via wet removal, and the remaining 12.4% is lost in the stratosphere. These results are in reasonable agreement with the assessment of Butler et al. [1991]. Assuming that one molecule of COCl$_2$ is produced for each molecule of CH$_3$CCl$_3$ oxidized by OH, we infer an annual tropospheric production rate of COCl$_2$ of 28 pptv per year (see Table 5).

#### 6.2. Tetrachloroethylene

The annual mean CCl$_4$ concentrations calculated as a function of altitude and latitude for an emission rate of 580 kt/yr [Class and Ballschmiter, 1987] are plotted in Figure 6. Our results are compared with the surface CCl$_4$ concentrations observed by Class and Ballschmiter [1987] at various sampling sites over the Atlantic and Indian Oceans in the years 1982-1986, and with measurements taken by Koppmann et al. [1993] on a cruise through the Atlantic Ocean made in August-September 1989. As can be seen in Figure 6, our results are in good agreement with the measured concentrations. Our calculations, similar to those of Derwent and Eggleton [1978], yield an average atmospheric residence time of 0.38 years. with about
98.4% of the annual \( \text{C}_2\text{Cl}_4 \) emissions destroyed by OH in the troposphere and only 1.6% destroyed in the stratosphere. If 0.47 molecules of COCl₂ are produced for each molecule of \( \text{C}_2\text{Cl}_4 \) oxidized by OH, our calculations imply a global COCl₂ source from \( \text{C}_2\text{Cl}_4 \) of about 11 pptv/yr.

### 6.3. Chloroform

Our model-calculated CHCl₃ concentrations were obtained assuming a total emission rate of 810 kt/yr with 40% distributed as an anthropogenic source and 60% distributed as an oceanic source as discussed above. As is illustrated in Figure 7, an emission rate of this magnitude and distribution yields reasonable agreement with all the measurements, except those of Singh et al. [1983]. (We found that model-calculated concentrations fell below observations when the total emission source of 610 kt/yr estimated by Khalil et al. [1983] was used.)

We estimate an atmospheric residence time for CHCl₃ of about 0.53 years with approximately 98.3% of the total budget lost in the troposphere and 1.7% in the stratosphere. If one molecule of COCl₂ is produced for each molecule of CHCl₃ oxidized by OH, then our calculations imply a tropospheric source of COCl₂ from CHCl₃ of about 47 pptv/yr.

### 6.4. Trichloroethylenne

In Figure 8, we compare model-calculated concentrations for \( \text{C}_2\text{HCl}_3 \) assuming an emission rate of 300 kt/yr [Gidel et al., 1983; A. McCulloch, private communication, 1992] with those measured by Koppmann et al. [1993]. Significant discrepancies between the model-calculated and observed concentrations are apparent. Because of \( \text{C}_2\text{HCl}_3 \)'s short atmospheric residence time of only 7 days a direct comparison of the model-calculated concentrations with observations is problematic. However, because of its relatively small yield of COCl₂ production, \( \text{C}_2\text{HCl}_3 \) is of only minor importance to the overall COCl₂ cycle, and thus uncertainties in its emissions and distribution have a negligible impact on our conclusions. We infer a tropospheric source of COCl₂ from \( \text{C}_2\text{HCl}_3 \) of about 6.4 pptv/yr. Because of \( \text{C}_2\text{HCl}_3 \)'s short lifetime, essentially all of the species is destroyed in the troposphere by OH, and direct injection to the stratosphere is thereby prevented.

### 6.5. Summary of Tropospheric Sources

Table 5 summarizes the source strengths of COCl₂ to the troposphere from the four RPP compounds. We estimate a total tropospheric rate of COCl₂ production of about 92 pptv/yr, with about half coming from CHCl₃, 30% coming from CH₃CCl₂, 12% from C₂Cl₄, and the reminder from C₂HCl₃. Although not illustrated in a figure, we find that the majority of the COCl₂ is produced in the lower troposphere and in the northern hemisphere; this is to be expected given the distribution of the RPP compounds and their emissions. Comparison of these results with those obtained by Helas and Wilson [1992] using a zero-dimensional box model indicate qualitative agreement with some small discrepancies. Our total COCl₂ source strength is about 10% higher than that of Helas and Wilson [1992], with about 25% and 10% higher source strengths arising from CHCl₃ and CH₃CCl₂, respectively, and 15% and 35% lower source strengths from C₂Cl₄ and C₂HCl₃, respectively. For the most part, these differences can be attributed to the different emission rates assumed for the parent compounds.

### 7. Fate of Tropospheric Phosgene

Figures 9 and 10 compare model-calculated distributions of tropospheric COCl₂ with measurements made by Wilson et al. [1988] and Singh [1976]. The agreement between measurements and simulations is reasonably good, with both the measurements and model calculations indicating an average northern hemispheric mixing ratio of about 15-20 pptv, with at most modest latitudinal and seasonal variations.

Table 6 summarizes the budget of tropospheric COCl₂ inferred by the 2-D model. Of the total 92 pptv of tropospheric COCl₂ produced annually by the oxidation of the RPP compounds, we find that 99.6% is directly removed from the atmospherically nitric oxide (NO) and hydroxyl (OH) will be produced.

---

**Table 5. Summary of Simulations of the RPP Compounds and Their COCl₂ Production Rates**

<table>
<thead>
<tr>
<th>RPP Compound</th>
<th>Release Rate, kt/yr</th>
<th>Average Concentration, pptv</th>
<th>Average Residence Time, yr</th>
<th>Phosgene Production Rate, pptv/yr</th>
<th>Percentage of Total Production COCl₂, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>810</td>
<td>22.8</td>
<td>0.53</td>
<td>47.0</td>
<td>50.8</td>
</tr>
<tr>
<td>CH₃CCl₂</td>
<td>614</td>
<td>152.9</td>
<td>5.59</td>
<td>27.7</td>
<td>29.9</td>
</tr>
<tr>
<td>C₂Cl₄</td>
<td>580</td>
<td>8.8</td>
<td>0.38</td>
<td>11.4</td>
<td>12.3</td>
</tr>
<tr>
<td>C₂HCl₃</td>
<td>300</td>
<td>0.4</td>
<td>0.028</td>
<td>6.4</td>
<td>7.0</td>
</tr>
</tbody>
</table>

**Figure 5.** Model-calculated (open symbols) and observed (solid symbols) CH₃CCl₂ concentrations. The open squares represent the lower troposphere, the open diamonds represent the upper troposphere, and the open circles represent the stratosphere. The calculated concentrations were obtained assuming a steady emission rate of 617 kt/yr distributed latitudinally. The solid squares represent annually averaged observations as a function of latitude obtained from the ALEGAGE remote surface network [Prinn et al., 1992].
Figure 6. Model-calculated (open symbols) and observed (solid symbols) \( \text{C}_3\text{Cl}_3 \) concentrations. The open squares represent the lower troposphere, the open diamonds represent the upper troposphere, and the open circles represent the stratosphere. The calculated concentrations were obtained assuming a steady emission rate of 580 kt/yr distributed latitudinally. The solid squares represent annually averaged observed surface concentrations as a function of latitude taken by Class and Ballschmitter [1987] and the solid circle represents averaged surface measurements taken by Koppmann et al. [1993].

Figure 7. Model-calculated (open symbols) and observed (solid symbols) CHCl\(_3\) concentrations. The open squares represent the lower troposphere, the open diamonds represent the upper troposphere and the open circles represent the stratosphere. The calculated concentrations were obtained assuming a steady emission rate of 810 kt/yr distributed latitudinally. The solid squares represent annually averaged observed surface concentrations as a function of latitude made by Khalil et al. [1983]. The solid diamonds represent averaged surface measurements made by Singh et al. [1983] over the Eastern Pacific in December 1981 and the solid circle represents surface measurements made by Rasmussen et al. [1982] at 30° S in November 1981.

Figure 8. Model-calculated (open symbols) and observed (solid symbols) \( \text{C}_3\text{HCl}_3 \) concentrations. The open squares represent the lower troposphere, the open diamonds represent the upper troposphere, and the open circles represent the stratosphere. The calculated concentrations were obtained assuming a steady emission rate of 300 kt/yr distributed latitudinally. The solid squares represent averaged hemispheric surface observations made by Koppmann et al. [1993] on a cruise through the Atlantic Ocean in August-September 1989.

Figure 9. The latitudinal and vertical distribution calculated for tropospheric COC\(_2\) (i.e., COCl\(_2\) produced from the tropospheric oxidation of the four RPP compounds). The open squares represent the lower troposphere, the open diamonds represent the upper troposphere, and the open circles represent the stratosphere. The solid square represents annually averaged airborne measurements made by Wilson et al. [1988] between Germany and Spitsbergen (50°-78° N) at altitudes of 5-12 km. The solid square represents surface measurements made by Singh et al. [1977] at a remote site in California (38° N) in 1976.

8. Fate of Stratospheric Phosgene

Inspection of Figure 9 reveals that our model simulations of the tropospheric COC\(_2\) cycle predict a stratospheric COC\(_2\) concentration of about 10-15 pptv. This concentration is considerably smaller than the levels of 20-30 pptv observed in the lower stratosphere by Wilson et al. [1988]. The reason for this discrepancy is the fact that the calculations from the previous section omitted the production of COC\(_2\) in the stratosphere. In this section we address this later aspect of the COC\(_2\) cycle with our 1-D stratospheric model.

As was discussed in section 2 and summarized in the bottom part of Table 1, we consider four sources of stratospheric COC\(_2\). These arise from the photolysis of CCL, the OH oxidation and photolysis of \( \text{C}_3\text{Cl}_3 \) and the oxidation of CH\(_2\text{ClCl}_3\) and CHCl\(_3\). (While OH-initiated oxidation of \( \text{C}_3\text{HCl}_3 \) produces COCl\(_2\), its contribution to stratospheric COC\(_2\) is negligible because of the
Figure 10. Model-calculated and observed tropospheric COCl₂ concentrations as a function of time of year in the northern hemisphere poleward of 30°N. The model-calculated concentrations are for the lower troposphere (boxes n = 1) (represented by pluses) and the upper troposphere (box n = 5) (represented by crosses) of the two-dimensional model using the COCl₂ sources from the oxidation of the RPP compounds. The observed concentrations are based on the mid tropospheric airborne measurements of Wilson et al. [1988] and are represented by solid squares.

The role of each of the five stratospheric sources relative to that which arises from the upward transport of tropospheric COCl₂ is indicated in Figure 11a, where profiles calculated with the 1-D stratospheric model for equinoctial conditions at midlatitudes are illustrated for each source and all sources together. While the tropospheric COCl₂ profile decreases monotonically from its concentration at the tropopause, the profiles which include stratospheric production increase in concentration in the lower stratosphere and generally reach a maximum at altitudes between 21 and 27 km. The exact altitude of the maximum depends on the species. The COCl₂ produced from C₂Cl₄, CHCl₃, and CH₂CCl₃ peaks at an altitude of about 22 km because of their reactivity toward OH, while COCl₂ from the unreactive CCl₄ peaks at about 27 km. Interestingly, a comparison of the profile which includes all sources with the profile from the midlatitude measurements of Wilson et al. [1988] indicates reasonably good agreement in both the concentration magnitude and profile shape in the lower stratosphere (see Figure 11).

The model-calculated budgets of stratospheric COCl₂ produced from CCl₄, C₂Cl₄, CHCl₃, and CH₂CCl₃ for global average conditions are presented in Table 7. Because of COCl₂’s relatively long lifetime against destruction in the stratosphere and its rapid removal rate in the troposphere, we find that a significant portion of the COCl₂ that is produced in the stratosphere is transported to and lost in the stratosphere.

Table 6. Model-Calculated Budget for Tropospheric COCl₂

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate, ppb/yr</th>
<th>Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total source (see Table 5)</td>
<td>92.4</td>
<td>100</td>
</tr>
<tr>
<td>Loss via cloud removal in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lower troposphere</td>
<td>70.9</td>
<td>76.7</td>
</tr>
<tr>
<td>Loss via cloud removal in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>upper troposphere</td>
<td>13.1</td>
<td>14.2</td>
</tr>
<tr>
<td>Loss via ocean deposition</td>
<td>8.0</td>
<td>8.7</td>
</tr>
<tr>
<td>Total wet deposition</td>
<td>92.0</td>
<td>99.6</td>
</tr>
<tr>
<td>Transport to and loss in</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>stratosphere</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total loss</td>
<td>92.4</td>
<td>100</td>
</tr>
</tbody>
</table>

Here, tropospheric COCl₂ is produced from the oxidation of the four RPP compounds.

Figure 11a. Calculated profiles for COCl₂ in the stratosphere for a solar zenith angle of 65°. The solid lines are the calculated profiles: A for tropospheric COCl₂ (no stratospheric source), B for stratospheric COCl₂ from CCl₄, C for stratospheric COCl₂ from C₂Cl₄, D for stratospheric COCl₂ from CHCl₃, E for stratospheric COCl₂ from CH₂CCl₃, and F is total COCl₂ (tropospheric plus stratospheric sources). The squares indicate the measurements of Wilson et al. [1988]. The concentration at the lower boundary (i.e., tropopause) for simulations A and F was chosen to be equal to the COCl₂ concentration obtained for the northern, upper tropospheric box in our 2-D model simulation (see Figure 9). Note that the resulting averaged stratospheric concentration obtained from our simulation of tropospheric COCl₂ using this boundary condition (i.e., profile A) is consistent with that obtained for the stratosphere in our 2-D box model simulation.

Wilson et al. [1988] indicates reasonably good agreement in both the concentration magnitude and profile shape in the lower stratosphere (see Figure 11).

Figure 11b. Calculated profiles for COCl₂ in the stratosphere for a solar zenith angle of 65°. The solid lines are calculated profiles: A is for our standard model, B for K₅ multiplied by a factor of 2, C for C₅(OH) multiplied by a factor of 5, D for including potential reaction of COCl₂ on sulfate aerosols with γ = 1, E for including potential reaction of COCl₂ on sulfate aerosols with γ = 10⁻², and F for including potential reaction of COCl₂ on sulfate aerosols with γ = 5x10⁻³.
transported to the troposphere before it is destroyed. As is indicated in Table 7, the fraction returned to the troposphere is estimated to be roughly one third in the case of CCl₄, two thirds in the case of that produced from C₂Cl₂ and four fifths in the case of stratospheric CCl₂ produced from CH₃CCl₃ and CHCl₃. The larger fractions returned to the troposphere for the CCl₂ produced from CH₃CCl₃, C₂Cl₂, and CHCl₃ are caused by the fact that this CCl₂ is generated at lower stratospheric altitudes, where it encounters less UV radiation and has a shorter distance to travel to reach the tropopause. As we discuss in the next section, the transport of stratospheric CCl₂ into the troposphere can have a significant impact on the stratospheric chlorine loading of these compounds and ultimately therefore on their ozone depletion potentials.

9. Effect of Phosgene Transport on Stratospheric Chlorine Loadings of Phosgene Parent Compounds

An important factor in determining the potential for a compound to deplete stratospheric ozone is its stratospheric chlorine loading, defined here as the percentage of the chlorine contained in the species that is emitted at the surface and ultimately released in the stratosphere as reactive chlorine capable of participating in the catalytic destruction of ozone. Estimates of the stratospheric chlorine loadings of CCl₂'s parent compounds are presented in Table 8 for a variety of model assumptions. (Note that we indicate absolute chlorine loadings in Table 8 rather than the more standard, chlorine loading potentials, which are normalized to the chlorine loading of CFC-11. The reason for this will be discussed in section 10.)

An indication of the effect of tropospheric-stratospheric transport of CCl₂ on the stratospheric chlorine loadings of CCl₂'s parent compounds can be obtained by comparing the results listed in Table 8 for the standard model with those listed for "Model 0," where exchange of CCl₂ across the tropopause was neglected. Because of tropospheric CCl₂'s relative short lifetime and stratospheric CCl₂'s long lifetime, we find that tropospheric-stratospheric CCl₂ transport tends to lower the stratospheric chlorine loadings of the phosgene parent compounds, and, in some cases the decrease can be significant. Most notable are CCl₂ and CHCl₃, because these species are destroyed efficiently in the lower stratosphere, major fractions (i.e., 70% for CCl₂ and 85% for CHCl₃) of the stratospheric CCl₂ produced from these compounds are returned to the troposphere and as a result, consideration of tropospheric-stratospheric transport tends to lower the stratospheric chlorine loadings of these two species. In some cases the decrease can be significant. In the case of CCl₂, the stratospheric chlorine loadings for these two species are so small, they are not effective agents of stratospheric ozone depletion, and thus the decreased chlorine loadings calculated for these two compounds will not affect overall predictions of ozone depletion from halocarbons.) The impact on the chlorine loading of CCl₄ is somewhat less pronounced (approximately 14%) because the CCl₂ from this compound is produced at higher stratospheric altitudes. A relatively small correction (i.e., 3%) to the chlorine loading of CH₃CCl₃ is predicted because the vast majority of the chlorine atoms from CH₃CCl₃ decomposition in the stratosphere are not converted into CCl₂. Recall that CCl₂ is only produced from CH₃CCl₃ via OH attack (see Table 1), while most of the stratospheric CH₃CCl₃ in our model is destroyed via photolysis.

The sensitivity of our results to variations in model parameters was investigated in a series of additional calculations, in model 1 we varied the stratospheric K₄ by factors of 2, in model 2 we varied (OH) in the stratosphere by factors of 5, in model 3 we included a reaction between CCl₂ and stratospheric sulfate aerosol; and in model 4 we include convective like transport from the lower troposphere to the stratosphere in the 2-D model. The inclusion of a (OH) sink via reaction with sulfate aerosol in model 3 was accomplished by modifying equation (12) for CCl₂ to include an additional loss with an effective first-order rate constant k₄ given by

\[ k₄ \text{effective} = v \gamma A/4 \]  

(15)
The stratospheric chlorine loading of a species is defined here as the percentage of the chlorine atoms released at the surface that are injected into the stratosphere as reactive chlorine capable of participating in the catalytic destruction of ozone. Values are percentages.

- Model 0 assumes no transport of tropospheric COCl\(_2\) to the stratosphere and no transport of stratospheric COCl\(_2\) to the troposphere. Parameters adopted for the standard model are described in the text. Model 1 investigates the effect of varying \(K_1\) in model 1A, \(K_1\) is multiplied by 2, and in model 1B, \(K_1\) is divided by 2. Model 2 investigates the effect of varying stratospheric CO(\(\text{OH}\)) in model 2A CO(\(\text{OH}\)) is multiplied by 5, and in model 2B, CO(\(\text{OH}\)) is divided by 5. Model 3 investigates the effect of including a reaction between stratospheric COCl\(_2\) and sulfate aerosol, in model 3A, \(\gamma = 1\), and in model 3B, \(\gamma = 5 \times 10^{-5}\). Model 4 investigates the effect of convective like transport from the lower troposphere to the stratosphere.

where \(v\) is the COCl\(_2\) thermal velocity, \(\gamma\) is probability of a reaction occurring per collision (and allowed to vary from \(5 \times 10^{-5}\) to 1), and \(A\) is the aerosol surface area (taken from World Meteorological Organization, WMO, [1991], as a function of altitude). The inclusion of convective like transport in model 4 was accomplished by altering the transport code in the 2-D model so that 50% of the transport from the troposphere to the stratosphere occurred by direct injection of air from the lower tropospheric boxes, as opposed to the standard model, where all such transport came from the upper tropospheric boxes. The results of our sensitivity calculations are summarized in Table 8 and Figure 11b.

Inspection of Table 8 reveals that the inclusion of a reaction with sulfate aerosol can cause a major shift in our results. For instance, note that when \(\gamma = 1\), the stratospheric chlorine loadings for phosgene parent compounds become equal to those obtained for our model 0 calculations. In this case all stratospheric COCl\(_2\) is destroyed in the stratosphere by the aerosol reaction, and there is no transport of stratospheric COCl\(_2\) to the troposphere. Hence our results in this case are identical to those in which we neglected the tropospheric-stratospheric exchange of COCl\(_2\). (Of course, when we let \(\gamma < 5 \times 10^{-4}\), the results approach those obtained for our standard model, since the reaction of COCl\(_2\) with the sulfate aerosol becomes too slow to have an impact.) However, it should be noted in this regard that in addition to changing the stratospheric chlorine loadings of the phosgene parent compounds, inclusion of a reaction of COCl\(_2\) with sulfate aerosol can also have a major effect on the distribution of COCl\(_2\) in the lower stratosphere. Note in Figure 11b that when \(\gamma > 5 \times 10^{-5}\), the rapid scavenging of COCl\(_2\) by sulfate aerosol causes its concentration to decrease instead of increase as a function of altitude in the lower stratosphere. This result is in direct contradiction with the observed profile of Wilson et al. [1988]. It would appear that the reaction of COCl\(_2\) with sulfate aerosol hypothesized in model 3 most likely has a \(\gamma < 5 \times 10^{-5}\) and thus has a negligible impact on the stratospheric chlorine loadings of the phosgene parent compounds (see Table 8).

Inspection of Table 8 reveals that variations in CO(\(\text{OH}\)) cause modest changes in our results, increasing the stratospheric OH concentrations by a factor of 5 leads to a 17 and 40% decrease in the stratospheric chlorine loadings of CH\(_2\)Cl\(_2\) and CHCl\(_3\), respectively. This occurs because an increase in stratospheric OH increases the yield of COCl\(_2\) from these two compounds in the stratosphere (see Table 1) and thus effectively increases the percentage of chlorine from these two compounds that can be returned to the troposphere as COCl\(_2\). Finally note that variations in eddy diffusion coefficients by a factor of 2 have a very small impact on our results, and inclusion of convective like transport in the troposphere has essentially no effect on our results. The lack of an impact from convective like transport can be attributed to the absence of strong vertical gradients in the distributions of COCl\(_2\) and its parent compounds (see Figures 5-10).

Another model assumption that bears some discussion is that concerning the role of Cl atoms as oxidizers of the RFP compounds in the troposphere; recall that we assumed that photochemical destruction of these compounds in the troposphere only occurred as a result of reaction with OH and we neglected any contribution that might occur as a result of a reaction with Cl. However, as was noted earlier, C\(_2\)Cl\(_4\) reacts extremely rapidly with Cl atoms. Moreover, the Cl-initiated oxidation of C\(_2\)Cl\(_4\) has been found to produce trichloroacetyl chloride (TCAC) and COCl\(_2\), in a molar ratio of roughly 3:1 [Santangelo et al., 1976]. If the Cl-initiated oxidation were a significant sink for C\(_2\)Cl\(_4\) and a significant fraction of the chlorine in TCAC produced from this reaction were transported to the stratosphere, the stratospheric chlorine loading for this compound could conceivably be significantly larger than the approximate 1-2% value obtained here in our standard model. It is interesting therefore to briefly consider the fate of tropospheric TCAC. One pathway for TCAC loss is photolysis, a major product being COCl\(_2\); and a
minor product being CCl₄ [Behnke and Zetzsch, 1991]. While the production of CCl₄ from TCAC could potentially increase the stratospheric chlorine loading of C₂Cl₂, the yield of CCl₄ appears to be quite small (less than 0.3% according to Behnke and Zetzsch) and thus should have a negligible impact. In addition to photoysis, TCAC can be removed from the atmosphere via wet removal: Calculations with the algorithm described in section 4 using He = 0.3 M/atm and k = 2.7 s⁻¹ [D. Worsnop, private communication, 1993] indicate that the lifetime against these removal processes is of order of 20 days and thus that stratospheric chlorine loading from TCAC is insignificant. Thus it appears likely on the basis of present kinetic and thermodynamic data that if a Cl-initiated oxidation pathway represented a major sink for C₂Cl₂, its stratospheric chlorine loading would be even smaller than the value estimated here.

10. Revised Estimates for ODPs of Phosgene Parent Compounds

The ozone depletion potential, or ODP, of a compound is defined as the steady state ozone reduction calculated for each unit mass of gas emitted per year into the atmosphere relative to that for a unit mass emission of CFC₁₃ [MWO, 1989]. Because we find that the inclusion of stratospheric/tropospheric exchange of COCl₂ causes a decrease in the stratospheric chlorine loadings of the phosgene parent compounds, one might assume that it would also cause an approximately equivalent decrease in the ODPs of these compounds, as indicated by the first two columns of Table 9 (calculated according to the semiempirical equation for ODPs given by Solomon et al. [1994]).

However, a thorough evaluation of the ODPs of the phosgene parent compounds requires consideration of an additional complication. The ODPs are expressed relative to the ozone depletion of CFC₁₃, and the destruction of CFC₁₃ in the stratosphere via photoysis produces COFCI [Jayanty et al., 1975]. COFCI is a compound with properties similar to that of COCl₂; it is a weak absorber in the near UV [Noelle et al., 1993] and most likely is hydrolyzed in water at a rate close to that of COCl₂ and thus like COCl₂ is subject to transport to the troposphere and removal by wet deposition. Such an effect would decrease the stratospheric chlorine loading of CFC₁₃ and, as a result, would effectively increase the ODP of other compounds, although the actual chlorine loadings of these other compounds would not be changed by the transport of COFCI.

Using the same model approach we used for COCl₂ and its parent compounds, along with spectroscopic data for CFC₁₃ and COFCI from DeMore et al. [1992] and Noelle et al. [1993], we estimate that approximately 21% of all COCl₂ produced in the stratosphere from the photoysis of CFC₁₃ is transported down to the troposphere. Since only one third of the Cl atoms in CFC₁₃ are converted to COFCI from photoysis, this implies that roughly 7% of the Cl from CFC₁₃ is returned to the troposphere in the form of COFCI and removed in precipitation. Thus we estimate an actual stratospheric chlorine loading for CFC₁₃ of 93% instead of 100% (see Table 8). This somewhat smaller chlorine loading for CFC₁₃ causes a slight upward revision in the ODPs of the phosgene parent compounds as indicated by the third column of Table 9. Note that in the cases of CCl₄, CH₃Cl, and C₂Cl₂, the decreases in their stratospheric chlorine loadings due to the cross-tropopause transport of COCl₂ are estimated to be larger than the decrease in the stratospheric chlorine loading of CFC₁₃ due to transport of COFCI, and thus we predict a net decrease in the ODPs of these species. The opposite is found for CH₃CCl₃, and thus in this case we actually predict a slight increase in its ODP.

11. Conclusions

An analysis of the cycle of atmospheric COCl₂ reveals two distinct subcycles. The tropospheric subcycle is driven by production from the OH-initiated oxidation of four reactive halocarbons, namely, CH₃CCl₃, C₂Cl₄, CHCl₃, and CH₃Cl. Our calculations indicate that COCl₂ produced from these compounds is removed from the atmosphere by hydrolysis in cloudwater with an average atmospheric lifetime of about 70 days. Simulations of this subcycle with a 2-D model yield reasonably good agreement with observations of tropospheric COCl₂ and its parent compounds. Our calculations suggest that it is unlikely that a significant fraction of the COCl₂ produced in the troposphere is transported and decomposed in the stratosphere and thus that tropospheric COCl₂ has an insignificant role in the depletion of stratospheric ozone.

The stratospheric COCl₂ subcycle is driven by production from the photochemical degradation of CCl₄, a compound which is essentially inert in the troposphere, as well as of CH₃CCl₃, CHCl₃, and C₂Cl₂. However, because of COCl₂'s weak absorption cross sections in the near and middle ultraviolet, we estimate that a significant fraction of the COCl₂ produced in the stratosphere (perhaps 40%) is probably returned to the troposphere and removed from the atmosphere by clouds. Thus

Table 9. Ozone Depletion Potentials for Phosgene Parent Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ozone Depletion Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ODP(0)</td>
</tr>
<tr>
<td>COCl₂</td>
<td>0.0030</td>
</tr>
<tr>
<td>CH₃CCl₃</td>
<td>0.086</td>
</tr>
<tr>
<td>C₂Cl₄</td>
<td>7.0x10⁻³</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.0102</td>
</tr>
<tr>
<td>CH₃CCl₃</td>
<td>4.9x10⁻⁴</td>
</tr>
<tr>
<td>CCl₄</td>
<td>(0.0010)</td>
</tr>
</tbody>
</table>

ODP(0) is that obtained using the formulation of Solomon et al. [1994] and neglecting the effect of COCl₂ transport (i.e., model 0); ODP(1) obtained by including the effect of COCl₂ tropospheric-stratospheric exchange (i.e., standard model); ODP(1)* is similar to ODP(1) but also includes the effect of the downward transport of stratospheric COCl₂ to the troposphere. Literature values are taken from WMO [1991]. Note that ODP(0) for CH₃CCl₃ is smaller than the values found in the literature because a shorter lifetime of 5.59 years was adopted here to be consistent with the most recent ALE/GAGE data [Prinn et al., 1992].

* Not available
unless some other sink for stratospheric COCl₂ exists, our calculations suggest the downward transport of stratospheric COCl₂ causes a decrease in the stratospheric chlorine loadings of the phosgene parent compounds. Factoring in a similar effect for CFCI from the photolysis of CFCI, we infer a downward revision in the ODPs of CCl₃, C₂Cl₂H, and CHCl₃ but a slight increase in the ODP of CH₂Cl₂.

Finally, our calculations suggest the need for a small correction to the global budget of stratospheric chlorine. For instance, Prather and Watson [1990] estimated that 13% of the total chlorine loading of the stratosphere is caused by CCl₃, 13% is caused by CH₂Cl₂, and 22% is caused by CFC-11. However, if about 13.8% of the chlorine atoms from CCl₃, 3.2% of those from CH₂Cl₂, and 6.5% of that from CFC-11 are transported back to the troposphere as COCl₂ or CFCI, the global input of chlorine to the stratosphere is about 4% smaller than that originally estimated by Prather and Watson [1990].

There are of course large uncertainties in the results presented here because of the many simplifications inherent in our model's formulation as well as the potential errors in the thermodynamic and kinetic data adopted in the model. However, the results perhaps point to a more fundamental uncertainty in our understanding of halocarbons and their impact on stratospheric ozone. The atmospheric degradation of halocarbons can lead to the production of a wide variety of intermediates. In some cases these intermediates may be long-lived enough to either enhance the amount of chlorine from reactive halocarbons that reaches the stratosphere or decrease the amount of chlorine from unreactive halocarbons that is liberated in the stratosphere. For this reason we believe that priority should continue to be given to research that unravels the detailed degradation pathways of halocarbons and the ultimate fate of the intermediate products of these pathways.

Acknowledgments. The research for this work was supported in part by funds from the European Chlorinated Solvent Association, the Halogenated Solvents Industry Alliance (USA), the Japanese Association for Hygiene of Chlorinated Solvents, and the National Science Foundation under grant ATM-8905901. Participation by P.H.W. was supported by the National Aeronautics and Space Administration under grant NAGW-1001.

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Khaili, M.A.K., R.A. Rasmussen, and S.D. Hoyt. Atmospheric chlorine-


Temperature-Dependent Kinetics Studies of the Reactions \( \text{Br}(^2P_{3/2}) + \text{CH}_3\text{SCH}_3 \rightleftharpoons \text{CH}_3\text{SCH}_2 + \text{HBr} \). Heat of Formation of the \( \text{CH}_3\text{SCH}_2 \) Radical

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Time-resolved resonance fluorescence detection of \( \text{Br}(^2P_{3/2}) \) atom disappearance or appearance following 266-nm laser flash photolysis of \( \text{CF}_2\text{Br}_2/\text{CH}_3\text{SCH}_3/\text{H}_2/\text{N}_2 \) and \( \text{Cl}_2\text{CO}/\text{CH}_3\text{SCH}_3/\text{HBr}/\text{H}_2/\text{N}_2 \) mixtures has been employed to study the kinetics of the reactions \( \text{Br}(^2P_{3/2}) + \text{CH}_3\text{SCH}_3 \rightleftharpoons \text{HBr} + \text{CH}_3\text{SCH}_2 \) and \( \text{CH}_3\text{SCH}_2 + \text{HBr} \rightleftharpoons \text{Br}(^2P_{3/2}) + \text{CH}_3\text{SCH}_3 \). Absolute entropies of \( \text{R}', \text{R}'\text{H}, \) and \( \text{RH} \) are well-characterized. The kinetic results have been employed to derive a value of the heat of formation of \( \text{CH}_3\text{SCH}_2 \) radical, an intermediate in the oxidation of the important atmospheric reduced sulfur compound dimethyl sulfide (\( \text{CH}_3\text{SCH}_2 \)).

Experimental Technique

The experimental approach involved coupling reactant radical (i.e., \( \text{Br} \) or \( \text{CH}_3\text{SCH}_3 \)) production by 266-nm laser flash photolysis of suitable precursors with time-resolved detection of ground-state bromine atom disappearance or appearance by atomic resonance fluorescence spectroscopy. A schematic diagram of the apparatus, as configured for bromine atom detection, can be found elsewhere. A diagram showing the geometry of the reaction cell as well as a discussion of heating and temperature measurement techniques is published elsewhere.

Introduction

Accurate thermochemical information for free-radical intermediates is essential to the analysis of reaction mechanisms in complex chemical systems. One experimental approach which can be employed to obtain thermochemical parameters for a radical involves measurement of temperature-dependent rate coefficients for the pair of reactions \( \text{RH} + \text{R}' \rightleftharpoons \text{R}'\text{H} + \text{R} \); the ideal reaction pair for such a study is one where the heats of formation and absolute entropies of \( \text{R}', \text{R}'\text{H}, \) and \( \text{RH} \) are well-characterized and where kinetic data for the two reactions can be obtained over the same temperature range.

In this paper we report the results of temperature-dependent kinetics studies of the following pair of reactions:

\[
\begin{align*}
\text{Br}(^2P_{3/2}) + \text{CH}_3\text{SCH}_3 & \rightarrow \text{CH}_3\text{SCH}_2 + \text{HBr} \quad (1) \\
\text{CH}_3\text{SCH}_2 + \text{HBr} & \rightarrow \text{Br}(^2P_{3/2}) + \text{CH}_3\text{SCH}_3 \quad (\text{-1})
\end{align*}
\]

The kinetic results have been employed to derive a value for the heat of formation of the \( \text{CH}_3\text{SCH}_2 \) radical, an intermediate in the oxidation of the important atmospheric reduced sulfur compound dimethyl sulfide (\( \text{CH}_3\text{SCH}_2 \)).

Methodology

Only those aspects of the experimental approach which are unique to this study are discussed below.

Because the temperature range of this study (386-604 K) was higher than in our previous studies of bromine atom kinetics, a different reaction cell was employed. The cell was constructed of quartz and had an internal volume of about 200 cm³. A diagram showing the geometry of the reaction cell as well as a discussion of heating and temperature measurement techniques is published elsewhere.

To avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The concentration of each component in the reaction mixtures was determined from measurements of the appropriate mass flow rates and the total pressure. The excess reactant (i.e., \( \text{CH}_3\text{SCH}_3 \) or \( \text{HBr} \)) concentrations were also determined in situ in the slow flow system by UV photometry using a 2-m absorption cell. The monitoring wavelengths employed were 228.8 nm for \( \text{CH}_3\text{SCH}_3 \) (Cd line) and 202.6 nm for \( \text{HBr} \) (Zn line). Absorption cross sections used to convert measured absorbances to concentrations were 1.16 x 10⁻²⁹ cm⁻¹ for \( \text{CH}_3\text{SCH}_3 \) and 1.02 x 10⁻¹⁸ cm² for \( \text{HBr} \).

The excess reagent concentration was usually measured upstream from the photolyte addition point; dilution factors required to correct the measured concentration to the actual reagent concentration never exceeded 1.1.

The gases used in this study had the following stated minimum purities: \( \text{N}_2, 99.9999\% \); \( \text{H}_2, 99.9999\% \); \( \text{HBr}, 99.9997\% \) (liquid phase in cylinder); \( \text{Cl}_2\text{CO}, 99.00\% \) (liquid phase in cylinder). Liquid samples were purchased from Aldrich and had the following stated purities: \( \text{CH}_3\text{SCH}_3, 99+\% \); \( \text{CF}_2\text{Br}_2, 99\% \). Nitrogen and hydrogen were used as supplied while \( \text{HBr}, \text{Cl}_2\text{CO}, \text{CH}_3\text{SCH}_3 \), and \( \text{CF}_2\text{Br}_2 \) were degassed at 77 K before being used to prepare gaseous mixtures with \( \text{N}_2 \).

Results

In our study of reaction 1, bromine atoms were generated by 266-nm laser flash photolysis of \( \text{CF}_2\text{Br}_2 \) (\( \text{[CF}_2\text{Br}_2 \)) ranged from...
2.3 \times 10^{13} \text{ to } 2.7 \times 10^{14} \text{ molecules cm}^{-2})

\text{CF}_2\text{Br}_2 + h\nu (266 \text{ nm}) \rightarrow \text{Br} + \text{CF}_2\text{Br}

(2)

The CF$_2$Br$_2$ absorption cross section at 266 nm is approximately $8 \times 10^{-22}$ cm$^2$ molecule$^{-1}$ while the quantum yield for Br production from CF$_2$Br$_2$ photolysis increases from unity at $\lambda = 248$ nm to approximately 2 at $\lambda = 193$ nm. Presumably, at $\lambda \geq 248$ nm, CF$_2$Br$_2$ photodissociates as indicated in reaction 2 with unit yield. To ensure rapid relaxation of any photolytically generated Br($^3P_2$), about 1 Torr of H$_2$ was added to the reaction mixture. The reaction

$\text{Br}^3P_2 + H_2 (v=0) \rightarrow \text{Br}^3P_2 + H_2 (v=1)$

(3)

is known to be fast with $k_1 = 6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In our study of reaction 1, CH$_3$SCH$_3$ radicals were generated as follows:

$\text{Cl}_2\text{CO} + h\nu (266 \text{ nm}) \rightarrow 2\text{Cl} + \text{CO}$

(4)

$\text{Cl}_2 + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_3 + \text{HCl}$

(5a)

$\text{Cl}_2 + \text{HBr} \rightarrow \text{Br}^3P_2 + \text{HCl}$

(6)

Reaction 5 is known to occur at a gas kinetic rate, and channel 5a is dominant under the relatively high-temperature, low-pressure conditions employed in this study. Typical concentrations of Cl$_2$CO and CH$_3$SCH$_3$ were $1 \times 10^{14}$ and $5 \times 10^{14}$ molecules cm$^{-2}$, respectively. The concentration of CH$_3$SCH$_3$ was kept sufficiently high that >80% of the photolytically generated Cl reacted with CH$_3$SCH$_3$, rather than with HBr ($k_2 = 2.25 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). In our study of reaction 1, the linear flow rate of the reaction mixture through the reactor and the photolysis laser repetition rate.

All experiments were carried out under pseudo-first-order conditions with the stable reactant in large excess (factors of $10^4$) over the free-radical reactant. Concentrations of photolytically generated radicals were typically around $3 \times 10^{11}$ cm$^{-3}$, although this experimental parameter was varied over a wide range (factor of 30). For both reactions studied, observed kinetics were found to be independent of the photolytic precursor concentration(s) and the concentration of photolytically generated radicals. Observed kinetics were also found to be independent of the linear flow rate of the reaction mixture through the reactor and the photolysis laser repetition rate.

In the absence of side reactions which regenerate or deplete the Br($^3P_2$) atom concentration, the observed Br($^3P_2$) temporal profile following the laser flash in studies of reaction 1 would be described by the relationship

$S(t) = a_1 \exp(-r_1t) + a_2 \exp(-r_2t) + a_3 \exp(-r_3t)$

(II)

where it can be shown that

$r_1 = 0.5[J_a + J_k + D]$  

(III)

$r_2 = 0.5[J_a + J_k - D]$  

(IV)

$r_3 = k'_r + k'_i + k_9$  

(V)

$a_1 = -(r_3 - r_2)a_2 + (r_2 - J_a)X + k'_rY + k'_iD / D$  

(VI)
Figure 2. Typical plot of $k'$ versus $[\text{CH}_3\text{SCH}_3]$ observed in the studies of reaction 1. The four closed circles are the data points obtained from the temporal profiles shown in Figure 1. The solid line is obtained from a linear least-squares analysis and gives the binomial rate coefficient shown in the figure in units of cm$^3$ molecule$^{-1}$ s$^{-1}$.

**Table 1: Summary of Kinetic Data for the Reaction**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (Torr)</th>
<th>$[\text{CH}_3\text{SCH}<em>3]</em>{\text{max}}$ (10$^{15}$ cm$^{-3}$)</th>
<th>$k_2 \pm 2\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>386</td>
<td>50</td>
<td>3.70</td>
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<td>409</td>
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<tr>
<td>486</td>
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<tr>
<td>487</td>
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<td>7-1684</td>
</tr>
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</tr>
<tr>
<td>604</td>
<td>50</td>
<td>1.51</td>
<td>25-2618</td>
</tr>
</tbody>
</table>

*Units are $\text{T} \times \text{K}$. $P$ (Torr), $[\text{CH}_3\text{SCH}_3]$ (10$^{15}$ molecules cm$^{-3}$), $k_2$ (s$^{-1}$), and $k_1$ (10$^{13}$ molecules cm$^{-1}$ s$^{-1}$).*

**Errors represent precision only.**

where

$$a_2 = [(r_1 - r_2)a_3 + (r_1 - J_b)k'X + k'_3Y + k'_4)/D$$ (VII)

$$a_1 = k'(r_1 - r_2) + k'_3/r_3) / ((J_b - r_3)(J_b - r_1) - k'k'_2)$$ (VIII)

where

$$k_1 = k_1[\text{CH}_3\text{SCH}_3], f = 1, 5$$ (IX)

$$k'_j = k_j[\text{HBr}], f = 1, 6$$ (X)

$$J_b = k'_1 + k'_7$$ (XI)

$$J_R = k'_2 + k_8$$ (XII)

$$D = [(J_b - r_2)^2 + 4k'_2k'_4]/2 = r_1 - r_2$$ (XIII)

$$X = [\text{Br}_2]/[\text{Cl}_2]$$ (XIV)

$$Y = [\text{CH}_3\text{SCH}_3]/[\text{Cl}_2]$$ (XV)

and $k_1$ and $k_2$ are first-order rate coefficients for the processes

$\text{CH}_3\text{SCH}_2 \rightarrow \text{loss by diffusion from the detector field}$

and $\text{Cl} \rightarrow \text{loss by diffusion from the detector field}$

**Figure 3. Typical Br$(^3P_3/2)$ atom temporal profile observed in the studies of reaction -1. Experimental conditions: $P = 25$ Torr, $T = 325$ K, $[\text{H}]_0 = 5.66 \times 10^{13}$ molecules cm$^{-3}$, $[\text{Cl}]_0 = 4.24 \times 10^{14}$ molecules cm$^{-1}$, $[\text{CH}_3\text{SCH}_3] = 5.53 \times 10^{14}$ molecules cm$^{-3}$, $[\text{Cl}_2] = 5 \times 10^{11}$ atoms cm$^{-2}$, and $[\text{HBr}] = 1.83 \times 10^{15}$ molecules cm$^{-3}$. The solid curve represents a nonlinear least-squares fit of the data to eq 11 and gives the following best-fit parameters: $a_1 = -2.244 \times 10^{-14}$, $a_2 = 3.618 \times 10^{-14}$, $a_3 = -7.69 \times 10^{-14}$, $a_4 = -8.167 \times 10^{-14}$, and $a_5 = 60 \times 10^{-14}$. The parameter $a_1$ was held fixed at $7.2 \times 10^{-14}$ s$^{-1}$.

The time-independent background of 1357 cts (measured immediately prior to the laser flash) has been subtracted from each data point. It should be noted that $r_1 = k_1$.

In the above equations, it is assumed that $k_1 = k_1$; this assumption is approximately correct in the temperature and pressure regime of our study and is employed only to simplify the mathematics, i.e., the determination of $k_1$ does not critically depend on its validity. A nonlinear least-squares analysis of each experimental temporal profile was employed to determine $r_1$, $r_2$, $a_1$, $a_2$, and $a_3$. Because $k_1$ and $k_2$ are well-known and $k_3$ is negligible compared to $k'_1 + k'_2$, $r_3$ was not treated as a variable in the fitting procedure. Under typical experimental conditions, $r_2$ was considerably larger than $r_1 + r_2$, a requirement for accurate evaluation of $r_1 + r_2$. The bimolecular rate coefficients of interest, $k_1(P,T)$, were determined from the slopes of plots of $r_1 + r_2$ versus [HBr] for data obtained with $[\text{CH}_3\text{SCH}_3]$ held constant (see eq XVI). It should be noted that accurate determination of $k_1$ in these experiments requires that the concentrations of $\text{CH}_3\text{SCH}_3$ and HBr be chosen with care. We require that $k'_1 \gg k'_2$ (at least for the larger HBr concentrations employed) so that the dominant contribution to $r_1 + r_2$ is from reaction -1, not from reaction 1.

Similar to the situation discussed above for the study of reaction 1, observation of Br$(^3P_3/2)$ temporal profiles that obey eq II, linear dependencies of $r_1 + r_2$ on [HBr], and invariance of $r_1 + r_2$ to variation in laser photon fluence and photolyte concentration suggests that reactions -1, -1, and 5-9 are the only processes other than possible impurity reactions which significantly affect the Br$(^3P_3/2)$ time history. A typical Br$(^3P_3/2)$ appearance temporal profile and a typical plot of $r_1 + r_2$ versus [HBr] observed in our study of reaction -1 are shown in Figures 3 and 4. Kinetic data for reaction -1 are summarized in Table 2, while best-fit values of $r_1$, $r_2$, $a_1$, $a_2$, and $a_3$ for data obtained at four representative temperatures are presented in Table 3.

Listed in Table 2 are values of the intercept of the $r_1 + r_2$ versus [HBr] plots from each temperature. As can be seen from eq XVI, this intercept is the sum of three terms, i.e., $k'_1$, $k_1$, and $k_2$. 

**Note:**

Reactant is CD$_3$SCD$_3$. 

**Summary of Kinetic Data for the Processes**

Reactant is CD$_3$SCD$_3$. 

**Summary of Kinetic Data for the Processes**

### Summary of Kinetic Data for the Reaction

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*Units are $\text{T} \times \text{K}$. $P$ (Torr), $[\text{CH}_3\text{SCH}_3]$ (10$^{15}$ molecules cm$^{-3}$), $k_2$ (s$^{-1}$), and $k_1$ (10$^{13}$ molecules cm$^{-1}$ s$^{-1}$).*

**Errors represent precision only.**
Reactions, from radical-polytate side reactions, from reactions contributions to Br(2P3/2) observed invariance of Br(2P3/2) accuracy of each measured bimolecular rate coefficient shown in the figure in units of cm³ molecule⁻¹ s⁻¹.

Since [CH₃SCH₃] is a known experimental parameter, 𝑘' can be subtracted from each intercept, yielding 𝑘₂(= 𝑘₁ + 𝑘₂). In our study of 𝑘₁(T) the observed background loss of Br(2P₃/2) was always quite small, i.e., 𝑘₁ < 40 s⁻¹; therefore, the values of 𝑘₂ listed in Table 2 are dominated by 𝑘₂. It can be seen from Table 2 that 𝑘₂ systematically decreases as the temperature increases. A likely explanation for the apparently large background loss of [CH₃SCH₃] is the presence of O₂ impurity possibly due to small leaks or the porosity of the Teflon tubing used in the flow system.

CH₃SCH₂ + O₂ + M → CH₃SCH₂O₂ + M (10)

A room temperature value of 5.7 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ has been reported for 𝑘₂ in 1 atm of SF₆. Hence, O₂ levels in the 10 mTorr range could account for our observed values for 𝑘₂ (Table 2). In any event the value of the intercept was never more than 25% and typically less than 10% of the maximum value of 𝑘₁ + 𝑘₂ at any temperature. We therefore conclude that the chemistry contributing to the intercept did not significantly impact the accuracy of our measurement of 𝑘₁(T).

As indicated in Tables 1 and 2, pressure dependence studies were carried out for reactions 1 and -1; as expected, no evidence for pressure-dependent rate coefficients was observed over the range investigated (20–200 Torr for reaction 1; 10–50 Torr for reaction -1). Arrhenius plots for reactions 1 and -1 are shown in Figure 5. The solid lines in Figure 5 are obtained from linear least-squares analyses of the ln 𝑘₂ versus 1/T data; these analyses give the following Arrhenius expressions in units of cm³ molecule⁻¹ s⁻¹:

\[
\begin{align*}
    k_1 &= (9.0 ± 2.9) \times 10^{-11} \exp(-236 ± 151)/T \\
    k_{-1} &= (8.6 ± 2.5) \times 10^{-11} \exp(836 ± 140)/T
\end{align*}
\]

Errors in the above expressions are 2σ and represent precision only. On the basis of observed precision and consideration of possible systematic errors (see below), we estimate the absolute accuracy of each measured bimolecular rate coefficient to be ±15% for 𝑘₁(T) values and ±25% for 𝑘_{-1}(T) values.

As discussed briefly above, a number of potential systematic errors in our kinetic measurements can be ruled out based on the observed invariance of Br(2P₃/2) temporal profiles to variations in laser photon fluence, photolyte concentrations, flow velocity through the reactor, and laser pulse repetition rate; these include contributions to Br(2P₃/2) kinetics from radical–radical side reactions, from radical–photolyte side reactions, from reactions involving radicals which are produced by reactant photolysis, or from reactions involving stable products which build up in concentration with successive laser flashes. In situ measurements of stable reactant (i.e., CH₃SCH₃ and HBr) concentrations greatly reduce another potential source of systematic error.

One type of kinetic interference which needs to be addressed is the potential contribution to measured rate coefficients from impurity reactions. The relatively unreactive nature of Br atoms makes it unlikely that impurity reactions were a problem in our study of reaction 1. The most likely impurity problem in our study of reaction -1 is from Br₂. Potential sources of Br₂ are impurity in the HBr; sample and residual Br₂ from heterogeneous reactions of HBr (presumably on metal surfaces of valves and fittings). There is no kinetic data in the literature for reaction 11.

CH₃SCH₂ + Br₂ → CH₃SCH₂Br + Br(2P₃/2) (11)

However, based on reported rate coefficients for reactions of Br₂ with alkyl radicals and thiyl radicals, it seems safe to assume that reaction 11 proceeds at a near gas kinetic rate. Since CH₃SCH₂, probably reacts with Br₂ 10–50 times faster than with HBr, the HBr concentrations must be several hundred times larger than the Br₂ concentration before Br₂ interferences can be considered unimportant. To investigate the Br₂ interference problem, a 2 m absorption cell was positioned in the slow flow system downstream from the reaction cell and employed to monitor Br₂ photometrically (at 404.7 nm) with typical CI₂CO/CH₃SCH₂/HBr/H₂/N₂ mixtures flowing through the system. No absorption was observed (i.e., 𝐼/𝐼₀ > 0.998) even at HBr levels as high as 5 × 10⁻¹⁴ molecules cm⁻³. Since the Br₂ absorption cross section at 404.7 nm is about 6 × 10⁻¹⁹ cm², these experiments suggest that [Br₂] < 0.0004 [HBr].

CH₃SCH₃ has a small absorption cross section at 266 nm (1.2 × 10⁻²⁰ cm²). An interference in our measurement of 𝑘₉ would be present if a significant fraction of the observed Br atom appearance were due to reaction of CH₃SCH₃ photoproducts (rather than CH₃SCH₂Br) with HBr. As discussed above, the CI atom photolyte, CI₂CO, has an absorption cross section at 266 nm of 2.3 × 10⁻²⁰ cm² with an effective CI atom yield of 2.1. All experiments to measure 𝑘₉ were carried out with [CI₂CO] greater than or equal to [CH₃SCH₃]. The concentration of any CH₃SCH₃ photofragments were therefore never more than ∼5% of the initial [CI], and since both CH₃S and CH₃ react more slowly with HBr than does CH₃SCH₃ (see ref 3 and the discussion in the next paragraph), it is concluded that CH₃SCH₃ photolysis did not represent a significant systematic error in our measurements. In our measurements of 𝑘₁, CH₃SCH₃ photo-
To examine this possibility, we have directly measured \( k_{1} \) at 573 K, the \( \text{H}_2\text{C-SCH}_2 \) bond strength is \( 30 \pm 3 \text{ kcal mol}^{-1} \). Hence, it is monitoring \( \text{Br}^2 \text{P}_3 \text{Br}^2 \) appearance following 266-nm laser rapidly enough that the rate-limiting formation for \( \text{CH}_3^2 \text{P}_3 \text{CH}_3 \) leads to the occasion that (see below) in conjunction with the best available values of this analysis.

Another potential systematic error in our study of reaction 1 centers around the possible occurrence of the reaction

\[
\text{CH}_3\text{SCH}_2 + \text{M} \rightarrow \text{CH}_3 + \text{CH}_3\text{S} + \text{M}
\]  

(12)

Using the \( \text{CH}_3\text{SCH}_2 \) heat of formation determined in this study (see below) in conjunction with the best available heats of formation for \( \text{CH}_3 \) and \( \text{CH}_3\text{S} \) leads to the conclusion that the \( \text{H}_2\text{C-SCH}_2 \) bond strength is \( 30 \pm 3 \text{ kcal mol}^{-1} \). Hence, it is conceivable that, near the high-temperature end of our range of experimental conditions (i.e., \( T \approx 400 \text{ K} \)), reaction 12 could occur rapidly enough that the rate-limiting step in production of bromine atoms was not reaction 1, but rather reaction 13.

\[
\text{CH}_3 + \text{HBr} \rightarrow \text{Br}^2 \text{P}_3 + \text{CH}_4
\]  

(13)

To examine this possibility, we have directly measured \( k_4 \) at 573 K by monitoring \( \text{Br}^2 \text{P}_3 \text{Br}^2 \) appearance following 266-nm laser flash photolysis of \( \text{Cl}_2\text{CO}/\text{CH}_4/\text{HBr}/\text{H}_2/\text{N}_2 \) mixtures, i.e., using the \( \text{Cl} + \text{CH}_4 \) reaction as a source of methyl radicals. A plot of \( r_1 + r_2 \) versus \( \text{HBr} \) for this experiment is shown in Figure 6; the slope, \( (2.09 \pm 0.13) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), is \( k_4 \) (573 K).

This value agrees well with the value \( 2.04 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) obtained via extrapolation of the Arrhenius expression we report elsewhere, which is based on kinetics studies carried out over the temperature range 257-422 K (k_4) = 1.3 \times 10^{-12} \exp(-233/7) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. When \( \text{CH}_3\text{SCH}_2 \) was employed in the reaction mixtures instead of \( \text{CH}_4 \), a significantly faster value, \( k_4 \) (573 K) = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, was obtained for the "apparent" rate coefficient (see Figure 5). This observation, coupled with the fact that the "apparent" activation energy (i.e., the slope of the In k vs T) plot did not change as a function of temperature, leads to the conclusion that reactions 12 and 13 were not a significant interference in our study of reaction 1.

Another possible interference in our measurement of \( k_4 \) (T) results from the presence of \( \text{H}_2 \) which was added to ensure that any atomic bromine formed in the \( \text{P}_3 \text{Br}_2 \) state was rapidly quenched to the \( \text{P}_3 \text{Br}_2 \) ground state. At the higher end of our temperature range the reaction

\[
\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}
\]  

(14)

becomes rapid enough to be significant. The hydrogen atom
Heat of Formation of CH3SCH2 Radical


Table 4: Thermochmical Parameters for the Reaction Br(2P3/2) + CH3SCH3 → CH3SCH2 + HBr

<table>
<thead>
<tr>
<th>T, K</th>
<th>ΔH, kcal mol⁻¹</th>
<th>ΔS, cal mol⁻¹ deg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2nd law</td>
<td>3rd law</td>
</tr>
<tr>
<td>470</td>
<td>-6.40 ± 0.58</td>
<td>6.67 ± 1.37</td>
</tr>
<tr>
<td>298</td>
<td>-5.98 ± 0.58</td>
<td>6.24 ± 1.37</td>
</tr>
<tr>
<td>0</td>
<td>-5.24 ± 0.58</td>
<td>5.50 ± 1.38</td>
</tr>
</tbody>
</table>

* Errors are 2σ and represent best estimate of absolute accuracy.

Discussion

 reaction mechanism included reactions 1, 5, 4, and 14-16. In order to access the contribution of this additional Br production process, we simulated the chemistry under typical experimental conditions at 583 K using a numerical integration routine. The reaction mechanism included reactions 1, 5, 4, and 14-16. We have found that addition to the sulfur atom is the dominant reaction pathway at T > 300 K. However, at the temperatures employed in this study, T < 386 K the adduct products is a crucial issue. Can we be sure that Br(2P3/2) + CH3SCH3 produces CH3SCH2 + HBr with unit yield, and can we be sure that CH3SCH2 + HBr produces Br(2P3/2) + CH3SCH3 with unit yield? In the case of the Br(2P3/2) + CH3SCH3 reaction, we have found that addition to the sulfur atom is the dominant reaction pathway at T ≤ 300 K. However, at the temperatures employed in this study, T ≥ 386 K, the adduct lifetime toward uninuclear decomposition back to reactants is so short that its existence is kinetically inconsequential. At temperatures around 400 K, we have obtained strong evidence that the dominant pathway for the Br(2P3/2) + CH3SCH3 reaction is hydrogen transfer. First, we find that at T = 405 K Br(2P3/2) reacts with CD3SCD3 a factor of 3.7 more slowly than with CH3SCH3 (Table 1); this result strongly suggests that the reaction mechanism involves breaking a carbon–hydrogen bond. Second, in experiments which will be published elsewhere, we have employed time-resolved tunable diode laser absorption spectroscopy to directly monitor HBr production from the Br(2P3/2) + CH3SCH3 reaction. Using the Br(2P3/2) + (CH3)2CH reaction as a "unit yield calibration", we find that the HBr yield from Br(2P3/2) + CH3SCH3 is near unity. For the CH3SCH2 + HBr reaction, qualitative thermochmical considerations suggest that production of CH3SCH3 + Br should be the dominant reaction pathway. Observed resonance fluorescence signal levels confirm that atomic bromine is produced with high yield. However, production of electronically excited bromine atoms, Br(2P3/2), is a possibility which warrants consideration.

CH3SCH2 + HBr → CH3SCH3 + Br(2P3/2) (−1)

If the CH3SCH2 + HBr reaction proceeded exclusively or in a significant fraction of the time via channel −1, then we would be overestimating the rate of the true reverse of reaction 1 and our reported enthalpy change for reaction 1 (see below) would be in error. A simple thermochmical argument based on the measured activation energy for reaction 1 can be used to place a reasonable upper limit on k1. It is reasonable to assume that the activation energy for reaction −1 is greater than −2.0 kcal mol⁻¹. Since the bromine atom spin–orbit splitting is 10.5 kcal mol⁻¹, reaction −1 must be endothermic by at least 3.7 kcal mol⁻¹, i.e., 10.5 - 2.0 = 8.5 kcal mol⁻¹ where 4.8 kcal mol⁻¹ is the measured activation energy for reaction 1. Taking 1 × 10⁻¹⁰ cm⁻³ molecule⁻¹ s⁻¹ as an upper limit A factor for reaction −1 (a polystyrenic + diatomic reaction) and 3.7 kcal mol⁻¹ as a lower limit activation energy for reaction −1 leads to the result k1 < 9.0 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 395 K and k1 < 4.1 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 583 K; comparison of these limits with the rate coefficients reported in Table 2 shows that upper limit branching ratios for formation of Br(2P3/2) are 0.013 at 395 K and k1 < 0.11 at 583 K. We conclude that it is safe to ignore the possible occurrence of reaction −1 in our thermochmical analysis.

Thermochemistry. From the Arrhenius parameters determined in this study, we can obtain the enthalpy change and entropy change associated with reaction 1. Our approach, the "second law method", employs the following relationships to obtain thermochmical parameters:

\[ ΔH_i = E_i - E_{-i} \]  
\[ ΔS_i = R \ln (A_i/A_{-i}) \]

where ΔH, ΔS, E, and A, are the enthalpy change, entropy change, activation energy, and A factor for reaction i. Thermochmical parameters for reaction 1 obtained from the second law analysis are tabulated in Table 4. The temperature 470 K is the arithmetic mean of the T ranges employed in the determinations of k(T) and k_1(T). Values of ΔH at 298 and 0 K were computed using heat capacity corrections obtained from the JANAF tables for Br and HBr and calculated using the structural information in Table 5 for CH3SCH2 and CH3SCH3. Second law values for ΔS at 298 K were computed from the relationship

\[ ΔG_{298} = ΔH_{298} - TΔS_{298} = -RT \ln (k_{M}(298 K)/k_{M}(298 K)) \]

where \( k_{M}(298 K) \) and \( k_1(298 K) \) were computed from the Arrhenius expressions reported above.

Jefferson et al.

Estimated uncertainties in the second and third law determinations of the barriers to internal rotation, kcal mol\(^{-1}\)

\[ V\bar{\eta}(CH_3) = 1.89 \text{ (doubly degenerate)} \]

and other uncertainties are from ab initio calculations at the MP2/6-31+G(2d) level\(^{112}\) (see text for further discussion).

Experimentally observed values from ref. 33. From ref. 34. Extremes of suggested barrier heights, the lower from ref 35 and the higher from ref 32; thermochrometric parameters calculated at extremes and averaged.

TABLE 6: Comparison of CH\(_3\)SCH\(_2\) and CH\(_3\)SCH\(_3\) vibrational frequencies, cm\(^{-1}\)

<table>
<thead>
<tr>
<th>CH(_3)SCH(_3)</th>
<th>CH(_3)SCH(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2998, 2998, 2990, 2970, 2930, 2930, 1444, 1444, 1439, 1331, 1315, 1030, 973, 940, 903, 743, 695, 282</td>
<td>3157, 3025, 3006, 2997, 2897, 1419, 1407, 1358, 1294, 991, 929, 866, 811, 689, 282, 281</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Values for** \( V\bar{\eta}(CH_3) \) **are**

\[ 173180 \]

**I\(_A\)(CH\(_3\))** **amu** \( \times 10^3 \)

3.24

**I\(_B\)(CH\(_3\))** **amu** \( \times 10^3 \)

1.77

**Units are kcal mol\(^{-1}\) for the thermochrometric parameters.** These values were arrived at using an assumed activation energy for the CH\(_3\)SCH\(_3\) + HI reaction of 1.0 ± 0.5 kcal mol\(^{-1}\).

An alternate approach for obtaining thermochrometric parameters is the "third law method" where the entropy change is calculated using standard statistical mechanical methods\(^{36}\) and employed in conjunction with an experimental value for \( K_m(T) \) to obtain \( D_H^T \) (from eq XIX). Absolute entropies as a function of temperature were obtained from the JANAF tables\(^{34}\) for Br and HBr, and calculated using the structural information in Table 5 for CH\(_3\)SCH\(_3\) and CH\(_3\)SCH\(_2\). The uncertainty in the third law \( AS \) value is based on estimated uncertainties in key structural parameters, most notably the low-frequency vibrational modes and internal rotation barriers in CH\(_3\)SCH\(_3\). The structural parameters for CH\(_3\)SCH\(_3\) listed in Table 5 are based on ab initio quantum chemical calculations carried out by McEwen and Golden\(^{31}\), and calculated bond angles and bond lengths (for the structure with \( C_i \) symmetry) agree well with those reported in a recent ab initio theoretical study by Baker and Dyke.\(^{37}\) McEwen finds that two structures with \( C_i \) and \( C_i \) symmetry, respectively, are very close in energy. The calculated frequency of the CH\(_3\) wag changes considerably between the two structures; its values (scaled downward by 5% from those actually calculated) are 281 cm\(^{-1}\) (\( C_i \)) and 396 cm\(^{-1}\) (\( C_i \)). Another major source of uncertainty is the barrier for internal rotation of the CH\(_3\) group. McEwen's calculations suggest that this barrier could be very large (6.15 kcal mol\(^{-1}\)) while Shum and Benson\(^{32}\) estimate a barrier of 1.40 kcal mol\(^{-1}\). We have carried out four separate calculations of the absolute entropy of CH\(_3\)SCH\(_3\) (\( S^U \)) using different pairs of the above values for the CH\(_3\) wag frequency and the barrier to CH\(_3\) internal rotation. Reported heat capacity corrections and third law \( AS \) values employ the average result with uncertainties adjusted to span the range of reasonable possibilities. The four calculations give \( S^U \) values which range from 70.84 to 73.09 cal mol\(^{-1}\) K\(^{-1}\); the average value is 71.89 cal mol\(^{-1}\) K\(^{-1}\).

Values for \( \Delta H_2 \) and \( \Delta H_2 \) for CH\(_3\)SCH\(_3\), which are given in Table 6, were calculated from our \( \Delta H_2 \) determinations using literature values for the heats of formation of Br,\(^{24}\) HBr,\(^{24}\) and CH\(_3\)SCH\(_3\).\(^{48}\) Simple averages of the second and third law enthalpies of reaction have been employed to obtain our reported heat of formation; this approach seems reasonable since (a) estimated uncertainties in the second and third law determinations do not differ greatly and (b) the second and third law values for \( \Delta H_T \) agree to within a few tenths of a kcal mol\(^{-1}\). The reported uncertainties in \( \Delta H_T \) represent 2\( \sigma \) estimates of absolute accuracy, since the 2\( \sigma \) error estimates for the individual second and third law determinations are significantly larger than the deviations of the two determinations from their mean, we take the larger of the (second and third law) error estimates to be the error for the mean. The possible small contribution from reaction -1\(^{11}\), i.e., a channel forming Br(\( ^2P, \)) (see above), represents an insignificant source of systematic error.

Comparison with Previous Research. To our knowledge there have been no previous kinetics studies of either reaction 1 or -1. The preexponential factor that we observe for reaction 1 is similar to those observed for other atom plus polyatomic hydrogen abstraction reactions. In the case of the reverse process, reaction -1, a significant negative activation energy is observed. It is interesting to note that in recent studies negative activation energies have been observed for reactions of carbon-centered radicals with HBr.\(^{41}\) and H\(_2\).\(^{42}\) While positive activation energies have been measured for reactions of sulfur-centered radicals with HBr.\(^{43}\) In fact, the Arrhenius parameters reported here for reaction -1 are similar to the Arrhenius parameters for the C\(_2\)H\(_4\) + HBr and t-C\(_3\)H\(_7\) + HBr reactions\(^{44}\).

While the experimental evidence for negative activation energies in reactions of carbon-centered radicals with HBr and H\(_2\) is very strong, the theoretical interpretation of this counterintuitive phenomenon is less clear. Apparently, reaction proceeds via formation of a weakly bound complex. As shown by Mozurkewich and Benson,\(^{43}\) if the transition state leading from reactants to complex (TS1) is loose and the transition state leading from complex to products is both tighter and lower in energy compared to TS1, than a negative activation energy should be observed. McEwen and Golden\(^{46}\) have reported a two-channel RRKM calculation that models the t-C\(_3\)H\(_7\) + HBr (DI) reactions as proceeding via formation of a weakly bound (CH\(_3\)H)\(_2\)I-H (D) complex. They were able to reproduce the kinetic results of Seetul et al.\(^{42}\) for t-C\(_3\)H\(_7\) + HI with complex binding energies as low as 3 kcal mol\(^{-1}\). Interestingly, their models which are capable of reproducing experimental \( k(T) \) values for t-C\(_3\)H\(_7\) + HI also predict an inverse kinetic isotope effect (KIE), i.e., \( k_D > k_H \); this prediction results from the fact that the transition state leading from complex to products becomes looser with the lower vibrational frequencies associated with deuterium substitution. No experimental determination of the KIE for t-C\(_3\)H\(_7\) + HBr has been reported. However, "normal" kinetic isotope effects are observed for CH\(_3\), C\(_2\)H\(_5\), and t-C\(_3\)H\(_7\) reactions with HBr, i.e., \( k_D > k_H \). A detailed theoretical study of the CH\(_3\) + HBr reaction, which has an activation energy of about -0.4 kcal mol\(^{-1}\),\(^{46}\) has been reported by Chen et al.\(^{46}\). They calculated a potential energy surface at the G1 level of theory and deduced

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the existence of a hydrogen-bridged complex with C3v symmetry which is bound by 0.28 kcal mol\(^{-1}\) and is formed without activation energy. Chen et al. calculated rate constants for CH\(_3\) + HBr, CH\(_3\) + DBr, and CD\(_3\) + HBr from RRKM theory with corrections for tunneling. By adjusting the height of the barrier toward dissociation to products, they were able to obtain values for \(k(T)\) which agreed fairly well with experiment.\(^{4,45}\) Furthermore, their calculated isotope effects agreed quantitatively with experiment.\(^{4}\)

Table 6 contains a comparison of our thermochemical results with previously reported values. Shum and Benson\(^{23}\) reported a value of \(\Delta H_{\text{f}}\) for CH\(_3\)SCH\(_2\) that is approximately 3.0 kcal mol\(^{-1}\) greater than the reported in this study; these investigators studied the iodination of CH\(_3\)SCH\(_2\) at elevated temperatures (650-650 K). Kinetic information was arrived at indirectly by monitoring the rate of change of [I2] and total pressure. In order to obtain their reported thermochemical results, Shum and Benson assumed a value of 1.0 \(\pm\) 0.5 kcal mol\(^{-1}\) for the activation energy for the reaction

$$\text{HI} + \text{CH}_2\text{SCH}_2 \rightarrow \text{I} + \text{CH}_3\text{SCH}_2$$ (17)

If the activation energy for reaction 17 is actually negative (as we report for the analogous CH\(_3\)SCH\(_2\) + HBr reaction), then the difference between Shum and Benson’s value for \(\Delta H(\text{CH}_3\text{SCH}_2)\) and the value reported in this study would be even larger. The only other experimental thermochemical information available in the literature is from a recent molecular beam photodissociation study of CH\(_3\)SCH\(_2\) by Ng and co-workers,\(^{8}\) in which they report a value of 91 \(\pm\) 2.5 kcal mol\(^{-1}\) for the C-H bond strength in CH\(_3\)SCH\(_2\); their result is in good agreement with our study; theee

**Acknowledgment.** We thank S. Wang for assisting with some of the preliminary experiments, M. L. McKee for providing theoretical calculations of structural parameters for CH\(_3\)SCH\(_2\), and R. E. Stiek for several helpful discussions. This research was supported by Grant ATM-9104807 from the National Science Foundation and Grant NAGW-1001 from the National Aeronautics and Space Administration.

**References and Notes**

HALOGEN AND SULFUR REACTIONS RELEVANT TO POLAR CHEMISTRY

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INTRODUCTION

It is widely hypothesized that catalytic cycles involving BrO$_x$ species play an important role in the episodic destruction of ground-level ozone which is observed in the springtime Arctic boundary layer, although the exact mechanism for production of BrO$_x$ radicals remains an open question [Barrie et al., 1988, Bottenheim et al., 1990, Finlayson-Pitts et al., 1990, McConnell et al., 1992]. The critical evidence linking ozone depletion with BrO$_x$ chemistry is an observed negative correlation between ozone and filterable bromine [Bottenheim et al., 1990; Kieser et al., 1992]. In a recent field study of springtime Arctic boundary layer chemistry [Kieser et al., 1992], ozone concentrations and ethane concentrations were found to be correlated; this observation suggests that chlorine atoms (which react rapidly with ethane) may also be an important catalyst for ozone destruction under springtime Arctic conditions.

The possibility that reactions occurring on surfaces of sea-salt aerosol particles can lead to significant production of halogen atoms in the marine boundary layer has received considerable attention in recent years. Production of photochemically labile X$_2$(g) (X = Cl, Br) via heterogeneous degradation of ozone (possibly involving free radical intermediates) is one suggested pathway for generation of gas phase bromine atoms [McConnell et al., 1992] and chlorine atoms [Zetzsch et al., 1988, Behnke and Zetzsch, 1989, Keene et al., 1990], however, recent laboratory and modeling studies [Behnke and Zetzsch, 1990; Chameides and Stelson, 1992a, 1992b] suggest that, at least in the case of chlorine, this pathway is not important in the atmosphere. On the other hand, it appears that CINO$_2$, generated via heterogeneous reaction of N$_2$O$_5$ vapor with moist NaCl(s), may represent a

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photolytic precursor for atmospherically significant levels of atomic chlorine, even in the remote marine boundary layer where NO\textsubscript{X} levels are typically quite low [Behnke and Zetzsch, 1990; Zetzsch and Behnke, 1992; Ganske et al., 1992]. The analogous reaction of N\textsubscript{2}O\textsubscript{5}(g) with NaBr(s) is one proposed source of springtime Arctic Br\textsubscript{O}\textsubscript{X} radicals [Finlayson-Pitts et al., 1990], although it has been pointed out that generation of sufficient levels of the photolytic precursor BrNO\textsubscript{2} would require a longer residence time for Arctic air than is actually observed [McConnell et al., 1992; Patterson and Husar, 1981]. The frequency of ice fogs in the springtime Arctic boundary layer suggests that heterogeneous chemistry similar to that which occurs in polar stratospheric clouds [Poole et al., 1992] may result in partitioning of XO\textsubscript{X} (X = CL,Br) species largely into the reactive forms X and XO.

Dimethylsulfide (CH\textsubscript{3}SCH\textsubscript{3}, DMS) is a key atmospheric sulfur species. Roughly half the global flux of sulfur into the atmosphere is thought to be natural in origin [Cullis and Hirschler, 1980; Schwartz, 1988] and a significant fraction of all natural sulfur enters the atmosphere as DMS volatilized from the oceans [Andreae, 1986; Bates et al., 1987]. Levels of DMS in polar regions typically peak during springtime when microorganisms which produce DMS are exposed to light after a long dark period [H. Berresheim, private communication]. Hence, under conditions which exist in the springtime Arctic marine boundary layer, reactions of chlorine and bromine atoms with DMS may play an important role in coupling the halogen and sulfur cycles.

Discussed below are the results of recent laboratory studies we have carried out to investigate the kinetics and mechanisms of the X + DMS reactions (X = CI,Br) [Stickel et al., 1992; Nicovich et al., 1992a]. We also present estimates of sea level (i.e., 760 torr) unimolecular decomposition rates for BrNO\textsubscript{2} which are based on kinetic and thermochemical information obtained in our recent study of the Br + NO\textsubscript{2} association reaction [Kreutter et al., 1990].

THE CL + DMS REACTION

Time-resolved resonance fluorescence detection of chlorine atoms following 266 nm laser flash photolysis of Cl\textsubscript{2}CO/DMS/N\textsubscript{2} mixtures has been employed to study the kinetics of R\textsubscript{1} over the temperature and pressure ranges 240-421K and 3-700 torr.

\[
\text{Cl} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}
\]  

A complete description of the experimental approach can be found in a recent publication describing our study of the Cl + CS\textsubscript{2} reaction [Nicovich et al., 1990]. In agreement with a recent competitive kinetics study [Nielsen et al., 1990], we find that R\textsubscript{1} is very fast, i.e., reaction occurs on essentially every Cl + DMS encounter. Measured rate coefficients at
240K, 297K, and 421K are plotted as a function of pressure in Figure 1. The reaction rate is found to increase with decreasing temperature as would be expected for a very fast reaction whose rate is determined by the magnitude of long range attractive forces between the reactants. The somewhat surprising aspect of the data in Figure 1 is our observation of a clear pressure dependence for $k_1$. It appears that reaction 1 occurs via both pressure-independent and pressure-dependent pathways; the pressure-dependent pathway must involve collisional stabilization of a $(\text{CH}_3)_2\text{S}-\text{Cl}$ adduct.

To gain further insight into the mechanism for reaction 1, we carried out a separate set of experiments where laser flash photolytic (LFP) production of Cl (via 248 nm photolysis of phosgene) was coupled with tunable diode laser absorption spectroscopy (TDLAS) to

![Figure 1](image_url)

**Fig. 1.** Rate constants for the Cl + $(\text{CH}_3)_2\text{S}$ reaction at three temperatures plotted as a function of pressure. The solid lines are "eyeball" fits to the data; their significance is simply as an aid in visualizing the observed pressure dependencies.
Table 1. Yield of HCl from the Cl + DMS reaction as a function of pressure at T = 297 K

<table>
<thead>
<tr>
<th>Buffer Gas</th>
<th>P (torr)</th>
<th>N(a)</th>
<th>HCl Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>0.6</td>
<td>2</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>19</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>4</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>10.1</td>
<td>4</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>2</td>
<td>0.62</td>
</tr>
<tr>
<td>N2(b)</td>
<td>5.0</td>
<td>2</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>2</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>203</td>
<td>2</td>
<td>0.51</td>
</tr>
</tbody>
</table>

(a) N = number of experiments
(b) includes one torr of CO2

measure the HCl product yield at 297K as a function of pressure. A detailed description of the LFP-TDLAS apparatus is given elsewhere [Stickel et al., 1992]. To obtain the HCl yield we carried out back-to-back experiments where the photolytically produced Cl reacted with DMS, then with ethane (C2H6); the yield of HCl from the Cl + C2H6 reaction is known to be unity. In all experiments, at least 0.6 torr CO2 was present in the reaction mixture to (a) facilitate rapid equilibration of the atomic chlorine spin-orbit states and (b) facilitate rapid relaxation of any HCl formed in the v = 1 level. Typical experimental HCl appearance temporal profiles are presented elsewhere [Stickel et al., 1992]. The results of the yield experiments are summarized in Table 1.

The HCl yield approaches unity as P → 0 but decreases with increasing pressure. Although extrapolation of kinetic and yield data to zero pressure is non-trivial, examination of the results in Figure 1 and Table 1 strongly suggests that the following relationship is obeyed:

\[ \Phi(P) = \frac{k_1(P \rightarrow 0)}{k_1 P} = 1 \]

where \( \Phi(P) \) is the HCl yield at pressure P.

The experiments described above demonstrate that hydrogen abstraction is the dominant pathway for reaction 1 in the low pressure limit. With increasing pressure, stabilization of a \((\text{CH}_3)_2\text{SCl}\) adduct apparently becomes competitive with the hydrogen
abstraction pathway. Under the pressure and temperature conditions of the springtime Arctic boundary layer, it appears that \( k_1 \approx 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and that 60-80\% of the overall reaction proceeds via the adduct-forming pathway. The fate of the stabilized adduct remains uncertain, although it clearly does not dissociate to Cl or HCl on the time scale of our experiments (several milliseconds). One interesting possibility is reaction with \( \text{O}_2 \) to form \((\text{CH}_3)_2\text{SO} + \text{ClO} \), this reaction could represent an unrecognized source of atmospheric \((\text{CH}_3)_2\text{SO} \). Another energetically feasible pathway for degradation of \((\text{CH}_3)_2\text{SCl} \) is unimolecular decomposition to \( \text{CH}_3\text{S} + \text{CH}_3\text{Cl} \), a process which could possibly represent an important source of atmospheric methyl chloride. Clearly, the atmospheric fate of \((\text{CH}_3)_2\text{SCl} \) warrants further investigation.

THE \( \text{BR} + \text{DMS} \) REACTION

Time-resolved resonance fluorescence detection of bromine atoms following 266 nm laser flash photolysis of \( \text{CF}_2\text{Br}_2/\text{DMS}/\text{H}_2/\text{N}_2 \) mixtures has been employed to study the kinetics of reaction 2 as a function of temperature and pressure:

\[
\text{Br} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}
\]  

(2)

A complete description of the experimental approach can be found in a recent publication describing our studies of the reactions \( \text{Br} + \text{H}_2\text{S} \rightarrow \text{SH} + \text{HBr} \) and \( \text{Br} + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{HBr} \) \[\text{Nicovich et al., 1992b}\]. Distinctly different kinetic behavior is observed in the two temperature regimes 260-310K and 375-425K.

In the low temperature regime, i.e., 260-310K, the dominant reaction pathway is found to be reversible adduct formation:

\[
\begin{align*}
\text{Br} + (\text{CH}_3)_2\text{S} + \text{M} & \rightarrow (\text{CH}_3)_2\text{SBr} + \text{M} \\
(\text{CH}_3)_2\text{SBr} + \text{M} & \rightarrow \text{Br} + (\text{CH}_3)_2\text{S} + \text{M}
\end{align*}
\]

(2a)  (-2a)

Observation of the kinetics of the approach to equilibrium allows evaluation of \( k_{2a}(P,T) \), \( k_{-2a}(P,T) \) and, therefore, \( K_{\text{eq}}(T) \) (\( K_{\text{eq}} = k_{2a}/k_{-2a} \)). Measured rate coefficients are summarized in Table 2. A van't Hoff plot of \( \ln K_p \) versus \( T^{-1} \) is shown in Figure 2. From the slope of the van't Hoff plot (and a small heat capacity correction) we obtain a value for the enthalpy change associated with reaction 2a, i.e., the \((\text{CH}_3)_2\text{S}-\text{Br} \) bond strength; the result is \( \Delta H_{298} = -14.5 \pm 1.2 \text{ kcal mole}^{-1} \). We have recently carried out similar measurements of the \((\text{CH}_3)_2\text{S}-\text{OH} \) bond strength \( [\text{Hynes et al., 1992}] \) and find it to be approximately equal to the...
Table 2. Rate constants for the reactions \( \text{Br} + (\text{CH}_3)_2\text{S} + \text{M} \rightleftharpoons (\text{CH}_3)_2\text{SBr} + \text{M} \) as a function of temperature and pressure (a)

<table>
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<tr>
<th>T</th>
<th>P</th>
<th>( k_{2a} )</th>
<th>( k_{-2a} )</th>
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<td>50</td>
<td>2.11</td>
<td>10,500</td>
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</table>

(a) Units are \( T(\text{K}), P(\text{torr}) \), \( k_{2a}(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) \), \( k_{-2a}(\text{s}^{-1}) \).

(b) Reactant was DMS-d6.

(c) Photolyte was Br\(_2\) (it was CF\(_2\)Br\(_2\) in all other experiments); Br\(_2\) was photolyzed at 355 nm.

\((\text{CH}_3)_2\text{S}-\text{Br}\) bond strength. Hence, a reasonable "guesstimate" for the \((\text{CH}_3)_2\text{S}-\text{Cl}\) bond strength is 14-15 kcal mole\(^{-1}\).

At temperatures above 375K, \((\text{CH}_3)_2\text{SBr}\) decomposition is so rapid that the addition reaction effectively does not occur. In this temperature regime sulfide reactivity toward atomic bromine follows the trend \((\text{C}_2\text{H}_5)_2\text{S} > (\text{CH}_3)_2\text{S} > (\text{CD}_3)_2\text{S}\), strongly suggesting that the dominant reaction pathway is hydrogen abstraction:

\[
\text{Br} + \text{CH}_3\text{SCH}_3 \rightarrow \text{HBr} + \text{CH}_3\text{SCH}_2
\]  \(\text{(R2b)}\)

Interestingly, we measure an activation energy for reaction 2b of 5.0 kcal mole\(^{-1}\), while the literature value for CH\(_3\)SCH\(_2\) heat of formation [Shum and Benson, 1985] suggests that
reaction 2b is endothermic by 9.0 kcal mole$^{-1}$, hence, our kinetic results strongly suggest that the C-H bond strength in DMS is 2-4 kcal mole$^{-1}$ weaker than currently thought.

Extrapolation of our kinetic data to conditions typical of the springtime Arctic boundary layer (760 torr, 230-270K) suggests that under the conditions of interest (a) addition of Br to DMS is four to five orders of magnitude faster than hydrogen abstraction, (b) the rate coefficient for the addition reaction is $(1.3 \pm 0.2) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

**Fig. 2.** van't Hoff plot for the equilibrium $\text{Br} + (\text{CH}_3)_2\text{S} \rightleftharpoons (\text{CH}_3)_2\text{SBr}$. Open circles are data obtained using $(\text{CD}_3)_2\text{S}$ as the sulfide reactant. Solid line is obtained from a least squares analysis; the slope gives $\Delta H(334K) = -14.6 \pm 1.1$ kcal mole$^{-1}$ while the intercept gives $\Delta S(334K) = -22.9 \pm 3.9$ cal mole$^{-1}$ deg$^{-1}$ (errors are $2\sigma$ and represent precision only).
and (c) the lifetime of the \((\text{CH}_3)_2\text{SBr}\) adduct toward unimolecular decomposition is 0.01-0.0001 seconds. The short lifetime of \((\text{CH}_3)_2\text{SBr}\) toward unimolecular decomposition suggests that the only atmospheric species capable of scavenging \((\text{CH}_3)_2\text{SBr}\) is \(\text{O}_2\).

\[(\text{CH}_3)_2\text{SBr} + \text{O}_2 \rightarrow (\text{CH}_3)_2\text{SO} + \text{BrO} \quad (3)\]

To search for \(\text{BrO}\) production from reaction 3, a separate set of experiments was carried out (at 297K) where time-resolved longpath absorption detection in the near ultraviolet was coupled with 248 nm laser flash photolysis of \(\text{CF}_3\text{Br}/\text{DMS}/\text{H}_2/\text{N}_2/\text{O}_2\) mixtures, a description of the apparatus is given elsewhere [Daykin and Wine, 1990]. Production of \(\text{BrO}\) was not observed, but a strong, broad, unstructured absorption feature with \(\lambda_{\text{max}} \approx 370\) nm was observed. Studies of the appearance kinetics of the absorption feature demonstrate rather conclusively that it is due to \((\text{CH}_3)_2\text{SBr}\), i.e., a plot of pseudo-first order appearance rate versus [DMS] is linear with slope equal to the (previously measured) \(k_2\) and intercept equal to the (previously measured) \(k_{-2a}\). At 50 torr total pressure the strength and temporal behavior of the transient absorption signal was independent of whether \(\text{N}_2\) or \(\text{O}_2\) was employed as the buffer gas, this observation suggests that \(k_3 < 3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). For assessing the potential role of reaction 3 in atmospheric chemistry under springtime Arctic boundary layer conditions, it will be necessary to extend the time-resolved absorption studies to higher \(\text{O}_2\) partial pressures and lower temperatures.

UNIMOLECULAR DECOMPOSITION OF \(\text{BrNO}_2\)

As mentioned in the introduction, Finlayson-Pitts et al. [1990] have proposed that \(\text{BrNO}_2\) (nitryl bromide), formed via the heterogeneous reaction of \(\text{N}_2\text{O}_5\) with \(\text{NaBr}\) on the surface of sea salt aerosol particles, may be an important photolytic precursor to \(\text{BrO}_X\) radicals in the springtime Arctic boundary layer. However, McConnell et al. [1992] have pointed out a potential problem with the Finlayson-Pitts et al. proposal — the residence time for an air mass in the Arctic may not be long enough for sufficient buildup of \(\text{BrNO}_2\) to occur prior to polar sunrise.

Recently, we reported a detailed study of the kinetics and thermochemistry of \(\text{Br} + \text{NO}_2\) association reaction [Kreutter et al., 1990]. Given in Table 3 are upper and lower limit lifetimes toward \(\text{BrNO}_2\) unimolecular decomposition (i.e., \(k_4^{-1}\)) under springtime Arctic boundary layer conditions; the lifetimes are obtained by extrapolation of our data [Kreutter et al., 1990] to 760 torr and low temperature.

\[\text{BrNO}_2 + \text{N}_2 \rightarrow \text{Br} + \text{NO}_2 + \text{N}_2 \quad (4)\]
The range of values for $k_4^{-1}$ which are consistent with our data is rather large because the possible roles of the (short lived) isomer BrONO and/or excited electronic state potential energy surfaces could not be quantified due to lack of information. Nonetheless, the data in Table 3 lead to an important conclusion. At temperatures typical of the wintertime and springtime Arctic, i.e., 220 - 260 K, the lifetime of BrNO$_2$ toward unimolecular decomposition is rather short, i.e., usually less than one day. Hence, bromine atoms would be released from the BrNO$_2$ reservoir not only when the sun comes up, but continuously during the dark BrNO$_2$ production period.

### Table 3. Lifetime of BrNO$_2$ toward unimolecular decomposition at atmospheric pressure

<table>
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<th>upper limit</th>
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</table>

**Acknowledgments:** The research described in this paper was supported by the NSF Atmospheric Chemistry Program (grant ATM-9104807), the NASA Upper Atmosphere Research Program (grant NAGW-1001), and the Georgia Tech Research Institute (internal grant E-8904-038).

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CH$_3$SH $\rightarrow$ CH$_3$S + HBr: Heats of formation of SH and CH$_3$S radicals, J. Phys. Chem., 96, 2518-2528, 1992b


Kinetics of the BrO + NO₂ Association Reaction. Temperature and Pressure Dependence in the Falloff Regime

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School of Earth & Atmospheric Sciences, School of Chemistry & Biochemistry, and Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332

Abstract

A laser flash photolysis-long path absorption technique has been employed to study the kinetics of the reaction BrO + NO₂ + M → products as a function of temperature (248–346 K), pressure (16–800 torr), and buffer gas identity (N₂,CF₄). The reaction is found to be in the falloff regime between third and second-order over the entire range of conditions investigated. This is the first study where temperature-dependent measurements of \( k_I(P,T) \) have been reported at pressures greater than 12 torr; hence, our results help constrain choices of \( k_I(P,T) \) for use in models of lower stratospheric BrO₃ chemistry. Approximate falloff parameters in a convenient form for atmospheric modeling are derived. © 1993 John Wiley & Sons, Inc.

Introduction

Despite its relatively low concentration (about 25 pptv) in the stratosphere, bromine plays an important role in stratospheric odd oxygen chemistry. Due to differences in the rates of formation and destruction of the HX reservoir species, under "normal" stratospheric conditions (i.e., unperturbed by heterogeneous chemistry) a much larger fraction of bromine is partitioned into the "active" form (Br + BrO) compared to chlorine. Hence, on a per molecule basis, bromine is thought to be 30–120 times more effective than chlorine as a catalyst for odd oxygen destruction [1]. The chlorine-to-bromine concentration ratio in the stratosphere is currently about 160 [1]; this ratio is expected to drop to about 100 over the next century as anthropogenic sources of both halogen species are greatly reduced [1].

The most important BrO₃ reservoir species in the lower stratosphere is bromine nitrate, which is formed via the BrO + NO₂ association reaction

\[
\begin{align*}
(1a) \quad \text{BrO} + \text{NO}_2 + \text{M} & \rightarrow \text{BrONO}_2 + \text{M} \\
(1b) \quad & \rightarrow \text{other products (?)}
\end{align*}
\]

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In fact, recent model calculations suggest that BrONO$_2$ is the dominant BrO species at altitudes below 35 km [2,3]. The calculated partitioning between BrONO$_2$ and BrO, the two most concentrated species, is critically dependent on the assumed values for $k_1(P,T)$.

Two studies of the kinetics of reaction (1) are reported in the literature. Sander et al. [4] employed both discharge flow and flash photolysis techniques to obtain values for $k_1(P,298\ K)$ over the pressure range 1–700 torr $N_2$, while Danis et al. [5] employed a laser flash photolysis-time resolved mass spectrometry technique to study the temperature dependence of $k_1$ (over the range 263–343 K) at low total pressures (4–12 torr $O_2$). Where the two studies overlapped, i.e., $T = 298\ K$ and $P = 4–12$ torr, the rate coefficients reported by Sander et al. [4] are about 25% faster than those reported by Danis et al. [5].

In this article we present the results of a study where 351 nm laser flash photolysis of Br$_2$/NO$_2$/N$_2$ (or CF$_4$) mixtures has been coupled with detection of BrO by time-resolved long path ultraviolet spectroscopy to study the kinetics of reaction (1) over the temperature and pressure ranges 248–346 K and 16–800 torr. The motivation for this study is primarily to improve the accuracy with which $k_1(P,T)$ values can be estimated under atmospheric conditions, particularly under the low temperature, high pressure conditions of the lower stratosphere. In addition, this study improves somewhat the accuracy with which $k_{1,\infty}(T)$, the rate coefficient in the high pressure limit, can be estimated.

**Experimental**

The kinetics of reaction (1) were investigated by monitoring the temporal behavior of BrO absorbance following 351 nm laser flash photolysis of Br$_2$/NO$_2$/N$_2$ (or CF$_4$) mixtures. The laser flash photolysis-long path absorption apparatus was similar to the one we employed recently to investigate the reactions of F and Cl atoms with HNO$_3$ [6] and the reactions of IO radicals with NO and NO$_2$ [7]. A schematic diagram of the apparatus and descriptions of the reaction cell and temperature measurement techniques can be found elsewhere [6]. As in the IO kinetics study [7], a 150 watt xenon arc lamp was employed as the probe light source.

The XeF laser photolysis beam was expanded by means of cylindrical lenses to be 11–12 cm wide and 2 cm high as it traversed the reactor. The xenon arc lamp beam was multipassed through the reactor at right angles to the photolysis beam using modified White cell optics [8]; 42 or 46 passes were employed, giving absorption path lengths through the photolyzed volume of 462 or 552 cm. Output radiation from the multipass cell was focused onto the entrance slit of a 0.22–m monochromator adjusted to transmit radiation at 338.3 nm, the peak of the strong 7–0 band of the BrO $A^2\Pi \rightarrow X^2\Sigma$ transition [9].

Reflective losses in the multipass system were minimized by using White cell mirrors coated for high reflectivity around 338 nm and reaction cell windows coated for maximum transmission around 338 nm. As a tradeoff between light throughput and resolution, the monochromator slit widths
were set at 200 μm (resolution 0.72 nm FWHM). Radiation exiting the monochromator was detected by a photomultiplier (Hamamatsu R928), the time-dependent output from which was monitored by a signal averager with 1.5 μs time resolution and 10 bit voltage resolution. The results of 32–512 laser shots were averaged to obtain data with suitable signal-to-noise ratio for quantitative kinetic analysis. Digitized voltage vs. time data were transferred to a small computer for storage and analysis.

In order to avoid accumulation of reaction or photolysis products, all experiments were carried out under “slow flow” conditions. The linear flow rate through the reaction cell was typically 2 cm s⁻¹, and the excimer laser repetition rate was 0.2 Hz. Hence, the gas mixture in the photolysis zone was replenished between laser shots. Br₂ and NO₂ were flowed into the reaction cell from 12–L bulbs containing dilute mixtures in nitrogen (Br₂) or zero grade air (NO₂). Preparation of the NO₂ bulb with air as the diluent gas prevented conversion of NO₂ to NO during storage. To prevent reaction of Br₂ with the antireflection coated reaction cell windows, a four-port gas input/output system was employed [6,7]. The NO₂/Br₂ mixture and 85–90% of the N₂ buffer gas entered the reactor through an inner port while the remaining 10–15% of the N₂ buffer gas entered the reactor through both outer ports. The gas mixture was exhausted through an inner port. The concentration of Br₂ was determined from the known bulb concentration, measurement of the appropriate mass flow rate, and the total pressure. The NO₂ concentration was measured in situ in the slow flow system by UV photometry using a 216.2 cm long absorption cell plumbed in series with the reaction cell. Radiation at 326.1 nm emitted by a cadmium pen-ray lamp was employed as the light source for NO₂ detection. With the combination of the Cd lamp light source and the band-pass filter employed to isolate the 326.1 nm line, we determined the effective NO₂ absorption cross section to be $(2.89 \pm 0.04) \times 10^{-19}$ cm². This value is in reasonable agreement with the recent measurements of Schneider et al. [10], who report $\sigma = 2.815 \times 10^{-19}$ cm² at 326.0 ± 0.5 nm. The absorption cross section for Br₂ at 326.1 nm is about $4.0 \times 10^{-20}$ cm² [11], which is too low to interfere with the photometric determination of the NO₂ concentration. UV photometry at 404.7 nm was used to determine the Br₂ concentration in each 12–L Br₂/N₂ bulb used. With the combination of an Hg pen-ray lamp light source and a band-pass filter employed to isolate the 404.7 nm line, we measured the effective Br₂ absorption cross section to be $5.95 \times 10^{-19}$ cm².

The gases used in this study were obtained from Matheson and had the following stated minimum purities: N₂, 99.999%; NO, 99.0%; O₂, 99.99%; and CF₄, 99.99%. Air was ultra zero grade with total hydrocarbons less than 0.1 ppm. The procedures employed to synthesize pure NO₂ from the NO + O₂ reaction are described elsewhere [7]. The Br₂ used in this study had a stated minimum purity of 99.94% (liquid phase). The Br₂ was transferred under nitrogen into a vial fitted with a high-vacuum stopcock and then degassed repeatedly at 77 K before being used to prepare Br₂/N₂ gas mixtures.
Results and Discussion

The following scheme was employed to generate BrO radicals:

\[(2) \quad \text{NO}_2 + h\nu(351 \text{ nm}) \rightarrow \text{NO} + \text{O} \]
\[(3) \quad \text{O} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br} \]
\[(4) \quad \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \]

Based on literature values for \(k_3\) and \(k_4\) [12,13] and the concentrations of \(\text{Br}_2\) and \(\text{NO}_2\) employed to measure values for \(k_1(P,T)\) (Table I), it was always the case that BrO production was at least 15 times faster than BrO removal, and that at least 70% of the photolytically generated oxygen atoms reacted with \(\text{Br}_2\) to produce BrO.

For the optical path lengths traversed by the probe beam through the reactor (around 13 meters in most experiments) and the \(\text{NO}_2\) concentrations employed (up to \(6.31 \times 10^{15}\) molecules per cm\(^3\)), a large fraction of the probe radiation was absorbed by \(\text{NO}_2\). Hence, destruction of \(\text{NO}_2\) by reactions (2) and (4) led to a noticeable difference between the (baseline) signal levels before and after the laser fired in experiments where \(\text{NO}_2\) was photolyzed in the absence of \(\text{Br}_2\). In the presence of \(\text{Br}_2\), the magnitude of the rapid baseline shift upon firing the laser was reduced due to the occurrence of reaction (3) in competition with reaction (4). A majority of the BrO generated via reaction (3) decayed by reacting with \(\text{NO}_2\) to form BrONO\(_2\) while, as will be discussed in more detail below, a small fraction decayed by reaction (5), a process which regenerates \(\text{NO}_2\).

\[(5) \quad \text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2 \]

Based on reported 338.3 nm absorption cross sections for BrO [9], \(\text{NO}_2\) [10], and BrONO\(_2\) [14], it appears that absorption of analytical light by BrONO\(_2\) was negligible, i.e., the BrONO\(_2\) absorption cross section is a factor of 4 smaller than the \(\text{NO}_2\) absorption cross section and more than a factor of 100 smaller than the BrO absorption cross section. Furthermore, Sander and Watson [15] have shown that if an elementary reaction results in an absorbance change due to removal of an absorbing excess reagent and/or formation of an absorbing product, the correct decay rate is obtained from the first-order decay of the overall absorbance by using the signal level at \(t \rightarrow \infty\) as the baseline. All of our kinetic data were analyzed in this manner. As typified by the data in Figure 1, the observed transmission after BrO had decayed away was found to be slightly lower than the transmission before the laser fired; this implies either that the BrONO\(_2\) absorption cross section at 338.3 nm is larger than reported in the literature, or that another species is formed whose absorbance more than offsets the increased transmission due to \(\text{NO}_2\) removal. A likely explanation for the lower than expected postdecay transmission is production of BrNO\(_2\) via the reaction of atomic bromine with \(\text{NO}_2\).

\[(6) \quad \text{Br} + \text{NO}_2 + M \rightarrow \text{BrNO}_2 + M \]
### Table I. Summary of kinetic data for the reaction BrO + NO$_2$ + N$_2$ products.

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</tbody>
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---

* Units are: $T$, K; concentration, $10^{16}$ molecules per cm$^3$; $k'$, s$^{-1}$; $k_1$, $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

* Experiment = measurement of one BrO temporal profile.

* Errors are 2σ and represent precision only.

* Corrected for contributions from the BrO + NO reaction.
Figure 1. Typical absorbance temporal profile. Experimental conditions: $T = 298 \, \text{K}$; $P = 40 \, \text{torr N}_2$; $1.59 \times 10^{15} \, \text{NO}_2$ per cm$^3$; $8.73 \times 10^{15} \, \text{Br}_2$ per cm$^3$; electronic time constant = $16 \, \mu\text{s}$; and 225 laser shots averaged. Note that the transmitted light level after absorbance has decayed away is lower than the pretrigger transmitted light level by 0.00048 volts, the equivalent of 0.041% absorption.

In our experiments, bromine atoms were generated via reactions (3) and (5), and also via 351 nm photolysis of Br$_2$. In fact, under typical experimental conditions, bromine atoms were in about three-fold excess over BrO. Values for $k_b(P,T)$ over the pressure and temperature range of this study are reported in the literature [16], but the BrNO$_2$ absorption spectrum is unknown. The possible systematic error resulting from BrNO$_2$ absorption will be discussed below after the kinetic data are presented. It is worth pointing out that the Br-to-BrO concentration ratio could have been reduced somewhat by employing 308 nm as the photolysis wavelength, i.e., XeCl laser rather than XeF laser. However, the excimer laser available for this study had been used for many years exclusively at fluoride wavelengths and, as a result, could not be passivated for operation with chloride gas mixtures.

To ensure that we were detecting the BrO radical, the spectrum of the absorbing species was mapped out over the wavelength range 333-339 nm. As expected [9], the 8-0 and 7-0 bands of BrO were clearly observed. The apparent BrO absorption cross section at the peak of the 7-0 band was estimated based on the measured laser fluence, the measured NO$_2$ and Br$_2$ concentrations, and the known rate coefficients for reactions (3) and (4) [12,13]. An absorption cross section of $(1.4 \pm 0.4) \times 10^{-17} \, \text{cm}^2$ was obtained (at 0.72 nm resolution). This agrees very well with the literature value of $(1.55 \pm 0.15) \times 10^{-17} \, \text{cm}^2$ at 0.4 nm resolution [9].

Reaction mixtures employed to study reaction (1) contained 0.007–0.226 torr NO$_2$, 0.116–0.322 torr Br$_2$, and 16–800 torr N$_2$ or CF$_4$ buffer gas. As mentioned above, a small amount of O$_2$ was also present in the reaction mixture because the NO$_2$ storage bulb contained air rather than N$_2$ as the diluent gas, typically, [O$_2$] ca. 10 [NO$_2$]. Concentrations of BrO radicals generated via reactions (2) and (3) were in the range $(0.4–8.5) \times 10^{12}$ molecules per cm$^3$; these concentrations were sufficiently low that contributions from the BrO self reaction were negligible. In all experiments, BrO removal was
dominated by reaction (1), but also had small contributions from reactions (5) and (7).

(7) \( \text{BrO} \rightarrow \text{loss by reaction with background impurities and diffusion or flow out of the detector field of view.} \)

Under the assumption that all processes contributing to BrO removal are first order or pseudo-first-order, the data can be analyzed using the following relationship:

\[
\ln\left( \frac{[\text{BrO}]_t}{[\text{BrO}]_0} \right) = \ln\left( \frac{S_t}{S_0} / \frac{S_t}{S_0} \right) - (k_1[\text{NO}_2] + k_3[\text{NO}] + k_7) t = k' t
\]

In eq. (I), \( t' \) represents a time shortly after the laser fires when BrO production is complete but little or no BrO decay has occurred, \( t'' \) represents a time after BrO removal has gone to completion but before \( \text{NO}_2, \text{BrONO}_2, \) and \( \text{BrNO}_2 \) diffuse or flow into or out of the detection volume, and \( S \) represents the signal level at time \( t \). The bimolecular rate coefficients of interest, \( k_1([M],T) \), are determined from the slopes of \( k'_\text{corr} \) vs. \( [\text{NO}_2] \) plots where \( k'_\text{corr} \) is the measured pseudo-first-order decay rate, \( k' \), corrected for the contribution from flash-generated NO:

\[
k'_\text{corr} = k' - k_3[\text{NO}]_f
\]

In eq. (II), \( [\text{NO}]_f \) is the concentration of flash-generated NO; the method used to determine \( [\text{NO}]_f \) is described below. Observation of BrO temporal profiles that are exponential (i.e., obey eq. (I)) and a linear dependence of \( k' \) on \( [\text{NO}_2] \) strongly suggests that reactions (1), (5), and (7) are, indeed, the only processes significantly contributing to BrO removal.

As mentioned above, all measured BrO pseudo-first-order decay rates were corrected for contribution from reaction of BrO with flash-generated NO using eq. (II). Values for \( [\text{NO}]_f \) were determined from the peak BrO absorption signals using the following relationships:

\[
[\text{BrO}]_r = \ln(S_r/S_n) / \sigma(\lambda,T)
\]

\[
[O]_0 = [\text{BrO}]_r / f
\]

\[
f = k_3[\text{Br}_2]/(k_3[\text{Br}_2] + k_4[\text{NO}_2])
\]

\[
[\text{NO}]_f = (2 - f) [O]_0
\]

In the above equations \( \sigma(\lambda,T) \) is the BrO absorption cross section (estimated at each temperature based on the results presented in ref. [9]), \( l \) is the absorption pathlength through the region photolyzed by the laser beam, and \( [\text{O}]_0 \) is the oxygen atom concentration immediately after the laser fired. At 298 K, the ratio \( k_3[\text{NO}]_f/k' \) decreased from about 0.12 at \( P = 16 \) torr to about 0.02 at \( P = 640 \) torr.

In making the correction for the reaction of BrO with flash-generated NO, it was assumed that the NO concentration was time-independent over the course of the BrO decay. Computer simulations of representative experiments indicated that the ratio \( [\text{NO}]_f/[\text{NO}]_r \) never exceeded 1.1 in any experiment. Hence, errors in evaluation of corrected pseudo-first-order BrO decay rates resulting from the approximation that [NO] was time-
independent never exceed 1%, and errors in evaluation of bimolecular rate coefficients, i.e., $k_1([M], T)$, resulting from this approximation never exceeded a few tenths of a percent.

In order to evaluate the magnitude of $k_7$, experiments were conducted where BrO removal was monitored following 351 nm laser flash photolysis of Br$_2$/O$_3$/N$_2$ mixtures.

(8) \[ \text{Br}_2 + h\nu(351 \text{ nm}) \rightarrow 2 \text{Br} \]

(9) \[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]

(7) \[ \text{BrO} \rightarrow \text{loss by reaction with background impurities} \]

Experiments were carried out using the lowest detectable BrO concentrations to minimize contributions to BrO removal from the self reaction. At all pressures and temperatures relevant to this study, we found that $k_7 < 3 \text{ s}^{-1}$. Observed intercepts of $k_{\text{con}}$ vs. [NO$_2$] plots also suggest a very small value for $k_7$; averaging the intercepts observed from experiments at all temperatures and pressures gives $k_7 = 9 \pm 140 \text{ s}^{-1}$, where the uncertainty represents two standard deviations of the average.

As typified by the data in Figures 2–4, well-behaved pseudo-first-order kinetics were observed in all experiments, i.e., BrO decays were exponential and decay rates increased linearly as a function of [NO$_2$]. The data in Figure 4 demonstrate, as expected, that the bimolecular rate coefficient, $k_1([M], T)$, increases with increasing pressure. Measured bimolecular rate coefficients are summarized along with other pertinent information in Tables I and II. Uncertainties in $k_1([M], T)$ given in the tables are 2σ and represent precision only. Small systematic errors are possible in the

![Figure 2. Typical plots of log (absorbance) vs. time obtained assuming that the post-decay transmitted light level is the correct baseline. Experimental conditions: $T = 298 \text{ K}; P = 40 \text{ torr N}_2$; [Br$_2$] in units of $10^{15}$ molecules cm$^{-3}$ (a) 6.7, (b) 8.7, (c) 6.8, and (d) 8.4; [NO$_2$] in units of $10^{16}$ molecules cm$^{-3}$ = (a) 0.62, (b) 1.59, (c) 2.70, and (d) 5.22; and number of laser shots averaged = (a) 128, (b) 225, (c) 128, and (d) 200. Solid lines are obtained from least-squares analyses and give the following pseudo-first-order decay rates in units of s$^{-1}$: (a) 306, (b) 878, (c) 1520, and (d) 2840. For the sake of clarity, temporal profiles are shifted on the absorbance scale; peak base absorbances are (a) 0.0060, (b) 0.0082, (c) 0.020, and (d) 0.010. Note that trace (b) is obtained from the data shown in Figure 1.](image-url)
NO$_2$ concentration determination, in the correction for reaction with flash-generated NO, and because of contributions to the absorbance signal from species other than BrO, NO$_2$, and BrONO$_2$ (the potential magnitude of errors resulting from BrNO$_2$ absorption is considered below). We estimate the accuracy of any measured rate coefficient, $k_1([M], T)$, to be ±20% (2σ).

Our kinetics studies of reaction (1) were restricted to $T \geq 248$ K because, for the range of NO$_2$ concentrations employed, dimerization becomes a significant problem at lower temperatures [17]. At the low temperature extreme of our study, a small fraction of NO$_2$ existed as the dimer $(\cdot$N$_2$O$_4\cdot$ in all experiments). Under experimental conditions where N$_2$O$_4$ levels were significant, i.e., low temperature (where the NO$_2$ $\rightarrow$ N$_2$O$_4$ equilibrium is
### Table II. Summary of kinetic data for the reaction BrO + NO₂ + CF₄ → products at T = 298 K.

<table>
<thead>
<tr>
<th>Concentrations¹</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
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<td>Br₂</td>
<td>NO₂</td>
<td>[NO₂]/[O]₀</td>
<td>no. of expts⁵</td>
<td>Range of k⁴</td>
<td>Uncorrected</td>
</tr>
<tr>
<td>518</td>
<td>4.5</td>
<td>1.10–3.35</td>
<td>630–910</td>
<td>6</td>
<td>419–1200</td>
<td>3.52 ± 0.44</td>
</tr>
<tr>
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<td>4.9</td>
<td>1.01–4.97</td>
<td>880–1000</td>
<td>6</td>
<td>634–3590</td>
<td>6.91 ± 0.70</td>
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<td>8.8</td>
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<td>330–880</td>
<td>6</td>
<td>1580–6890</td>
<td>12.2 ± 0.78</td>
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<tr>
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<td>3.1</td>
<td>1.03–3.23</td>
<td>590–600</td>
<td>5</td>
<td>2560–7840</td>
<td>24.6 ± 1.6</td>
</tr>
<tr>
<td>20700</td>
<td>3.8</td>
<td>1.00–4.02</td>
<td>440–460</td>
<td>5</td>
<td>3660–15,900</td>
<td>40.1 ± 2.6</td>
</tr>
</tbody>
</table>

¹ Units are: concentration, 10¹⁵ molecules per cm³; k₁, s⁻¹; k₁, 10⁻¹³ cm³ molecule⁻¹ s⁻¹.

² Errors are 2σ and represent precision only.

³ Corrected for contributions from the BrO + NO reaction.

⁴ Experiments = measurement of one BrO temporal profile.
shifted toward $\text{N}_2\text{O}_4$) and low pressure (where higher concentrations of $\text{NO}_2$ are employed due to the slower $\text{BrO} + \text{NO}_2$ rate coefficient), a potential interference could result from the reaction

$$\text{BrO} + \text{N}_2\text{O}_4 \rightarrow \text{BrONO}_2 + \text{NO}_2$$

A plot of $k'$ vs. $[\text{NO}_2]$ for our data at $T = 248 \text{ K}, P = 16 \text{ torr}$ is shown in Figure 5. A linear dependence of $k'$ on $[\text{NO}_2]$ is observed; the slope gives an apparent $\text{BrO} + \text{NO}_2$ rate coefficient of $4.83 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a reasonable intercept of $34 \pm 36 \text{ s}^{-1}$ (uncertainty is $2\sigma$, precision only). If we assume that $k_{10} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, then a simulated $k'$ vs. $[\text{NO}_2]$ plot with a slope of $4.83 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can be obtained by assuming a value of $3.01 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_1 (248 \text{ K}, 16 \text{ torr N}_2)$. However, the simulated $k'$ vs. $[\text{NO}_2]$ plot differs from the experimental plot in two important ways (see Fig. 5). First, the simulated plot is not as linear as the experimental plot, i.e., it displays a small but distinct upward curvature. Secondly, the intercept of the simulated plot is distinctly negative, i.e., $-184 \pm 96 \text{ s}^{-1}$ (uncertainty is $2\sigma$, precision only). The observed positive intercept of the $k'$ vs. $[\text{NO}_2]$ plot for data obtained at the lowest temperature and pressure of our study strongly suggests that reaction (10) did not contribute significantly to BrO removal over the range of experimental conditions employed. Therefore, analysis of all low temperature data employed the good approximation that $k_{10}[\text{N}_2\text{O}_4] \ll k_1[\text{NO}_2]$.

As mentioned above, one potential source of systematic error in our data analysis procedure results from the fact that a species other than $\text{BrO}, \text{NO}_2$, and $\text{BrONO}_2$ appears to absorb probe radiation at $338.3 \text{ nm}$. The probable absorbing species is $\text{BrNO}_2$, produced via reaction (6). The kinetics of reaction (6) as a function of temperature and pressure are well characterized [16]. The bimolecular rate coefficients $k_1$ and $k_6$ are similar in magnitude but

![Figure 5. Plots of $k'$ vs. $[\text{NO}_2]$ for (a) experimental data at $T = 248 \text{ K}, P = 16 \text{ torr}$ and (b) a simulation with $k_1$ assumed equal to $3.01 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{10}$ assumed equal to $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Note the significant nonlinearity in the simulated $k'$ vs. $[\text{NO}_2]$ data. Lines are obtained from linear least-squares analyses and give equal slopes ($4.83 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) but significantly different intercepts.](image-url)
have somewhat different temperature and pressure dependences. Over the range of temperatures and pressures employed in this study, the ratio \( k_l/k_o \) varies from 1.4 in the low \( P \), low \( T \) extreme (16 torr, 248 K) to 0.4 in the high \( P \), high \( T \) extreme (800 torr, 346 K). As discussed above, the kinetic data reported in Tables I and II were obtained based on an analysis which assumed a time-independent baseline equal to \( S_{post} \), the postdecay signal level. The assumption that all absorbance not due to \( \text{BrO}, \text{NO}_2 \), or \( \text{BrONO}_2 \) is attributable to \( \text{BrNO}_2 \) leads to a time-dependent baseline which, since the time constant for baseline change is different from the time constant for \( \text{BrO} \) attenuation, should be accounted for in the data analysis [15]. To address this problem, we have reanalyzed the 346 K, 640 torr, and 248 K, 16 torr data sets using a time-dependent baseline calculated from our kinetic data for reaction (6) [16] under the assumptions that (a) all absorbance at \( t = t'' \) not attributable to \( \text{BrO}, \text{NO}_2 \), or \( \text{BrONO}_2 \), is due to \( \text{BrNO}_2 \), and (b) removal of \( \text{BrNO}_2 \) via reaction (11) is negligible on the time scale of interest.

(11) \[
\text{Br} + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2
\]

The results of a typical reanalysis are summarized in Figures 6 and 7. Individual pseudo-first-order decay rates computed using the time-dependent baseline differ from those computed using the time-independent baseline by 2–6% with the largest differences coming at the lowest \( \text{NO}_2 \) concentrations. Bimolecular rate coefficients obtained using the two methods of analysis differ by less than 2% in the high pressure, high temperature case (the more exact analysis gives a slightly higher rate coefficient), and by less than 5% in the low pressure, low temperature case (the more exact analysis gives a slightly lower rate coefficient). Because the errors associated with neglecting the time-dependent baseline are small and identification of the fourth absorbing species as \( \text{BrNO}_2 \) is somewhat tenuous, we have chosen to report rate coefficients obtained using the less exact time-independent baseline analysis. The above-mentioned accuracy estimate of ±20% for individual values of \( k_l([M], T) \) includes possible systematic errors due to the time-independent baseline assumption. It is worth noting that a small systematic error in the shape of reported fall off curves probably results from the time-independent baseline assumption, because high pressure rate coefficients are expected to be slightly underestimated while low pressure rate coefficients are expected to be slightly overestimated.

Our results demonstrate that reaction (1) is in the “falloff” regime between third- and second-order kinetics over the temperature and pressure ranges investigated. Troe and co-workers [18–21] have shown that bimolecular rate coefficient vs. pressure curves (i.e., falloff curves) for association reactions can be approximated by the three-parameter equation

\[
k_l([M], T) = k_{i,0}([M], T)F_{LH}F([M], T)
\]

where \( F_{LH} \) is the Lindemann-Hinshelwood factor.

\[
F_{LH} = X/(1 + X)
\]

\[
X = k_{i,0}([M], T)[M]/k_{i,0}(T)
\]

In the above equations, \( k_{i,0}([M], T) \) is the rate coefficient for reaction (i) in the low-pressure-third-order limit, \( k_{i,0}(T) \) is the rate coefficient for reaction
BrO + NO₂ ASSOCIATION REACTION

Figure 6. Solid circles are experimental transmitted 338.3 nm probe intensity vs. time data for an experiment at $T = 346\, K$, $P = 640$ torr N₂ with $[\text{NO}_2] = 7.75 \times 10^{14}$ molecules cm$^{-3}$, and $[\text{Br}_2] = 6.7 \times 10^{15}$ molecules cm$^{-3}$. The dashed line is the expected "baseline" transmitted probe intensity assuming that BrNO₂ is transparent at 338.3 nm. The solid line is calculated assuming that the difference between the postdecay experimental signal level and the postdecay dashed line level can be attributed to absorption by BrNO₂; the BrNO₂ absorption cross section required to account for the difference is $1.14 \times 10^{-18}$ cm$^2$.

(i) in the high-pressure-second-order limit, and $F([M], T)$ is the parameter which characterizes the broadening of the falloff curve due to the energy dependence of the rate coefficient for decomposition of the energized adduct. $F([M], T)$ can be calculated from the spectroscopic and thermodynamic properties of the adduct.

For parameterization of the temperature and pressure dependences of atmospheric association reactions, the following approximate form for $F([M], T)$

Figure 7. Plots of log (absorbance) vs. time for the data shown in Figure 6. In trace (a), the baseline is assumed to be time-independent and equal to the postdecay value of the solid line in Figure 6. In trace (b) the baseline (B) is assumed to be time-dependent with $B(t)$ given by the solid line in Figure 6. Solid lines are obtained from least-squares analyses and give the following pseudo-first-order decay rates in units of s$^{-1}$: (a) 1290 and (b) 1360.
is typically employed [13,22]:

\[(X) \quad F([M], T) = F_c(M, T)[1+(\log[M]/2)]^{-1}\]

In eq. (X), \(F_c(M, T)\) is the broadening parameter at the center of the falloff curve, i.e., when \(k\text{,}_0[M] = k\text{,}_\infty\). The NASA panel for data evaluation assumes \(F_c(N_2, T) = 0.6\) for all reactions at all temperatures [13]. On the other hand, the IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry employs \(F_c\) values which are both reaction and temperature dependent. For reaction (1) the IUPAC panel recommends \(F_c(N_2, T) = \exp(-T/327)\) [22]; the recommended value at 298 \(K\), \(F_c = 0.402\), is based on the detailed analysis of Sander et al [4]. We have fit our data to eqs. (VII) and (X) using both \(F_c(N_2, T) = 0.6\) and \(F_c(N_2, T) = \exp(-T/327)\). Corresponding values for \(F_c(CF_4, T)\) were computed from the relationship [18]

\[(XI) \quad \frac{F_c(CF_4, 298 K)}{F_c(N_2, 298 K)} = \left[ \frac{k\text{,}_0(CF_4, 298 K)Z_{LJ}(N_2, 298 K)}{k\text{,}_0(N_2, 298 K)Z_{LJ}(CF_4, 298 K)} \right]^{0.14}\]

In eq. (XI), \(Z_{LJ}(M, 298 K)\) is the Lennard-Jones collision frequency for \(BrONO_2 - M\) encounters; it is calculated using a relationship and Lennard-Jones parameters given elsewhere [23].

Experimental data along with best fit (to our data only) falloff curves for \(M = N_2\) at 298 \(K\) are shown in Figure 8 while experimental data along with best fit (to our data only) falloff curves for \(M = N_2\) at 268 \(K\) and 346 \(K\) are shown in Figure 9. Rate coefficients reported in the two previous studies of \(BrO + NO_2\) kinetics [4,5] are also plotted in Figures 8 and 9. The fits for the two different choices of \(F_c\) are virtually indistinguishable over the range of pressures where our data were obtained although, as expected, values for \(k\text{,}_\infty(T)\) obtained using the two different \(F_c\) parameterizations differ considerably; the \(k\text{,}_\infty(T)\) values obtained using \(F_c = \exp(-T/327)\) are...
Figure 9. Falloff curves for the reaction BrO + NO₂ → NO₂ + N₂ products at 268 K and 346 K. Closed squares and circles are rate coefficients reported in this article at 268 K and 346 K, respectively; open squares and circles are rate coefficients reported by Danis et al. [5] at 263 K and 343 K, respectively. Solid lines are the best fits of our data only to eqs. VII and X with $F_r = \exp(-T/327)$. Dashed lines are the best fits of our data only to eqs. VII and X with $F_r = 0.6$. Best fit values for $k_{i,0}$ and $k_{i,\infty}$ are given in Table III.

Undoubtedly closer to the real high pressure limit rate coefficients because (a) $F_r$ is expected to be temperature dependent [18–21] and (b) the 298 K value $\exp(-298/327) = 0.402$ is supported by the experimental and theoretical results of Sander et al. [4]. Best fit falloff parameters are summarized in Table III.

Examination of Figure 8 shows that our 298 K results agree very well with the extensive 298 K study of Sander et al. [4], who used two different experimental techniques (one of which was very similar to ours) to measure $k_1(N_2, 298 K)$ over the pressure range 1–700 torr. On the other hand, as shown in Figures 7 and 8, the low pressure rate coefficients reported by Danis et al. [5] in O₂ buffer gas are lower than our (extrapolated) low pressure rate coefficients by about 25%. It has now been established that the lower rate coefficients reported by Danis et al. can be attributed to heterogeneous loss of NO₂ in their slow flow system [24]. Hence, it appears that values of $k_1(P, T)$ for use in stratospheric models should be based on our results and the 298 K results of Sander et al. [4]. This approach leads

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<th>$T$</th>
<th>$M$</th>
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<td></td>
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<tr>
<td>346 ± 1</td>
<td>N₂</td>
<td>3.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* Units are: $T$, K; $k_{i,0}$, $10^{-31}$ cm$^6$ molecule$^{-2}$ s$^{-1}$; $k_{i,\infty}$, $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

* These $F_r$ values are for N₂; $F_r(CF₄) = 1.056 F_r(N₂)$. 

Table III. Summary of "best fit" falloff parameters for reaction (1).
to the following two sets of recommended falloff parameters ($k_{1,0}$ values are for N$_2$ buffer gas):

I. $F_c = 0.6$

\[ k_{1,0} = 5.2 \times 10^{-31} (T/300)^{-3.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \]
\[ k_{1,\infty} = 6.9 \times 10^{-12} (T/300)^{-2.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

II. $F_c = \exp(-T/327)$

\[ k_{1,0} = 5.4 \times 10^{-31} (T/300)^{-3.2} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \]
\[ k_{1,\infty} = 1.4 \times 10^{-11} (T/300)^{-1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

Either of the above sets of falloff parameters can be employed to accurately compute $k_1(P,T)$ over the range of temperatures and pressures relevant to the atmosphere. However, it should be kept in mind that the values for $k_{1,0}$ and $k_{1,\infty}$ given above are parameters which only approximate the actual low- and high-pressure-limit rate coefficients. Because data are available near the low pressure limit, and because derived values for $k_{1,0}$ are only weakly dependent on the choice of $F_c$, we expect that the reported $k_{1,0}$ values are within ±20% of the actual low pressure limit rate coefficient. On the other hand, because data are not available near the high pressure limit, and because derived values for $k_{1,\infty}$ are strongly dependent on the choice of $F_c$, the uncertainty in the actual high pressure limit rate coefficient is rather high, i.e., at least a factor of two. If accurate values for $F([M],T)$ could be calculated from available spectroscopic and thermodynamic information about BrONO$_2$, then a reasonably accurate value for $k_{1,\infty}$ could be obtained by extrapolation of available kinetic data. However, for reasons discussed below, available structural and thermodynamic information for XONO$_2$ species must be viewed with skepticism. Measurements of $k_1(P,T)$ up to very high pressures, i.e., tens of atmospheres, would provide the data needed for accurate evaluation of $k_{1,\infty}$ (and $F_c$).

One interesting aspect of reaction (1) is the magnitude of the low-pressure-limit termolecular rate coefficient. Theoretical values of $k_{1,0}$ have been calculated using RRKM theory [5] and the factorized expression of Troe [5,23]; theoretical values for $k_{1,0}$ are slightly lower than experimental low pressure rate coefficients; for typical N$_2$ collisional efficiency factors of 0.1 to 0.3, this means that theoretical $k_{1,0}$ values are about a factor of five too low to be consistent with experiment. As pointed out by DeMore, et al. [25], “Even though isomer formation seems to have been ruled out for the ClO + NO$_2$ reaction (i.e., the isomer stability is too low to make a significant contribution to the measured rate constant), this does not eliminate the possibility that BrO + NO$_2$ leads to more than one stable compound. In fact, if the measured low pressure limit rate constant for BrO + NO$_2$ is accepted, it can only be theoretically reconciled with a single isomer, BrONO$_2$, which would have a 6–7 kcal mol$^{-1}$ stronger bond than ClONO$_2$! This would fix the heat of formation of BrONO$_2$ to be the same as ClONO$_2$, an unlikely possibility.” Interestingly, a similar situation exists when comparing the measured low-pressure-limit rate coefficient for the IO + NO$_2$ reaction [7], with those for ClO + NO$_2$ and BrO + NO$_2$. Clearly, the thermochemistry of XONO$_2$ ($X = Br, I$) requires further investigation, as does the possible formation of isomers such as OXNO$_2$, XOONO, or OXONO. Regarding XONO$_2$ thermochemistry, we have recently become aware of a theoretical study which suggests a higher than expected value for the
BrONO$_2$ bond dissociation energy [24]; the higher bond dissociation energy, if correct, would lead to good consistency between calculated $k_{1,0}(T)$ values and experimental low pressure rate coefficients [24].

Acknowledgment

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Bibliography


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Temperature-Dependent Kinetics Studies of the Reactions $\text{Br}(^2P_{3/2}) + \text{H}_2\text{S} \leftrightarrow \text{SH} + \text{HBr}$ and $\text{Br}(^2P_{3/2}) + \text{CH}_3\text{SH} \leftrightarrow \text{CH}_3\text{S} + \text{HBr}$. Heats of Formation of SH and CH$_3$S Radicals

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Time-resolved resonance fluorescence detection of $\text{Br}(^2P_{3/2})$ atom disappearance or appearance following 266-nm laser flash photolysis of CF$_2$Br$_2$/H$_2$S/H$_2$/N$_2$, CF$_2$Br$_2$/CH$_3$SH/H$_2$/N$_2$, Cl$_2$CO/H$_2$S/HBr/N$_2$, and CH$_3$SSCH$_3$/HBr/H$_2$/N$_2$ mixtures has been employed to study the kinetics of the reactions $\text{Br}(^2P_{3/2}) + \text{H}_2\text{S} \rightarrow \text{SH} + \text{HBr}$ (1, -1) and $\text{Br}(^2P_{3/2}) + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{HBr}$ (2, -2) as a function of temperature over the range 273-431 K. Arrhenius expressions in units of $10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ which describe the reactions are $k_1 = (14.2 \pm 3.4) \exp((-2752 \pm 90)/T)$, $k_2 = (4.40 \pm 0.92) \exp((-971 \pm 73)/T)$, $k_3 = (9.24 \pm 1.15) \exp((-386 \pm 41)/T)$, and $k_4 = (1.46 \pm 0.21) \exp((-399 \pm 41)/T)$; errors are 2σ and represent precision only.

By examining $\text{Br}(^2P_{3/2})$ equilibration kinetics following 355-nm laser flash photolysis of Br$_2$/CH$_3$SH/H$_2$/N$_2$ mixtures, a 298 K rate coefficient of $(1.7 \pm 0.5) \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ has been obtained for the reaction $\text{CH}_3\text{S} + \text{Br}_2 \rightarrow \text{CH}_3\text{SBr} + \text{Br}$. To our knowledge, these are the first kinetic data reported for each of the reactions studied. Measured rate coefficients, along with known rate coefficients for similar radical + H$_2$S, CH$_3$SH, HBr, Br$_2$ reactions are considered in terms of possible correlations of reactivity with reaction thermochemistry and with IP - EA, the difference between the ionization potential of the electron donor and the electron affinity of the electron acceptor. Both thermochemical and charge-transfer effects appear to be important in controlling observed reactivities. Second and third law analyses of the equilibrium data for reactions 1 and 2 have been employed to obtain the following enthalpies of reaction in units of kcal mol$^{-1}$: for reaction 1, $\Delta H_{\text{mol}} = 3.64 \pm 0.43$ and $\Delta H_{\text{mol}} = 3.26 \pm 0.45$; for reaction 2, $\Delta H_{\text{mol}} = -0.14 \pm 0.28$ and $\Delta H_{\text{mol}} = -0.65 \pm 0.36$. Combining the above enthalpies of reaction with the well-known heats of formation of Br, HBr, H$_2$S, and CH$_3$SH gives the following heats of formation for the RS radicals in units of kcal mol$^{-1}$: $\Delta H_f^\circ(\text{SH}) = 34.07 \pm 0.72$, $\Delta H_f^\circ(\text{CH}_3\text{S}) = 34.18 \pm 0.68$, $\Delta H_f^\circ(\text{CH}_3\text{SH}) = 31.44 \pm 0.54$, and $\Delta H_f^\circ(\text{CH}_3\text{S}) = 29.78 \pm 0.44$; errors are 2σ and represent estimates of absolute accuracy. The SH heat of formation determined from our data agrees well with literature values but has reduced error limits compared to other available values. The CH$_3$S heat of formation determined from our data is near the low end of the range of previous estimates and is 3-4 kcal mol$^{-1}$ lower than values derived from recent molecular beam photodissociation studies.

Introduction

Accurate thermochemical information for free-radical intermediates is essential to analysis of reaction mechanisms in complex chemical systems. One experimental approach which can be employed to obtain thermochemical parameters for a radical R involves measurement of temperature-dependent rate coefficients for the pair of reactions RH + R' $\rightarrow$ R'H + R; the ideal reaction pair for such a study is one where the heats of formation and absolute entropies of R, R', and RH are well characterized and where kinetic data for the two reactions can be obtained over the same temperature range.

In this paper we report the results of temperature-dependent kinetics studies of the following four reactions:

1. $\text{Br}(^2P_{3/2}) + \text{H}_2\text{S} \rightarrow \text{SH} + \text{HBr}$
2. $\text{SH} + \text{HBr} \rightarrow \text{Br}(^2P_{3/2}) + \text{H}_2\text{S}$
3. $\text{Br}(^2P_{3/2}) + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{HBr}$
4. $\text{CH}_3\text{S} + \text{HBr} \rightarrow \text{Br}(^2P_{3/2}) + \text{CH}_3\text{SH}$

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Heats of Formation of SH and CH₃S Radicals

The kinetic results have been employed to derive the most precise (and hopefully the most accurate) values currently available for the heats of formation of SH and CH₃S, two radicals which are important intermediates in the oxidation of a number of atmospheric reduced sulfur compounds including H₂S, CH₃SH, CH₃SCH₃, and CH₃SSCH₃. To our knowledge there are no kinetic studies of any of the reactions 1, -1, 2, and -2 reported in the literature.

Experimental Technique

The experimental approach involved coupling reactant radical (i.e., Br, SH, CH₃S) production by laser flash photolysis of suitable precursors with time-resolved detection of ground state bromine atom disappearance or appearance by resonance fluorescence spectroscopy. A schematic diagram of the apparatus, as configured for bromine atom detection, can be found elsewhere. A description of the experimental methodology is given below.

A Pyrex-jacketed reaction cell with an internal volume of 150 cm³ was used in all experiments; a diagram showing the geometry of the reaction cell is published elsewhere. The cell was maintained at a constant temperature by circulating ethylene glycol (T > 298 K) or methanol (T < 298 K) from a thermostatically controlled bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket was inserted into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment.

The reactant radicals Br, SH, and CH₃S were generated by 266-nm laser flash photolysis of CF₂Br₂, Cl₂CO/H₂S, and CH₃SSCH₃, respectively. In a few experiments Br atoms were generated by 355-nm laser flash photolysis of Br₂. Third (355 nm) or fourth (266 nm) harmonic radiation from a Quantaray Model DCR-2 Nd:YAG laser provided the photolytic radiation. The laser could deliver up to 3 × 10¹⁴ photons per pulse at 266 nm and up to 1 × 10¹⁵ photons per pulse at 355 nm; the maximum repetition rate was 10 Hz and the pulse width was approximately 6 ns.

A bromine resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the bromine atoms produced photolytically or as a reaction product. The resonance lamp consisted of an electrodeless microwave discharge through about 1 Torr of a flowing mixture containing a trace of Br₂ in helium. The flows of a 0.2% Br₂ in helium mixture and pure helium into the lamp were controlled by separate needle valves, thus allowing the total pressure and Br₂ concentration to be adjusted for optimum signal-to-noise ratio. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell, the lamp output passed through a flowing gas filter containing 30 Torr cm of methane in nitrogen. The methane filter prevented radiation at wavelengths shorter than 140 nm (including impurity emissions from excited oxygen, hydrogen, nitrogen, and chlorine atoms) from entering the reaction cell, but transmitted the strong bromine lines in the 140-160-nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and resonance lamp beam and was imaged onto the photocathode of a solar blind photomultiplier with a CsI photocathode. The region between the reaction cell and the photomultiplier was purged with N₂ to prevent absorption of fluorescence photons by O₂, N₂O, and other trace gases in the laboratory air. Signals were processed using photon counting techniques in conjunction with multichannel scaling. A large number of laser shots were typically averaged to obtain a bromine atom temporal profile with signal-to-noise sufficient for quantitative kinetic analysis. It is worth noting that the resonance fluorescence detection scheme is sensitive to both ground-state (7P/2) and spin-orbit excited-state (7P, 1D) bromine atoms.

Tests were carried out to evaluate the sensitivity of the detection system toward O, H, Cl, CO, and Br using 266-nm laser flash photolysis of O₂/N₂, CH₃SH/N₂, Cl₂CO/N₂, and CF₂Br₂/H₂/N₂ mixtures as the respective sources for O, H, Cl + CO, and Br (the reason for adding H₂ to the CF₂Br₂/N₂ mixture is discussed below). Production of 1 × 10¹⁵ O₂ or H₂ cm⁻³ resulted in no observable signal. Similarly, production of 1 × 10¹⁴ Cl cm⁻³ + 5 × 10¹⁴ CO cm⁻³ resulted in no observable signal. The detection sensitivity for Br atoms was sufficient to obtain a bromine atom temporal profile to be followed down to [Br] < 1 × 10¹² atoms cm⁻³ with a reasonable level of signal averaging.

The emission spectrum of the bromine lamp (transmitted through the methane filter) was measured using a scanning vacuum UV monochromator (resolution = 0.05 nm) and the same solar blind photomultiplier as was employed in the kinetics experiments. In addition to the 7P — 3P and 7P — 1D bromine transitions, major impurity emissions were the 7P — 2D, 7P — 2D, and 3D — 2P transitions of atomic nitrogen at 174 nm (strong), 149 nm (strong), and 141 nm (weak), respectively, and the 7P — 2P transitions of atomic carbon at 166 nm (weak). The above-mentioned sensitivity tests confirmed that N(3P), N(3D), and/or C(3P) were not produced in sufficient quantity in the reaction cell (by multiphoton photodissociation of N₂ or Cl₂CO) to be detected via fluorescence excited by impurity lamp emissions; if these were not the case, then fluorescence signal would have been observed following 266-nm laser flash photolysis of O₂/N₂, CH₃SH/N₂, and/or Cl₂CO/N₂ mixtures. The tests described above demonstrate quite conclusively that the detection system was specific to bromine atoms.

To avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was in the range 1.5-4.5 cm s⁻¹ (and the laser repetition rate was varied over the range 1-10 Hz (5 Hz typical)). Hence, no volume element of the reaction mixture was subjected to more than a few laser shots. Reactants and radical photolytic precursors were flowed into the reaction cell from bulbs (12 L volume) containing dilute mixtures in nitrogen while hydrogen and additional nitrogen were flowed directly from their storage cylinders. Except where specified in later discussions, all gases were premixed before entering the reactor. The concentrations of each component in the reaction mixtures were determined from measurements of the appropriate mass flow rates and the total pressure. The excess reactant (i.e., H₂S, CH₃SH, or HBr) concentration was also determined in situ in the slow flow system by UV photometry. Monitoring wavelengths, light sources, and absorption cross sections relevant to the photometric measurements are summarized in Table I. Since it was normally the case that more than one species in the reaction mixtures absorbed at the monitoring wavelength, the excess reactant concentration was usually measured upstream from the photolyte addition point; dilution factors required to correct the measured concentration to the actual reactor concentration never exceeded 1.1. Some experiments were carried out with the absorption cell positioned downstream from the reactor. Although the determinations of the excess reactant concentration were less precise in this experimental configuration (due to the presence in the absorption cell of more than one absorbing species), ex-

| Table I: Parameters Relevant to in Situ Monitoring of H₂S, CH₃SH, and HBr |
|--------------------------|------------------|------------------|
| species | λ nm | light source | λ isolation |
| H₂S    | 202.6 | A | M | 57.5' |
|        | 228.8 | B | BPF | 4.58' |
| CH₃SH  | 202.6 | A | M | 87.1 (ref 67) |
|        | 213.9 | A | M | 14.8 |
| HBr    | 202.6 | A | M | 10.2 (ref 24) |

* A, zinc hollow cathode lamp; B, cadmium penray lamp. A, 1/cm monochromator; BPF, band-pass filter. *Measured during the course of this investigation. **
perimental results were found to be independent of whether the absorption cell was positioned upstream or downstream relative to the reactor.

The gases used in this study had the following stated minimum purities: N₂, 99.999%; H₂, 99.999%; Cl₂, 99.99%; HBr, 99.8%; H₂S, 99.5%; CH₃SH, 99.5%. Nitrogen and hydrogen were used as supplied. When Cl₂, HBr, H₂S, and CH₃SH were degassed repeatedly at 77 K before being used to prepare mixtures with N₂. It is not worth noting that HBr gas samples taken directly from the storage cylinder contained significant (25-50%) levels of a noncondensable (at 77 K) impurity which was determined by weighing to be H₂. The stated minimum purity of the CF₂Br₂ liquid sample was 99.9%. It was transferred under nitrogen into a vial fitted with a high vacuum stopcock and subjected to repeated freeze (77 K)-pump-chuckle cycles before being used to prepare gaseous mixtures with N₂.

Results and Discussion

In studies of reactions 1 and 2 bromine atoms were generated by 266-nm laser flash photolysis of CF₂Br₂ ((CF₂Br₂) ranging from 0.2 x 10⁻¹⁰ to 11 x 10⁻¹⁰ molecules cm⁻³):

CF₂Br₂ + hν(266 nm) → Br + CF₂Br

(3)

The CF₂Br₂ absorption cross section at 266 nm is approximately 8 x 10⁻²⁰ cm⁻² molecule⁻¹ while the quantum yield for Br production from CF₂Br₂ photolysis increases from unity at λ ≥ 248 nm to around 2 at λ = 193 nm. Presumably, at λ ≥ 248 nm CF₂Br₂ photodissociates as indicated in reaction 3 with unit yield. To ensure rapid relaxation of any photolytically generated Br(P₃/₂), about 1 Torr of He was added to the reaction mixture. The reaction

Br(P₃/₂) + H₂(o=0) → Br(P₃/₁) + H₂(o=1)

(4)

is known to be fast with k₁ = 6 x 10⁻¹² cm³ molecule⁻² s⁻¹. In studies of reaction 1, SH radicals were generated as follows:

Cl₂CO + hν(266 nm) → 2Cl + CO (5)

Cl + H₂S → SH + HCl (6)

The Cl₂CO concentration was typically 1 x 10⁻¹³ molecules cm⁻³ while the H₂S concentration was typically 1 x 10⁻¹⁴ molecules cm⁻³. We have recently shown that k₁ = 3.6 x 10⁻¹⁰ exp(-210/Th) cm³ molecule⁻² s⁻¹ and k₂ = 2.25 x 10⁻¹⁰ exp(-400/Th) cm³ molecule⁻² s⁻¹. Cl + H₂ → Br(P₃/₁) + HCl

(7)

Based on the above rate coefficients, experimental conditions were maintained where >90% of the photolytically generated Cl reacted with H₂S and <10% reacted with HBr. The Cl₂CO absorption cross section at 266 nm is approximately 1 x 10⁻¹⁰ molecules cm⁻³ while the quantum yield for Cl₂CO photodissociation at 253.7 nm has been shown to be unity. Reaction 5 actually occurs in a two-step process involving a CICO intermediate. However, even in the unlikely event that CICO is produced without internal excitation, the CICO lifetime toward decomposition to Cl + CO is short compared to the experimental time scale (hundreds of microseconds) for SH removal. Reaction 1 was studied employing reaction mixtures containing no H₂ in order to avoid potential complications from the reaction Cl + H₂ → HCl + H.

(5) Stated purity of liquid phase in cylinder.
(9) Tauldar, R.; Vaghiangia, G. L.; Ravishakara, A. R., to be published.

In the absence of side reactions which regenerate or deplete the Br(P₃/₂) atom concentration, the observed Br(P₃/₂) temporal profile following the laser flash in studies of reactions 1 and 2 would be described by the relationship

ln(S₂/S₁) = ln |[Br(P₃/₂)]₀/[Br(P₃/₂)]₁| = k₁[S₀][Sₘ] + k₂

(I)

In the above relationship, S₀ and S₁ are the signal levels immediately after the laser fires and at some later time t, [Br(P₃/₂)]₀ and [Br(P₃/₂)]₁ are the bromine atom concentrations corresponding to S₀ and S₁, and k₂ is the first-order rate coefficient for the process

Br(P₃/₂) → loss by diffusion from the detector field of view and reaction with background impurities (9).

The bimolecular rate coefficients of interest, k₂[P,T], are determined from the slopes of k₁ versus [S,R,S] plots. Observation of Br(P₃/₂) temporal profiles which are exponential (i.e., obey eq 1), linear dependencies of k₂ on [S,R,S], and invariance of observed

The rate coefficient for the following reaction(s)

\[ k = k_{\text{HBr}} \]

is the rate coefficient for the following reaction(s)

\[ \text{concentrations after photolysis and (in the case of the SH + HBr} \]

For the reaction systems of interest, removal of RS radical has occurred, \( f \) is the fraction of RS

\[ \text{study) reaction 6 have gone to completion, but before significant} \]

and \( C \)

rate coefficient for Br

relationship

\[ \text{Kinetic data for reactions 1 and 2 are summarized in Tables 11} \]

ruled out by the above set of observations. A typical Br(2P3,0)

flash in studies of reactions

\[ \text{processes which affect the Br(} \]

psuedo-first order \( \text{Br(} \text{P}_3\text{)}e \text{ decay rate.} \]

Errors represent precision only.

TABLE II: Summary of Kinetic Data for the Reactions \( \text{Br(} \text{P}_3\text{)} \) + 

\[ \text{H}_2\text{S} \rightarrow \text{SH} + \text{HBr} \]

kinetics to variations in laser photon fluence and photolyte concentration strongly suggest that reactions 1 and 9 are the only processes which affect the \( \text{Br(} \text{P}_3\text{)}e \) time history, although reactions of \( \text{Br(} \text{P}_3\text{)}e \) with impurities in the RS samples are not

units are \( T \) (K), \( P \) (Torr); \( \text{[H}_2\text{S]} \) (10^14 molecules cm^-2); \( k' \) (s^-1); \( k_1 \) (10^-3 cm^3 molecule^-1 s^-1) . \( \text{Expt} \) = measurement of a single pseudo-first-order \( \text{Br(} \text{P}_3\text{)}e \) decay rate. \( \text{Errors} \) represent precision only.

TABLE III: Summary of Kinetic Data for the Reaction \( \text{Br(} \text{P}_3\text{)} \) + 

\[ \text{CH}_2\text{SH} \rightarrow \text{CH}_3\text{S} + \text{HBr} \]

kinetics to variations in laser photon fluence and photolyte concentration strongly suggest that reactions 1 and 9 are the only processes which affect the \( \text{Br(} \text{P}_3\text{)}e \) time history, although reactions of \( \text{Br(} \text{P}_3\text{)}e \) with impurities in the RS samples are not

units are \( T \) (K), \( P \) (Torr); \( \text{[CH}_2\text{SH]} \) (10^14 molecules cm^-2); \( k' \) (s^-1); \( k_1 \) (10^-3 cm^3 molecule^-1 s^-1) . \( \text{Expt} \) = measurement of a single pseudo-first-order \( \text{Br(} \text{P}_3\text{)}e \) decay rate. \( \text{Errors} \) represent precision only.

In the absence of side reactions that remove or produce \( \text{Br(} \text{P}_3\text{)}e \), the observed \( \text{Br(} \text{P}_3\text{)}e \) temporal profile following the laser flash in studies of reactions -1 and -2 would be described by the relationship

\[ S = k_0C_2(k_3 - k_4)^{-1}\left(\exp(-k_0t) - \exp(-k_3t)\right) + C_1\exp(-k_4t) \]

In eq II, \( S \) and \( k_4 \) are as defined above, \( k_0 \) is the pseudo-first-order rate coefficient for \( \text{Br(} \text{P}_3\text{)}e \) appearance, and the parameters \( C_1 \) and \( C_2 \) are defined as follows:

\[ C_1 = \alpha[R,S]_0 \]

\[ C_2 = \alpha[\text{Br(} \text{P}_3\text{)}e]_0 \]

In the above equations \( [R,S]_0 \) and \( [\text{Br(} \text{P}_3\text{)}e]_0 \) are the radical concentrations after photolysis and (in the case of the SH + HBr study) reaction 6 have gone to completion, but before significant removal of \( R,S \) radicals has occurred, \( f \) is the fraction of \( R,S \) radicals which are removed via a reaction which produces Br, and \( \alpha \) is the proportionality constant which relates \( S \) to \( [\text{Br(} \text{P}_3\text{)}e]_0 \). For the reaction systems of interest, we expect that

\[ k_0 = k_{\text{HBr}} + k_{10} \]

\[ f = k_{\text{HBr}}/k_10 \]

where \( i = 1 \) or 2, \( R = \text{H} \) for \( i = 1 \) and \( \text{CH}_2 \) for \( i = 2 \), and \( k_{10} \) is the rate coefficient for the following reaction(s)

\[ \text{R} + \text{S} \rightarrow \text{first-order loss by processes which do not produce Br} \]

errors in the above expressions are 2e and represent precision only. On the basis of observed precision and consideration of possible
TABLE IV: Summary of Kinetic Data for the Reaction SH + HBr → Br(2P5/2) + H2S

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (Torr)</th>
<th>no of expts</th>
<th>[HBr]max</th>
<th>range of k,</th>
<th>range of k2</th>
<th>k10 ± 2σ</th>
<th>k2 ± 2σ</th>
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<tr>
<td>299</td>
<td>100</td>
<td>7</td>
<td>161</td>
<td>590-2910</td>
<td>29-45</td>
<td>49 ± 106</td>
<td>176 ± 10</td>
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<td>321</td>
<td>100</td>
<td>6</td>
<td>125</td>
<td>411-2980</td>
<td>24-35</td>
<td>64 ± 76</td>
<td>209 ± 8</td>
</tr>
<tr>
<td>341</td>
<td>100</td>
<td>5</td>
<td>153</td>
<td>626-4050</td>
<td>28-39</td>
<td>92 ± 140</td>
<td>253 ± 14</td>
</tr>
<tr>
<td>402</td>
<td>100</td>
<td>7</td>
<td>117</td>
<td>1100-4740</td>
<td>31-37</td>
<td>302 ± 286</td>
<td>385 ± 34</td>
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<tr>
<td>423</td>
<td>100</td>
<td>12</td>
<td>91.2</td>
<td>622-4330</td>
<td>23-43</td>
<td>112 ± 140</td>
<td>457 ± 22</td>
</tr>
</tbody>
</table>

*Units are T (K); P (Torr); [HBr] (1014 molecules cm⁻³); k, k2 (s⁻¹); k10 (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). *Expt is measurement of a single Br(2P5/2) temporal profile. *Errors represent precision only.

TABLE V: Summary of Kinetic Data for the Reaction CHS + HBr → Br(2P5/2) + CH₂SH

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (Torr)</th>
<th>no of expts</th>
<th>[HBr]max</th>
<th>range of k,</th>
<th>range of k2</th>
<th>k10 ± 2σ</th>
<th>k2 ± 2σ</th>
</tr>
</thead>
<tbody>
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<td>273</td>
<td>100</td>
<td>10</td>
<td>77.9</td>
<td>261-2870</td>
<td>11-29</td>
<td>99 ± 114</td>
<td>347 ± 29</td>
</tr>
<tr>
<td>295</td>
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<td>247 ± 116</td>
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<td>11</td>
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<td>16-29</td>
<td>81 ± 50</td>
<td>363 ± 12</td>
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<td>14</td>
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<td>382 ± 20</td>
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<td>10</td>
<td>69.4</td>
<td>436-2770</td>
<td>9-23</td>
<td>18 ± 130</td>
<td>383 ± 28</td>
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<td>100</td>
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<td>473-2970</td>
<td>14-20</td>
<td>49 ± 82</td>
<td>438 ± 21</td>
</tr>
<tr>
<td>366</td>
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<td>6</td>
<td>56.4</td>
<td>225-2960</td>
<td>25-49</td>
<td>65 ± 26</td>
<td>468 ± 8</td>
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<tr>
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<td>8</td>
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<td>294-3120</td>
<td>30-37</td>
<td>55 ± 42</td>
<td>546 ± 12</td>
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<tr>
<td>426</td>
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<td>54.7</td>
<td>287-3341</td>
<td>24-44</td>
<td>22 ± 77</td>
<td>592 ± 25</td>
</tr>
</tbody>
</table>

*Units are T (K); P (Torr); [HBr] (1014 molecules cm⁻³); k, k2 (s⁻¹); k10 (10⁻¹⁵ cm³ molecule⁻¹ s⁻¹). *Expt is measurement of a single Br(2P5/2) temporal profile. *Errors represent precision only.

Figure 3. Typical Br(2P5/2) atom temporal profile observed in the studies of RS + HBr reactions (R = H₂SCH). Reaction: CH₃S + HBr. Experimental conditions: T = 330 K, P = 100 Torr, (CH₃SCH)j = 3.29 X 10¹³ molecules cm⁻³, [HBr] = 9.12 X 10¹¹ molecules cm⁻³, number of laser shots averaged = 5000. The solid line is obtained from a nonlinear least-squares analysis and gives the following best-fit parameters: k₁ = 2270 s⁻¹, k₂ = 15 s⁻¹, C₁ = 7470, C₂ = 396.

Figure 4. Typical plot of k₁ versus [HBr] observed in the studies of the RS + HBr reactions (R = H₂SCH). Reaction: CH₃S + HBr. T = 330 K, P = 100 Torr. The solid line is obtained from a linear least-squares analysis and gives the bimolecular rate coefficient shown in the figure. The open circle is the data point obtained from the temporal profile shown in Figure 3.

Figure 5. Arrhenius plots. Solid lines are obtained from least-squares analyses which yield the Arrhenius expressions given in the text.
The occurrence of reaction 2b seems unlikely since the C-H bond in CH₃SH is thought to be about 6 kcal mol⁻¹ stronger than the S-H bond.¹⁹ ²⁰ For the similar though considerably more exothermic reactions of CI and OH radicals with CH₃SH, abstraction of a methyl hydrogen is known to be a very minor reaction channel.²¹ ²² Since channel 2b is probably not significantly endothermic, the yield of CH₃SH from reaction 2 is probably smaller than the (very small) yields of CH₂S from the reactions of CI and OH with CH₃SH. Assuming the RS-Br bond strength to be 57 kcal mol⁻¹, i.e., intermediate between published estimates of the RS-CI²³ and RS-I²⁴ bond strengths, reactions 2c and 2d are highly endothermic. Using the CH₃S and SH heats of formation derived from our data (see below) to calculate the enthalpy change for reaction 2c leads to the conclusion that this reaction is endothermic by 4.6 kcal mol⁻¹ assuming an A factor of 1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for k₂, and an activation energy equal to the endothermicity suggests that reaction 2c could contribute no more than 1% to the measured k₂ at 431 K and much less at lower temperatures. Recent unpublished experiments in our laboratory have observed kinetic evidence for reversible adduct formation in the Br + CH₂S reaction at temperatures below 235 K. A T ≥ 273 K, the temperature range of interest for this study, our results suggest that the adduct lifetime is too short for its existence to be kinetically important.

As an experimental check on the above conclusions, experiments were carried out where Br(P3/2) kinetics were observed following 355-nm laser flash photolysis of Br₂/CH₃SH/HBr/H₂/N₂ mixtures. To avoid complications from a heterogeneous dark reaction between Br₂ and CH₃SH, it was necessary to inject Br₂ into the gas flow just upstream from the reaction zone. Long-wavelength photolysis was necessary in order to completely avoid production of CH₃S and H via photodissociation of CH₃SH. Following Br(P3/2) production by the laser flash, the following reactions occur:

\[ \text{Br}(P3/2) + \text{CH₃SH} \rightarrow X' + Y \]  \hspace{1cm} (2)

\[ X' + \text{Br₂} \rightarrow X\text{Br} + \text{Br}(P3/2) \]  \hspace{1cm} (11)

\[ X' + \text{HBr} \rightarrow \text{XH} + \text{Br}(P3/2) \]  \hspace{1cm} (12)

\[ \text{Br}(P1/2) + \text{H₂} \rightarrow \text{Br}(P3/2) + \text{H₂} \]  \hspace{1cm} (4)

Assuming that all reactions are first order or pseudo first order and that Br(P3/2) deactivation to Br(P1/2) is instantaneous on the time scale for the occurrence of reactions 2, 11, and 12, the rate equations for the above reaction scheme can be solved analytically:

\[ \frac{[\text{Br}(P3/2)]}{[\text{Br}(P3/2)]_0} = \frac{(Q + \lambda_1) \exp(\lambda_1 t) - (Q + \lambda_2) \exp(\lambda_2 t)}{(\lambda_1 - \lambda_2)^{-1}} \]  \hspace{1cm} (VII)

where

\[ \lambda_1 = 0.5[(a^2 - 4b)^{1/2} - a] \]  \hspace{1cm} (VIII)

\[ \lambda_2 = -0.5[(a^2 - 4b)^{1/2} + a] \]  \hspace{1cm} (IX)

\[ Q = k_1[\text{Br}_2] + k_{12}[\text{HBr}] + k_{13} \]  \hspace{1cm} (X)

\[ a = Q + k_1[\text{CH₃SH}] + k_{10} = (\lambda_1 + \lambda_2) \]  \hspace{1cm} (XI)

\[ b = k_4Q + k_{13}k_1[\text{CH₃SH}] = \lambda_1\lambda_2 \]  \hspace{1cm} (XII)

Values for k₁₂ were always found to be relatively small, ranging from 14 to 127 s⁻¹ for the 45 double-exponential decays which were analyzed. For a set of experiments where [HBr] is varied at constant (low) [Br₂], a plot of (Q - k₁₃) versus [HBr] should, according to eq X, be linear with slope = k₁₃ and intercept = k₁₁[Br₂]. With the exception of CH₃S, 298 K rate coefficients for reactions of all possible radicals X' with HBr are known and are significantly different from each other; in units of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ the rate coefficients of interest are 1.7 for X' = CH₃S (SH) (this work), 3.9 for X' = CH₃S (CH₃S), 30 for X' = CH₃S, and 65 for X' = H₂.²₅ Hence, determination of k₁₃ as described above should provide strong evidence concerning the identity of X'.

Typical Br(P3/2) temporal profile observed following 355-nm laser flash photolysis of Br₂/CH₃SH/HBr/H₂/N₂ mixtures is shown in Figure 6, while typical plots of (Q - k₁₃) versus [HBr] are shown in Figure 7. The data in Figure 7 suggest that k₁₃(298 K) = 4.6 × 10⁻¹₂ cm³ molecule⁻¹ s⁻¹; considering the nature of the fitting procedure, we estimate the uncertainty in k₁₃(298 K) to be ±30%. This determination of k₁₃(298 K) strongly supports the contention that the dominant reaction channel for the Br(P3/2) + CH₃SH reaction is production of CH₃S + HBr. The intercepts of the plots in Figure 7 indicate that the CH₃S + Br₂ reaction is very fast, i.e., k₄ = (1.7 ± 0.5) × 10⁻¹₀ cm³ molecule⁻¹ s⁻¹. To our knowledge there are no measurements of k₄ reported in the literature.

\[ \text{CH₃S} + \text{Br}_2 \rightarrow \text{CH₃SBr} + \text{Br}(P3/2) \]  \hspace{1cm} (14)

Values, very fast rate coefficients have recently been reported for the reactions of alkyl radicals²⁶ and SD radicals²⁷ with Br₂.
actions of HBr

Reactivity in these systems seems to correlate with properties that reflect the strength of long-range attractive forces, particularly those associated with stabilization of transition state vicinities separation. The highly polarizable nature of both CH₃S and Br₂, the low ionization potential of CH₃S (8.06 eV), and the large electron affinity of Br₂ (∼2.55 eV) are electronic properties which contribute to the very fast rate of reaction 14.

Potential Systematic Errors. As discussed briefly above, a number of potential systematic errors in our kinetic measurements can be ruled out based on the observed invariance of Br(2P₁/₂) kinetics from radical-radical side reactions, from radical–photolyte side reactions, from reactions involving radicals which are produced by photolytic dissociation (H and CH₃S from CH₃SH photolysis, for example) or from reactions involving stable products which build up in concentration with successive laser flashes. In situ measurements of stable reactant (i.e., H₂S, CH₃SH, HBr) concentrations greatly reduce another potential source of systematic error.

One type of kinetic interference which needs to be addressed is the potential contribution to measured rate coefficients from impurity reactions. The relatively unreactive nature of Br atoms makes it unlikely that impurity reactions were a problem in our studies of reactions 1 and 2. Gas chromatographic analyses of the H₂S and CH₃SH samples were carried out using a flame photometric detector and/or for sulfur-containing impurities; none were observed, lending further confidence that impurity reactions were not a problem. The most likely impurity problem in our studies of reactions 1 and 2 is from Br₂. Potential sources of Br₂ are impurity in the HBr sample, residual Br₂ (from Br₂ recombination) not swept out of the reaction zone between laser flashes, and catalytic formation of Br₂ from heterogeneous reactions of HBr (presumably on the metal surfaces of valves and fittings). As discussed above, reactions 14 and 15 are very fast (the 298 K rate coefficient for the SD + Br₂ reaction has recently been reported to be 9.8 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ [27]).

Since SH and CH₃S react with Br₂ several hundred times faster than with HBr, the HBr concentration must be several thousand times larger than the Br₂ concentration before Br₂-interference can be considered to be unimportant. To investigate the Br₂ interference problem, a 2-m absorption cell was positioned in the flow system downstream from the reaction cell and employed to monitor Br₂ photometrically (at 404.7 nm) with typical CH₂CO/H₂S/HBr/N₂ or CH₃SSCH₃/HBr/H₂/N₂ mixtures flowing through the system. No absorption was observed (i.e., I/I₀ > 0.998) even at HBr levels as high as 1 × 10⁻⁷ molecules cm⁻³. Since the Br₂ absorption cross section at 404.7 nm is 6 × 10⁻¹⁹ cm⁻², the experiments suggest that [Br₂] < 0.0002[HBr].

Another potential systematic error in our studies of reactions 1 and 2 concerns the possibility that SH and CH₃S are produced in vibrationally or electronically excited states and do not relax much more rapidly than they react. The spin–orbit splittings in SH and CH₃S are 377 cm⁻¹ to 257 cm⁻¹, respectively, i.e., only slightly larger than the average collision energy at 298 K (kT ∼ 0.02 cm⁻¹ at 298 K). Hence, extremely rapid equilibration of the SH and CH₃S spin orbit states via collisions with the nitrogen buffer gas can be safely assumed. It is known from infrared chemiluminescence experiments that much of the available exothermicity of the CI + H₂S reaction appears as vibrational excitation in the HCl product, but that the SH product is formed with little or no internal excitation. Furthermore, vibrational relaxation of SH by H₂S is expected to be a very efficient process due to the near resonance (Δυ ∼ 40 cm⁻¹) between the SH vibrational frequency²⁸ and the S–H stretch frequencies in H₂S.²⁹ Hence, it seems safe to conclude that SH was thermalized in our study of reaction 1. Black and Jusinski have studied the time dependence for populating the ground vibrational level of CH₃S following 248-nm pulsed laser photolysis of CH₃SSCH₃ in the presence of a number of inert collision partners.³⁰ They find that nearly all CH₃S is produced in excited vibrational levels, but that relaxation is very efficient. A phenomenological rate coefficient of 5.1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ was measured for populating the ground vibrational level (from the unknown initial vibrational state distribution) via collisions with N₂. Hence, under our experimental conditions (Table V), CH₃S relaxation times ranged from 0.02 to 0.2 µs while CH₃S reaction times ranged from 300 to 4000 µs.

As mentioned above, the SH + HBr experiments were carried out with no H₂ added to the reaction mixtures in order to avoid potential complications from the CI + H₂ reaction. This variation in experimental conditions does, however, introduce a different possible complication. As mentioned in the Experimental Section, the resonance fluorescence detection technique is sensitive to both bromine atom spin–orbit states, and the relative sensitivities for detecting the two states are different and difficult to quantify. If Br(2P₁/₂) was generated in significant quantity, and if its relaxation to Br(2P₁/₂) occurred on the same time scale as the SH + HBr reaction, then temporal profiles for appearance of the fluorescence signal would deviate systematically from the quantity we actually want to measure—the temporal profile for appearance of bromine atoms. Rate coefficients for deactivation of Br(2P₁/₂) by N₂ and HBr are, in units of cm³ molecule⁻¹ s⁻¹, 2.5 × 10⁻¹⁷ and ∼ 1 × 10⁻¹⁸,³¹,³² respectively. Hence for the N₂ and HBr levels employed (Table IV), any Br(2P₁/₂) generated via HBr photolysis, via reaction 7, or via reaction 2 was deactivated to Br(2P₁/₂) on a time scale which was faster by factors of 3–20 than the time scales for the occurrence of reaction 1. Although the rate coefficient for Br(2P₁/₂) deactivation by H₂S does not appear to

\[ \text{HS + Br}_2 \rightarrow \text{HSBr + Br}(2P_{1/2}) \]
TABLE VI: Kinetic Parameters, Enthalpy Changes, and IP - EA Values for a Series of Hydrogen Transfer Reactions \( R + XH \rightarrow RH + X \)

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>( A )</th>
<th>( E_{in} )</th>
<th>( k(298 \text{ K}) )</th>
<th>ref</th>
<th>(-\Delta H^{\text{m}})</th>
<th>IP(R) - EA(XH)</th>
<th>IP(XH) - EA(R)</th>
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<tr>
<td>Br</td>
<td>HS</td>
<td>140</td>
<td>5.5</td>
<td>0.013</td>
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<td>11.9</td>
<td>11.86</td>
<td>6.83</td>
</tr>
<tr>
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<td>0.1</td>
<td>11.69</td>
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<tr>
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<td>12.85</td>
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<td>13.5</td>
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<td>Cl</td>
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<tr>
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<tr>
<td>CH,S</td>
<td>Br</td>
<td>13</td>
<td>-1.1</td>
<td>83</td>
<td>24</td>
<td>13.7</td>
<td>7.9</td>
<td>10.7</td>
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<td>270</td>
<td>24</td>
<td>8.9</td>
<td>6.5</td>
<td>11.0</td>
</tr>
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</table>

* Units for \( A \) and \( k(298 \text{ K}) \) are \( 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and units for \( E_{in} \) are kcal mol\(^{-1}\). * Units are kcal mol\(^{-1}\); values are computed using heats of formation from this work (SH and CH,S), ref 24 (\( \text{CH}_3 \text{CH}_2 \text{H}, F-\text{C}_2 \text{H}_5 \)), ref 28 (i-C,H,SH), and ref 68 (all others). * Units are electronvolts; ionization potentials and electron affinities taken from ref 28. * \( TW^* \) = this work. * The unknown (but presumably very small) EA(XH) is assumed to be 0.2 eV.

be known, it appears likely (based for example on analogy with the known fast rate for \( \text{Br}^{(P_2)} \) deactivation by \( \text{H}_2\text{O} \)) that H,S levels of \( 1 \times 10^{-6} \) molecules cm\(^{-3}\) were sufficient to contribute significantly to the overall rate of \( \text{Br}^{(P_2)} \) deactivation.

Comparison of Reaction Rates for a Series of Radical + H,S, CH,S, HBr Reactions. To our knowledge, there are no previous kinetic studies of reactions 1, -1,2, or -2 with which to compare our results. However, kinetic data are available for many similar reactions. Kinetic parameters, reaction enthalpies, and relevant electronic properties for a series of hydrogen-transfer reactions involving free-radical attack on H,S, CH,S, and HBr are summarized in Table VI.

When one considers series of similar reactions such as those in Table VI, a correlation between the activation energy (in the exothermic direction) and the reaction exothermicity is often observed. Such correlations were clearly established by Evans and Polanyi in the 1930s and are heavily documented in the literature. Examination of Table VI, however, shows the correlation between activation energy and reaction exothermicity to be rather poor. Only the small subset of reactions Cl, OH, SH + HBr appear to follow such a trend.

As mentioned above when considering the very fast rate observed for the CH,S + Br\(_2\) reaction, it is often possible to correlate reactivity with properties that reflect the strength of long-range attractive forces, particularly those associated with stabilization of transition states via charge separation. For some classes of reactions, reactivity is found to be strongly correlated with the parameter IP - EA, the difference between the ionization potential of one reactant and the electron affinity of the other reactant. Bayes and co-workers have observed that low values of IP - EA correlate with enhanced reactivity in the alkyl + O\(_2\) reactions.\(^{39,40}\) Gutman and co-workers have observed a similar reactivity trend for the reactions of alkyl radicals with Cl\(_2\),\(^{41}\) Br\(_2\),\(^{42}\) H\(_2\), and HBr.\(^{43,44}\) Recent work in our laboratory has confirmed the reactivity trend in the alkyl + HBr series (Table VI). Anderson and co-workers have observed correlations between IP - EA and reactivity in reactions of OH and SD radicals with halogen molecules.\(^{45,46}\) and in the reactions of Br, Cl, F, O, and OH radicals with CNOS and with O\(_2\).\(^{47}\) The property IP - EA has been found to correlate with both activation energies \(^{28,47,48}\) and A factors.\(^{49}\) As discussed by Abbatt et al.,\(^{50}\) the barrier (i.e., activation energy) to reaction can be lowered through an interaction with low-lying ionic states. Presumably, the ionic character of the reaction potential energy surface in the region of the transition state is enhanced when IP - EA is relatively small; this ionic character presumably lowers the barrier by increasing the stability of charge separation at the transition state. The long-range electronic interaction which can occur when IP - EA is relatively low can result in formation of highly polar, loose transition states, an effect which leads to abnormally large A factors.

Examination of the kinetic parameters and IP - EA values in Table VI leaves little doubt that ionic interactions exert an important influence on reactivity in the reactions considered. The low ionization potential of CH,S and high electron affinity of Cl allow these reactants to interact via a charge-transfer mechanism at large separation, thus leading to a very large A factor and very fast reaction rate. Differences in reactivity of H,S and CH,S toward Cl and OH correlate very well with the value of IP(R) - EA(XH). For Br(\(P_2\)) reactions with H,S and CH,S, however, the above correlation would predict faster rate coefficients than are actually observed as a result of the high electron affinity of Br. The reactions of Cl and OH with H,S and CH,S, all of which are significantly exothemic, are barrierless processes. However, the thermoneutral Br(\(P_2\)) + CH,S reaction has an activation energy of 0.8 kcal mol\(^{-1}\) and the endothermic Br(\(P_2\)) + H,S reaction has an activation energy 1.9 kcal mol\(^{-1}\) larger than the endothermicity. It seems clear that Br(\(P_2\)) can form (very weakly bound) long-range polar complexes with H,S and CH,S. However, the unfavorable thermochemistry of the Br + RSH reactions apparently leads to significant barriers for H atom transfer within the complexes, such that complex dissociation back to reactants can compete effectively with the H-transfer reaction.

Observed A factors for the radical + HBr reactions in Table VI follow the well-established trend of decreasing with increasing complexity of the reactant radical (i.e., atomic vs 2-atomic vs polyatomic).\(^{49}\) As mentioned above, alkyl + HBr reactivity correlates well with the alkyl radical ionization potential, i.e., the lower the radical ionization potential, the faster the reaction, alkyl + HBr reactivity does not correlate with reaction exothermicity.
Errors are 2σ and represent best estimates of absolute accuracy.

On the other hand, for the Cl, OH, and SH reactions with HBr, a reasonable correlation of activation energy with reaction exothermicity is observed. These reactions apparently proceed through transition states which are not strongly influenced by ionic interactions. The thermoneutral CH₃S + HBr reaction appears to be an intermediate case. Unlike the alkyl + HBr reactions, the CH₃S + HBr reaction does have a positive activation energy. However, the barrier is much smaller than one would predict based on the ΔH° versus Eₚ trend observed for the Cl, OH, SH + HBr reactions. Apparently, the low ionization potential of CH₃S facilitates ionic interactions which reduce but do not eliminate the barrier.

SH and CH₃S Thermochernistry. From the Arrhenius parameters determined in this study we can obtain the enthalpy changes and entropy changes associated with reactions 1 and 2. One approach, the "second law method", employs the following relationships to obtain thermochemical parameters for reaction 1:

\[ ΔH = E_α - E_β \]
\[ ΔS = R \ln \left( \frac{A_α}{A_β} \right) \]

where \( A_α \) and \( E_α \) are the A factor and activation energy for reaction \( i \). Thermochemical parameters for reactions 1 and 2 obtained from the second law analyses are tabulated in Table VII. The temperature, 360 K for reaction 1 and 333 K for reaction 2, is defined as the arithmetic mean of the \( T' \) ranges employed in the temperature determinations. Absolute entropies as a function of temperature were obtained from the JANAF tables\(^{(50)}\).

The analysis presented above is based on the idea that reactions -1 and -2 are the reverse of reactions 1 and 2. In the case of reactions 1 and 2 we know that the reacting bromine atom was in the \( P(3/2) \) ground state because sufficient \( \mathrm{H}_2 \) was present in the reaction mixtures to instantaneously (on the time scale for Br reaction) deactivate any photolytically generated Br(\( P(3/2) \)). Hence, the reverse reactions we wish to determine the rates of are

\[ \mathrm{SH} + \mathrm{HBr} \rightarrow \mathrm{H}_2 \mathrm{S} + \mathrm{Br}(\mathrm{P}(1/2)) \]
\[ \mathrm{CH}_3 \mathrm{S} + \mathrm{HBr} \rightarrow \mathrm{CH}_3 \mathrm{SH} + \mathrm{Br}(\mathrm{P}(1/2)) \]

Clearly, if reactions -1 and/or -2 proceed exclusively or a significant fraction of the time via channels 1b and/or 2b, then we would be overestimating the rate of the true reverse reaction(s) and our reported enthalpy changes would be in error. Simple thermochemical arguments based on the measured activation energies for reactions 1 and 2 can be used to place reasonable upper limits on \( k_{τ1} \) and \( k_{τ2} \). Our measured activation energy for reaction 1 is 5.5 kcal mol\(^{-1} \). It is reasonable to assume that the activation energy for reaction -1a is greater than -1.0 kcal mol\(^{-1} \). Since the bromine atom spin-orbit splitting is 10.5 kcal mol\(^{-1} \), reaction 1b must be endothermic by at least 4.0 kcal mol\(^{-1} \). Taking \( 1 \times 10^{-11} \) cm\(^{-1} \) molecule\(^{-1} \) s\(^{-1} \) as an upper limit A factor for reaction -1b and 4.0 kcal mol\(^{-1} \) as a lower limit activation energy for reaction -1b leads to the result \( k_{τ1} \approx 299 \) K \( < 1.2 \times 10^4 \) molecule\(^{-1} \) cm\(^{-1} \) s\(^{-1} \) and \( k_{τ2} \approx 423 \) K \( < 8.6 \times 10^{10} \) molecule\(^{-1} \) cm\(^{-1} \) s\(^{-1} \), i.e., \( k_{τ1} \approx k_{τ2} \approx 1.6 \times 10^8 \) at 299 K and \( k_{τ1} \approx k_{τ2} \approx 0.19 \) at 423 K. We have repeated the second and third law analyses of the reaction data assuming that the above upper limits were the correct values for \( k_{τ1} \). Under this scenario, the second law ΔH values for reaction 1 which are given in Table VII would be increased by 0.29 kcal mol\(^{-1} \) while the third law ΔH values for reaction 1 would be decreased by 0.09 kcal mol\(^{-1} \). Our measured activation energy for reaction 2 is 0.8 kcal mol\(^{-1} \). If we assume as above that the activation energy for reaction -2a is greater than -1.0 kcal mol\(^{-1} \), then we are led to the conclusion that reaction -2b must be endothermic by at least 8.7 kcal mol\(^{-1} \). Taking \( 1 \times 10^{-11} \) cm\(^{-1} \) molecule\(^{-1} \) s\(^{-1} \) as an upper limit A factor for reaction -2b and 8.7 kcal mol\(^{-1} \) as a lower limit activation energy for reaction -2b leads to the result \( k_{τ3} \approx 273 \) K \( < 1.1 \times 10^{14} \) molecule\(^{-1} \) cm\(^{-1} \) s\(^{-1} \) and \( k_{τ4} \approx 426 \) K \( < 3.4 \times 10^{10} \) molecule\(^{-1} \) cm\(^{-1} \) s\(^{-1} \), i.e., \( k_{τ3} \approx k_{τ4} \approx 0.1 \times 10^9 \) at 273 K and \( k_{τ3} \approx k_{τ4} \approx 5.7 \times 10^4 \) at 426 K. Clearly, the contribution of channel 2b to our measured values for \( k_{τ4} \) must be negligible over the entire temperature range investigated.

The enthalpy changes for reactions 1 and 2 determined in this study can be combined with the accurately known heats of formation of Br, HBr, H₂S, and CH₃SH\(^{29,30} \) (Table VII) to obtain SH and CH₃S heats of formation. Values for ΔH°(RS) and

<table>
<thead>
<tr>
<th>reaction</th>
<th>( T, K )</th>
<th>( \Delta H^\circ, \text{kcal mol}^{-1} )</th>
<th>( \Delta S^\circ, \text{cal mol}^{-1} \text{deg}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>360</td>
<td>3.54 ± 0.32</td>
<td>3.96 ± 0.21</td>
</tr>
<tr>
<td>2</td>
<td>333</td>
<td>-0.03 ± 0.17</td>
<td>-0.17 ± 0.32</td>
</tr>
<tr>
<td>298</td>
<td>-0.08 ± 0.19</td>
<td>-0.20 ± 0.28</td>
<td>3.48 ± 1.09</td>
</tr>
<tr>
<td>0</td>
<td>-0.59 ± 0.27</td>
<td>-0.71 ± 0.36</td>
<td></td>
</tr>
</tbody>
</table>

\( \Delta H^\circ, \Delta S^\circ \) for reactions 1 and 2.
Table VIII: Gas-Phase Heats of Formation

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>$\Delta H_f^{298}$ (kJ/mol)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>51.634 ± 0.001</td>
<td>52.103 ± 0.001</td>
<td>50</td>
</tr>
<tr>
<td>HBr</td>
<td>28.184 ± 0.014</td>
<td>26.735 ± 0.014</td>
<td>50</td>
</tr>
<tr>
<td>HBr</td>
<td>-6.367 ± 0.060</td>
<td>-8.710 ± 0.040</td>
<td>19</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>35.62 ± 0.19</td>
<td>34.28 ± 0.19</td>
<td>50</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-2.50 ± 0.14</td>
<td>-3.47 ± 0.14</td>
<td>23</td>
</tr>
<tr>
<td>CH$_3$S</td>
<td>-5.09 ± 0.12</td>
<td>-4.96 ± 0.12</td>
<td>28</td>
</tr>
<tr>
<td>CH$_3$SSCH$_3$</td>
<td>-1.63 ± 0.24</td>
<td>-5.78 ± 0.24</td>
<td>28</td>
</tr>
<tr>
<td>SH</td>
<td>34.07 ± 0.72</td>
<td>34.18 ± 0.68</td>
<td>this work</td>
</tr>
<tr>
<td>S$_2$H</td>
<td>33.5 ± 1.2</td>
<td>33.1 ± 1.1</td>
<td>57</td>
</tr>
<tr>
<td>CH$_3$S</td>
<td>33.9 ± 1.5</td>
<td>33.9 ± 1.5</td>
<td>58</td>
</tr>
<tr>
<td>SH</td>
<td>31.44 ± 0.54</td>
<td>29.78 ± 0.44</td>
<td>this work</td>
</tr>
<tr>
<td>HBr</td>
<td>33.7 ± 2.1</td>
<td>32.4 ± 2.0</td>
<td>59</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>31.2 ± 2.0</td>
<td>30.5 ± 2.0</td>
<td>60</td>
</tr>
<tr>
<td>S$_2$H</td>
<td>29.3 ± 2.0</td>
<td>29.3 ± 2.0</td>
<td>61</td>
</tr>
<tr>
<td>SH</td>
<td>35.4 ± 1.5</td>
<td>35.5 ± 2</td>
<td>65</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>34.2 ± 1.5</td>
<td>34.2 ± 1.5</td>
<td>66</td>
</tr>
</tbody>
</table>

*Units are kcal mol$^{-1}$. These values are obtained by coupling the kinetic data of Colussi and Benson (ref 59) with different values (ranging from 44 to 49 kcal mol$^{-1}$) for the benzyl radical heat of formation. Critical review.

Table IX: Bond Strengths Derived Using the SH and CH$_3$S Heats of Formation Determined in This Study in Conjunction with Other Heats of Formation Given in Table VIII

<table>
<thead>
<tr>
<th>bond</th>
<th>$D_{0}$ (kcal/mol)</th>
<th>$D_{298}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-H</td>
<td>83.23 ± 0.78</td>
<td>84.12 ± 0.74</td>
</tr>
<tr>
<td>HS-H</td>
<td>89.91 ± 0.91</td>
<td>91.18 ± 0.87</td>
</tr>
<tr>
<td>H$_2$C-S</td>
<td>72.58 ± 1.05</td>
<td>74.47 ± 1.01</td>
</tr>
<tr>
<td>H$_2$C-S</td>
<td>69.84 ± 0.79</td>
<td>71.24 ± 0.69</td>
</tr>
<tr>
<td>H$_2$C-S</td>
<td>85.96 ± 0.68</td>
<td>87.35 ± 0.58</td>
</tr>
<tr>
<td>H$_2$C-S-SCH$_3$</td>
<td>72.15 ± 0.85</td>
<td>73.56 ± 0.75</td>
</tr>
<tr>
<td>H$_2$C-S-SCH$_3$</td>
<td>64.51 ± 1.32</td>
<td>65.34 ± 1.00</td>
</tr>
</tbody>
</table>

*Units are kcal mol$^{-1}$. *Computed using $\Delta H_f^{298}$(CH$_3$S) = 35.3 ± 0.5 kcal mol$^{-1}$ as reported in ref 24.

$\Delta H_f^{298}$(R,S) are given in Table VIII. Simple averages of the second and third law enthalpies of reaction have been employed to obtain our reported R,S heats of formation; this approach seems reasonable since (a) estimated uncertainties in the second and third law determination do not differ greatly and (b) the second and third law values for $\Delta H_f^c$(R,S) agree to within a few tenths of a kcal mol$^{-1}$ for both SH and CH$_3$S. The reported uncertainties in $\Delta H_f^c$(R,S) represent 2σ estimates of absolute accuracy, since the 2σ error estimates for the individual second and third law determinations are significantly larger than the deviation of the two determinations from their mean, we take the larger of the (second and third law) error estimates to be the error estimate for the mean. In the case of SH, we increase the uncertainty by an additional 0.1 kcal mol$^{-1}$ to account for the fact that reaction 1 could have a small but not negligible channel forming Br$_2$(PH$_3$) (see above). Our estimated uncertainties in $\Delta H_f^c$(R,S) of 0.44-0.72 kcal mol$^{-1}$ are substantially smaller than those reported previously (Table VIII). The SH or CH$_3$S heat of formation represents the least well-known parameter required for evaluation of a number of bond dissociation energies (BDEs); in Table IX we give values for these BDEs derived using our reported values for $\Delta H_f^c$(R,S) in conjunction with the other heats of formation given in Table VIII. For consistency, we employ the JANAF$^{50}$ value of 34.82 ± 0.19 kcal mol$^{-1}$ for $\Delta H_f^{298}$(CH$_3$) to derive H$_2$C-SH, H$_2$C-S, and H$_2$C-SCH$_3$ bond strengths. It should be pointed out, however, that combining our recent measurement of the CH$_3$ + HBr rate coefficient with the literature value for the Br + CH$_4$ rate coefficient leads to a value of 35.3 ± 0.5 kcal mol$^{-1}$ for $\Delta H_f^{298}$(CH$_3$)$_2$; bond strengths derived using this value for the methyl heat of formation are given in parentheses in Table IX.

Values for $\Delta H_f^c$(R,S) reported in this study are compared with literature values in Table VIII. The current JANAF$^5$ recommendations are based on measurements of the SH ionization potential$^{54,55}$ and the appearance potential of SH$^+$ from photodissociation of H$_2$S$^5$. Hwang and Benson have obtained a value for $\Delta H_f^{298}$(SH) based on a study of the I$_2$ + H$_2$S reaction at 555-595 K$^{3}$; derivation of $\Delta H_f^{298}$(SH) from their kinetic data required the assumption that the activation energy for the SH + HI reaction is 1 ± 1 kcal mol$^{-1}$. A value for $\Delta H_f^{298}$(SH) has recently been obtained by Nourbakhsh et al. based on time-of-flight measurements of CH$_3$H and SH photofragments from 193-nm photodissociation of CH$_3$SH in a supersonic molecular beam$^{58}$. Within combined uncertainties, the results reported in this study agree with all three literature values mentioned above. However, the error limits in the present study are somewhat smaller than those reported previously.

Values for $\Delta H_f^c$(CH$_3$S) reported in this study are compared with literature values in Table VIII. An early determination of $\Delta H_f^{298}$(CH$_3$S), reported by Colussi and Benson$^{35}$ involved studying the kinetics of benzylmethyl sulfide pyrolysis; their data analysis required knowledge of the benzyl radical heat of formation. A number of subsequent evaluations of $\Delta H_f^{298}$(CH$_3$S) have appeared in the literature$^{28,60,61}$ which involve reevaluation of Colussi and Benson's results based on different assumed values for $\Delta H_f^{298}$(benzyl); the recommendation of Lias et al.$^{62}$ which shows the best agreement with our results, is based on an assumed benzyl heat of formation of 49 kcal mol$^{-1}$ as recommended by Tang$^{63}$; Janousek et al.$^{64}$ have measured the electron affinity of CH$_3$S and combined their result with gas-phase acidity data for CH$_3$SH$^+$ to derive a value for $\Delta H_f^{298}$(CH$_3$S) which agrees quite well with our findings. Shum and Benson$^{65}$ have studied the kinetics of the I$_2$ + CH$_3$SH reaction over the temperature range 476-604 K and obtain a lower limit value for $\Delta H_f^{298}$(CH$_3$S) which is consistent with our findings. Hence, the value for $\Delta H_f^{298}$(CH$_3$S) which we obtain from kinetics studies of reactions 2 and -2 seems to be consistent with (but more precise than) most earlier work, although uncertainties in the heat of formation of benzyl radical$^{65,62}$ somewhat hinders the comparison. However, an interesting discrepancy exists between our results and the recent molecular beam photofragmentation studies of Nourbakhsh et al.$^{58,66}$ These authors have obtained three independent measurements of $\Delta H_f$ (CH$_3$S) based on time-of-flight measurements of photofragments from 193-nm photodissociation of CH$_3$SH$^{58}$, CH$_3$SSCH$_3$$^{66}$, and CH$_3$SCH$_3$; they reported values for $\Delta H_f$ (CH$_3$S) (with uncertainties of 1.5-2 kcal mol$^{-1}$) which are all 3-4
2528 kcal mol\(^{-1}\) higher than the value of 31.44 \(\pm\) 0.54 kcal mol\(^{-1}\) obtained in this study. The error in our determination of \(k_1/k_2\) needed to rationalize a 3–4 kcal mol\(^{-1}\) increase in \(\Delta H_{r0}(\text{CH}_3\text{S})\) is a factor of several hundred in the direction where \(k_1\) would have to be slower or \(k_2\) would have to be faster; errors of this magnitude seem unlikely.

Summary

Time-resolved resonance fluorescence detection of \(\text{Br}(^3\text{P}_3)\) disappearance following 266-nm laser flash photolysis of \(\text{CF}_2\text{Br}_2/\text{H}_{2}\text{S}/\text{H}_2/\text{N}_2\), \(\text{CF}_2\text{Br}_2/\text{CH}_3\text{SH}/\text{H}_2/\text{N}_2\), \(\text{Cl}_2\text{CO}/\text{H}_{2}\text{S}/\text{HBr}/\text{N}_2\), and \(\text{CH}_3\text{SSCH}_3/\text{HBr}/\text{H}_2/\text{N}_2\) mixtures has been employed to study the kinetics of reactions 1, 2, -1, and -2 as a function of temperature. In units of \(10^{-17}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), Arrhenius expressions which describe our results are \(k_1 = (14.2 \pm 3.4) \exp\left[-(2752 \pm 90)/T\right]\), \(k_2 = (4.40 \pm 0.92) \exp\left[-(971 \pm 73)/T\right]\), \(k_3 = (9.24 \pm 1.15) \exp\left[-(386 \pm 41)/T\right]\), and \(k_{-2} = (1.46 \pm 0.21) \exp\left[-(399 \pm 41)/T\right]\). By examining \(\text{Br}(^3\text{P}_3)\) equilibration kinetics following 355-nm laser flash photolysis of \(\text{Br}_2/\text{CH}_3\text{SH}/\text{H}_2/\text{N}_2\) mixtures, a 298 K rate coefficient of \((1.7 \pm 0.5) \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) has been obtained for the \(\text{CH}_3\text{S} + \text{Br}_2\) reaction. To our knowledge, these are the first kinetic data reported for each of the reactions studied. Comparison of \(A\) factors and activation energies for reactions 1, -1, 2, and -2 with known kinetic parameters for other radical + \(\text{H}_2\text{S}, \text{CH}_3\text{SH}, \text{HBr}\) hydrogen-transfer reactions suggests that both thermochemistry and electronic properties (i.e., IP - EA) exert important influences on observed reaction rates.

Second and third law analyses of the equilibrium data, i.e., \(k_1/k_1\), and \(k_3/k_{-2}\), have been employed to obtain the enthalpy changes associated with reactions 1 and 2. At 298 K, reaction 1 is endothermic by 3.64 kcal mol\(^{-1}\) while reaction 2 is exothermic by 0.14 kcal mol\(^{-1}\). Combining the experimentally determined enthalpies of reaction with the well-known heats of formation of \(\text{Br}, \text{HBr}, \text{H}_2\text{S}, \) and \(\text{CH}_3\text{SH}\) gives the following heats of formation for RS radicals in units of kcal mol\(^{-1}\): \(\Delta H_{r0}(\text{SH}) = 34.07 \pm 0.72\), \(\Delta H_{r0}(\text{CH}_3\text{S}) = 34.18 \pm 0.68\), \(\Delta H_{r0}(\text{CH}_3\text{S}) = 31.44 \pm 0.54\); \(\Delta H_{r0}(\text{CH}_3\text{S}) = 29.78 \pm 0.44\); errors are 2\(\sigma\) and represent estimates of absolute accuracy. The SH heat of formation determined from our data agrees well with literature values but has reduced error limits compared to other available values. The \(\text{CH}_3\text{S}\) heat of formation determined from our data is near the low end of the range of previous estimates and is 3–4 kcal mol\(^{-1}\) lower than values derived from recent molecular beam photodissociation studies.

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Laser flash photolysis studies of atmospheric free radical chemistry using optical diagnostic techniques


Physical Sciences Laboratory, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332

ABSTRACT

Some recent studies carried out in our laboratory are described where laser flash photolytic production of reactant free radicals has been combined with reactant and/or product detection using time-resolved optical techniques to investigate the kinetics and mechanisms of important atmospheric chemical reactions. Discussed are (1) a study of the radical-radical reaction \( \text{O} + \text{BrO} \rightarrow \text{Br} + \text{O}_2 \) where two photolysis lasers are employed to prepare the reaction mixture and where the reactants O and BrO are monitored simultaneously using atomic resonance fluorescence to detect O and multipass UV absorption to detect BrO; (2) a study of the reaction of atomic chlorine with dimethylsulfide (\( \text{CH}_3\text{SCH}_3 \)) where atomic resonance fluorescence detection of Cl is employed to elucidate the kinetics and tunable diode laser absorption spectroscopy is employed to investigate the HCl product yield; and (3) a study of the aqueous phase chemistry of \( \text{Cl}_2^- \) radicals where longpath UV absorption spectroscopy is employed to investigate the kinetics of the \( \text{Cl}_2^- + \text{H}_2\text{O} \) reaction.

1. INTRODUCTION

The combination of reactant radical production by laser flash photolysis (LFP) with reactant and product detection by time-resolved optical techniques (TROT) has proven to be a powerful method for investigating the kinetics and mechanisms of important atmospheric chemical reactions. While not without limitations, this approach offers several advantages over other commonly used techniques. First, studies can be carried out which employ both short reaction times and low radical concentrations, thus minimizing interferences from secondary reactions. Secondly, in gas phase studies a wide range of pressure, covering more than five orders of magnitude for some detection techniques (0.001 - 200 atmospheres), is experimentally accessible. Finally, and probably most importantly, the chemistry of interest occurs in complete isolation from reactor surfaces, so interferences from heterogeneous reactions can be completely avoided.

In this paper some recent LFP-TROT studies conducted in our laboratory are described. These include a study of the kinetics of the radical-radical reaction \( \text{O} + \text{BrO} \rightarrow \text{Br} + \text{O}_2 \), a kinetic and mechanistic study of the \( \text{Cl} + \text{CH}_3\text{SCH}_3 \) reaction, and a study of the potentially important cloudwater reaction of \( \text{Cl}_2^- \) radicals with \( \text{H}_2\text{O} \), where very sensitive detection of \( \text{Cl}_2^-\text{(aq)} \) by multipass UV absorption spectroscopy provides information not attainable using less sensitive detection techniques.

2. THE \( \text{O} + \text{BrO} \) REACTION

The radical-radical reaction of ground state atomic oxygen (\( \text{O} = \text{O}(^3\text{P}) \)) with bromine monoxide is the rate-determining step in a potentially important mid-stratospheric ozone destruction cycle:
The only value for the $\text{BrO} + \text{O}$ rate coefficient reported in the literature, $k_2(298 \text{ K}) = (2.5^{+2.5}_{-1.8}) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, is based on measurements of O atom consumption rates and Br atom production rates observed in a study which was actually designed to measure the O + Br$_2$ rate coefficient.$^1$

Traditionally, most studies of radical-radical reaction kinetics have employed flow tube techniques.$^2$ Advantages of the flow tube method which make it well-suited for studying radical-radical reactions include the following: (1) absolute concentrations of unstable chemical species can be readily determined via chemical titration; (2) unstable reactants can be generated in spatially separated regions, thus allowing improved control over potential chemical interferences; and (3) multiple detection axes can be readily employed. Our study of O + BrO kinetics attempts to preserve the advantages of the flash photolysis method (discussed in the introduction), while also incorporating some of the advantages of the flow tube method. The experimental approach is an improved version of one we have employed previously to study the kinetics of the O + HO$_2$$^{14}$ and O + ClO$^5$ reactions. Despite improvements in experimental sophistication, however, the O + BrO study has proven quite challenging due to difficulties in controlling interferences from unwanted side reactions.

To study O + BrO kinetics, a reaction mixture containing O$_3$, Br$_2$, and N$_2$ is subjected to 248 nm laser flash photolysis using a KrF excimer laser. Concentrations are $(5-30) \times 10^{14}$ O$_3$ per cm$^3$, $(3-20) \times 10^{12}$ Br$_2$ per cm$^3$, and 25-150 Torr N$_2$. The laser fluence is sufficient to produce O atoms in 5-10 fold excess over Br$_2$:

$$\text{O}_3 + h\nu(248 \text{ nm}) \rightarrow \text{O}(^3\Pi) + \text{O}_2(^1\Delta), \quad \Phi = 0.9$$

$$\text{O}(^3\Pi) + \text{O}_2(X^3\Sigma) \rightarrow \text{O}(^3\Pi) + \text{N}_2 \quad \Phi = 0.1$$

Ozone photolysis at 248 nm produces primarily electronically excited singlet products.$^6$ However, at the N$_2$ levels employed in the experiment, relaxation of O($^3\Pi$) to ground state O($^3\Pi$)(??O) atoms occurs on a sub-microsecond time scale.$^7$ Subsequent to O($^3\Pi$) relaxation, O atoms titrate Br$_2$ to BrO and the catalytic cycle defined by reactions (1) and (2) converts all remaining O atoms to O$_2$:

$$\text{O} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br}$$

$$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$$

$$\text{BrO} + \text{O} \rightarrow \text{Br} + 2\text{O}_2$$

The O + BrO reaction is sufficiently exothermic to generate atomic bromine in the excited spin-orbit electronic state Br($^2\Pi_{3/2}$). However, relaxation to the ground electronic state, Br($^2\Pi_{1/2}$), via collisions with N$_2$ is rapid compared to the time scale for bromine atom reaction.$^8$ The kinetics of reactions (1) and (5) are well established, having been investigated recently in our laboratory.$^8,10$ as well as elsewhere.$^{11}$

If the chemistry in the O$_3$/Br$_2$/N$_2$ photolysis system were completely described by reactions (1) - (5), then we could evaluate the O + BrO rate coefficient based on measurements of the O atom decay rate at long
times after the laser flash, i.e., when $[\text{Br}_2] \to 0$. However, there are complicating side reactions which must be considered:

$$\text{BrO} + \text{BrO} \rightarrow 2 \text{Br} + \text{O}_2, \quad \Phi = 0.84 \tag{6a}$$

$$\rightarrow \text{Br}_2 + \text{O}_2, \quad \Phi = 0.16 \tag{6b}$$

$$\text{O}_2(\Delta) + \text{O}_3 \rightarrow \text{O} + 2 \text{O}_2 \tag{7}$$

The kinetics of reactions (6a), (6b), and (7) are reasonably well-established.\textsuperscript{11} Reaction (6b) results in regeneration of some $\text{Br}_2$ on the time scale for $\text{O}$ decay. The relatively slow reaction (7) prevents complete decay of $\text{O}$ atoms. Instead, a near-steady-state situation is established at long time after the excimer laser flash where $\text{O}$ production via reaction (7) and $\text{O}$ loss via reactions (2) and (5) occur at similar rates; as a result, quantitative information about the $\text{O} + \text{BrO}$ rate coefficient is not easily obtained from the oxygen atom temporal profile. To circumvent the above complications, we employ a second photolysis laser. After the near-steady state oxygen atom concentration is established, 532 nm radiation (Nd:Yag laser, 2nd harmonic, 7 ns pulsewidth) is employed to photolyze a small fraction of the remaining $\text{O}_3$, thus perturbing the steady state $\text{O}$ atom concentration. Computer simulations show that relaxation of the $\text{O}$ atom concentration back to steady state is dominated by the $\text{O} + \text{BrO}$ reaction.

A schematic diagram of the apparatus for the $\text{O} + \text{BrO}$ kinetics study is shown in Figure 1. A "slow flow" configuration is employed such that the reaction mixture is essentially static on the time scale of the experiment (10-50 milliseconds) but is completely replaced during the 5-10 seconds between excimer laser flashes. The reaction cell is jacketed to allow control of temperature by flowing a cooled or heated fluid through the outer jacket (which is not shown in Figure 1). Ground state oxygen atoms are monitored by time-resolved atomic resonance fluorescence spectroscopy\textsuperscript{10} while $\text{BrO}$ radicals are monitored by time-resolved UV absorption spectroscopy at 338.3 nm, the peak of the strongest band in the $\text{BrO}$ A-X spectrum;\textsuperscript{12} details of our application of the long path absorption technique are given elsewhere.\textsuperscript{13,14} A dual channel signal averager simultaneously accumulates the $\text{O}_3$ fluorescence signal in the multichannel scaling mode (i.e., photon counting techniques are employed to process the fluorescence signal) and the $\text{BrO}$ absorption signal in the peak height analysis mode. A segmented aperture optical integrator is employed to make the excimer laser photolysis beam spatially uniform. Hence, the excimer laser photolysis flash produces a spatially uniform concentration of oxygen atoms. Several hundred flashes are typically averaged to obtain the desired $\text{O}$ and $\text{BrO}$ temporal profiles. The shot-to-shot stability of the excimer laser is about $\pm 10\%$. Because experimental conditions are such that $[\text{O}]_o > [\text{Br}_2]$, ten percent fluctuations in excimer laser fluence result in very small shot-to-shot variations in $[\text{BrO}]_o$.

Results from a typical experiment are summarized in Figures 2-4; the experimental conditions employed to obtain the results in Figures 2-4 are as follows: $T = 298\text{K}$; $P = 50 \text{Torr}$; $[\text{O}_3]_o = 7.68 \times 10^{14}$ per cm$^2$; $[\text{Br}_2]_o = 1.56 \times 10^{13}$ per cm$^2$; $[\text{O}]_o = 8.6 \times 10^{13}$ per cm$^2$; time delay between the excimer and Nd:Yag laser pulses = 0.025 seconds. Observed $\text{O}$ and $\text{BrO}$ temporal profiles are shown in Figure 2. At short times when $[\text{O}]$ is very high, the fluorescence signal is reduced due to radiation trapping effects; hence, the fluorescence signal is proportional to the $\text{O}$ atom concentration only after the signal has decayed significantly from its peak value. Computer simulations of the $\text{O}$, $\text{BrO}$, and $\text{Br}_2$ temporal profiles are shown in Figure 3. The simulations were obtained by numerical integration of the rate equations assuming that the chemistry governing the desired temporal profiles is described completely by reactions (1), (2), (5), (6), and (7), and using the best available kinetic data from the literature;\textsuperscript{11} since $[\text{BrO}]$ values are based (at least in part) on the simulations, an iterative procedure was required in order to allow the value of $k_t$ determined from our data to be used in the simulations. Comparison of simulated $\text{O}$ and $\text{BrO}$ temporal profiles with experiment shows qualitative but not quantitative agreement. The simulated $\text{O}$ decay to
steady state is somewhat faster than that observed experimentally, the simulated BrO appearance rate is a little slower than that observed experimentally, and the simulated BrO decay is a little faster than that observed experimentally. Typically, we find that the simulated BrO concentration at the time the Nd:Yag laser fires is about 10% lower than the concentration derived from the measured BrO absorbance using the best available literature value for the BrO absorption cross section at 338.3 nm\textsuperscript{12} to convert absorbance to concentration. The difference between observed and simulated O and BrO temporal profiles could indicate that the chemistry in the model is incomplete or that one or more rate coefficients for reactions (1), (2), (6), and/or (7) are inaccurate. Another possibility which may account for all observations is the production of electronically excited oxygen, O\(_2\) (A), as a product of the O + BrO reaction. The oxygen atom fluorescence data around the time that the 532 nm laser fires is shown in Figure 4. The solid "base line" is obtained from fitting the data in the -10 to -0.1 ms and 7 to 14 ms time intervals to a double exponential decay function. The relaxation of the O atom population generated by the 532 nm laser is found to be exponential; for the data shown in Figure 4, the relaxation time (\(\tau\)) is 950 microseconds. A plot of \(k' (\equiv \tau^{-1})\), the pseudo-first order rate of O atom relaxation back to steady state following the 532 nm laser pulse, versus [BrO] is shown in Figure 5; the BrO concentrations are those obtained from the computer simulations of system chemistry. Also shown in Figure 5 is the \(k'\) versus [BrO] data corrected for the contribution to the O decay from the O + Br\(_2\) reaction; in this case (which is typical of all pressures and temperatures examined) about 10% of the oxygen atom decay is attributable to the O + Br\(_2\) reaction. The slope of the corrected \(k'\) versus [BrO] plot gives a rate coefficient of 4.8 \(\times 10^{11}\) cm\(^2\)molecule\(^{-1}\)s\(^{-1}\) for the O + BrO reaction at 298 K in 50 Torr N\(_2\).

![Diagram](image)

**Fig. 1.** Apparatus for the O + BrO kinetics study.
Fig. 2. Typical O and BrO temporal profiles. T = 298 K, P = 50 Torr. 
\([O]_0, [O_3], \text{ and } [Br_2]_0\) in units of \(10^{13} \text{ cm}^{-3}\) = 76.8, 8.6, and 1.56, respectively.

Fig. 3. Computer simulation of temporal profiles. Experimental conditions same as Fig. 2, but no 532 nm laser pulse.

Fig. 4. O atom temporal profile around the time that the 532 nm laser fires; same data as in Fig. 2 but with scales expanded.

Fig. 5. Plots of \(k'\) versus \([\text{BrO}]\). 
\(T = 298 \text{ K}, P = 50 \text{ Torr. Open circles are corrected for the O + Br}_2\) contribution.
We have investigated the kinetics of the O + BrO reaction at 298 K over the pressure range 25 - 150 Torr and at 50 Torr pressure over the temperature range 233 - 328 K. We find that $k_5(298 \text{ K}) = (4.4 \pm 0.6) \times 10^{11} \text{ cm}^3\text{molecule}^{-1}\text{ s}^{-1}$ and that $k_5(T) = (2.4 \pm 0.4) \times 10^{11} \exp\left[\frac{(190 \pm 100)}{T}\right] \text{ cm}^3\text{molecule}^{-1}\text{ s}^{-1}$, i.e., $k_5$ increases slightly with decreasing temperature; "negative activation energies" are often observed for radical-radical reactions because the potential energy surface typically contains a minimum corresponding to a bound intermediate complex (BrOO in the case of reaction (5)).

At this time the O + BrO kinetic results reported above must be considered preliminary. In particular, the potential importance of $O_2('\Delta)$ or $O_2('\Sigma)$ production from reaction (5) needs to be addressed. As mentioned above, a high yield of $O_2('\Delta)$ from reaction (5) could account for important differences between observed and simulated O and BrO temporal profiles; however, $O_2('\Delta)$ production could have only a small effect on the simulated BrO concentration at the time the 532 nm laser fires and, therefore, would not significantly alter reported values for $k_5$. Production of $O_2('\Sigma)$ as a product of the O + BrO reaction is potentially a more serious problem because the $O_2('\Sigma) + O_3$ reaction is several orders of magnitude faster than the $O_2('\Delta) + O_3$ reaction. (15)

$$O_2('\Sigma) + O_3 \rightarrow O + 2 O_2$$

(8)

Hence, any O atoms which reacted with BrO to form $O_2('\Delta)$ would immediately be regenerated via reaction (8). Since efficient $O_2('\Sigma)$ quenchers which are also chemically inert in the $O_2/Br_2/N_2$ photolysis system do not seem to be available, direct evidence for $O_2('\Sigma)$ production will require observation of its infrared emission in an experimental system where $O_2$ is not present. Adiabatic correlation arguments as well as statistical arguments (i.e., arguments based on the assumption that all sets of energetically accessible product quantum states are equally probable) suggest that the $O_2('\Sigma)$ yield from reaction (5) should be very small; however, experimental confirmation that this is the case would be highly desirable. Our results indicate that the O + BrO reaction is considerably faster than previously thought, even though we are observing only those reaction channels which produce $O_2$ in the $X^\Sigma$ or $1\Delta$ states.

3. KINETIC AND MECHANISTIC STUDY OF THE CI + CH$_3$SCH$_3$ REACTION

It has recently been suggested that significant chlorine concentrations may be present in the marine boundary layer, possibly as a result of ClNO$_2$ or Cl$_2$ generation via reactions on surfaces of marine aerosol particles. A recent competitive kinetics study of reaction (9) at 298 K in one atmosphere of air suggests that this reaction is extraordinarily fast, i.e., $k_9(298 \text{ K}) = 3.2 \times 10^{16} \text{ cm}^3\text{molecule}^{-1}\text{ s}^{-1}$.

$$Cl + CH_3SCH_3 \rightarrow \text{products}$$

(9)

Combining the above result with the findings of our study of the kinetics and mechanism of the OH + CH$_3$SCH$_3$ (DMS, dimethylsulfide) reaction suggests that $k_9/k_{10} \sim 50$ at 298 K and one atmosphere of air.

$$OH + CH_3SCH_3 \rightarrow \text{products}$$

(10)

DMS is the dominant reduced sulfur species in the marine boundary layer and its primary removal mechanism from the atmosphere is thought to be reaction with OH. Hence, if Cl concentrations in the marine boundary layer are as large as $10^4$ atoms per cm$^3$, and if reaction (9) is as fast as the available kinetic data suggest, then the Cl + DMS reaction could be very important in marine atmospheric chemistry.

The above considerations have led us to carry out a detailed study of the kinetics and mechanism of the Cl + DMS reaction. Laser flash photolysis of Cl$_2$CO (phosgene) at 266 nm was combined with time-
resolved atomic resonance fluorescence detection of chlorine atoms to measure values for $k_9$ as a function of temperature and pressure. A complete description of the experimental approach can be found in a recent publication describing our study of the complex Cl + CS$_2$ reaction. All experiments were carried out under pseudo-first order conditions with DMS in large excess over chlorine atoms. Observed chlorine atom decays were exponential and increased linearly as a function of [DMS], as would be expected if chlorine atom removal is dominated by reaction with DMS. The bimolecular rate coefficients of interest, $k_9(P,T)$, are obtained from the slopes of plots of $k'$, the pseudo-first order decay rate, versus DMS concentration; measured rate coefficients at 239 K, 297 K, and 421 K are plotted as a function of pressure in Figure 6. Our results confirm that reaction (9) occurs on virtually every Cl-DMS encounter. The reaction rate is found to increase with decreasing temperature as would be expected for a very fast reaction whose rate is determined by the magnitude of long range attractive forces between the reactants. The surprising aspect of the data in Figure 6 is our observation of a clear pressure dependence for $k_9$, at least at temperatures of 297 K and below. Reaction (9) appears to occur via both pressure-independent and pressure-dependent pathways; the pressure-dependent pathway must involve collisional stabilization of a (CH$_3$)$_2$S-Cl adduct.

![Graph showing rate constants for the Cl + DMS reaction as a function of temperature and pressure.](image)

**Fig. 6.** Rate constants for the Cl + DMS reaction as a function of temperature and pressure.
To gain further insight into the mechanism for reaction (9), we have carried out additional experiments where laser flash photolytic production of Cl (via 248 nm photolysis of phosgene) has been coupled with tunable diode laser absorption spectroscopy (TDLAS) to measure the HCl product yield at 297 K as a function of pressure. A schematic of the LFP-TDLAS apparatus is shown in Figure 7. The excimer laser photolysis beam and the diode laser probe beam traverse the one-meter-long reaction cell coaxially; the beams are combined and separated using dichroic optics. The experiments are carried out under slow flow conditions as described above for the O + BrO study. An absorption cell is positioned in the flow system upstream from the reaction cell to allow UV photometric monitoring of the Cl₂CO concentration. Other important components of the apparatus are a He/Ne alignment laser, a liquid helium closed cycle refrigerator which cools the diode laser housing, electronics for controlling the diode laser frequency via temperature or current tuning, an infrared monochromator for diode laser mode isolation, and infrared detectors with associated electronics for monitoring the transmitted intensities of the probe and reference beams. To obtain the HCl yield we carry out back-to-back experiments where the photolytically produced Cl reacts with DMS, then with ethane (C₂H₆); the yield of HCl from the Cl + C₂H₆ reaction is known to be unity. About 1 Torr of CO₂ is added to the reaction mixture to facilitate rapid relaxation of any Cl₂ which is formed in the v = 1 level. Typical data, obtained in 10 Torr N₂ buffer gas, are shown in Figure 8. It is clear from the data in Figure 8 that HCl is a major product of reaction (9). However, it is also clear that the HCl yield is less than unity. A plot of the HCl yield as a function of pressure is shown in Figure 9. The HCl yield approaches unity as P → 0, but decreases with increasing pressure.

![Fig. 7. Apparatus for LFP-TDLAS measurements of the HCl yield from the Cl + DMS reaction.](image)
Fig. 8. Typical HCl yield data. 
P = 10 Torr, T = 298 K. Ethane and DMS concentrations in units of $10^{14}$ cm$^3$ are 1.5 and 1.1, respectively. The diode laser is swept back and forth through an HCl absorption feature, thus obtaining a concentration measurement every 50 $\mu$s.

Fig. 9. Pressure dependence of the HCl yield from the Cl + DMS reaction.
Possible reaction channels for the Cl + DMS reaction include the following:

\[ \text{Cl} + \text{CH}_3\text{SCH}_3 \rightarrow [\text{CH}_3\text{S(Cl)}\text{CH}_3]^* \rightarrow \text{CH}_3\text{SCH}_2 + \text{HCl} \]  
(11a)

\[ \rightarrow \text{CH}_3\text{SCI} + \text{CH}_3 \]  
(11b)

\[ \rightarrow \text{CH}_3\text{S} + \text{CH}_3\text{Cl} \]  
(11c)

\[ \rightarrow \text{CH}_3\text{S(Cl)}\text{CH}_3 \]  
(11d)

Comparison of the kinetic data and the HCl yield data strongly suggests that reaction (11a) is the dominant channel in the low pressure limit, but that reaction (11d) becomes competitive at higher pressures. Whether the adduct formed via reaction (11d) is stable on the time scale of our experiment, or decomposes to products other than HCl or Cl, remains to be determined.

4. LABORATORY STUDIES OF FREE RADICAL CHEMISTRY IN CLOUD WATER

Free radical reactions occurring in cloud water play a role in the generation of acid precipitation and may affect gas phase concentrations of key species such as \( \text{O}_3, \text{HO}_2 \), and \( \text{NO}_x \) in the remote troposphere. In recent years we have developed a laser flash photolysis - long path absorption (LFP-LPA) technique for studying the kinetics of aqueous phase free radical reactions, and applied the technique to studies of potential importance in cloud chemistry. The improved sensitivity afforded by the LPA detection technique has allowed us to carry out kinetics studies employing much lower radical concentrations than have typically been employed in pulse radiolysis and/or flash photolysis studies; examples of results which could only be obtained because of this improved detection sensitivity include (1) our measurement of the rate coefficient for the slow \( \text{SO}_4^- + \text{H}_2\text{O} \) reaction and (2) our demonstration that previous measurements of the \( \text{SO}_4^- + \text{HSO}_3^- \) rate coefficient had not (as had been suggested in the literature) been affected by secondary reactions which regenerate \( \text{SO}_4^- \).

In order to further improve the ultimate detection limit of our LFP-LPA apparatus, we have recently constructed a new reactor which is considerably longer than the reactor we employed in earlier studies. A cylindrical lens is employed to expand the excimer laser photolysis beam in the horizontal direction, thus allowing a 10 cm wide region of the reaction cell to be photolyzed. We typically employ 34 passes of the probe light through the reactor, giving an absorption pathlength of ~340 cm.

Chlorine radical chemistry initiated by, for example, pulse radiolysis of \( \text{N}_2\text{O} \)-saturated chloride solutions, is quite complex; the following three rapid equilibria are thought to be involved:

\[ \text{OH} + \text{Cl}^- \leftrightarrow \text{HOCl}^- \]  
(12,-12)

\[ \text{HOCl}^- + \text{H}^+ \leftrightarrow \text{Cl} + \text{H}_2\text{O} \]  
(13,-13)

\[ \text{Cl} + \text{Cl}^- \leftrightarrow \text{Cl}_2^- \]  
(14,-14)

At relatively high [\( \text{Cl}^- \)] and [\( \text{H}^+ \)], the radical pool in the above equilibria exist almost entirely as \( \text{Cl}_2^- \), a species which absorbs strongly in the near UV (\( \epsilon_{\text{abs}} = 8800 \text{ M}^{-1}\text{cm}^{-1}, \lambda_{\text{abs}} = 340 \text{ nm} \)); both \( \text{HOCl}^- \) and Cl also absorb in the near UV, but not as strongly as \( \text{Cl}_2^- \). A convenient method for generating chlorine radicals by flash photolysis is as follows:
\[
\begin{align*}
S_2O_8^{2-} + hv & \rightarrow 2 SO_4^- \quad (15) \\
SO_4^- + Cl^- & \rightarrow Cl + SO_4^{2-} \quad (16)
\end{align*}
\]

\(S_2O_8^{2-}\) can be photolyzed efficiently at the excimer laser wavelength 248 nm, and does not react at an appreciable rate with \(SO_4^-\), OH, Cl, \(Cl_2^-\), or \(HOCl^-\). Reaction (16), which happens to be the dominant sink for chloride in cloud water,\(^{24}\) is reasonably fast with \(k_{16}(298\ K) \approx 2.6 \times 10^4\ M^{-1}s^{-1}\) in the limit of zero ionic strength.\(^{24,25}\)

In a recent study of chlorine radical chemistry initiated by reaction (16) McElroy\(^{26}\) concludes that the \(Cl_2^- + H_2O\) reaction proceeds at a rate of \(1300\ s^{-1}\), a result which, if correct, has important implications for chlorine radical chemistry in cloud water.

\[
Cl_2^- + H_2O \rightarrow \text{products} \quad (17)
\]

We have tried to observe a first order decay of \(Cl_2^-\) under conditions of high \(Cl^-\) (0.1 M) and low pH (1.1). These experiments were carried out using extremely low \(Cl_2^-\) concentrations (in the nanomolar range) to minimize contributions from the \(Cl_2^-\) self reaction; the \([S_2O_8^{2-}]\) and \([SO_4^-]\) employed in our study are about three orders of magnitude lower than employed by McElroy.\(^{26}\) Typical data are shown in Figure 10. At very low radical concentrations, we observe decay rates slower than \(10\ s^{-1}\) which decrease with decreasing laser power at constant \([S_2O_8^{2-}]\); these observations suggest that even the very slow decays we observe are not due to reaction (17), but instead were due to a radical-radical reaction. It is possible (or even likely) that if reaction (17) occurs, the product is a radical species which would rapidly react to regenerate \(Cl_2^-\), i.e., OH, Cl, or \(HOCl^-\). Experiments are currently in progress to examine this possibility.

![Fig. 10. \(Cl_2^-\) temporal profiles observed following 248 nm laser flash photolysis of \(10^{-3}\ M \ S_2O_8^{2-}/0.1\ M\ Cl^-/0.08\ M\ H^+\). Higher laser power was employed to obtain (a). Best fit first order decay rates are (a) \(15.8\ s^{-1}\) and (b) \(7.3\ s^{-1}\).]
5. ACKNOWLEDGMENTS

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6. REFERENCES


Isotope Effects in Gas-Phase Chemistry

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Chapter 7

Deuterium Substitution Used as a Tool for Investigating Mechanisms of Gas-Phase Free-Radical Reactions

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Results are presented and discussed for a number of gas phase free radical reactions where H/D isotope effects provide valuable mechanistic insights. The cases considered are (1) the reactions of OH, NOx, and CI with atmospheric reduced sulfur compounds, (2) the reactions of OH and OD with CH3CN and CD3CN, and (3) the reactions of alkyl radicals with HBr and DBr.

A major focus of modern chemical kinetics research is on understanding complex chemical systems of practical importance such as the atmosphere and fossil fuel combustion. In these applications, accurate information on reaction mechanisms (i.e., product identities and yields) as well as reaction rate coefficients is often critically important. Since detailed experimental kinetic and mechanistic information for every reaction of importance in a complex chemical system is often an unrealizable goal, it is highly desirable to develop a firm theoretical understanding of well studied reactions which can be extrapolated to prediction of unknown rate coefficients and product yields.

In recent years it has become apparent that many reactions of importance in atmospheric and combustion chemistry occur via complex mechanisms involving potential energy minima (i.e., weakly bound intermediates) along the reaction coordinate. The OH + CO reaction is one of the best characterized examples (1). While theoretical descriptions can sometimes be employed to rationalize experimental observations (1-3), a theoretical framework does not yet exist for predicting complex behavior. In this paper we discuss some experimental studies carried out in our laboratory over the last several years which were aimed at characterizing the kinetics and mechanisms of a number of complex chemical reactions of practical interest. Mechanistic details were deduced in part from studies of the
effects of temperature, pressure, and \([O_2]\) on reaction kinetics and from direct observation of reaction products. However, studies of \(H/D\) isotope effects were also employed as a tool for deducing reaction mechanisms; information obtained from the isotope effect studies is highlighted in the discussion.

The chemical processes we have chosen for discussion are (1) the reactions of \(OH\), \(NO_3\), and \(Cl\) with atmospheric reduced sulfur compounds (2) the reactions of \(OH\) and \(OD\) with \(CH_3CN\) and \(CD_3CN\), and (3) the reactions of alkyl radicals with \(HBr\) and \(DBr\). The experimental methodology employed to investigate the above reactions involved coupling generation of reactant radicals by laser flash photolysis with time resolved detection of reactants and products by pulsed laser induced fluorescence (\(OH\) and \(OD\)), atomic resonance fluorescence (\(Cl\) and \(Br\)), and long path tunable dye laser absorption (\(NO_3\)).

The Reactions of \(OH\), \(NO_3\), and \(Cl\) with Atmospheric Reduced Sulfur Compounds

Dimethylsulfide (\(CH_3SCH_3\), DMS) emissions into the atmosphere from the oceans are thought to account for a significant fraction of the global sulfur budget \((4)\). It has been suggested that DMS oxidation in the marine atmosphere is an important pathway for production of cloud condensation nuclei and, therefore, that atmospheric DMS can play a major role in controlling the earth’s radiation balance and climate \((5)\). Hence, there currently exists a great deal of interest in understanding the detailed mechanism for oxidation of atmospheric DMS.

It is generally accepted that the \(OH\) radical is an important initiator of DMS oxidation in the marine atmosphere \((4)\). Several years ago, we carried out a detailed study of the kinetics and mechanism of the \(OH + DMS\) reaction \((6)\). We found that \(OH\) reacts with DMS via two distinct pathways, one of which is only operative in the presence of \(O_2\) and one of which is operative in the absence or presence of \(O_2\) (see Figure 1). The rate of the \(O_2\)-dependent pathway increases with increasing \([O_2]\), increases dramatically with decreasing temperature, and shows no kinetic isotope effect, i.e., \(CH_3SCH_3\) and \(CD_3SCD_3\) react at the same rate. These observations indicate that the \(O_2\)-dependent pathway involves formation of a weakly bound adduct which reacts with \(O_2\) in competition with decomposition back to reactants.

\[
\begin{align*}
OH + CH_3SCH_3 + M &\rightarrow (CH_3)SOH + M \quad (1-1) \\
(CH_3)SOH + O_2 &\rightarrow \text{products} \quad (2)
\end{align*}
\]

The absence of a kinetic isotope effect strongly suggests that none of the three elementary steps in the above mechanism involve breaking a C-H bond.
Figure 1. Arrhenius plots for the OH + CD₃SCD₃ reaction in 700 Torr N₂, air, and O₂. \( k_{\text{obs}} \) is the slope of a plot of the pseudo-first order OH decay rate versus the CD₃SCD₃ concentration under conditions where the adduct (CD₃)₂SOH is removed much more rapidly than it is formed. (Reproduced from reference 62. Copyright 1987 American Chemical Society.)
The O$_2$-independent channel for the OH + DMS reaction proceeds with a 298K rate coefficient of $4.4 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$; in one atmosphere of air, the O$_2$-independent channel is dominant at $T > 285$K while the O$_2$-dependent channel dominates at lower temperatures (6). We find that the rate of the O$_2$-independent channel is pressure independent but increases slightly with increasing temperature (small positive activation energy). Furthermore, the O$_2$-independent channel displays a significant kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} = 2.3$ at 298K. Based upon the observed positive activation energy and significant isotope effect, we have postulated (6) that the O$_2$-independent pathway is a direct hydrogen abstraction reaction, i.e., there is no potential energy minimum (corresponding to an OH-DMS adduct) on the potential energy surface connecting reactants with products.

$$\text{OH} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{H}_2\text{O}. \quad (3)$$

Interestingly, Domine et al. (7) have recently observed production of C$_2$H$_5$ + CH$_3$OH from the reaction of OH with C$_2$H$_5$SCH$_3$ at low pressure and in the absence of O$_2$, although the branching ratio for production of C$_2$H$_5$ + CH$_3$SOH remains rather uncertain. By analogy, Domine et al.'s results suggest that the O$_2$-independent pathway in OH + DMS may involve cleavage of the relatively weak C-S bond rather than the C-H bond.

$$\text{OH} + \text{CH}_3\text{SCH}_3 \rightarrow [(\text{CH}_3)_2\text{SOH}] \rightarrow \text{CH}_3 + \text{CH}_3\text{SOH} \quad (4)$$

If the O$_2$-independent pathway for OH + DMS is reaction 4 rather than reaction 3, then the H/D isotope effect we have observed (6) would, to our knowledge, be the largest secondary isotope effect known for a gas phase reaction. Clearly, direct determination of the product yields from the O$_2$-independent channel of the OH + DMS reaction could have a major impact not only on our understanding of atmospheric sulfur oxidation, but also on our understanding of chemical reactivity in general and kinetic isotope effects in particular.

In coastal marine environments where NO$_x$ levels are relatively high, it is generally believed that NO$_x$ can compete with OH as an initiator of DMS oxidation (4). The 298K rate coefficient for the NO$_x$ + DMS reaction is known to be about $1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (8-13) and a significant negative activation energy has been reported (12). The reaction of NO$_x$ with DMS could proceed via direct H or O atom transfer or via formation of long-lived adduct.

$$\text{NO}_x + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HNO}_3 \quad (5)$$
$$\text{NO}_x + \text{CH}_3\text{SCH}_3 \rightarrow (\text{CH}_3)_2\text{SO} + \text{NO}_2 \quad (6)$$
$$\text{NO}_x + \text{CH}_3\text{SCH}_3 + \text{M} \rightarrow (\text{CH}_3)_2\text{SONO}_4 + \text{M} \quad (7,7)$$
Attempts to detect NO$_2$ as a reaction product have been unsuccessful (9,12) suggesting that O atom transfer via either a direct mechanism or via adduct decomposition is unimportant. As pointed out by Atkinson et al. (8), the NO$_3$ + DMS reaction is several orders of magnitude faster than the known rates of H-abstraction of, for example, relatively weakly bound aldehydic hydrogens by NO$_3$; this fact, coupled with the observed negative activation energy (12), strongly suggests that the NO$_3$ + DMS reaction does not proceed via a direct H-abstraction pathway. By the process of elimination, it is generally accepted that the initial step in the NO$_3$ + DMS reaction is adduct formation, i.e., reaction (7).

In a recent study of the kinetics of NO$_3$ reactions with organic sulfides (13), we observed a large kinetic isotope effect for the NO$_3$ + DMS reaction; at 298K NO$_3$ reacts with CH$_3$SCH$_3$ a factor of 3.8 more rapidly than with CD$_3$SCD$_3$. The observed isotope effect, coupled with the observation that at 298K C$_2$H$_5$SC$_2$H$_5$ reacts with NO$_3$ a factor of 3.7 more rapidly than does CH$_3$SCH$_3$, clearly demonstrates that the adduct decomposes via a process which involves C-H bond cleavage. A very recent chamber study by Jensen et al. (14) confirms the magnitude of our reported isotope effect and reports quantitative observation of HNO$_3$ as a reaction product.

\[
(CH_3)_2SONO_2 + M \rightarrow CH_3SCH_3 + HNO_3 + M \quad (8)
\]

As we discuss elsewhere (13), the postulate that the NO$_3$ + DMS reaction proceeds via reactions 7, -7, and 8 appears to be consistent with all available product data.

It is interesting to compare and contrast kinetic and mechanistic findings for the NO$_3$ + DMS reaction, with those for the reaction of OH with CH$_3$SH. Like NO$_3$ + DMS, the OH + CH$_3$SH reaction becomes faster with decreasing temperature (15-18), suggesting that the initial step in the mechanism is adduct formation.

\[
OH + CH_3SH + M \rightarrow CH_3S(OH)H + M \quad (9)
\]

Also, as appears to be the case for NO$_3$ + DMS, the OH + CH$_3$SH reaction is known to give H-abstraction products with unit yield (19).

\[
CH_3S(OH)H + M \rightarrow CH_3S + H_2O \quad (10)
\]

Hence, there are important similarities between the NO$_3$ + DMS and OH + CH$_3$SH reactions. However, there are also important differences. First, at 298K the OH + CH$_3$SH reaction is about 30 times faster than the NO$_3$ + DMS reaction. Secondly, while NO$_3$ + DMS displays a large H/D kinetic isotope effect (see above), isotope effects in OH reactions with CH$_3$SH, CD$_3$SH, and CH$_3$SD are minimal (17,18). These reactivity differences can be rationalized by postulating that decomposition of (CH$_3$)$_2$SONO$_2$ to products competes relatively unfavorably with decomposition back to
reactants (i.e. \( k_7 > > k_4 \)), whereas decomposition of \( \text{CH}_3\text{S(OH)}\text{H} \) to products is much faster than decomposition back to reactants (i.e. \( k_8 << k_10 \)). Hence, the rate of the adduct → product step, which should be sensitive to isotopic substitution, strongly influences the overall rate of the \( \text{NO}_3 + \text{DMS} \) reaction but does not influence the overall rate of the \( \text{OH} + \text{CH}_3\text{SH} \) reaction.

Recently in our laboratory we have investigated the kinetics of chlorine atom reactions with \( \text{CH}_3\text{SH}, \text{CD}_3\text{S}D, \text{H}_2\text{S}, \text{and} \text{D}_3\text{S} \) (20) as a function of temperature. There have been no previous reports of the temperature dependence of the \( \text{Cl} + \text{CH}_3\text{SH} \) rate coefficient and no previous kinetics studies of \( \text{Cl} \) reactions with \( \text{CD}_3\text{SD} \) or \( \text{D}_3\text{S} \). Nesbitt and Leone (21,22) have shown that, at 298K, the \( \text{Cl} + \text{CH}_3\text{SH} \) reaction occurs at a gas kinetic rate (\( k = 1.84 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \)) and that \( \frac{k_{11}}{k_{12}} = 45 \).

\[
\text{Cl} + \text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{S} + \text{HCl} \quad (11)
\]

\[
\text{Cl} + \text{CH}_3\text{SH} \rightarrow \text{CH}_2\text{SH} + \text{HCl} \quad (12)
\]

Several kinetics studies of the \( \text{Cl} + \text{H}_2\text{S} \) reaction have been reported (21,23-27) with published 298K rate coefficients spanning the range (4.0 - 10.5) \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}. Two temperature dependence studies (26,27) both conclude that the \( \text{Cl} + \text{H}_2\text{S} \) rate coefficient is temperature independent. Internal state distributions in the \( \text{HCl} \) product of \( \text{Cl} + \text{H}_2\text{S} \) and \( \text{Cl} + \text{CH}_3\text{SH} \) (28,29) and the \( \text{SH} \) product of \( \text{Cl} + \text{H}_2\text{S} \) (29) have also been reported.

Arrhenius plots for reactions of \( \text{Cl} \) with \( \text{H}_2\text{S}, \text{D}_2\text{S}, \text{CH}_3\text{SH}, \text{and} \text{CD}_3\text{SD} \) are shown in Figure 2. Arrhenius expressions derived from our data are as follows (units are \( 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \); errors are 2\( \sigma \), precision only):

\[
\text{Cl} + \text{H}_2\text{S}: \quad k = (3.60 \pm 0.26) \exp [(210 \pm 20)/T], \quad 202-430K
\]

\[
\text{Cl} + \text{D}_2\text{S}: \quad k = (1.65 \pm 0.27) \exp [(225 \pm 45)/T], \quad 204-431K
\]

\[
\text{Cl} + \text{CH}_3\text{SH}, \text{CD}_3\text{SD}: \quad k = (11.9 \pm 1.7) \exp [(151 \pm 38)/T], \quad 193-430K
\]

Kinetic data for \( \text{CH}_3\text{SH} \) and \( \text{CD}_3\text{SD} \) were indistinguishable so one Arrhenius expression incorporating all data is presented. One important aspect of our results is that all reactions are characterized by small but well-defined negative activation energies, suggesting that long range attractive forces between \( \text{S} \) and \( \text{Cl} \) are important in defining the overall rate coefficient. Our interpretation of observed kinetic isotope effects follows the same arguments as employed above in the comparison of \( \text{NO}_3 + \text{DMS} \) with \( \text{OH} + \text{CH}_3\text{SH} \). In the case of the \( \text{Cl} + \text{CH}_3\text{SH} \) reaction, adduct decomposition to products is apparently fast compared to adduct decomposition back to reactants whereas in the case of the \( \text{Cl} + \text{H}_2\text{S} \) reaction the two adduct decomposition pathways occur at competitive rates. This argument seems
Figure 2. Arrhenius plots for the reactions of chlorine atoms with H₂S (○), D₂S (●), CH₃SH (□), and CD₃SD (■). Error bars are 2σ and represent precision only. Solid lines are obtained from linear least squares analyses which yield the Arrhenius parameters given in the text.
reasonable since we expect H$_2$S(Cl)H to be a less strongly bound species than CH$_3$S(Cl)H, thus making adduct decomposition back to reactants considerably more rapid for Cl + H$_2$S than for Cl + CH$_3$SH. The relative stabilities of the adducts can be predicted based on the facts that a methyl group releases electron density to the sulfur atom more efficiently than does a hydrogen atom (30), and that the ionization potential of CH$_3$SH is about 1 ev lower than the ionization potential of H$_2$S (31), thus facilitating the formation of a more stable charge transfer complex in the Cl + CH$_3$SH case.

**The Reactions of OH and OD with CH$_3$CN and CD$_3$CN**

Acetonitrile (CH$_3$CN) is present at significant levels in both the troposphere and the stratosphere, and has been implicated in stratospheric ion chemistry (32-35). Reaction with OH is generally thought to be a major atmospheric removal mechanism for acetonitrile (35). Early studies of the kinetics of the OH + CH$_3$CN reaction demonstrated that $k$(298K) - 2 x 10$^{-14}$ cm$^3$ molecule$^{-1}$s$^{-1}$ and that $E_a$ = 2 kcal mole$^{-1}$ (36-41); it has generally been thought that reaction proceeds via a direct H-abstraction mechanism (40-42).

We recently carried out a detailed study of the hydroxyl reaction with acetonitrile which demonstrates that the reaction mechanism is considerably more complex than previously thought (43). The kinetics of the following four isotopic variants were investigated:

$$\begin{align*}
\text{OH} + \text{CH}_3\text{CN} & \rightarrow \text{products} \quad (13) \\
\text{OH} + \text{CD}_3\text{CN} & \rightarrow \text{products} \quad (14) \\
\text{OD} + \text{CH}_3\text{CN} & \rightarrow \text{products} \quad (15) \\
\text{OD} + \text{CD}_3\text{CN} & \rightarrow \text{products} \quad (16)
\end{align*}$$

All four reactions were studied at 298K as a function of pressure and O$_2$ concentration, while reactions 13 and 14 were also studied as a function of temperature.

Experiments which employed N$_2$ buffer gas gave some results which appear inconsistent with the idea that reactions 13 - 16 occur via direct H (or D) abstraction pathways. First, rate coefficients for reactions 13 and 14 (but not reactions 15 and 16) increase with increasing pressure over the range 50 - 700 Torr; the largest increase, nearly a factor of two, is observed for reaction 14. Second, observed isotope effects on the (high pressure limit) 298K rate coefficients are not as would be expected for an H (or D)-abstraction mechanism. Measured 298K rate coefficients in units of 10$^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ are $k_{13} = 2.48 \pm 0.38$, $k_{14} = 2.16 \pm 0.11$, $k_{15} = 3.18 \pm 0.40$, and $k_{16} = 2.25 \pm 0.28$ (errors are 20%). If the dominant reaction pathway is H (or D) abstraction we would expect reactions 13 and 15, which break C-H
bonds, to be faster by a factor of two or more than reactions 14 and 16, which break C-D bonds. Observed differences in reactivity are quite small, although reaction 15 does appear to be somewhat faster than the other reactions.

The observed kinetics in the absence of O\textsubscript{2} can best be reconciled with a complex mechanism which proceeds via formation of an energized intermediate, i.e.

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{CN} & \rightarrow \text{energized complex} \rightarrow \text{products} \\
\text{M, } k_v & \rightarrow \text{adduct}
\end{align*}
\]

Such an energized intermediate could decompose to produce CH\textsubscript{2}CN + H\textsubscript{2}O or other products, decompose back to reactants, or be collisionally stabilized at sufficiently high pressures. Hence, the reaction proceeds at a finite rate at low pressure but shows an enhancement in the rate as the pressure is increased. Such a mechanism is well documented for the important atmospheric reactions of OH with CO and HNO\textsubscript{3} (44) and has recently been observed in our laboratory for the Cl + DMS reaction (45). The pressure, temperature, and isotopic substitution dependences of the elementary rate coefficients \( k_v, k_m, k_o, \) and \( k_e \) interact to produce the observed complex behavior.

Perhaps the most conclusive evidence that the OH + CH\textsubscript{3}CN reaction proceeds, at least in part, via formation of an intermediate complex comes from experiments carried out in reaction mixtures containing O\textsubscript{2}. Observed OH temporal profiles in the presence of CH\textsubscript{3}CN and O\textsubscript{2} are non-exponential and suggest that OH is regenerated via a reaction of O\textsubscript{2} with a product of reaction 13. Two possibilities are as follows:

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{CN} & \rightarrow \text{CH}_3\text{CN} + \text{H}_2\text{O} \quad (13a) \\
\text{CH}_3\text{CN} + \text{O}_2 & \rightarrow \rightarrow \text{OH} + \text{other products} \quad (17) \\
\text{OH} + \text{CH}_3\text{CN} + \text{M} & \rightarrow \text{adduct} + \text{M} \quad (13b) \\
\text{adduct} + \text{O}_2 & \rightarrow \rightarrow \text{OH} + \text{other products} \quad (18)
\end{align*}
\]

In the mixed-isotope experiments, we observe that OD is regenerated from OD + CH\textsubscript{3}CN + O\textsubscript{2} and that OH is regenerated from OH + CD\textsubscript{3}CN + O\textsubscript{2}; these findings conclusively demonstrate that an important channel for the hydroxyl + acetonitrile reaction involves formation of an adduct which lives long enough to react with O\textsubscript{2} under atmospheric conditions, and also places considerable constraints on possible adduct + O\textsubscript{2} reaction pathways.
plausible set of elementary steps via which OH can be regenerated in the
OH + CD₃CN + O₂ reaction is shown in Figure 3. The mechanism in-
volves OH addition to the nitrogen atom, followed by O₂ addition to the
cyano carbon atom, isomerization, and decomposition to D₂CO + DOCN +
OH. Further studies are needed to establish whether or not OD as well as
OH is generated from OH + CD₃CN + O₂ and whether or not OH as well
as OD is generated from OD + CH₃CN + O₂. Further studies are also
needed to directly detect end products of the adduct + O₂ reactions(s).

The Reactions of Alkyl Radicals with HBr and DBr

The thermochemistry and kinetics of alkyl radicals are subjects of consid-
erable importance in many fields of chemistry. Accurate evaluation of alkyl
radical heats of formation are required for determination of primary,
secondary, and tertiary bond dissociation energies in hydrocarbons, for
establishing rates of heat release in combustion, and for relating unknown
"reverse" rate coefficients to known "forward" values. Kinetic data for
numerous alkyl radical reactions are needed for modeling hydrocarbon
combustion.

Recent direct kinetic studies (46-51), primarily by Gutman and
coworkers (46-49), strongly suggest that alkyl + HX reactions have negative
activation energies, a finding which seems counter-intuitive for apparently
simple hydrogen abstraction reactions. It should be noted, however, that
one recent direct study (52) reports much slower rate coefficients compared
to other direct studies (46,48,50,51) and positive activation energies for the
reactions of t-C₄H₉ with DBr and DI.

Motivated initially by the desire to obtain improved thermochemical
data for sulfur-containing radicals of atmospheric interest, we developed a
method for studying radical + HBr(DBr) reactions by observing the appear-
ance kinetics of product bromine atoms (53). We have recently applied the
same experimental approach to investigate the kinetics of the following
reactions (54):

\[
\begin{align*}
\text{CH}_3 + \text{HBr} &\rightarrow \text{Br} + \text{CH}_4 \\
\text{CD}_3 + \text{HBr} &\rightarrow \text{Br} + \text{CD}_3\text{H} \\
\text{CH}_3 + \text{DBr} &\rightarrow \text{Br} + \text{CH}_3\text{D} \\
\text{C}_2\text{H}_5 + \text{HBr} &\rightarrow \text{Br} + \text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_5 + \text{DBr} &\rightarrow \text{Br} + \text{C}_2\text{H}_5\text{D} \\
t\text{-C}_6\text{H}_{13} + \text{HBr} &\rightarrow \text{Br} + (\text{CH}_3)\text{CH} \\
t\text{-C}_6\text{H}_{13} + \text{DBr} &\rightarrow \text{Br} + (\text{CH}_3)\text{CD}
\end{align*}
\]
Figure 3. Plausible set of elementary steps for the reaction OH + CD_3CN + O_2 → D_2CO + DOCN + OH. Adduct decomposition to products is shown as a single step; in reality, it probably occurs via two sequential steps with either D_2CO or OH coming off before the other. (Reproduced from reference 43. Copyright 1991 American Chemical Society.)
The isotope effect studies were motivated by a recent theoretical investigation of the \( \text{t-C}_5\text{H}_5 + \text{HI}, \text{DI} \) reactions (55) which suggests that negative activation energies for alkyl + HX reactions should be accompanied by inverse kinetic isotope effects, i.e., \( k_H/k_D < 1 \).

In Table I our results (54) are compared with other available direct kinetic data for reactions 19 - 25. The negative activation energies and fast rate coefficients for alkyl + HBr reactions reported by Gutman and coworkers (46,47,49) are confirmed in our study. In fact, the activation energies derived from our data are consistently a little lower, i.e., more negative, than those reported by Gutman and coworkers and the 298K rate coefficients obtained in our study are consistently more than a factor of two faster than those reported by Gutman and coworkers. Our 298K rate coefficient for the \( \text{t-C}_5\text{H}_5 + \text{HBr} \) reaction exceeds the values reported by Russell et al. (46) and Richards et al. (50) by a factor of 2.7, but is in excellent agreement with the value reported by Seakins and Pilling (51); interestingly, the experimental technique employed by Seakins and Pilling was very similar to the technique employed in our study. Our 298K rate coefficient for the \( \text{t-C}_5\text{H}_5 + \text{DBr} \) reaction exceeds the value reported by Richards et al. (50) by a factor of 2.7 and exceeds the value reported by Müller-Markgraf et al. (52) by more than two orders of magnitude. As discussed in some detail by Gutman (56), the probable source of error in the Müller-Markgraf et al. study (52) is neglect of heterogeneous loss of \( \text{t-C}_5\text{H}_5 \) in their data analysis.

Traditionally, hydrogen transfer reactions such as \( \text{R} + \text{HX} \rightarrow \text{RH} + \text{X} \) have been thought of as "direct" metathesis reactions with a barrier along the reaction coordinate and a single transition state located at the potential energy maximum. Rationalization of observed negative activation energies for \( \text{R} + \text{HX} \) reactions has centered around the postulate that product formation proceeds via formation of weakly bound \( \text{R} \cdots \text{XH} \) complexes (45-48,55). As shown by Mozurkewich and Benson (57), if the transition state leading from reactants to complex (TS1) is loose and the transition state leading from complex to products is both tighter and lower in energy compared to TS1, then a negative activation energy for the overall reaction should be observed. McEwen and Golden (55) have carried out a two channel RRKM calculation that models the \( \text{t-C}_5\text{H}_5 + \text{HI(DI)} \) reactions as proceeding through a weakly bound complex; they were able to reproduce the kinetics results of Seetula et al. (48) for \( \text{t-C}_5\text{H}_5 + \text{HI} \) assuming complex binding energies as low as 3 kcal mole\(^{-1}\). Probably the most interesting aspect of McEwen and Golden's study is the fact that models which were capable of reproducing experimentally observed (48) \( k(T) \) values for \( \text{t-C}_5\text{H}_5 + \text{HI} \) also predicted an inverse kinetic isotope effect (KIE), i.e., \( \text{t-C}_5\text{H}_5 + \text{DI} \) was predicted to be faster than \( \text{t-C}_5\text{H}_5 + \text{HL} \). The predicted inverse KIE results from the fact that the transition state leading from complex to products becomes looser with lower vibrational frequencies associated with deuterium substitution. Contrary to McEwen and Golden's prediction for \( \text{t-C}_5\text{H}_5 + \text{HI} \), we observe normal KIE's for \( \text{CH}_3 \text{C}_5\text{H}_5 \) and \( \text{t-C}_5\text{H}_5 \) reactions with HBr. Richards et al. (50) also observe a normal KIE for the \( \text{t-C}_5\text{H}_5 + \text{HBr} \) reaction.
Table I. Comparison of our results (reference 54) with other direct determinations of alkyl + HBr(DBr) rate coefficients.*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Exptl Method</th>
<th>Range of T</th>
<th>A°</th>
<th>-E/R°</th>
<th>k,(298K)*</th>
<th>Reference</th>
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<tr>
<td>CH₃ + HBr</td>
<td>LFP - PIMS</td>
<td>296 - 532</td>
<td>0.87</td>
<td>160 ± 110</td>
<td>1.49</td>
<td>47</td>
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<td></td>
<td>LFP - RF</td>
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<td>1.36</td>
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<td>60</td>
</tr>
<tr>
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<td>297</td>
<td></td>
<td>3.35</td>
<td></td>
<td>54</td>
</tr>
<tr>
<td>CH₃ + DBr</td>
<td>VLPP</td>
<td>608 - 1000</td>
<td>0.32</td>
<td>0 ± 500</td>
<td>0.32</td>
<td>61</td>
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<tr>
<td></td>
<td>LFP - RF</td>
<td>267 - 429</td>
<td>1.07</td>
<td>130 ± 55</td>
<td>1.66</td>
<td>54</td>
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<tr>
<td>CD₃ + HBr</td>
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<td>295 - 532</td>
<td>1.0</td>
<td>410 ± 110</td>
<td>3.96</td>
<td>47</td>
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<tr>
<td></td>
<td>LFP - RF</td>
<td>259 - 427</td>
<td>1.33</td>
<td>539 ± 78</td>
<td>8.12</td>
<td>54</td>
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<tr>
<td>CH₃ + DBr</td>
<td>LFP - RF</td>
<td>298 - 415</td>
<td>(0.92)</td>
<td>(580)</td>
<td>6.44</td>
<td>54</td>
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<tr>
<td>t-C₃H₇ + HBr</td>
<td>VLPP</td>
<td>296 - 532</td>
<td>0.99</td>
<td>700 ± 110</td>
<td>10.4</td>
<td>46</td>
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<td></td>
<td>LFP - DLA</td>
<td>297</td>
<td></td>
<td>10</td>
<td></td>
<td>50</td>
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<tr>
<td></td>
<td>LFP - RF</td>
<td>298</td>
<td></td>
<td>32</td>
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<td>51</td>
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<tr>
<td></td>
<td>LFP - RF</td>
<td>297 - 429</td>
<td>1.07</td>
<td>963 ± 152</td>
<td>27.1</td>
<td>54</td>
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<tr>
<td>t-C₃H₇ + DBr</td>
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<tr>
<td></td>
<td>LFP - RF</td>
<td>298 - 415</td>
<td>(1.03)</td>
<td>(919)</td>
<td>22.5</td>
<td>54</td>
</tr>
</tbody>
</table>

a. Units are T, E/R: degrees K; A, k,(298K): 10⁻¹² cm³molecule⁻¹s⁻¹.
b. LFP: laser flash photolysis; PIMS: photoionization mass spectrometry; RF: resonance fluorescence; IRE: infrared emission; VLPP: very low pressure pyrolysis; DLA: diode laser absorption; VLPP: very low pressure photolysis.
c. Parentheses indicate Arrhenius parameters which are based on experiments at only two temperatures.
d. Calculated from Arrhenius parameters when temperature dependent data were obtained. Error limits not quoted due to inconsistencies in methods used by different groups to arrive at uncertainties; most values of k,(298K) have absolute accuracies in the 15-30% range.
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**HBr reaction.** It does appear, however, that the magnitude of the KIE is reduced as the activation energy becomes more negative, i.e., the observed KIE is largest for \( R = \text{CH}_3 \) and smallest for \( R = \text{t-CH}_3 \). Chen et al. have recently calculated a potential energy surface for the \( \text{CH}_3 + \text{HBr} \) reaction at the G3 level of theory and deduced the existence of a hydrogen bridged complex which is bound by 0.28 kcal mole\(^{-1}\) and is formed without activation energy (58). They have also calculated rate coefficients for \( \text{CH}_3 + \text{HBr}, \text{CH}_3 + \text{DBr}, \) and \( \text{CD}_3 + \text{HBr} \) from RRKM theory with corrections for tunneling evaluated using the Wigner method (59). Their calculated isotope effects agree quantitatively with our measured isotope effects, a result which lends strong support to the idea that the methyl-HBr complex is hydrogen-bridged rather than bromine-bridged.

**Summary**

Experimental kinetic data have been presented and discussed for a number of reactions where H/D isotope effects provide valuable mechanistic insights. For the reactions of atmospheric free radicals with reduced sulfur compounds, isotope effect studies provide information not only about C-H or S-H bond cleavage versus other reactive pathways but also on the relative rates of adduct decompositions back to reactants versus on to products. For the reaction of hydroxyl radicals with acetonitrile, isotope effect studies conclusively demonstrate the intermediacy of a long-lived adduct and also provide site-specific information which places important constraints on the detailed mechanism for hydroxyl generation from the adduct + \( \text{O}_2 \) reaction. For the \( \text{CH}_3 + \text{HBr} \) reaction, comparison of observed and theoretical isotope effects supports the view that reaction proceeds via formation of a very weakly bound, hydrogen-bridged addition complex. In one case considered, namely the \( \text{O}_2 \)-independent channel for the \( \text{OH} + \text{CH}_3\text{SCH}_3 \) reaction, there exist potential problems in relating experimental observations (6,7) to existing prejudices concerning the nature of kinetic isotope effects.

**Acknowledgments**

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Introduction

The thermochemistry and kinetics of alkyl radicals are subjects of considerable importance in many fields of chemistry. Accurate evaluation of alkyl radical heats of formation is required for determination of primary, secondary, and tertiary bond dissociation energies in hydrocarbons, for establishing rates of heat release in combustion, and for relating unknown "reverse" rate coefficients to known "forward" values. Kinetic data for numerous alkyl radical reactions are needed for modeling hydrocarbon combustion.

Despite the importance of alkyl radical kinetics and thermochemistry, and an extensive literature which dates back several decades, important discrepancies in the database have persisted.

Recent direct kinetic studies, primarily by Gutman and co-workers, strongly suggest that alkyl + HX reactions have negative activation energies; while this finding seems counterintuitive for apparently simple hydrogen-transfer reactions, it can resolve the above-mentioned discrepancy in alkyl radical heats of formation since all earlier iodination and bromination studies were analyzed under the assumption that alkyl + HX reactions have small, positive activation energies. However, it should be noted that one recent direct study reports much slower rate coefficients (compared to other direct studies) and positive activation energies for the reactions of t-C4H9 with DBr and D2.

Motivated initially by the desire to obtain improved thermochemical data for sulfur-containing radicals of atmospheric interest, we developed a method for studying radical + HBr(DBr) reactions by observing the appearance kinetics of product bromine atoms. In this paper we report the results of a series of experiments where time-resolved monitoring of bromine atom appearance was employed to investigate the kinetics of the following reactions:

CH3 + HBr \rightarrow Br + CH4 (1)
CD3 + HBr \rightarrow Br + CD4 (2)
C2H5 + DBr \rightarrow Br + C2H4 (3)
C2H5 + HBr \rightarrow Br + C2H4 (4)
C2H5 + DBr \rightarrow Br + C2H4 (5)
l-C4H9 + HBr \rightarrow Br + (CH3)2CH (6)
l-C4H9 + DBr \rightarrow Br + (CH3)2CD (7)

The isotope effect studies have been motivated by a recent theoretical study of the t-C4H9 + HI, DI reactions, which suggests that negative activation energies for alkyl + HX reactions should be accompanied by inverse kinetic isotope effects, i.e., kH/kD < 1.

Experimental Technique

The experimental approach involved coupling alkyl radical production by laser flash photolysis of suitable precursors with time-resolved detection of bromine atom appearance by resonance fluorescence spectroscopy. A schematic diagram of the apparatus, as configured for bromine atom detection, can be found elsewhere.

A Pyrex, jacketed reaction cell with an internal volume of 150 cm3 was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol (T > 298 K) or methanol (T < 298 K) from a thermostatically controlled bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket was injected into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment.

Alkyl radicals were produced by 266-nm pulsed laser photolysis of R1/HBr/N2 mixtures (R = CH3, CD3, C2H5, l-C4H9) or by 355-nm pulsed laser photolysis of Cl2/RH/HBr/N2 mixtures (R = CH3, C2H5). Third or fourth harmonic radiation from a Quanta Ray Model DCR-2 Nd:YAG laser provided the photolytic ra-

References

Reaction Kinetics of Alkyl + HBr(DBr)

The laser could deliver up to $3 \times 10^{14}$ photons per pulse at 266 nm and up to $1 \times 10^{17}$ photons per pulse at 355 nm; the maximum repetition rate was 10 Hz, and the pulse width was approximately 6 ns. A bromine resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the photolytically produced atoms. The resonance lamp consisted of an electrodeless microwave discharge through about 1 Torr of a flowing mixture containing a trace of Br2 in helium. The flows of a 0.2% Br2 in helium mixture and pure helium into the lamp were controlled by separate needle valves, thus allowing the total pressure and Br2 concentration to be adjusted for optimum signal-to-noise ratio. Radiation was guided out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell, the lamp output passed through a flowing gas filter containing 50 Torr-cm of methane in nitrogen. The methane filter prevented radiation at wavelengths shorter than 140 nm (including impurity emissions from excited oxygen, hydrogen, and nitrogen atoms) from entering the reaction cell but transmitted the strong bromine lines in the 140-160-nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and resonance lamp beam and was imaged onto the photocathode of a solar blind photomultiplier. Signals were processed by using photon counting techniques in conjunction with multichannel scaling. A large number of laser shots were typically averaged to obtain a bromine atom temporal profile with signal-to-noise ratio sufficient for quantitative kinetic analysis. It is worth noting that the resonance fluorescence detection scheme is sensitive to both ground state ($^{3}P_{2}$) and spin-orbit excited state ($^{3}P_{1/2}$) bromine atoms.

To avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was in the range 2-10 cm s$^{-1}$, and the laser repetition rate was varied over the range 5-10 Hz (5 Hz typical). Hence, no volume element of the reaction mixture was subjected to more than a few laser shots. The alkyl iodides, ethane, Cl2, HBr, and DBr flowed into the reaction cell from bulbs (12-L volume) containing dilute mixtures in nitrogen while methane, hydrogen, and additional nitrogen were flowed directly from their storage cylinders. All gases except Cl2 (see below) were premixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The concentrations of HBr and DBr were also determined by in situ UV photometry at 202.6 nm (Zn* line). A zinc hollow cathode lamp was employed as the light source for the photometric measurement, and a quartz meter monochromator was used to isolate the 202.6-nm line. The absorption cross sections needed to convert measured absorbances into concentrations were determined during the course of this investigation and were found to be 1.02 $\times 10^{-19}$ cm$^2$ for HBr and 9.7 $\times 10^{-19}$ cm$^2$ for DBr. The measured HBr cross section agrees well with values reported by Goodeve and Taylor and by Huebert and Martin but is $\sim 20$% higher than the value reported by Romand and $\sim 20$% lower than the value of Nee et al. Experimental results were found to be independent of whether the 2 m long absorption cell was positioned upstream or downstream relative to the reaction cell.

The gases used in this study had the following stated minimum purities: N2, 99.999%; H2, 99.999%; HBr, 99.999%; Cl2, 99.999%; CH4, 99.999%; CH2, 99.999%; CH3, 99.999%; CI, 99.999%; Br2, 99.98%; DBr, 99.98%; D2, 99.99%. All gases except CI2, Cl, and HBr were purified by repeated freeze (77 K)-pump-thaw cycles. It is worth noting that the HBr and DBr gas samples taken directly from their storage cylinders contained significant (25-50$\%$) levels of a noncondensable impurity which was determined by weighing to be H2(D$_2$).

The liquids used in this study had the following stated minimum purities: CH3I, 99.5%; CD3I, undetermined chemical purity and 99.5+ atom % $^2$D; CH2I, 99%; t-C6H5I, 95%. All liquid samples were transferred under nitrogen into vials fitted with high-vacuum stopcocks and were subjected to repeated freeze (77 K)-pump-thaw cycles before being used to prepare gaseous RI/N2 mixtures. When not in use, the vials were stored in the dark at 278 K.

Results and Discussion

In most experiments, alkyl radicals were generated by 266-nm laser flash photolysis of the appropriate alkyl iodide (RI) in the range 1-12 $\times 10^3$ molecules cm$^{-3}$:

$$\text{RI} + h\nu(266 \text{ nm}) \rightarrow \text{R} + \text{I}, \text{R} = \text{CH}_3, \text{CD}_3, \text{C}_2\text{H}_5, t-\text{C}_6\text{H}_5, 9\text{CH}_3$$

(8)

Reactions 1 and 4 were also studied using the following alternate alkyl production scheme:

$$\text{Cl}_2 + h\nu(355 \text{ nm}) \rightarrow 2 \text{Cl}$$

(9)

$$\text{Cl} + \text{RH} \rightarrow \text{R} + \text{HCl}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5$$

(10)

When the alternate production scheme was applied, Cl2 (concentration $\sim 1 \times 10^3$ molecules cm$^{-3}$) was injected into the gas flow just upstream from the reaction zone to suppress the heterogeneous dark reaction between Cl2 and HBr. Also, RH was added to the reaction mixture in sufficient quantity that (a) production of alkyl radicals was essentially instantaneous on the time scale for the alkyl + HBr reaction and (b) nearly all Cl (99%) reacted with RH rather than with HBr. Observed kinetics were found to be independent of the choice of alkyl radical production scheme. As will be discussed in more detail below, the invariance of observed kinetics to the alkyl radical source rules out some potential sources of systematic error.

Reactions 1-5 are sufficiently exothermic that the bromine atom product could be formed in the spin-orbit excited state. Br($^{3}P_{1/2}$). To ensure that relaxation of Br($^{3}P_{1/2}$) was not rate-limiting in defining observed Br appearance rates, all experiments were carried out with 0.2-2 Torr of H2 added to the reaction mixture. The reaction

$$\text{Br}^2(P_{1/2}) + \text{H}_2(c = 0) \rightarrow \text{Br}^2(P_{1/2}) + \text{H}_2(c = 1)$$

(11)

is known to be fast, with $k_1 \sim 6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. All experiments were carried out under pseudo-first-order conditions with HBr in large excess (typically a factor of 106) over the alkyl radical. Concentrations of photolytically generated radicals were typically in the range 5-10 $\times 10^9$ cm$^{-3}$, although this experimental parameter was varied over a wide range (factor of 20). Observed kinetics were found to be independent of both the alkyl iodide concentration and the concentration of photolytically generated radicals.

In the absence of side reactions that remove or produce Br, the observed temporal profile following the flash would be described by the relationship

$$S_t = k_4C_t(k_4 - k_3)^{-1} \left[ \exp(-k_3t) - \exp(-k_4t) \right] + C_2 \exp(-k_4t)$$

(1)

In eq 1, $S_t$ is the fluorescence signal level at time $t$ (proportional to [Br]). $k_3$ and $k_4$ are the pseudo-first-order rate coefficients for Br appearance ($k_3$) and disappearance ($k_4$), and the parameters $C_1$ and $C_2$ are defined as follows:

$$C_1 = a[R]_0$$

(II)

$$C_2 = a[Br]_0$$

(III)

In the above equations [R]$_0$ and [Br]$_0$ are the alkyl and Br concentrations after photolysis and reaction 10 have gone to completion.

(18) Stated purity of liquid phase in cylinder.
f is the fraction of alkyl radicals that are removed via a reaction. Considerations are either primary or secondary. k_s is the rate coefficient for the following reaction(s):  

\[
 k_s = k_{[\text{HBr(DBr)}]} / k_a \quad (i = 1-7)
\]

where \( k_a \) is the rate coefficient for the following reaction(s):  

\[
 \text{R} \rightarrow \text{first-order loss by processes that do not produce Br} \quad (12)
\]

A nonlinear least-squares analysis of each experimental temporal profile was employed to determine \( k_a, k_s, C_1, \) and \( C_2 \). The bimolecular rate coefficients of interest, \( k_s(P,T) \), were determined from the slopes of \( k_s \) vs \([\text{HBr(DBr)}] \) plots. Typical data are shown in Figures 1 and 2. It is worth pointing out that the accuracy with which \( k_s \) could be determined via the nonlinear least-squares fitting technique was quite good because it was always the case that \( k_s \gg k_a \) and \( C_1 \gg C_2 \). Observation of Br temporal profiles that are well described by eq (1), a linear dependence of \( k_a \) on \([\text{HBr(DBr)}] \), and invariance of \( k_a \) to variation in laser photon fluence and photolyte concentration suggest that the alkyl + HBr(DBr) reaction and reaction 13 (\( k_{13} \sim k_a \)) are the only processes that significantly affect the Br time history (once photolysis and CI reaction with RH and HBr are complete). One potential interference that is not ruled out by the above observations is reaction of alkyl radicals with impurities which are either present in the HBr sample or produced via dark reactions of HBr with other components in the reaction mixture; impurity reactions are considered below when potential systematic errors are discussed.

<table>
<thead>
<tr>
<th>( [\text{HBr}] ) (10^10 molecules cm^{-3})</th>
<th>( k_s ) (10^{-12} cm^3 molecule(^{-1} \text{s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.45 (a) 5.61 (b)</td>
<td>7.81 (a) 8.24 (b)</td>
</tr>
</tbody>
</table>

Figure 1. Typical Br atom temporal profiles. Reaction: \( \text{C}_2\text{H}_5 + \text{HBr} \). Experimental conditions: \( T = 298 \text{ K} \), \( P \) (Torr) = (a) 100, (b) 50. Solid and dashed lines are obtained from linear least-squares analyses of the solid and open circle data points, respectively, and give the following bimolecular rate coefficients in units of 10^{-12} cm^3 molecule^{-1} s^{-1}: (a) \( k_s \sim 8.24 \pm 0.65 \), (b) \( k_s \sim 7.81 \pm 0.51 \). Arrows indicate the two points obtained from the data shown in Figure 1.

One interesting aspect of the data in Figure 2 is the relatively large value for \( k_{12} \), i.e., the relatively large intercept in the \( k_s \) vs \([\text{HBr}] \) plot. The observed values for \( k_{12} \) were typically larger than expected if background removal of alkyl radicals was due only to reaction with their photolytic precursors and to diffusion out of the detector field of view. At low \([\text{HBr(DBr)}] \), where \( k_{12} > k_s[\text{HBr(DBr)}] \) (\( i = 1-7 \)), fluorescence signal levels were considerably reduced; this indicates that the process responsible for background alkyl radical removal did not result in production of bromine atoms. The magnitude of \( k_{12} \) tended to increase with decreasing temperature and with increasing complexity of the alkyl radical, suggesting that a process responsible for significant background removal of alkyl radicals was reaction with \( \text{O}_2 \):

\[
 \text{R} + \text{O}_2 + \text{N}_2 \rightarrow \text{RO}_2 + \text{N}_2
\]

The \( \text{O}_2 \) levels required to account for observed \( k_{12} \) values are around 0.01 Torr—significantly higher than expected \( \text{O}_2 \) impurity levels in the \( \text{N}_2 \) buffer gas. Hence, a small leak in the slow flow system is the probable source of \( \text{O}_2 \). The presence of a reactive impurity at the levels encountered in our experiments is not expected to introduce systematic error into the kinetic measurements. However, when the condition \( k_{12} \ll k_s[\text{HBr(DBr)}] \) is not met at least for the highest \( \text{HBr(DBr)} \) concentrations employed in a particular rate coefficient determination, the precision of the derived value for \( k_s(P,T) \) is reduced; the worst case in this regard was the \( k_s \) measurement at \( T = 415 \text{ K} \), where \( k_{12} / k_s(\text{max}) \approx 0.28 \) (Table 1).

Kinetic data for reactions 1-7 are summarized in Table 1, and Arrhenius plots for reactions 1, 3, 4, and 6 are shown in Figure 3. The solid lines in Figure 3 are obtained from linear least-squares analyses of the ln \( k_s(P,T) \) vs \( T^{-1} \) data; these analyses give the following Arrhenius expressions in units of cm^3 molecule^{-1} s^{-1}:

\[
 k_s = (1.36 \pm 0.10) \times 10^{-12} \exp[(233 \pm 23)/T]
\]

\[
 k_s = (1.07 \pm 0.17) \times 10^{-12} \exp[(130 \pm 55)/T]
\]

\[
 k_s = (1.33 \pm 0.33) \times 10^{-12} \exp[(539 \pm 78)/T]
\]

\[
 k_s = (1.07 \pm 0.34) \times 10^{-12} \exp[(963 \pm 152)/T]
\]

Errors in the above expressions are \( 2\sigma \) and represent precision only. As reported previously by Gutman and co-workers, it is found that alkyl + HBr(DBr) rate coefficients increase with decreasing...
Errors are indicated. *(Refer to reaction number in text.)

N$_2$ buffer gas was employed as alkyl source except where indicated. *($^i$) refers to reaction number in text. *N$_2$ buffer gas except where indicated. *Exp$^*$ = measurement of a single Br temporal profile. *Errors are 2$\sigma$ and represent precision only. *C$_{\text{CH}_3}$/C$_{\text{H}_2}$ photolysis employed as CH$_4$ source. CH$_4$ used as buffer gas. i.e. [CH$_4$] $\sim$ 9.6 x 10$^{17}$ molecules cm$^{-3}$. *C$_{\text{C}_2\text{H}_6}$/C$_{\text{CH}_3}$ photolysis employed as C$_2$H$_6$ source: [C$_2$H$_6$] $\sim$ 1.6 x 10$^{18}$ molecules cm$^{-3}$. Temperature, i.e., activation energies are negative. Pressure variations within the range 10-300 Torr of N$_2$ revealed no evidence of a pressure dependence for any of the reactions studied. On the basis of observed precision and consideration of possible systematic errors (see below), we estimate the absolute accuracy of each measured rate coefficient, $k_i(T)$, to be $\pm$20%.

Potential Systematic Errors. As discussed briefly above, a number of potential systematic errors in our kinetic measurements can be ruled out on the basis of the observed invariance of Br temporal profiles to variations in laser photon fluence, photolysis concentrations, and flow velocity through the reactor; these include contributions to Br kinetics from radical-radical side reactions, from radical-R$_i$ side reactions, or from reactions involving stable products which build up in concentration with successive laser flashes. In situ measurement of HBr(DBr) concentrations greatly reduces another potential source of systematic error.

It is well-known that UV photolysis of CH$_3$I produces vibrationally hot methyl radicals, and both ethyl and tert-butyl radicals are likely to be produced in excited vibrational states from R$_1$ photolysis. However, it is generally thought that under our experimental conditions relaxation to a thermalized vibrational distribution occurs much more rapidly than chemical reaction. Our experiments employing the C$_3$H$_7$/R$_1$ source provide further evidence that we are indeed observing reactions of thermalized alkyl radicals. On the basis of the best available thermochemical data, the Cl + C$_2$H$_4$ reaction is slightly endothermic and the Cl + C$_3$H$_7$ reaction is only slightly exothermic; hence, these reactions cannot produce vibrationally hot alkyl radicals.

Another potential interference could have resulted if primary photolysis of R$_1$ or secondary photolysis of hot alkyl radicals led to generation of hydrogen atoms. The reaction

$$\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br} \quad (15)$$

is thought to proceed with $k_9(T)$ $\sim$ 6 x 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Hence, if the H atom concentration was significant compared to the alkyl radical concentration, we would systematically overestimate methyl radical reaction rates and systematically underestimate tert-butyl radical reactions rates. The experiments employing the C$_3$H$_7$/R$_1$ source provide evidence that H atom production was not a problem in our CH$_3$ + HBr study. Significant H atom production is expected when 355-nm photolysis is employed and the only H precursors are RH and HBr. Furthermore, secondary photolysis of alkyl radicals does not seem possible because (a) the radicals are born with little internal energy and, therefore, cannot be excited via a single photon process at 355 nm and (b) nearly all alkyl radical formation is delayed in time until after the laser flash is over.

Another possible interference that must be addressed is the role of Br$_2$ impurity. Potential sources of Br$_2$ are impurity in the HBr sample, residual Br$_2$ (from Br recombination) not swept out of the reaction zone between laser flashes, and catalytic formation of Br$_2$ from heterogeneous reactions of HBr (presumably on the metal surfaces of valves and fittings). Since alkyl + Br$_2$ reactions are about an order of magnitude faster than the corresponding alkyl + HBr reactions, the condition [Br$_2$] < 0.001 [HBr] must

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molecules cm⁻². Since the Br₂ absorption cross section at 404.7 nm is about 6 x 10⁻¹⁸ cm², these experiments suggest that [Br₂] < 0.0025[HBr]. A second set of observations which confirm that Br₂ levels were very low is the small values for C₂ obtained from the data analysis in all experiments. The experiments employing the Cl₂/RH photolysis source are particularly important in this regard because (a) the Br₂ absorption cross section at 355 nm (8.4 x 10⁻²⁰ cm²) is considerably larger than at 266 nm and (b) it is known that BrCl and/or Br₂ can be generated from heterogeneous reaction between Cl₂ and HBr. Taking these two features into account because (a) the Br₂ absorption cross section at 355 nm (8.4 x 10⁻²⁰ cm²) is considerably larger than at 266 nm and (b) it is known that BrCl and/or Br₂ can be generated from heterogeneous reaction between Cl₂ and HBr. Taking these two features into account because (a) the Br₂ absorption cross section at 355 nm (8.4 x 10⁻²⁰ cm²) is considerably larger than at 266 nm and (b) it is known that BrCl and/or Br₂ can be generated from heterogeneous reaction between Cl₂ and HBr.

As discussed above, the experiments that employed the Cl₂/RH alkyl radical source were of value for assessing the importance of several potential interferences. However, the use of Cl₂/RH photolysis for generating alkyl radicals introduces an additional chemistry complication which requires consideration, namely the reaction of alkyl radicals with Cl₂:

\[
\text{R} + \text{Cl}_2 \rightarrow \text{RCI} + \text{Cl}
\]  

Rate coefficients for reaction 16 at 298 K are 2.1 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ for R = CH₃ and 1.85 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for R = C₂H₅. For [Cl₂] = 1 x 10¹³ molecules cm⁻³, as employed in our experiments, reaction with Cl₂ was negligible alkyl removal mechanism in the experiments with R = CH₃ but did account for 2-7% of alkyl removal in the experiments with R = C₂H₅. However, the Cl atom product of reaction 16 reacts instantaneously (on the time scale for R + HBr reaction) to regenerate R (yield >95%) or produce Br (yield <5%). We conclude from the above discussion that reaction 16 did not significantly alter observed Br temporal profiles.


**TABLE II: Comparison of Our Results with Other Direct Determinations of kᵢ (i = 1-7)**

<table>
<thead>
<tr>
<th>reaction (i)</th>
<th>expli method*</th>
<th>range of T</th>
<th>A'/E/R</th>
<th>kᵢ(298 K)'</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ + HBr (1)</td>
<td>LFP-PIMS</td>
<td>296-332</td>
<td>0.87</td>
<td>160 ± 110</td>
<td>1.49</td>
</tr>
<tr>
<td>CD₃ + HBr (2)</td>
<td>LFP-RE</td>
<td>257-422</td>
<td>1.36</td>
<td>233 ± 23</td>
<td>2.97</td>
</tr>
<tr>
<td>CH₃ + DBr (3)</td>
<td>VLPP</td>
<td>608-1000</td>
<td>0.32</td>
<td>0 ± 500</td>
<td>0.32</td>
</tr>
<tr>
<td>C₂H₅ + HBr (4)</td>
<td>LFP-RF</td>
<td>267-429</td>
<td>1.07</td>
<td>130 ± 55</td>
<td>1.66</td>
</tr>
<tr>
<td>C₂H₅ + DBr (5)</td>
<td>LFP-RF</td>
<td>298-415</td>
<td>(0.92)</td>
<td>(580)</td>
<td>6.44</td>
</tr>
<tr>
<td>r-C₂H₅ + HBr (6)</td>
<td>LFP-PIMS</td>
<td>296-332</td>
<td>0.99</td>
<td>700 ± 110</td>
<td>10.4</td>
</tr>
<tr>
<td>LFP-RE</td>
<td>297</td>
<td>10</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFP-RF</td>
<td>298</td>
<td>32</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFP-RF</td>
<td>297-429</td>
<td>1.07</td>
<td>963 ± 152</td>
<td>27.1</td>
<td>this work</td>
</tr>
<tr>
<td>r-C₂H₅ + DBr (7)</td>
<td>VLPP</td>
<td>295-384</td>
<td>(8.3)</td>
<td>(1180)</td>
<td>0.16</td>
</tr>
<tr>
<td>LFP-DLA</td>
<td>297</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFP-RF</td>
<td>298</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFP-RF</td>
<td>298-415</td>
<td>(1.03)</td>
<td>(919)</td>
<td>22.5</td>
<td>this work</td>
</tr>
</tbody>
</table>

*Units are T, E/R, degrees K, A', kᵢ(298 K)', 10⁻¹² cm³ molecule⁻¹ s⁻¹. The letter i refers to reaction numbers in the text. LFP, laser flash photolysis; PIMS, photoionization mass spectrometry; RE, resonance fluorescence; IRE, infrared emission; VLPP, very low pressure pyrolysis; DLA, diode laser absorption; VLPP, very low pressure photolysis.


Figure 3. Arrhenius plots for the CH₃ + HBr(1), CD₃ + HBr(3), C₂H₅ + HBr(4), and r-C₂H₅ + HBr(6) reactions. Solid lines are obtained from linear least-squares analyses and yield the following Arrhenius expressions in units of 10⁻¹² cm³ molecule⁻¹ s⁻¹: A' = 1.36 exp(233/T); k₁ = 1.07 exp(130/T); k₂ = 1.33 exp(539/T); k₃ = 1.07 exp(963/T). Error bars represent 2σ precision only. Arrows indicate the rate coefficients measured using the Cl₂/RH alkyl radical source.

be met before Br₂ interference can be considered negligible. Two experimental observations lead us to conclude that Br₂ levels were very low in our experiments. In one set of experiments the 2-m absorption cell was positioned in the slow flow system downstream from the reaction cell and employed to monitor Br₂ photometrically (at 404.7 nm) with typical RI/HBr/H₂/N₂ reaction mixtures flowing and the laser firing (λ = 266 nm). No absorption was observed (i.e., I/I₀ > 0.997) even at HBr levels as high as 10⁻⁴ molecular cm⁻³. Since the Br₂ absorption cross section at 404.7 nm is about 6 x 10⁻¹⁸ cm², these experiments suggest that [Br₂] < 0.0025[HBr]. A second set of observations which confirm that Br₂ levels were very low is the small values for C₂ obtained from the data analysis in all experiments. The experiments employing the Cl₂/RH photolysis source are particularly important in this regard because (a) the Br₂ absorption cross section at 355 nm (8.4 x 10⁻²⁰ cm²) is considerably larger than at 266 nm and (b) it is known that BrCl and/or Br₂ can be generated from heterogeneous reaction between Cl₂ and HBr. Taking these two features into account because (a) the Br₂ absorption cross section at 355 nm (8.4 x 10⁻²⁰ cm²) is considerably larger than at 266 nm and (b) it is known that BrCl and/or Br₂ can be generated from heterogeneous reaction between Cl₂ and HBr.

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\]

Rate coefficients for reaction 16 at 298 K are 2.1 x 10⁻¹² cm³ molecule⁻¹ s⁻¹ for R = CH₃ and 1.85 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for R = C₂H₅. For [Cl₂] = 1 x 10¹³ molecules cm⁻³, as employed in our experiments, reaction with Cl₂ was negligible alkyl removal mechanism in the experiments with R = CH₃ but did account for 2-7% of alkyl removal in the experiments with R = C₂H₅. However, the Cl atom product of reaction 16 reacts instantaneously (on the time scale for R + HBr reaction) to regenerate R (yield >95%) or produce Br (yield <5%). We conclude from the above discussion that reaction 16 did not significantly alter observed Br temporal profiles.

Comparison with Previous Work. Available kinetic data for alkyl radical reactions with HBr and DBr are summarized in Table II. The negative activation energies and fast rate coefficients for alkyl + HBr reactions reported by Gutman and co-workers\(^{(3,5)}\) are confirmed in our study. However, the activation energies derived from our data are consistently a little lower, i.e., more negative, than those reported by Gutman and co-workers. The 298 K rate coefficients obtained in our study are consistently more than a factor of 2 faster than those reported by Gutman and co-workers. We observe "normal" kinetic isotope effects (i.e., R + HBr is faster than R + DBr) which decrease in magnitude with increasing complexity of the alkyl radical (and with decreasing activation energy). The 209\(^{\circ}\) kinetic isotope effect we observe for \(\text{t-C}_2\text{H}_5 + \text{HBr(DBr)}\) at 298 K is an excellent agreement with the isotope effect observed by Richards et al.\(^{(28)}\) By far the most studied of the alkyl + HBr(DBr) reactions are those involving the tert-butyl radical. A majority of recent work, including our own, suggests that \(k_8(298 \text{ K}) \approx 1 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(E_{\text{a}} = -1 \text{ kcal mol}^{-1}\).\(^{(1,8)}\) The exception is the very low pressure photolysis study of reaction 7 by Müller-Markgraf et al.\(^{(10)}\) They report \(k_8(293 \text{ K}) = 1.5 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and a significant positive activation energy (\(+2 \text{ kcal mol}^{-1}\)). As discussed by Richards et al.\(^{(28)}\) the probable source of the error in the Müller-Markgraf et al. study is neglect of heterogeneous loss of \(t\text{-C}_2\text{H}_5\) in their data analysis. The only study of reactions 6 and 7 where kinetic data were obtained by monitoring the decay of \(t\text{-C}_2\text{H}_5\) is the work of Russell et al.\(^{(8)}\) who coupled time-resolved photoionization mass spectrometry with 193-nm laser flash photolysis of 4,4-dimethyl-1-pentene or 2,2,4,4-tetramethyl-3-pentanone; they obtained the results \(k_6(298 \text{ K}) = 1.0 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(E_{\text{a}} = -1.4 \pm 0.2 \text{ kcal mol}^{-1}\). Subsequently, Richards et al.\(^{(1)}\) also generated \(t\text{-C}_2\text{H}_5\) radicals by 193-nm laser flash photolysis of 4,4-dimethyl-1-pentane but obtained kinetic data by monitoring the appearance of the \((\text{CH}_3)\text{CH}\)CH using tunable diode laser spectroscopy as the monitoring technique; they found \(k_6(298 \text{ K}) = 1.9 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(E_{\text{a}} = -1.4 \pm 0.2 \text{ kcal mol}^{-1}\).\(^{(1,8)}\) In excellent agreement with Russell et al. We find that \(k_6(298 \text{ K})\) is a factor of 2.7 faster than reported by Russell et al.\(^{(8)}\) and by Richards et al.\(^{(1)}\) and that \(E_{\text{a}} = -1.9 \pm 0.3 \text{ kcal mol}^{-1}\), i.e., 0.5 kcal mol\(^{-1}\) lower than reported by Russell et al. Seakins and Pilling\(^{(5)}\) have measured \(k_6(298 \text{ K})\) using 351-nm laser flash photolysis of azoisobutane as the \(t\text{-C}_2\text{H}_5\) source and, as in our study, employing time-resolved resonance fluorescence monitoring of product bromine atoms as the kinetic probe. Interestingly, they find \(k_6(298 \text{ K}) = (3.2 \pm 1.0) \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) in excellent agreement with our result. Any attempt to explain the difference between the rate coefficients reported in this study and those reported by Gutman and co-workers\(^{(3,5)}\) and by Richards et al.\(^{(1)}\) would be speculation on our part, since the alkyl + HBr(DBr) reactions appear to have been kinetically isolated from potential side reactions in all cases. Systematic error in determination of the HBr(DBr) concentration is one possibility. For example, Russell et al. report that HBr samples were degassed prior to use,\(^{(8)}\) while we find that gas taken directly from the HBr storage cylinder can contain up to 50% H\(_2\) impurity; hence, a large fraction of the gas flow that Russell et al. thought was HBr could have been unreactive \(H_2\), thus leading to under-estimation of the alkyl + HBr rate coefficients. Arguing against the above explanation, however, is the fact that Richards et al., who report that HBr and DBr samples were repeatedly degassed at 77 K prior to use,\(^{(1)}\) also obtained relatively slow rate coefficients for reactions 6 and 7.

Alkyl Radical Thermochemistry. Arrhenius parameters for reactions 1, 4, and 6 derived in this study can be combined with the best available Arrhenius parameters for the reverse (Br + RH) reactions to obtain entropies and enthalpies of reaction, using the "second-law method":

\[
\begin{align*}
\text{Br} + \text{CH}_3 & \rightarrow \text{CH}_3 + \text{HBr} \\
\text{Br} + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_5 + \text{HBr} \\
\text{Br} + (\text{CH}_3)\text{CH} & \rightarrow \text{t-C}_2\text{H}_5 + \text{HBr}
\end{align*}
\]


- Br + CH\(_3\) → CH\(_3\) + HBr
- Br + C\(_2\)H\(_4\) → C\(_2\)H\(_5\) + HBr
- Br + (CH\(_3\))\(_2\)CH → t-C\(_2\)H\(_5\) + HBr

The second-law method employs the following relationships to obtain thermochemical parameters for reaction \(i\):

- \(\Delta H_i = E_f - E_i\) \hspace{1cm} (VI)
- \(\Delta S_i = R \ln (A_i / A_o)\) \hspace{1cm} (VII)

where \(A_i\) and \(E_i\) are the A-factor and activation energy for reaction \(i\). The literature values for Arrhenius parameters for reactions 1, 4, and 6 which we have adopted are summarized in Table III. For \(k_{1,4}\), we adopt the recent direct determination of Seakins and Pilling\(^{(5)}\). For \(k_6\), we take the average of recent direct determinations by Seakins and Pilling\(^{(5)}\) and by Russell et al. \(^{(8)}\) (which are in excellent agreement). We combine the Seakins and Pilling determination of \(k_6\) with the temperature-dependent ratios \(k_6/k_1, k_6/k_4, k_6/k_{17}\) reported by Coomber and Whittle\(^{(6)}\) to obtain an Arrhenius expression for \(k_6\): 

\[
\text{Br} + \text{CH}_3\text{CHF}_2 → \text{CH}_3\text{CF}_2 + \text{HBr}
\]

(17)

Thermochemical parameters for reactions 1, 4, and 6 obtained from the second-law analysis are given in Table IV. The temperature in each case is defined as the arithmetic mean of the \(T_f\) ranges employed in the determinations of \(k\), (this work) and \(k_o\) (Table III). Values for \(\Delta H_k\) at 298 K were computed using heat capacity corrections obtained from Burcat (CH\(_2\))\(^{31}\) Chen et al. (C\(_3\)H\(_2\))\(^{32}\) and Manion and Golden (t-C\(_2\)H\(_5\))\(^{33}\); the corrections calculated by Manion and Golden are based in large part on the experimental and theoretical studies of Pacansky and co-workers.\(^{(30)}\) \(\Delta S_k\) at 298 K were computed in the relationship

\[
\Delta G_{298} = \Delta H_{298} - T \Delta S_{298} = RT \ln K_m(298 \text{ K}) = RT \ln (k(298 \text{ K}) / k(298 \text{ K}))
\]


calculated using standard statistical mechanical methods and employed in conjunction with experimental values for $K_e(T)$ to obtain $\Delta H_f$ (using eq VIII). Absolute entropies as a function of temperature were obtained from Burcat\textsuperscript{21} except in the cases of $C_2H_5$ and $t-C_6H_{13}$, where updated entropy calculations are available. Third-law entropy changes for reactions 1, 4, and 6 are given in Table IV. Uncertainties in the third-law $\Delta S$ values are estimated on the basis of uncertainties in key structural parameters. The uncertainties in calculated entropy changes increase with increasing alkyl radical complexity, due in large part to uncertainties in the magnitudes of internal rotation barriers for $C_2H_5$ and particularly for $t-C_6H_{13}$. In units of cal mol$^{-1}$ K$^{-1}$, the 298 K entropies of $C_2H_5$, $C_3H_7$, and $t-C_6H_{13}$ used in our third-law determinations are 48.06, 58.98, and 75.70, respectively.

The enthalpy changes for reactions 1, 4, and 6 determined in this study can be combined with the accurately known heats of formation of Br, HBr, and RH\textsuperscript{22,23} to obtain alkyl radical heats of formation. Values for $\Delta H^0_f(R)$ are given in Table V along with $\Delta H^0_f(R-H)$ bond strengths derived by combining the $\Delta H^0_f(R)$ values with known heats of formation for RH and H\textsuperscript{22,23}. Simple averages of the second- and third-law enthalpies of reaction have been obtained to yield our reported values for $\Delta H^0_f(R)$, this approach seems reasonable since (a) estimated uncertainties in the second- and third-law determinations are similar and (b) the second- and third-law values for $\Delta H^0_f$ (reaction 1) agree to within a few tenths of a kilocalorie per mole in all three cases. The relatively low activation energies for reactions 4 and 6 reported in this study leads to heats of formation for $C_3H_7$ and $t-C_6H_{13}$ which are 0.4 and 0.5 kcal mol$^{-1}$ higher than those reported by Russell et al.\textsuperscript{4,5} although our results agree with those of Russell et al.\textsuperscript{4,5} within combined uncertainties. As discussed briefly under Introduction, Tsang has critically reviewed the literature and, showing a preference for thermochemical data from bond scission and recombination studies of simple alkanes and radicals over thermochemical data from ionization and bromination studies, has recommended values for the heats of formation of a number of alkyl radicals including $C_3H_7$ and $t-C_6H_{13}$. Our value for $\Delta H^0_f(C_2H_5)$ is 0.5 kcal mol$^{-1}$ larger than the value recommended by Tsang, although in agreement within combined uncertainties. Our value for $\Delta H^0_f(t-C_6H_{13})$ is 0.2 kcal mol$^{-1}$ smaller than the value recommended by Tsang under the assumption that all barriers to internal rotation are zero but 1.1 kcal mol$^{-1}$ larger than the value recommended by Tsang under the assumption that all internal rotation barriers are 2.4 kcal mol$^{-1}$; a recent ab initio calculation\textsuperscript{26} predicts that the barriers to methyl rotation are 1.51 kcal mol$^{-1}$. The alkyl radical heats of formation reported in this study are significantly higher than those recommended by McMillen and Golden\textsuperscript{27} in a critical review which showed a preference for results from ionization and bromination studies over those from bond scission and recombination studies; as discussed in detail by Gunman and co-workers,\textsuperscript{1,28} the apparently incorrect assumption by McMillen and Golden of small positive activation energies for alkyl + HX reactions appears to completely account for the discrepancy. As discussed above, Müller-Markgraf et al.\textsuperscript{18} observe a significant positive activation energy for reaction 7; hence, these authors derive a value for $\Delta H^0_f(r-C_6H_{13})$ which is 2.9 kcal mol$^{-1}$ lower than the value reported in this study.

Mechanism for Alkyl + HX Reactions. Traditionally, hydrogen-transfer reactions such as $R + HX \rightarrow RH + X$ have been thought of as "direct" metathesis reactions with a barrier along the reaction coordinate and a single transition state located at the potential energy maximum. Rationalization of observed negative activation energies for $R + HX$ reactions requires the postulate that reaction proceeds via formation of a weakly bound $R-HX$ ($k$ = 4.12 kcal mol$^{-1}$) as shown by Mzejurkewich and Benson.\textsuperscript{40} If the transition state leading from reactants to complex (TS1) is loose and the transition state leading from complex to products is both tighter and lower in energy compared to TS1, then a negative temperature dependence for the overall reaction should be observed. McEwen and Golden\textsuperscript{12} have carried out a two-channel RRKM calculation that models the $r-C_6H_{13} + HX(DI)$ reactions as proceeding through a weakly bound complex; they were able to reproduce the kinetic results of Seestula et al.\textsuperscript{41} for $r-C_6H_{13} + HX$ with complex binding energies as low as 3 kcal mol$^{-1}$. One interesting aspect of McEwen and Golden's study is the fact that models which were capable of reproducing experimentally observed $k(T)$ values for $r-C_6H_{13} + HI$ also predicted an inverse kinetic isotope effect (KIE), i.e. $k_{HI} < k_{HBr}$; the inverse KIE results from the fact that the transition state leading from complex to products becomes looser with the lower vibrational frequencies associated with deuterium substitution. Contrary to McEwen and Golden's predictions for $r-C_6H_{13} + HI$, we observe normal KIEs for $CH_3$, $C_2H_5$, and $r-C_6H_{13}$ reactions with HBr, i.e. $k_{HBr} > k_{H}$; Richards et al.\textsuperscript{14} also observe a normal KIE for the $r-C_6H_{13} + HBr$ reaction. It does appear, however, that the magnitude of the KIE is reduced as the activation energy becomes more negative i.e., the observed KIE is largest for $R = CH_3$ and smallest for $R = r-C_6H_{13}$. Further experimental and theoretical studies of alkyl + HX reaction dynamics are clearly needed before a detailed understanding of these complex chemical reactions will be forthcoming.

Acknowledgment. We thank P. W. Seakins and M. J. Pilling for making their results on $Br + C_2H_5$, $Br + (CH_3)CH_2$, and $r-C_6H_{13} + HBr$ available to us before publication and J. A. Manion and D. M. Golden for calculation of $r-C_6H_{13}$ thermodynamic functions. We also thank D. M. Golden and D. Gutman for several helpful discussions. This work was supported by Grants ATM-8802386 and ATM-9104807 from the National Science Foundation and Grant NAGW-1001 from the National Aeronautics and Space Administration.

Note Added in Proof. We have recently become aware of a theoretical study of the $CH_3 + HBr$ reaction by Chen, Tschiukow-Roux, and Rauk; two of the authors (N.N. and J.G.) of this paper are involved in this work. These authors have calculated a potential energy surface for the $CH_3 + HBr$ reaction at the G1 level of theory and deduced the existence of a hydrogen-bridged complex with $C_2$ symmetry which is bound by 0.28 kcal mol$^{-1}$ and is formed without activation energy. They have also calculated rate constants for $CH_3 + HBr$, $CH_3 + DBr$, and $CD_3 + HBr$ from RRKM theory with corrections for tunneling evaluated using the Wigner method. Their calculated isotopic effects agree quantitatively with those reported in this paper.

Registry No. $IC_3H_{15}$: 74-88-4; $IC_7H_{15}$: 75-03-6; $I-C_7H_{15}$: 558-17-8; $Cl_2H$: 7782-50-5; $CH_2H$: 74-82-8; $HCH_3$: 74-84-0; $HBr$: 10035-10-6; $CH_3$: 2025-36-1; $r-C_6H_{13}$: 1605-73-8; H: 1323-74-0. D. 7782-33-0.

Kinetics and Thermochemistry of the Br(2P3/2) + NO2 Association Reaction

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A laser flash photolysis–resonance fluorescence technique has been employed to study the kinetics of the Br(2P3/2) + NO2 association reaction as a function of temperature (259–432 K), pressure (12.5–700 Torr), and buffer gas identity (He, Ar, H2, N2, CO, CO2, SF6). The reaction is found to be in the falloff regime between first and second order over the entire range of conditions investigated. At temperatures below 350 K, the association reaction is found to be irreversible on the time scale of the experiment (~30 ms). At higher temperatures reversible addition is observed, allowing equilibrium constants for BrNO2 formation and dissociation to be determined. Second- and third-law analyses of the equilibrium data are in only fair agreement and lead to the following thermochemical parameters for the association reaction: ΔHf,BrNO2 = −19.6 ± 1.7 kcal mol⁻¹, ΔHf,KNO2 = −18.6 ± 2.0 kcal mol⁻¹, ΔSf,KNO2 = −29.3 ± 4.2 cal mol⁻¹ K⁻¹; ΔHf,Br(NO2) = 17.0 ± 1.8 kcal mol⁻¹ (uncertainties are 2σ estimates of absolute accuracy). The value for ΔHf,K determined in this study has been employed to calculate k2, the low-pressure third-order rate coefficient in the strong collision limit, by using the method of Troe. Calculated values of k2 are inconsistent with experimental results unless ΔHf,K is assigned a value near the lower limit derived from analysis of the high-temperature data. These studies have established the gas-phase kinetics for BrNO2 and the absolute entropy of BrNO2 results from the complete lack of knowledge of the energies and degeneracies of the electronic states of BrNO2. The procedure developed by Troe and co-workers has been employed to extrapolate experimental falloff curves to the low- and high-pressure limits. Derived values for k4,M(298K) are estimated to be in the falloff regime between third and second order over the entire pressure range investigated. At temperatures above 350 K, bromine atom regeneration from BrNO2 decomposition occurred on the experimental time scale for reaction 1, i.e., 10⁻³ to 10⁻⁴ s. Analysis of the resultant double-exponential decays has allowed the first determinations of both BrNO2 unimolecular dissociation rate coefficients and the BrNO2 heat of formation.

Introduction

The reactions of fluorine and chlorine atoms with NO2 have been studied extensively in cryogenic matrices and in the gas phase.11 These studies have established the gas-phase kinetics of the F + NO2 association reaction22 and have demonstrated that both the nitrite (XONO) and the nitryl halide (XNO2) isomers are produced.12 Under atmospheric conditions, CiONO is the major product of the Cl + NO2 reaction; the CINO2 yield is only about 0.2.4 Until very recently, the only information about the reaction

Br(2P3/2) + NO2 + M → BrNO2 + M

(1a)

→ BrONO + M

(1b)

came from cryogenic matrix studies,13,14 which demonstrated that BrNO2 is the dominant product, i.e., k1 >> k1b; this observation has now been extended to the gas phase.14 Another gas-phase BrNO2 reaction has recently been observed as a product of the heterogeneous reaction of NO2 vapor with solid NaBr.15 Nitryl bromide could act as a reservoir for Br2O in the lower stratosphere, and it has recently been suggested16 that photolysis of Br2O (formed via the N2O3(g) + NaBr(s) reaction) may initiate chain reactions that result in the recently observed ground-level arctic ozone hole.17,18 Hence, there currently exists a great deal of interest in understanding the reaction kinetics, photochemistry, and thermochemistry of nitryl bromide.

The only reported kinetic study of reaction 1 is the work of Mellouki et al.19 who employed a discharge flow technique with EPR and mass spectrometric analysis to measure k1, at 298 K in helium buffer gas over the pressure range 0.6–2.1 Torr; they report the low-pressure limit rate coefficient k1He(298K) = (3.7 ± 0.7) × 10⁻³¹ cm⁶ molecule⁻² s⁻¹.

In this paper, we report the results of an experimental study that employed the laser flash photolysis–resonance fluorescence technique to study the kinetics of reaction 1 over a wide range of temperatures (259–432 K), pressure (12.5–700 Torr), and buffer gas identity (N2, He, Ar, H2, CO, CO2, SF6). These data allow accurate values for k1(P,T) to be obtained over the pressure–temperature regime of atmospheric interest and provide the first data that can be used to estimate (with a rather large uncertainty) k1, the rate coefficient in the high-pressure limit. At temperatures above 350 K, bromine atom regeneration from BrNO2 decomposition occurred on the experimental time scale for reaction 1, i.e., 10⁻³ to 10⁻⁴ s. Analysis of the resultant double-exponential decays has allowed the first determinations of both BrNO2 unimolecular dissociation rate coefficients and the BrNO2 heat of formation.

(14) Yarwood, G.; Niki, H., private communication.

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The Br(P3/2) + NO2 Association Reaction

Experimental Technique

A schematic diagram of the laser flash photolysis-resonance fluorescence apparatus, as configured for bromine atom detection, is shown elsewhere. A description of the experimental methodology is given below.

A Pyrex-jacketed reaction cell with an internal volume of 150 cm³ was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol or methanol from a thermostatically controlled bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket was injected into the reaction zone through a vacuum seal, thus allowing measurement of the temperature inside the reaction cell but transmitted the strong bromine lines to the photomultiplier.

Bromine atoms were produced by 266-nm pulsed laser photolysis of CF2Br2/NO2/M or Br2/NO2/M mixtures; a majority of experiments employed a CF2Br2 as the bromine atom precursor. Fourth harmonic radiation from a Quanta Ray Model DCR-2 Nd:YAG laser provided the photolytic light source. The laser could deliver up to 3 × 10^16 photons/pulse at a repetition rate of up to 10 Hz; the pulse width was 6 ns.

A bromine resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the photolytically produced atoms. The resonance lamp consisted of an electrode less microwave discharge through about 1 Torr of a flowing mixture containing a trace of Br2 in helium. The flows of a 0.2% Br2 in helium mixture and pure helium into the lamp were controlled by separate needle valves, thus allowing the total pressure and Br2 concentration to be adjusted for optimum signal-to-noise ratio. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell, the lamp output passed through a flowing gas filter containing 50 Torr cm of methane in nitrogen. The methane filter prevented radiation at wavelengths shorter than 140 nm (including impurity emissions from excited oxygen, hydrogen, chlorine, and nitrogen atoms) from entering the reaction cell but transmitted the strong bromine lines in the 140-160 nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and the resonance lamp beam and was imaged onto the photocathode of a solar blind photomultiplier. Signals were processed by using photon-counting techniques in conjunction with multichannel scaling. For each bromine atom decay measured, signals from a number of laser shots were averaged in order to obtain a well-defined temporal profile over (typically) three 1/6 times of decay.

To avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reaction cell was in the range 1-3 cm s⁻¹, and the laser repetition rate was varied over the range 1-10 Hz (5 Hz typical). Hence, no volume element of the reaction mixture was subjected to more than a few laser shots. CF2Br2, Br2, and NO2 were flowed into the reaction cell from bulbs (12-L volume) containing dilute mixtures in buffer gas. The photolyte (CF2Br2 or Br2) mixture, NO2 mixture, buffer gas, and a small amount of hydrogen were premixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The concentration of NO2 in the reaction mixture was also determined by in situ UV photometry at 366 nm. A mercury pen-ray lamp was employed as the light source for the photometric measurement, and an interference filter was used to isolate the three closely spaced Hg lines around 366 nm from other lamp emissions. For the lamp-filter combination employed, the "effective" NO2 absorption cross section has been previously determined to be 5.75 × 10⁻⁹ cm² molecule⁻¹ s⁻¹. Since the equilibrium concentration of Br(P3/2) is negligible over the temperature range of our study, all measured bromine atom temporal profiles should be considered as representative of removal of ground-state atoms, Br(P3/2); in the discussion that follows Br = Br(P3/2).

All experiments were carried out under pseudo-first-order conditions with NO2 in large excess over Br. Hence, in the absence of side reactions that remove or produce Br, the Br temporal profile following the laser flash would be described by the relationship

\[
\text{ln} \left( \frac{[\text{Br}]_0}{[\text{Br}]} \right) = (k_I[\text{NO2}] + k_d) t = k' t
\]

where \(k_d\) is the rate coefficient for the process

\[
\text{Br} \rightarrow \text{first-order loss by diffusion from the detector field of view and/or reaction with background impurities (8)}
\]

References:


Supplementary Information:


Absorption cross sections for Br2 at 266 nm are ~2 × 10⁻²⁰ cm² and 2.7 × 10⁻²⁰ cm², respectively. To minimize production of NO from the side reaction

\[
O + NO_2 \rightarrow NO + O_2
\]

rather large concentrations of CF2Br2 (or Br2) and low laser powers were typically employed. Observed kinetics were independent of laser power and photolyte concentration over wide ranges; concentrations of photolytically produced bromine atoms ranged from 3 × 10⁻⁶ to 30 × 10⁻⁶ atoms cm⁻³. Observed kinetics were also found to be independent of whether reaction 2 or reactions 3-5 was employed as the bromine atom source.

To ensure rapid relaxation of bromine atoms in the spin–orbit excited Br(P3/2) state, about 1 Torr of H2 was added to the reaction mixture. The reaction

\[
\text{Br}(P_{3/2}) + N_2(298 \text{K}) \rightarrow \text{Br}(P_{3/2}) + H_2(298 \text{K})
\]

is known to be fast, with \(k \approx 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). Since the equilibrium concentration of Br(P3/2) is negligible over the temperature range of our study, all measured bromine atom temporal profiles should be considered as representative of removal of ground-state atoms, Br(P3/2); in the discussion that follows Br = Br(P3/2).

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\]


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over a mathematical expression that an be used to compute k,([N, ,T)

studies were restricted to T z 259 K because NO 2 dimerization

coefficient nu, k,([M],T), are summarized in Table I. Kinetics

purposes of atmospheric modeling, it is convenient to generate

became a problem at lower temperatures.21

are shown in Figures 1 and 2. Measured bimolecular rate

creased linearly with increasing [NO 2] but was independent of

were

suggest that reactions I and 8 are, indeed, the only processes that

in laser photon fluence and photolyte concentration strongly

linear dependence of k’ on [NO 2], and invariance of k’ to variation

in laser photon fluence and photolyte concentration strongly

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significantly affect the Br time history.

Kinetics at T < 350 K. For all experiments carried out at

temperatures below 350 K, well-behaved pseudo-first-order kinetics

were observed, i.e., Br temporal profiles obeyed eq 1, a linear dependence of k’ on [NO 2], and invariance of k’ to variation in laser photon fluence and photolyte concentration strongly suggest that reactions 1 and 8 are, indeed, the only processes that significantly affect the Br time history.

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were observed, i.e., Br temporal profiles obeyed eq 1, a linear dependence of k’ on [NO 2], and invariance of k’ to variation in laser photon fluence and photolyte concentration strongly suggest that reactions 1 and 8 are, indeed, the only processes that significantly affect the Br time history.

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Parametrization of k,([N 2],T) for Atmospheric Modeling. For purposes of atmospheric modeling, it is convenient to generate a mathematical expression that can be used to compute k,([N 2],T) over the range of relevant temperatures and pressures (the effi-
The Br$^{(3P)}$ + NO$_2$ Association Reaction

\[ A = 4.24 \times 10^{-31} (T/300)^{1/2} \text{cm}^3 \text{molecule}^{-2} \text{s}^{-1} \]
\[ B = 2.65 \times 10^{-18} (T/300)^{3/2} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \]

Falloff curves calculated by substituting the above parameters into eq II are compared with measured rate coefficients in Figure 3; the parametrization represents the experimental data very well.  

Kinetics at $T > 350$ K. At temperatures above 350 K, bromine atom regeneration due to a secondary reaction became evident.  

Observed Br temporal profiles were independent of laser fluence and CF$_3$Br$_2$ concentration but varied as a function of [NO$_2$] and [M] in the manner expected if unimolecular decomposition of BrNO$_2$ was the source of regenerated Br. Assuming that BrNO$_2$ regeneration was occurring, the relevant kinetic scheme controlling Br removal includes not only reactions 1 and 8 but also the additional reactions:

\[
\text{BrNO}_2 + M \rightarrow \text{Br} + \text{NO}_2 + M
\]  

(1)

BrNO$_2$ → first-order loss by processes that do not regenerate Br atoms (9)

Assuming that all processes affecting Br and BrNO$_2$ concentrations are first order, the rate equations for reactions 1, 1, 8, and 9 can be solved analytically:

\[
\left[ \text{Br} \right] / \left[ \text{Br} \right]_0 = \left[ \left( Q + \lambda_1 \right) \exp (\lambda_1 t) - \left( Q + \lambda_2 \right) \exp (\lambda_2 t) \right] / (\lambda_1 - \lambda_2)
\]

(V)

where

\[
\lambda_1 = 0.5 \left[ (a^2 - 4b)^{1/2} - a \right]
\]

(VI)

\[
\lambda_2 = -0.5 \left[ (a^2 - 4b)^{1/2} - a \right]
\]

(VII)

\[
Q = k_{1,1} + k_9
\]

(VIII)

\[
a = Q + k_4 + k_9,[\text{NO}_2] = -(\lambda_1 + \lambda_2)
\]

(IX)

\[
b = k_4 Q + k_9 k_1 [\text{NO}_2] = \lambda_1 \lambda_2
\]

(X)

Observed temporal behaviors for Br atoms were fit to the double-exponential eq V by using a nonlinear least-squares method to obtain values for $\lambda_1$, $\lambda_2$, and $Q$ for each decay. The background Br atom loss rate in the absence of NO$_2$ ($k_9$) was directly measured at each temperature and pressure; $k_4$ ranged from 10 to 90 s$^{-1}$.  

Rearrangement of the above equations shows that the fit parameters $\lambda_1$, $\lambda_2$, and $Q$ can be related to the rate coefficients of interest as follows:

\[
k_1 = -(Q + k_4 + \lambda_1 + \lambda_2)/[\text{NO}_2]
\]

(XI)

\[
k_9 = (\lambda_1 \lambda_2 - k_4 Q)/k_1 [\text{NO}_2]
\]

(XII)

\[
k_{1,1} = Q - k_4
\]

(XIII)

Typical Br atom temporal profiles observed in the high-temperature experiments are shown in Figure 4 along with best fits to eq V.  

The results for all high-temperature experiments are summarized in Table II. The equilibrium constants, $K_p$, given in Table II are computed from the relationship

\[
K_p = k_{1,1}/k_9 RT = K_{1,1} RT
\]

(XIV)

It is worth noting that values for $k_1([\text{NO}_2], T)$ obtained from the least-squares analyses are consistent with those expected based on extrapolation of data from $T < 350$ K. We believe that reported values for $k_1$, even at high temperature where Br regeneration is fast, are accurate to within ±20%. Absolute uncertainties in reported values for $k_1$ are somewhat more difficult to assess. Inspection of Table II shows that the precision in multiple determinations of $k_{1,1}$ at a particular temperature and pressure (for varying [NO$_2$]) is quite good, even at low T and low P, where $k_4$ contributes about as much as $k_9$ to the parameter $Q$.  

An inherent assumption in our analysis is that the only significant BrNO$_2$ loss process that results in Br atom production is reaction 1; as long as this assumption is correct (it almost certainly is), we believe the absolute accuracy of our reported $k_{1,1}$ values is ±30% over the full range of temperature and pressure investigated.

Figure 4. Typical Br$^{(3P)}$ Br temporal profiles observed at $T > 350$ K. Experimental conditions: $T = 411$ K, $P = 30$ Torr, $M =$ N$_2$, CF$_3$Br$_2$.  

Figure 5. van't Hoff plot for the reaction Br + NO$_2$ → BrNO$_2$. The small numbers inside the data points indicate the number of individual experiments that were averaged to obtain the particular point. The solid line is obtained from a weighted least-squares analysis and gives the second-law thermochmical parameters $\Delta H_m = -18.64 \pm 0.49$ kcal mol$^{-1}$ (slope) and $\Delta S_m = -26.94 \pm 1.40$ cal mol$^{-1}$ deg$^{-1}$ (intercept). The dotted line is obtained from a third-law analysis with $K_p$ at 401 K assigned the value obtained by interpolation using the second-law method; third-law thermochmical parameters are $\Delta H_m = -20.77$ kcal mol$^{-1}$ and $\Delta S_m = -32.24$ cal mol$^{-1}$ deg$^{-1}$. 

BrNO$_2$ Thermochemistry. A van't Hoff plot for the equilibrium defined by reactions 1 and 1 is shown in Figure 5. Since

\[
\ln K_p = (\Delta S/\text{R}) - (\Delta H/\text{RT})
\]

(XV)

the enthropy change associated with reaction 1 is obtained from the slope of the van't Hoff plot while the entropy change is ob-
TABLE II: Results of the Br + NO₂ + N₂ → BrNO₂ + N₂ Approach-to-Equilibrium Experiments

<table>
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<tr>
<th>T</th>
<th>P</th>
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<th>BrBr₂</th>
<th>NO₂</th>
<th>Q</th>
<th>-λ₁</th>
<th>-λ₂</th>
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</table>

*Units are as follows: T; K; P, Torr; concentrations, 10⁻³/cm³; Q, 10⁻¹⁷/cm³ K; λ; k₄, k₅, k₆, k₇; kₛ, 10⁻¹⁷/cm³ molecule⁻¹ s⁻¹; Kₛ, atm⁻¹.

*BrNO₂* is planar with an N-Br bond length of 2.1 Å, N-O bond lengths of 1.2 Å, and an O-N-O bond angle of 125°; these estimates are expected to be reasonably accurate. In the presence of information about *BrNO₂* electronic states, we assumed that the electronic contribution to the *BrNO₂* entropy is zero, i.e., a singlet ground state with no low-lying excited states. All parameters used in the calculation of the entropy change for reaction 1 are summarized in Table III.

The entropy change calculated from the third-law analysis, ΔSₘₐₓ = -32.24 cal mol⁻¹ K⁻¹, differs substantially from the entropy change obtained from the second-law analysis (see above). Hence, the value for ΔHₘₐₓ obtained from the third-law analysis, ΔHₘₐₓ = -20.77 kcal mol⁻¹, differs by 2.13 kcal mol⁻¹ from the value obtained from the second-law analysis. The major source of uncertainty in the calculation of ΔS appears to be in the electronic contribution to the *BrNO₂* entropy. For example, if the ground electronic state of *BrNO₂* were assumed to be a triplet rather than a singlet, the difference between the second- and third-law en-
The Br(2P3/2) + NO2 Association Reaction


TABLE III: Molecular Parameters Used in Calculations of ΔS and k1,0SC

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<thead>
<tr>
<th>Species</th>
<th>ν, cm⁻¹</th>
<th>g ₀</th>
<th>g ₁</th>
<th>E₀, kcal mol⁻¹</th>
<th>I, amu Å²</th>
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* g₀, g₁ = degeneracies of the ground and first excited electronic states, respectively. * E₀ = energy difference between the ground and first excited electronic states. * BrNO2 structure estimated based on information for CINO2, CINO2, and BrNO from ref 31 (see text). * Estimated based on parameters for CINO2 and BrONO2 given in ref 32.

The tropics would be reduced from 5.30 to 3.12 cal mol⁻¹ K⁻¹. Until the source of the difference between the second- and third-law results is better understood, it seems prudent to report the average of the two values and adjust error limits so as to encompass all reasonable possibilities. Using this approach, we report ∆H₂⁹₀ = -19.7 ± 1.7 kcal mol⁻¹ and ∆S₂⁹₀ = 29.6 ± 4.2 cal mol⁻¹ K⁻¹, where the errors are 2σ estimates of absolute accuracy.

The parameters in Table III have been employed to correct the above enthalpies and entropies to 298 and 0 K values. We obtain the following results: ∆H₂⁹₀ = -19.6 ± 1.7 kcal mol⁻¹, ∆H₂⁹₀ = -18.6 ± 2.0 kcal mol⁻¹ (the Br-NO₂ bond dissociation energy), ∆S₂⁹₀ = -29.3 ± 4.2 cal mol⁻¹ K⁻¹. In conjunction with known heats of formation for Br and NO₂,¹¹ our value for ∆H₂⁹₀ leads to the result of ∆H₂⁹₀(BrNO₂) = 17.0 ± 1.8 kcal mol⁻¹. Uncertainties in the above thermochemical parameters are 2σ and include both precision and estimates of systematic errors.

Comparison of Theoretical k₁,0SC with Experiment. Since reaction 1 appears to be a barrierless process, our experimental value for -ΔH₁⁹₀ can be equated with E₀, the critical energy for BrNO₂ dissociation. Hence, our experimental value for ∆H₁⁹₀ can be employed to calculate k₁,0SC, the low-pressure limit value for k₁ in the "strong collision" limit, which is related to k₁,0 via the relationship

\[ k₁,0 = \beta k₁,0SC \] (XVI)

where \( \beta \) is the collisional efficiency (0 < \( \beta \) < 1). For collisions of an energized adduct with N₂ at 298 K, \( \beta \approx 0.3 \) is typical.⁴²

On the basis of analytical solutions of the master equation for an exponential collision model, it has been shown⁴¹ that the temperature dependence of \( \beta₁ \) can be approximated by the expression

\[ \beta₁ = \beta₀(1 - \beta₁ T/2) \] (XVII)

where \( \beta₀ \) is the average energy removed from the energized adduct per collision and \( F₂ \) is given by the expression⁴²

\[ F₂ = \sum \left( \frac{RT}{s(s-1)} \right) \left( \frac{1}{E₂ + \alpha(E₂)} \right) \] (XVIII)

where \( s \) is the number of adduct vibrational degrees of freedom, \( \alpha(E₂) \) is the Whitten-Rabinovich parameter, and \( E₂ \) is the adduct zero-point energy, for BrNO₂ = 6, 18.6 kcal mol⁻¹ (as determined in this study), \( \alpha(E₂) = 0.949 \), and \( E₂ = 7.441 \) kcal mol⁻¹. We have employed eq XVIII to calculate the temperature

**TABLE IV: Comparison of Theoretical and Experimental Low-Pressure Third-Order Rate Coefficients k₁,0(N₂,T)**

<table>
<thead>
<tr>
<th>( E_0 ), kcal mol⁻¹</th>
<th>16.6</th>
<th>20.6</th>
<th>259.26 K</th>
<th>298.26 K</th>
<th>346.26 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta k₁,0SC ), 10⁻¹² cm³ molecule⁻¹ s⁻¹</td>
<td>1.27</td>
<td>0.94</td>
<td>0.73</td>
<td>0.52</td>
<td>0.36</td>
</tr>
</tbody>
</table>

* \( \beta(N₂,298K) \) assumed to be 0.3; temperature dependence of \( \beta₁ \), calculated from eq XVII with (\( \Delta E \)) assumed to be temperature independent.

The methodology employed to calculate \( k₁,0SC \) was developed by Troe,¹³,³³ the relevant equations are summarized in a "user-friendly" form by Patrick and Golden.³² Values for \( k₁,0SC \) have been calculated for N₂ buffer gas at the three experimental temperatures 259, 298, and 346 K and for three choices of I₀. The temperature dependence of \( k₁,0SC \) can be approximated by the expression

\[ k₁,0 = \beta_0(1 - \beta_1 T/2) \] (XVII)

where \( \beta_0 \) is the average energy removed from the energized adduct per collision and \( F_k \) is given by the expression

\[ F_k = \sum \left( \frac{RT}{s(s-1)} \right) \left( \frac{1}{E_k + \alpha(E_k)} \right) \] (XVIII)

where \( s \) is the number of adduct vibrational degrees of freedom, \( \alpha(E_k) \) is the Whitten-Rabinovich parameter, and \( E_k \) is the adduct zero-point energy, for BrNO₂ = 6, 18.6 kcal mol⁻¹ (as determined in this study), \( \alpha(E_k) = 0.949 \), and \( E_k = 7.441 \) kcal mol⁻¹. We have employed eq XVIII to calculate the temperature

of bound excited states falls rapidly as the size of the system increases due to the much steeper increase of state density with internal energy for molecules with more degrees of freedom. For a four-atom system such as BrNO, reaction on an excited-state potential energy surface could contribute to $k_{11}$ if a bound, very low lying excited state existed. The existence of a reaction channel leading to formation of the BrONO isomer is another potential complication. Only the BrNO$_2$ isomer observed when Br and NO$_2$ are codeposited into argon matrices at ~10 K. Although near-ultraviolet photolysis of matrix isolated BrNO$_2$ does result in isomerization to BrONO, recent work by Yarwood and Nikiforov carried out a study where reaction products were monitored by STIR spectroscopy during UV photolysis of Br$_2$/NO$_2$ mixtures; they observed BrNO$_2$ as a reaction product but did not observe BrONO even though (by analogy with ClONO) the 1725-cm$^{-1}$ band of BrONO should have a strong Q branch and, therefore, be relatively easy to detect. Hence, the available evidence argues against the existence of a significant channel for BrONO formation.

**Extrapolation of Experimental Results To Obtain $k_{11}$ and $k_{28}$**

Under all experimental conditions employed in this study, reaction 1 is found to be in the "falloff" region between third and second order. Troe and co-workers have shown that bimolecular rate coefficient versus pressure curves (i.e., falloff curves) for addition reactions can be approximated by the three-parameter equation

$$k([M],T) = k_0(T) F_{LH}(F([M],T)) \tag{XIX}$$

where $F_{LH}$ is the Lindemann–Hinshelwood factor:

$$F_{LH} = C/(1 + C) \tag{XX}$$

$$C = k_d(M,T)[M]/k_w(T) \tag{XI}$$

and $F([M],T)$ is a parameter that characterizes the broadening of the falloff curve due to the energy dependence of the rate coefficient for the decomposition of the energized adduct. $F([M],T)$ is the product of strong collision and weak collision broadening factors:

$$F([M],T) = F^SC([M],T) F^WC([M],T) \tag{XXII}$$

Both the strong collision and weak collision broadening factors are parametrized as a pressure-independent parameter raised to a pressure-dependent power:

$$F^SC([M],T) = F^SC_{c}(T)^{x([M],T)} \tag{XXIII}$$

$$F^WC([M],T) = F^WC_{c}(T)[M]^{x([M],T)} \tag{XXIV}$$

$$x([M],T) = ([\log C - 0.12]/(\log C + 0.12))^{1/1} \tag{XXV}$$

$$N^SC = 0.75 - 1.27 \log F^SC_{c}(T)$$

$$D = 0.1 + 0.6 \log F^SC_{c}(T)$$

$$\delta = +1 \text{ if } C > 1, \delta = -1 \text{ if } C < 1$$

$$x([M],T) = ([\log C - 0.12]/(\log C + 0.12))^{1/1} \tag{XXVI}$$

$$N^SC = 0.7 + 0.35 \delta - 0.25 \log \beta_4$$

$$D = \log C + 0.085 \delta - 0.17 \log \beta_4$$

$$\delta = -0.2 - 0.12 \log \beta_4$$

where the parameter $S_K$ in equation XXVI is defined below. $F^SC_{c}$ can be estimated from structural information about the adduct (Table III), where estimation of $F^SC_{c}$ requires knowledge of the efficiency of energy transfer between the energized adduct and the buffer gas.

Values for $F^SC_{c}$ have been determined by Luther and Troe in tabular form as a function of the reduced Kassel integral parameters $S_K$ and $B_K$. $S_K$ is given by the relationship

$$S_K = S_{em} + (E_{em} - E_0)/RT \tag{XXVII}$$

where $E_{em}$ is the Arrhenius activation energy for unimolecular decomposition of the adduct in the high-pressure limit (an ill-defined parameter) and $S_{em}$ is the effective number of transition-state oscillators. $S_{em}$ can be estimated from the vibrational partition function of the adduct molecule:

$$S_{em} = \sum_{n=1}^{\infty} \exp(\Delta V_{n}/kT) - 1 \tag{XXVIII}$$

The parameter $B_K$ is approximated by

$$B_K = B'(S_K - 1)/(T - 1) \tag{XXIX}$$

where

$$B' = (E_0 + a(E_0)E_0(RT)^{-1} \tag{XXX}$$

Although the value of $E_0$ is highly uncertain, for a barrierless process such as reaction 1, the relationship $S_K - S_{em} < 2$ is usually obeyed. Comparison of preliminary fits of the experimental data to eq XIX suggest that the values of $F^SC_{c}(T)$ calculated with $S_K - S_{em}$ set equal to 2 are more appropriate for modeling the falloff behavior of reaction 1 than are $F^SC_{c}(T)$ values calculated for lower values of $S_K - S_{em}$ ($F^SC_{c}(T)$ decreases with increasing $S_K - S_{em}$ and with increasing $T$). Hence, our falloff analysis assumes that $S_K - S_{em} = 2$.

To a good approximation, $F^WC_{c}(M,T)$ can be calculated from the expression

$$F^WC_{c}(M,T) = \beta(M,T)^{0.14} \tag{XXXI}$$

To apply eq XXXI, we fix $\beta(N_2,298 K)$ at a typical value of 0.32 employ eq XVII (with $\Delta E$ assumed temperature independent) to calculate $\beta(N_2, T)$, and employ equation XXXII to calculate $\beta(M,298 K)$:

$$\beta(M,298 K) = k_d(M,298 K)Z_{du}(N_2,298 K) \tag{XXXII}$$

$$\beta(M,298 K) = k_d(N_2,298 K)Z_{du}(M,298 K) \tag{XXXII}$$

In eq XXXII, $Z_{du}(M,T)$ is the Lennard-Jones collision frequency for BrNO$_2$–M encounters; it was calculated from the Lennard-Jones parameters in Table III by using a relationship given elsewhere. Equation XXXII requires knowledge of $k_d(M,T)$ in order to compute $\beta(M,T)$, which is then used to calculate $k_d(M,T)$. Clearly, an iterative procedure must be employed in order to arrive at internally consistent values for $\beta(M,T)$ and $k_d(M,T)$. However, because the low end of our experimental pressure range is very close to the low-pressure limit, nearly exact initial estimates of $k_d(M,298 K)/k_d(N_2,298 K)$ could be made.

Using calculated values for $F^SC_{c}(T)$ (with $S_K - S_{em}$ set equal to 2), we have determined the parameters $k_{11}(M,T)$, $k_{28}(T)$, and $F^WC_{c}(M,T)$ by fitting our data to eq XIX using a least-squares method subject to the constraints that (1) $k_d(M,T)$ must be independent of buffer gas identity, (2) $\beta(N_2,298 K)$ is 0.3, and (3) eqs XVII (with $\Delta E$ assumed temperature independent), XXXII, and XXIII must be obeyed. Falloff parameters obtained from the analysis are given in Table V. Best-fit falloff curves for $N_2$ buffer gas at 259 and 346 K, and for CF$_3$, N$_2$, and He buffer gases at 298 K are plotted and compared with experimental rate coefficients in Figures 6 and 7. Because all experimental data were obtained in the low-pressure half of the falloff curves, i.e., where $k_{11}(M,T)$ and $k_{28}(T)$ are much less sensitive to the choice of $F_{LH}$ than is the extrapolated value for $k_{11}(M,T)$, the absolute accuracy of our $k_{11}(M,T)$ values is quite good—we estimate the uncertainties to be ±20%. On the other hand, the absolute accuracy of $k_{28}(T)$ is estimated to be no better than a factor of 2, although the derived small positive activation energy for $k_{28}(T)$ is probably correct as long as reaction
proceeds predominantly on the ground electronic state surface. Smith has shown that recombination into even weakly bound excited electronic states of the adduct, particularly states with high vibrational energy, can grossly affect the shape of the falloff curve near the high-pressure limit. The falloff analysis described above is based on the assumption that excited electronic states of BrNO₂ play no role in the association process. As discussed above, comparison of thermochemical parameters obtained from second- and third-law analyses as well as comparison of theoretical values for k₁,SC with experiment lead to the suspicion that excited electronic states of BrNO₂ may indeed be important. Rate coefficient measurements of k₁ at high pressure along with ab initio calculations that characterize all low-lying bound electronic states of BrNO₂ are needed before the high-pressure behavior of k₁(T) can be considered well characterized.

Comparison with Previous Work. The only published study of Br + NO₂ kinetics with which to compare our results is the recent low-pressure study of Mellouki et al.¹⁹ These authors employed a discharge flow technique with EPR and mass spectrometric diagnostics to study reaction 1 at 298 K in helium buffer gas at pressures of 0.6–21 Torr. The bimolecular rate coefficients reported by Mellouki et al. are considerably faster than predicted based on extrapolation of our results to lower pressure. Mellouki et al. corrected their rate coefficients downward to account for Br removal via the fast secondary reaction

\[
\text{Br} + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2 \quad (10)
\]

and to account for Br removal by reaction 1 with NO₂ as the third body (both of these interferences were negligible under our experimental conditions) to obtain the termolecular rate coefficient k₁,SC(He,298 K) = \(3.7 \pm 0.7\) \(\times 10^{-11}\) cm³ molecule⁻² s⁻¹. We find that k₁,SC(He,298 K) = \(2.75 \pm 0.55\) \(\times 10^{-11}\) cm³ molecule⁻² s⁻¹. *Units are \(10^{-11}\) cm³ molecule⁻² s⁻¹.

Comparison of kinetic data for the homologous series of X + NO₂ reactions is of limited instructional value because the F + NO₂ and Cl + NO₂ reactions are thought to proceed primarily via channels that lead to the XNO₂ product, whereas the Br + NO₂ reaction seems to form exclusively the BrNO₂ isomer.¹²-¹⁴ No information is available concerning the isomer(s) that are formed from the I + NO₂ reaction. Reported k₁(M,T) values for the F + NO₂ and Cl + NO₂ reactions are faster by factors of 2–5 than the corresponding k₁(M,T) values reported in this study and by Mellouki et al.¹⁹ The I + NO₂ reaction follows the same trend: i.e. reported values of k₁(M,T) for I + NO₂ are slightly lower than the corresponding Br + NO₂ rate coefficients. All reported studies of F + NO₂ and Cl + NO₂ kinetics except one relative rate study by Glavas and Heicklen⁶ have been restricted to pressures \(\leq 200\) Torr of N₂ where only slight deviations from low-pressure-limit behavior were observed. Estimates of k₁(M,T) for both F + NO₂ and Cl + NO₂ have been obtained by using very approximate extrapolation procedures; the resulting k₁(M,T) values are \(3 \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹ for F + NO₂ and \(1 \times 10^{-10}\) cm³ molecule⁻¹ s⁻¹ for Cl + NO₂. Although these values for k₁ are used to compute rate coefficients over the high-pressure limit regime, their absolute uncertainties are large—probably a factor of 2 or greater. The best known k₁ value in the X + NO₂ series is for the I + NO₂ reaction. van den Bergh and Troe have studied the NO₂-catalyzed recombination of iodine atoms at 320–450 K and 1–200 atm of helium.⁴¹ From analysis of their data they obtained k₁(M,T) = \(6.6 \times 10^{-11}\) cm³ molecule⁻¹ s⁻¹, about a factor of 2 faster than our extrapolated value for k₁(298 K); in van den Bergh and Troe’s experiment, the high-pressure limit was not reached even at a pressure of 200 atm. It is worth noting that we actually obtained slightly better fits to our data when Fₑ values somewhat smaller than those summarized in Table V were employed; the k₁ values associated with these lower Fₑ values are higher than those summarized in Table V and in better agreement with the high-pressure I + NO₂ results of van den Bergh and Troe.⁴¹ We did not employ

\[
\Delta H^\circ _{298 K} = (2.75 \pm 0.55) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}.
\]

\[
\Delta H^\circ _{298 K} = (2.75 \pm 0.55) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}.
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\]

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\]

\[
\Delta H^\circ _{298 K} = (2.75 \pm 0.55) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-2} \text{ s}^{-1}.
\]
the lower \( P_1 \) values in our falloff analysis because they can only be rationalized if \( S_E - S_W \) is assumed to be larger than the "normal" upper limit value of 2. As mentioned above, the "true" value for \( k, (298 \text{K}) \) remains uncertain by at least a factor of 2.

Heats of reaction for the \( X + NO_2 \rightarrow XNO_2 \) reactions are summarized in Table VI. While the X-NO\(_2\) bond strengths decrease monotonically in the order \( F > Cl > Br \), the BrNO\(_2\) bond strength determined in this study is identical within experimental uncertainty to the INO\(_2\) dissociation energy determined by Troe and co-workers.\(^{11} \) It should be noted that the potential contribution of an IONO species to the iodine recombination experiments has yet to be adequately addressed.

**Summary**

The kinetics of the \( \text{Br}(P_2) + NO_2 \) association reaction have been investigated as a function of temperature (259–432 K), pressure (12.5–700 Torr), and bath gas identity (He, Ar, H\(_2\), N\(_2\), CO\(_2\), CF\(_4\), SF\(_6\)). At temperatures below 350 K, the association reaction is irreversible on the (∼30 ms) time scale of the experiment. The 21 rate coefficients obtained with N\(_2\) as the buffer gas were fit to the expression recommended by the NASA panel for chemical kinetics and photochemical data evaluation for use in parametrizing the pressure and temperature dependences of association reaction rate coefficients for atmospheric modeling purposes;\(^{20} \) the best-fit parameters are \( A = 4.24 \times 10^{11}(T/300)^{24} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}(\sim k,_{A}) \) and \( B = 2.66 \times 10^{-11}(T/300)^{26} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}(\sim k,_{B}) \).

At temperatures above 350 K, reversible addition has been observed. Rate coefficients for BrNO\(_2\) formation and decomposition have been determined over the temperature range 374–432 K. Second- and third-law analyses of the data yields somewhat different thermochemical parameters. The major uncertainty in the calculated third-law entropy change appears to be the electronic entropy of BrNO\(_2\). Averaging the second- and third-law results and choosing error limits to encompass all reasonable possibilities, we report the following thermochemical parameters for reaction 1: \( \Delta H^\circ_{\text{prod}} = -19.6 \pm 1.7 \text{ kcal mol}^{-1}, \Delta S^\circ_{\text{prod}} = -18.6 \pm 2.0 \text{ kcal mol}^{-1}, \Delta S^\circ_{\text{prod}} = -29.3 \pm 4.2 \text{ cal mol}^{-1} \text{ K}^{-1}, \Delta H^\circ_{\text{prod}} = -17.0 \pm 1.8 \text{ kcal mol}^{-1} \text{ (uncertainties are 2σ estimates of absolute accuracy)}.

Our experimental value for \( \Delta H^\circ_{\text{prod}} \) has been employed to calculate \( k,_{A}(T) \), the low-pressure rate coefficient in the strong collision limit, using the method of Troe.\(^{21} \) Calculated values for \( k,_{A}(T) \) are inconsistent with experimental results unless \( \Delta H^\circ_{\text{prod}} \) is assigned a value near the lower limit derived from the high-temperature data, i.e., 16.6 kcal mol\(^{-1}\). Systematic errors in the calculations could result from the assumptions that (a) reaction occurs entirely on the ground electronic state potential energy surface and (b) formation of the BrONO isomer is unimportant; experimental data are available that suggest that assumption b is valid,\(^{12-14} \) but no information is available to validate assumption a.

The procedure developed by Troe and co-workers\(^{21,30,37-39} \) has been employed to extrapolate experimental falloff curves to the low- and high-pressure limits. Derived values for \( k,_{A}(M,298 \text{K}) \) in units of \( 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) range from 2.75 for \( M = \text{He} \) to 6.54 for \( M = \text{CO}_2 \). Values for \( k,_{A}(N_2,T) \) in units of \( 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) are 3.73 at 259 K, 4.61 at 298 K, and 3.21 at 346 K; the temperature dependence of \( k,_{A}(N_2,T) \) is consistent with the theoretical temperature dependence for \( A k,_{A}(T) \). Values for \( k,_{A}(N_2,T) \) in units of \( 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \) are 2.86 at 259 K, 3.22 at 298 K, and 3.73 at 346 K. Uncertainties in derived values for \( k,_{A} \) are estimated to be ±20%, whereas uncertainties in derived values of \( k,_{A}(T) \) are considerably larger—a factor of 2 or more; however, the derived small positive activation energy for \( k,_{A}(T) \) is probably correct. Experimental data up to pressures of several hundred atmospheres and ab initio calculations that characterize the low-lying bound electronic states of BrNO\(_2\) are needed before the magnitude of \( k,_{A} \) can be considered well established.

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Thermochemistry and kinetics of the Cl + O₂ association reaction

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Laser flash photolysis of Cl₂/O₂ mixtures has been employed in conjunction with Cl(¹P₂) detection by time-resolved resonance fluorescence spectroscopy to investigate equilibration kinetics for the reactions Cl + O₂ → ClO₂ at temperatures of 181-200 K and O₂ pressures of 15-40 Torr. The third-order rate coefficient for the association reaction at 186.5 ± 5.5 K is (8.9 ± 1.9) x 10⁻¹³ cm⁶ molecule⁻² s⁻¹ and the equilibrium constant (Kₑ) at 185.4 K is 17.9 atm⁻¹ (factor of 1.7 uncertainty). A third law analysis of our data leads to a value for the Cl-O₂ bond dissociation energy of 4.76 ± 0.49 kcal mol⁻¹.

1. Introduction

The existence of the ClOO radical was first postulated by Porter and Wright [1] to explain ClO production following flash photolysis of Cl₂/O₂ mixtures.

\[
\begin{align*}
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl}, \quad (1) \\
\text{Cl} + \text{O}_2 + \text{M} & \rightarrow \text{ClOO} + \text{M} \quad (2) \\
\text{ClOO} + \text{M} & \rightarrow \text{Cl} + \text{O}_2 + \text{M}, \quad (2^-) \\
\text{Cl} + \text{ClOO} & \rightarrow 2\text{ClO}, \quad (3a) \\
& \rightarrow \text{Cl}_2 + \text{O}_2, \quad (3b) \\
\text{ClO} + \text{Cl} & \rightarrow \text{ClOO} \quad \text{products} \quad (4)
\end{align*}
\]

Subsequent flash photolysis work by Burns and Nornish [2] supports the above mechanism. An early thermochemical estimate by Benson and Buss [3] suggested that ClOO is a very weakly bound species with a bond dissociation energy, \( D_b (\text{ClOO}) \), of 8 ± 2 kcal mol⁻¹. The only kinetic information for reaction (2) comes from a flash photolysis study by Nicholas and Nornish [4]; these investigators measured temporal profiles for ClO appearance following flash photolysis of Cl₂/O₂ mixtures, and modeled their results using the mechanism suggested by Porter and Wright [1] (see above), to obtain the rate coefficient \( k_2 (298 \text{ K}) = 1.7 \times 10^{-23} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \) in N₂ + O₂ bath gas.

The ClOO radical was first observed directly by ESR spectroscopy in cryogenic matrices [5], although subsequent work [6-9] was needed to correct the misassigned spectrum as being due to ClOO rather than ClO. The first infrared spectroscopic observation of ClOO was reported by Arkell and Schwager [10], who found the fundamental vibrational frequencies to be 1441, 407, and 373 cm⁻¹. Arkell and Schwager produced ClOO by photolysis of Cl₂/O₂ and OClO cryogenic matrices. Direct observation of ClOO in the gas phase was first reported by Johnsson et al. [11]; these authors employed molecular modulation spectroscopy to observe both the ultraviolet and infrared spectra of ClOO, and to obtain kinetic information about reactions (3) and (4). More recent flash photolysis [12], molecular modulation [13], and theoretical [14-16] studies provide additional information concerning the branching ratio for reaction (3) as well as ClOO thermochemistry, structure, and excited electronic state energies. An evaluation of all published information leads to a recommended equilibrium constant for Cl + O₂ = ClOO of 2.3 x 10⁻²² exp(3000/T) cm⁶ molecule⁻¹, and a recommended third-order rate coefficient for reaction (2) of \( 2.0 \times 10^{-32} \times (T/300)^{-1/4} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \) [17].

While ClOO plays an important role in laboratory studies of ClO₂ chemistry, it has not been considered an important species in atmospheric chemistry. However, interest in the potential role of ClOO in
the chemistry of the lower stratosphere has increased dramatically in recent years with the realization that increasing levels of CIO in the atmosphere are largely responsible for the Antarctic ozone hole [18]. In the wintertime Antarctic lower stratosphere, heterogeneous reactions in polar stratospheric clouds (PSCs) can convert the reservoir species HCl and ClONO$_2$ into the photochemically more labile species Cl$_2$ and HOCI [19,20]. As a result, high levels of CIO are produced at the expense of HCl and ClONO$_2$, and catalytic odd oxygen destruction cycles involving the ClO+ClO [21] and BrO+ClO [22] rate-limiting reactions become very rapid; both of these cycles involve ClOO as an intermediate. Also, it has recently been suggested that OCIO photo-isomerization to ClOO may be an important mechanism for odd oxygen destruction under Antarctic springtime conditions [23], although the quantum yield for photo-isomerization may be too low for this process to be of atmospheric importance [24]. Under the low temperature, high pressure conditions which exist in the springtime Antarctic lower stratosphere, the currently recommended equilibrium constant [17] (see above) suggests that equilibrium ClOO levels exceed levels of Cl atoms. Hence, ClOO could play an important role in Antarctic stratospheric chemistry if its reactions with key species occur sufficiently rapidly.

In this study we report a series of kinetics experiments aimed at directly measuring $k_1$ and $k_{-2}$, and, therefore, the equilibrium constant ($=k_1/k_{-2}$). Our results suggest that both the association and dissociation reactions are faster, and that the Cl–OO bond is about 1 kcal mol$^{-1}$ weaker, than previously thought.

2. Experimental technique

All experiments involved coupling laser flash photolysis of Cl$_2$/O$_2$ mixtures with Cl atom detection by time-resolved resonance fluorescence spectroscopy. A complete description of the experimental technique can be found elsewhere [25]. Chlorine atoms were monitored using the closely spaced $^2$D$_{3/2,3/2}$–$^2$P$_{3/2}$ doublet at 118.9 nm; these transitions are in accidental coincidence with a "window" in the O$_2$ absorption spectrum.

The gases used in this study had the following stated minimum purities: O$_2$, 99.99%; Cl$_2$, 99.99%. Oxygen was used as supplied while chlorine was degassed at 77 K before use.

3. Results and discussion

In all experiments, Cl($^2$P$_J$) was produced by 355 nm pulsed laser photolysis of Cl$_2$. Both theoretical [26] and experimental [27] information suggests that photolysis of Cl$_2$ around 355 nm produces almost exclusively ground state chlorine atoms, Cl($^2$P$_{3/2}$); the fraction of photolytically generated atoms in the $^2$P$_{1/2}$ spin–orbit excited state is probably less than the equilibrium fraction, which is only $6 \times 10^{-4}$ at a typical experimental temperature of 190 K. Reported rate coefficients for quenching of Cl($^2$P$_{1/2}$) by O$_2$ in units of $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ are $210 \pm 50$ [28], $230 \pm 30$ [29], $1.7 \pm 0.4$ [30], and $1.3 \pm 0.3$ [31]. Based on observed reaction times (see table 1) it appears that Cl($^2$P$_{1/2}$) deactivation was faster than chemical reaction of Cl($^2$P$_J$) under our experimental conditions, though only by factors of three to six if the slower literature values for the deactivation rate [30,31] are correct. The above discussion suggests that although the fraction of Cl atoms in the $^2$P$_{1/2}$ state could have varied somewhat over the experimental time scale for Cl decay, this fraction was so small at all reaction times that observed reactivity can be attributed entirely to Cl($^2$P$_{3/2}$). Furthermore, negligible systematic error is introduced by the assumption that the observed temporal evolution of the Cl($^2$P$_{3/2}$) fluorescence signal is identical to the temporal evolution of the total chlorine atom population.

When Cl$_2$/O$_2$ mixtures are subjected to 355 nm laser flash photolysis and experimental conditions are maintained where radical–radical reactions are unimportant, i.e. low radical concentrations and short reaction times, the Cl atom temporal profile should be controlled by the following reactions:

$\text{Cl} + \text{O}_2 + \text{O}_2 = \text{ClOO} + \text{O}_2$, \hspace{1cm} (2, -2)

Cl–loss by diffusion from the detector field of view and reaction with background impurities, \hspace{1cm} (5)
### Table 1

Results of the \( \text{Cl} + \text{O}_2 + \text{O}_2 = \text{ClO}_2 + \text{O}_2 \) approach-to-equilibrium experiments

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<th>( p_{\text{He}} ) (Torr)</th>
<th>( \text{Concentrations} ) (10(^{11}) cm(^{-3}))</th>
<th>( Q ) (s(^{-1}))</th>
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\[
a = Q + k_3 + k_2 [O_2] = - (\lambda_1 - \lambda_2),
\]

\[
b = k_3 Q + k_4 k_2 [O_2] = \lambda_1 \lambda_2.
\]

CIOO→loss by processes that do not generate Cl.

The rate equations for the above scheme can be solved analytically as long as all Cl and C100 loss processes are first order.

\[
[\text{Cl}] / [\text{Cl}]_0 = (Q + \lambda_1 \exp(\lambda_1 t) - (Q + \lambda_2 \exp(\lambda_2 t))/ (\lambda_1 - \lambda_2),
\]

where

\[
\lambda_1 = 0.5((a^2 - 4b)^{1/2} - a),
\]

\[
\lambda_2 = -0.5((a^2 - 4b)^{1/2} + a),
\]

\[
Q = k_{-2} + k_6,
\]

A double-exponential decay is predicted. Good quality experimental data can be fit to eq. (7) to obtain values for three parameters \( \lambda_1, \lambda_2, \) and \( Q \). Values for \( k_5 \) can be estimated based on measurements in \( N_2 \) and \( O_2 \) buffer gases at temperatures (> 250 K) where equilibrium CIOO levels are negligible and on low temperature measurements in \( N_2 \) buffer gas; over the range of temperatures (181–200 K) and \( O_2 \) pressures (15–40 Torr) investigated, estimated values for \( k_5 \) range from 50 to 100 s\(^{-1}\). The elementary rate coefficients \( k_2, k_{-2}, \) and \( k_6 \) can be obtained from the fit parameters using the following relationships:
\[ k_2 = - (\lambda_1 + \lambda_2 + k_3 + Q)/[O_2], \]  
\[ k_6 = (\lambda_1 \lambda_2 - k_3 Q)/k_2 [O_2], \]  
\[ k_{-2} = Q - k_6. \]

It should be noted that the parameter \( Q \) represents the sum of all first-order ClOO removal processes. Therefore, eqs. (10) and (15) require the assumption that the only important ClOO loss process that regenerates Cl atoms is reaction \((-2)\); for the chemical system of interest, this assumption should be valid.

When mixtures containing 0.17-4.5 mTorr \( O_2 \) and 15-40 Torr \( O_3 \) were subjected to 355 nm laser flash photolysis, the expected double-exponential decays were observable, but only at very low temperatures, i.e. \( T \leq 200 \) K. A typical Cl temporal profile, observed at \( T = 182 \) K and \( p \approx 90 \) Torr, is shown in fig. 1. The solid line in fig. 1 represents the best fit of the data to eq. (7) while the dashed line represents the Cl temporal profile expected based on an evaluation of previously published results [17]; clearly, the approach of laser-flash generated Cl into equilibrium with ClOO is much faster than expected based on previous work while the equilibrium concentration ratio \([Cl]/[ClOO]\) is much higher than expected. These differences between observed and expected kinetic behavior (fig. 1) made this study experimentally much more difficult than we had anticipated. An experimental problem (the viscosity of the 50% methanol-50% ethanol cooling fluid) limited the accessible temperature regime to \( T > 180 \) K. The requirement that relatively large \( O_2 \) concentrations be employed in order to drive the equilibrium to significant ClOO production resulted in sensitivity problems, as did the short multichannel scaler dwell times which were required to observe the very rapid equilibration process. The above problems severely limited the range of temperatures and oxygen pressures where quantitative data could be obtained.

Summarized in table 1 are results derived from analyses of 28 Cl atom temporal profiles obtained under experimental conditions where double-exponential decays were observed. The equilibrium constants, \( K_p \), given in table 1 were computed from the relationship

\[ K_p = K_i/RT = k_2/k_{-2}RT. \]

Non-linear least squares analyses were employed to extract values for \( \lambda_1, \lambda_2, Q, \) and the extrapolated signal level at \( t = 0 \) from the experimental temporal profiles. Values for \( k_2, k_{-2}, k_6, \) and \( K_p \) were then calculated as described above.

Values for \( k_2 \) obtained from the 26 experiments at \( 181 < T < 192 \) K are plotted as a function of \( O_2 \) concentration in fig. 2 (although \( k_2 \) is expected to increase with decreasing temperature, it should change very little over the relatively narrow temperature range 181-192 K). The spread in the data results from the fact that, under the conditions of our experiments, reaction \((-2)\) typically contributed significantly to the rate of approach into equilibrium \( (= k_2 [O_2] + k_{-2}) \); hence, uncertainties in individual \( k_2 \) determinations are rather large. The solid line in fig. 2 is obtained from a linear least squares analysis of the \( k_2 \) versus \([O_2]\) data. As expected for a three atom system like \( Cl + O_2 \), the data are well represented by a straight line passing through the origin (the standard deviation of the intercept is ten times larger than the absolute value of the intercept), thus indicating that reaction \((2)\) is in its low pressure termolecular limit under our experimental conditions. The termolecular rate coefficient, \( k_2^H \), can be evaluated in two different ways. From the slope of the
Fig. 2. Plot of $k_2$ versus $[O_2]$ for all data obtained at temperatures between 181 and 192 K. The solid line is obtained from a linear least squares analysis and gives the termolecular rate coefficient $k^{III}_{2} = (8.8 \pm 2.5) \times 10^{-33}$ cm$^6$ molecule$^{-2}$ s$^{-1}$.

plot in fig. 2 we obtain $k^{III}_{2} = (8.8 \pm 2.5) \times 10^{-33}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. Alternatively, by simply averaging the 26 values of $k_2/[O_2]$, we obtain $k^{III}_{2} = (9.0 \pm 3.3) \times 10^{-33}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. Since we do not prefer one method of analysis over the other, and since we believe that systematic errors are small compared to uncertainties resulting from precision, we report the rate coefficient

$$k^{III}_{2} = (8.9 \pm 2.9) \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

at $T = 186.5 \pm 5.5 \text{ K}$, where the uncertainty is $2\sigma$ and represents absolute accuracy.

A van 't Hoff plot for the equilibrium defined by reactions (2) and (−2) is shown in fig. 3. Since

$$\ln K_p = \Delta S/R - \Delta H/RT$$

the enthalpy change associated with reaction (2) can, in principle, be determined from the slope of the van 't Hoff plot while the entropy change can, in principle, be determined from the intercept. However, because our experiments were limited to a rather narrow temperature range, this "second law" analysis gives rather imprecise results. The solid line in fig. 3 is obtained from a linear least squares analysis of the In $K_p$ versus $1/T$ data with all data points included; it yields the results $\Delta H^{0}_{90} = -5.15 \pm 1.41$ kcal mol$^{-1}$ and $\Delta S^{0}_{90} = -21.94 \pm 7.51$ cal mol$^{-1}$ deg$^{-1}$ (errors are $2\sigma$). The dashed line in fig. 3 is obtained from a linear least squares analysis which excludes the two data points at $T = 200$ K. It gives the result $\Delta H^{0}_{96} = -7.00 \pm 1.63$ kcal mol$^{-1}$ and $\Delta S^{0}_{96} = -31.92 \pm 8.74$ cal mol$^{-1}$ deg$^{-1}$ (errors are $2\sigma$). The error bar represents the estimated $2\sigma$ uncertainty in $K_p$ at 185.4 K.

A potentially more accurate approach for obtaining CIOO thermochemical parameters is the "third law" method, where the measured equilibrium constant at a particular temperature is employed in conjunction with a calculated entropy change to determine $\Delta H$. At 185.4 K, the temperature where the solid and dashed lines in fig. 3 cross, our experiments indicate that $K_p = 18.9$ atm$^{-1}$; the estimated $2\sigma$ uncertainty in $K_p$ (185.4 K) is a factor of 1.7 (see error bar in fig. 3). While high resolution spectroscopic data for CIOO are not available, reasonable structural parameters can be deduced from the estimates
of Arkell and Schwager [10] and from the SCF-MO calculations of Hinchliffe [15]. We assume a Cl-O bond length of 1.835 Å, an O-O bond length of 1.31 Å, and a Cl-O-O bond angle of 112.5°. The vibrational frequencies for ClOO, 373, 407, and 1441 cm⁻¹, are taken from infrared measurements in cryogenic matrices [10]; only the high frequency vibration, which does not contribute to the entropy at $T<300$ K, has been observed in the gas phase [11]. Ab initio calculations suggest that ClOO has a doublet ground state with no excited doublet or quartet states low enough in energy to contribute to the ClOO entropy at $T<300$ K [16]. Using the above information, we calculate $\Delta S^0_{185.4}$ (ClOO) = 59.52 ± 1.09 cal mol⁻¹ deg⁻¹ and $\Delta S^0_{185.4}$ (reaction (2)) = -23.18 ± 1.09 cal mol⁻¹ deg⁻¹. The uncertainty in $\Delta S^0$ (ClOO) is 2σ and is based on the following estimated uncertainties in the ClOO structural parameters and low frequency vibrations: O-O bond length, ±0.12 Å; Cl-O bond length, ±0.05 Å; bond angle, ±5°; each of the two low frequency vibrations, ±100 cm⁻¹. It is worth noting that the value we calculate for $\Delta S^0_{185.4}$ (ClOO), 64.50 cal mol⁻¹ deg⁻¹, is 1.50 cal mol⁻¹ deg⁻¹ larger than the value reported by Johnston et al. [11]. If we use the same ClOO bond angle and bond lengths in our calculation as Johnston et al. used in their calculation (those suggested by Arkell and Schwager [10]), the two results differ by almost exactly $R \ln 2$, i.e. the electronic contribution to the ClOO entropy.

Using our experimental value for $K_2$ at 185.4 K and our calculated value for $\Delta S^0_{185.4}$, we compute from eq. (17) the enthalpy change $\Delta H^0_{185.4}$ (reaction (2)) = -5.58 ± 0.41 kcal mol⁻¹. Making the appropriate heat capacity corrections, one obtains the results $\Delta H^0_{185.4}$ (reaction (2)) = -5.56 ± 0.47 kcal mol⁻¹ and $\Delta H^0_2$ (reaction (2)) = 4.76 ± 0.49 kcal mol⁻¹ (≈ the Cl-OO bond dissociation energy). In conjunction with known heats of formation for Cl and O₂ [32], our value for $\Delta H^0_{185.4}$ (reaction (2)) leads to a value of 23.4 ± 0.5 kcal mol⁻¹ for the ClOO heat of formation at 298 K, previous work has lead to a recommended ClOO heat of formation of 22.5 ± 1 kcal mol⁻¹ [17].

Literature data with which we can compare our results are sparse. The only published measurement of $k_2$ was reported over twenty years ago by Nicholas and Norrish [4]. Their experiment involved flash photolysis of Cl₂/O₂/N₂ mixtures. Complex analysis of the time-resolved production of ClO, measured by photographic recording of absorption in the UV region, was employed to extract a value for $k_2$. Nicholas and Norrish reported $k_2^{III} = (1.7 ± 0.3) \times 10^{-33}$ cm⁶ molecule⁻² s⁻¹ at 298 K in N₂+O₂ buffer gas, a factor of 5.2 slower than the value for $k_2^{III}$ determined in this study at 186.5 ± 5.5 K in O₂ buffer gas. If both determinations of $k_2^{III}$ are correct, and if N₂ and O₂ are assumed to be equally efficient at stabilizing the ClOO adduct, then the activation energy for reaction (2) is -1.6 kcal mol⁻¹, i.e. somewhat smaller than one would "guesstimate" [17] but within the range of reasonable values. There are no quantitative kinetic data for reaction (-2) in the literature, though values for $k_2^{III}$ have been estimated by several groups [11-13] using measured equilibrium constants in conjunction with the value for $k_2^{III}$ reported by Nicholas and Norrish [4]; these estimates range from $(2.55-4.67) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K. Our data give $k_2^{III} = 1.8 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 185 K. Assuming that the activation energy for reaction (2) is -1 ± 1 kcal mol⁻¹ and using our measured enthalpy of reaction of -5.47 ± 0.44 kcal mol⁻¹ (averaged over the range 180-300 K), we estimate the activation energy for reaction (-2) to be 6.5 ± 1.4 kcal mol⁻¹. This leads to a best estimate for $k_2^{III}$(298 K) of $(1.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, i.e. 30-55 times faster than previous estimates [11-13]. In a recent study of ClOOCl photochemistry, Molina et al. also report evidence that ClOO decomposition is faster than previously thought [33].

Published values for $k_2$(298 K) are based on analyses of ClOO and ClO temporal behavior in molecular modulation [11,13] and flash photolysis [12] studies. In all cases, complex kinetic behavior had to be modeled to extract rate parameters and equilibrium constants. Radical-radical processes such as reactions (3) and (4) were important in these studies [11-13] and greatly complicated the kinetic analyses. Reported values for $k_2$(298 K) range from 0.090 to 0.165 atm⁻¹. Using the thermochemical parameters determined in this study in conjunction with eq. (17), we calculate $K_2$(298 K) = 0.071 atm⁻¹, somewhat lower than the literature values [11-13].

After our preliminary results were reported [34], two other groups undertook investigations of the Cl,
O₂, CIOO equilibrium [35,36]. Both groups employed time-resolved UV absorption to monitor CIOO following flash photolytic generation of Cl in the presence of O₂. Neither study obtained kinetic data for reactions (2) and (–2). However, because O₂ concentrations up to 1 atm [35] or 100 atm [36] could be employed, equilibrium constants could be determined at temperatures up to 250 K in one study [35] and up to 300 K in the other study [36]. Reported enthalpy changes for reaction (2) are −0.1 kcal mol⁻¹ at 215 K [35] and −0.53 kcal mol⁻¹ at 240 K [36], i.e. in excellent agreement with the enthalpy change reported in this study. All three recent determinations suggest that the CIOO bond strength is weaker by 1.0–1.3 kcal mol⁻¹ than previously thought [17].

Acknowledgement

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References

[34] A preliminary report of this study was presented at the XVIIth Informal Conference on Photochemistry, Santa Monica, CA (January, 1989).
Kinetics and Mechanism of the Reaction of Hydroxyl Radicals with Acetonitrile under Atmospheric Conditions

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The pulsed laser photolysis-pulsed laser induced fluorescence technique has been employed to determine absolute rate coefficients for the reaction OH + CH₃CN (1) and its isotopic variants, OH + CD₂CN (2), OD + CH₃CN (3), and OD + CD₃CN (4). Reactions 1 and 2 were studied as a function of pressure and temperature in N₂, N₂/O₂, and He buffer gases. In the absence of O₂ all four reactions displayed well-behaved kinetics with exponential OH decays and pseudo-first-order rate constants which were proportional to substrate concentration. Data obtained in N₂ over the range 50–700 Torr at 298 K are consistent with k₁ showing a small pressure dependence. The Arrhenius expression obtained by averaging data at all pressures is k₁(T) = (1.13 ± 0.03) x 10⁻¹² exp[(-1130 ± 90)/T] cm³ molecule⁻¹ s⁻¹. The kinetics of reaction 2 are found to be pressure dependent with k₂(298 K) increasing from (1.21 ± 0.12) x 10⁻¹⁴ to (2.16 ± 0.11) x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ over the pressure range 50–700 Torr of N₂ at 298 K. Data at pressures >600 Torr give k₂(T) = (9.4±0.4) x 10⁻¹⁴ exp[(-1180 ± 250)/T] cm³ molecule⁻¹ s⁻¹. The rates of reactions 3 and 4 are found to be independent of pressure over the range 50–700 Torr of N₂ with 298 K rate coefficients given by k₃ = (3.18 ± 0.40) x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ and k₄ = (2.25 ± 0.28) x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹. In the presence of O₂ each reaction shows complex (non-pseudo-first-order) kinetic behavior and/or an apparent decrease in the observed rate constant with increasing [O₂], indicating the presence of significant OH or OD regeneration. Observation of regeneration of OH in (2) and OD in (3) is indicative of a reaction channel which proceeds via addition followed by reaction of the adduct, or one of its decomposition products, with O₂. The observed OH and OD decay profiles have been modeled by using a simple mechanistic scheme to extract kinetic information about the adduct reactions with O₂ and branching ratios for OH regeneration. A plausible mechanism for OH regeneration in (2) involves OH addition to the nitrogen atom followed by O₂ addition to the cyano carbon atom, isomerization, and decomposition to D₂CO + DOCN + OH. Our results suggest that the OH + CH₃CN reaction occurs via a complex mechanism involving both bimolecular and termolecular pathways, analogous to the mechanisms for the important atmospheric reactions of OH with CO and HNO₃.

Introduction

It is now generally accepted that acetonitrile (CH₃CN) is present at ppt levels in the stratosphere. Attempts to understand the role of acetonitrile in stratospheric positive ion chemistry and its contribution to the stratospheric NO₂ budget require a detailed understanding of its atmospheric sources, emission rates, and oxidation mechanism. Acetonitrile was first proposed as a com-
The reaction of hydroxyl radicals with acetonitrile


dominate the stratospheric positive cluster ions by Arnold et al., who used a rocket-borne ion mass spectrometer to identify cluster ions of the type H+(H2O)n, where X = mass 41, l = 1, 2, and n = 0, 1, 2, 3. These ions have been termed non-proton hydrates (NPH) to distinguish them from proton hydrates (PH) of the form H+(H2O)n, which had been predicted to be present in the stratosphere and also observed experimentally. Subsequent experiments using balloon-borne mass spectrometers determined ion concentration profiles in the 25-40 km region and, although the identification of X as CH3CN remained controversial, were used to infer stratospheric mixing ratios for neutral CH3CN and even for the OH radical. The first definitive identification of X as CH3CN came from field and laboratory measurements of Schlager and Arnold, who used electric-field-induced collisional activation to fragment the NPH clusters and produce mass 15, identified as CH3+, as a product. The totally unexpected observation of NPH and inferred free CH3CN mixing ratios in the ppm range has led to a number of efforts to identify the source of the CH3CN and model its atmospheric profiles.

While it now appears that the only significant sources of CH3CN involve emission at the Earth’s surface, modeling efforts have been hampered by the paucity of data on emission rates, tropospheric concentration profiles, and atmospheric degradation processes. Three major deficiencies identified by Arijs et al. in a recent review of stratospheric positive ion measurements and acetonitrile detection are (a) accurate measurements of rate constants for the atmospheric reactions of CH3CN, in particular with OH, (b) a detailed study of the emission sources of CH3CN, and (c) a better knowledge of atmospheric eddy diffusion processes.

This work addresses the first of the above-mentioned data requirements, the rate and mechanism of reaction I under atmospheric conditions. Six previous studies of reaction I have employed the flash photolysis–resonance fluorescence and discharge flow-EPR techniques. While the most recent studies have employed the flash photolysis–resonance fluorescence and atmospheric degradation processes.

In this work, we have employed a pulsed laser photolysis–pulsed laser induced fluorescence (PLP-PLIF) technique to study reaction I as a function of pressure and temperature in N2, N2/O2, and He buffer gases. Studies of the isotopic variants, reactions 2, 3, and 4, have been performed in an attempt to shed light on the detailed reaction mechanism. Our results are inconsistent with the view that reaction I is pressure independent and proceeds exclusively via a direct hydrogen abstraction mechanism.

Experimental Section

The PLP-PLIF apparatus has been described in detail elsewhere. Modifications and a brief review of its operation are given below. Three different reaction cells were used, with most of the experiments being performed in a Pyrex cell which had an internal diameter of 4 cm and a length of 50 cm. Two side arms, 4 cm i.d. and 14 cm long, which terminated in Brewster angle windows were attached to the center of the cell. The photolysis laser passed through these side arms across the direction of gas flow while the probe laser passed along the length of the cell. Fluorescence was detected through a third side arm, 4 cm i.d. and 5 cm long, perpendicular to the photolysis and probe beams. The central 25 cm length of the cell was jacketed to permit the flow of heating or cooling fluid from a thermostated bath. Detailed descriptions of the other two reaction cells, which were constructed of Pyrex and brass, are given elsewhere. A copper-constantan thermocouple with a stainless steel jacket was inserted into the reaction zone through a vacuum seal, allowing measurement of the gas temperature under the precise pressure and flow conditions of the experiment.

OH and OD were produced by the pulsed laser photolysis of H2O2, HNO3, or DNO3 using the 193-nm (ArF) and 248-nm (KrF) outputs from an excimer laser or the 266-nm fourth harmonic output from a Nd:YAG laser. Pulsed laser induced fluorescence using a Nd:YAG laser pumped, frequency-doubled dye laser was used for OH(D) detection. Excitation was via the Q1 line of the A2Σ+–X1Π(1–0) transition at 282 nm for OH and 287 nm for OD. All kinetic studies were performed with a line-narrowing etalon in the dye laser cavity giving an estimated line width of 0.1 cm⁻¹ at 280 nm. The laser could be reproducibly scanned on and off the OH(D) line by pressure tuning using N2 gas. Fluorescence in the 0–0 and 1–0 bands was detected by an EMI 9813QB photomultiplier after passing through collection optics and filters to discriminate against Rayleigh scattering and Raman scattering from N2 and/or O2. The photomultiplier output

was appropriately terminated and fed to a 100-MHz waveform analyser to obtain the peak voltage averaged for (typically) 100 laser shots. To ensure that we were, in fact, producing and monitoring OD, a laser excitation spectrum of the A-X(0–0) band was obtained by scanning the unconverted dye laser. In this case the photomultiplier output was processed by a boxcar averager and the output digitized and stored in a small computer. The excitation spectrum was assigned by comparison with a simulated spectrum of the six main branches calculated from the term energies of Clyne et al.19 Intensities were calculated for a 300 K Boltzmann population distribution by using the formula of Earns, and convoluting over the laser bandwidth. The experimental and simulated spectra, shown in Figure 1, are in good agreement and confirm that we were producing and monitoring OD.

Kinetic information was obtained by varying the delay between the photolysis and probe lasers using a digital delay generator. Signal was collected for 15–20 delays, varying from 0 to 20 ms, in order to map out an OH(D) decay profile over three 1/e times.

In order to avoid the accumulation of photolysis or reaction products all experiments were carried out under "slow flow" conditions with the linear flow rate through the reactor varied between 1 and 5 cm s⁻¹. In a typical experiment the flows were set in the absence of CH₃CN to give the desired pressure. A CH₃CN/N₂ mixture was then added incrementally to the flow and a range of pseudo-first-order rate constants measured. The throttling valves in the flow system were not adjusted to keep the pressure constant during this process and hence there was some variation in total pressure over the course of an experiment. Bulbs containing 5% acetonitrile in N₂ were prepared manometrically and the concentration of acetonitrile in the reaction mixture was calculated from flow rates and reactor total pressure. The flow rates and total pressure were measured by using calibrated mass flow meters and a capnograph manometer. The response of the mass flow meter which measured the mixture containing CH₃CN was corrected for its presence by calibrating with CH₃CN/N₂ and CH₃CN/H₂O mixtures. For a 5% CH₃CN/N₂ mixture the correction was 7% and for the 6% CH₃CN/H₂O mixture used in the two sets of He buffer experiments the correction was 17%. These corrections were somewhat larger than the 5% and 12% corrections calculated by using a formula supplied by the manufacturer.

In order to assess the possibility of complications arising from isotopic exchange between H₂O and CD₃CN the infrared spectra of CH₃CN, CD₃CN, and CD₃CN/H₂O mixtures were measured. For the CD₃CN/H₂O mixtures, no evidence for isotopic exchange was observed on a time scale of 15 min.

Chemicals. The pure gases used in this study had the following stated minimum purities: N₂, 99.999%; O₂, 99.99%. Air was zero grade, <1 ppm total hydrocarbons. H₂O (90%) was obtained from FMC Corp.; it was further concentrated and purified by bubbling buffer gas through the sample for several days before use in experiments. HNO₃ (70% in H₂O) was used in a 30/70 mixture with H₂SO₄ (95%); both were Fisher AR grade. DNO₃ (99 atom % D, 70% solution in D₂O) and D₂SO₄ (99 atom % D) were obtained from ICN Biomedicals. CH₃CN, UV grade (99.99%) was obtained from Burdick & Jackson. CD₃CN (>99.9% chemical purity and 99 atom % D) was obtained from Aldrich. Acetonitrile samples were degassed and purified by trap to trap distillation before use.

Results and Discussion

Experiments in the Absence of Oxygen. All experiments were performed under pseudo-first-order conditions with [CH₃CN] ≫ [OH]. Typical initial OH concentrations were 1 × 10¹¹ to 3 × 10¹² molecules cm⁻³ while CH₃CN concentrations were in the range 1 × 10¹⁰ to 3 × 10¹¹ molecules cm⁻³. Under these conditions we expect the temporal profile of OH to be governed by the following reactions (for H₂O₂ precursor):

\[
\text{H}_2\text{O}_2 + hν → 2\text{OH} \\
\text{OH} + \text{CH}_3\text{CN} → \text{products}
\]

and reaction with background impurities (6)

\[
\text{OH} → \text{loss by diffusion, reaction with H}_2\text{O treatment}
\]

Since [CH₃CN] >> [OH] observed OH decays were expected to follow simple first-order kinetics:

\[
\ln([\text{OH}]_0/\text{[OH]})_t = k(t) \times [\text{CH}_3\text{CN}] + k_d_t = k't
\]

The bimolecular rate constant, k', is determined from the slope of a k' vs [CH₃CN] plot. Observation of OH temporal profiles which are exponential, a linear dependence of k' on [CH₃CN] and invariance of k' to variations in laser photolysis energy would serve to confirm the above mechanism. Factor of 5 variations in laser photolysis energy were carried out under a variety of experimental conditions and found to have no effect on observed kinetics; these observations confirmed that radical-radical side reactions had a negligible effect on OH kinetics.

OH decay profiles obtained at different CH₃CN concentrations in 600 ± 20 Torr of N₂ are shown in Figure 2. Some scatter and curvature is evident in this data which results from instabilities in the photolysis or probe laser. This scatter, which was particularly prevalent for high-pressure data where the signal to noise ratio was low, is reflected in the rather low precision of some of the rate constants obtained, particularly for k₁. However, there were no systematic deviations from exponential behavior for any OH and OD decays in the absence of oxygen. Figure 6d, for example, shows an OH decay in 450 Torr of N₂; this decay, which was measured on a day the system was particularly stable, shows excellent linearity for greater than 4 1/e times.

All decays were analyzed for at least three 1/e times: typical 2e errors in measured decay rates were <10% although at high pressures 2e errors as large as 15% were obtained. Figure 3 shows plots of k' vs acetonitrile concentration observed in studies employing N₂ buffer gas at high pressure. The results of all studies in the absence of O₂ are summarized in Tables 1–11; quoted errors in tables are 2σ and represent precision only. A plot of the 298 K rate constants for reactions 1 and 2 as a function of pressure is shown in Figure 4. To avoid congestion on the plot, the data are shown with 1σ error bars. The data for k₄ show a clear pressure dependence, increasing by almost a factor of 2 over the pressure range 40–700 Torr. The pressure dependence is confirmed by the results at higher temperature which show a trend firmmed by the results at higher temperature which show a trend.
R.ction of Hydroxyl Radicals with Acetonitrile

TABLE I: Summary of Kinetic Data for \( \text{OH} + \text{CH}_3\text{CN} \)

<table>
<thead>
<tr>
<th>T. K</th>
<th>photolysis wavelength* nm</th>
<th>press.° Torr</th>
<th>( k_1 \times 10^{14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>377</td>
<td>266</td>
<td>600-680</td>
<td>6.11 ± 0.69</td>
</tr>
<tr>
<td>370.5</td>
<td>266</td>
<td>550-650</td>
<td>5.71 ± 0.52</td>
</tr>
<tr>
<td>366</td>
<td>266</td>
<td>45-55</td>
<td>5.07 ± 0.19</td>
</tr>
<tr>
<td>352.5</td>
<td>266</td>
<td>46-60</td>
<td>4.71 ± 0.24</td>
</tr>
<tr>
<td>345.5</td>
<td>248</td>
<td>120-150</td>
<td>5.40 ± 0.7</td>
</tr>
<tr>
<td>338.5</td>
<td>266</td>
<td>50-60</td>
<td>3.61 ± 0.91</td>
</tr>
<tr>
<td>336</td>
<td>266</td>
<td>580-650</td>
<td>3.68 ± 0.50</td>
</tr>
<tr>
<td>318</td>
<td>248</td>
<td>650-700</td>
<td>3.15 ± 0.13</td>
</tr>
<tr>
<td>318</td>
<td>248</td>
<td>112-142</td>
<td>3.30 ± 0.55</td>
</tr>
<tr>
<td>298</td>
<td>266</td>
<td>600-700</td>
<td>2.81 ± 0.28</td>
</tr>
<tr>
<td>298</td>
<td>193</td>
<td>587-623</td>
<td>2.43 ± 0.22</td>
</tr>
<tr>
<td>298</td>
<td>268</td>
<td>580-650</td>
<td>2.15 ± 0.35</td>
</tr>
<tr>
<td>298</td>
<td>268</td>
<td>520-570</td>
<td>2.56 ± 0.22</td>
</tr>
<tr>
<td>298</td>
<td>248</td>
<td>246-294</td>
<td>2.64 ± 0.22</td>
</tr>
<tr>
<td>298</td>
<td>248</td>
<td>149-171</td>
<td>2.47 ± 0.23</td>
</tr>
<tr>
<td>298</td>
<td>266</td>
<td>130-160</td>
<td>2.41 ± 0.58</td>
</tr>
<tr>
<td>298</td>
<td>248</td>
<td>78-98</td>
<td>2.37 ± 0.12</td>
</tr>
<tr>
<td>298</td>
<td>266</td>
<td>46-60</td>
<td>2.17 ± 0.22</td>
</tr>
<tr>
<td>298</td>
<td>248</td>
<td>30-49</td>
<td>2.22 ± 0.12</td>
</tr>
<tr>
<td>278</td>
<td>248</td>
<td>180-235</td>
<td>2.30 ± 0.13</td>
</tr>
<tr>
<td>278</td>
<td>248</td>
<td>600-700</td>
<td>1.88 ± 0.24</td>
</tr>
<tr>
<td>278</td>
<td>248</td>
<td>100-120</td>
<td>1.84 ± 0.18</td>
</tr>
<tr>
<td>273</td>
<td>248</td>
<td>625-721</td>
<td>1.99 ± 0.13</td>
</tr>
<tr>
<td>256.5</td>
<td>248</td>
<td>550-600</td>
<td>1.46 ± 0.09</td>
</tr>
<tr>
<td>256.5</td>
<td>248</td>
<td>100-130</td>
<td>1.38 ± 0.08</td>
</tr>
</tbody>
</table>

*Photolytic precursor was \( \text{H}_2\text{O} \); except for (1) when \( \text{HNO}_3 \) was used. ° Buffer gas was \( \text{N}_2 \). Errors are 2σ.

The situation for reaction 1 is rather clear because the precision of the data is not as good as for reaction 2. The data for \( \text{N}_2 \) is consistent with \( k_1 \), showing a small pressure dependence. However, the data would also be consistent with a pressure-independent \( k_1 \) value of \( (2.48 ± 0.38) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). The data in He, which consist of one high- and one low-pressure series of experiments, are pressure independent over the range 30-600 Torr. For reactions 3 and 4, within the precision of the limited data set which encompasses two high- and two low-pressure rate constants for each reaction, the data suggests that \( k_1 \) and \( k_2 \) are independent of pressure over the range 50-700 Torr. The temperature dependence of \( k_1 \) is plotted in Arrhenius form in Figure 5 along with the temperature dependence of \( k_1 \) at high pressure (i.e., \( P > 600 \text{ Torr} \)). For reaction 1 all data were weighted equally in the calculation of the expression

\[
k_1(T) = (1.1 \times 10^{-12}) \times 10^{12} \exp[-(1130 ± 90)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

For reaction 2 the data at \( T > 298 \text{ K} \) confirm the observed pressure dependence at 298 K; these data suggest that the high-pressure limit is approached at progressively lower pressures as the temperature decreases. The observed pressure dependences suggest that, over the temperature range of our experiments, \( k_2 \) is close to its high-pressure limit at nitrogen pressures of 600 Torr.
due to OH regeneration and not to the detection of a second constant and varying amounts of O, present, is shown in Figure 5. Oxygen was present in the reaction mixture.

The data for $P > 600$ Torr give the Arrhenius expression

$$k_p(T) = \left(9.4 \times 10^{-15}\right) \exp(-1180/250) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

Measured 298 K rate constants are summarized in Table IV together with the Arrhenius expressions for reactions 1 and 2. The mechanistic implications of these results are discussed below.

Experiments in the Presence of Oxygen. Although determination of the effective rate constant for reaction 1 in air was a central objective of the present work, initial experiments gave indications of severe complications from secondary chemistry when oxygen was present in the reaction mixture. This took the form of nonexponential decays with the apparent regeneration of OH. A set of typical OH temporal profiles, with (CH₃CN) or greater. The data for $P > 600$ Torr give the Arrhenius expression

$$k_p(T) = \left(9.4 \times 10^{-15}\right) \exp(-1180/250) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

The voltages are the means ± standard error of 5 x 100 shot averages.

or greater. The data for $P > 600$ Torr give the Arrhenius expression

$$k_p(T) = \left(9.4 \times 10^{-15}\right) \exp(-1180/250) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

Experimental conditions: 298 K; 450 Torr total pressure, 50/50 N₂/O₂. Solid lines are obtained from the simulations described in the text. The plots have been displaced vertically for clarity.

In order to attempt to distinguish between regeneration from the products of (1a) or (1b), we examined reaction 2 in the presence of O₂. Trace b in Figure 7 shows an OH temporal profile for reaction 2 in 100 Torr of air at 256 K together with the temporal profile which would be expected from the rate constant measured in N₂. Again the deviation from exponential behavior and the presence of OH regeneration is clear. Similar results were obtained in a number of experiments at 300 K. In this case the interpretation of the data is relatively unambiguous since any CD₃CN formed in reaction 2 cannot react with O₂ to regenerate OH. Either massive isotope exchange between CD₃CN and H₂O₂ must have taken place or OH regeneration must have occurred via a process which involves an OH adduct. The former explanation can be rejected on two counts. First, as noted above, IR spectra of mixtures of CD₃CN and H₂O₂ showed no indications of isotopic exchange taking place. Second, since the concentrations of CD₃CN and H₂O₂ were 7.1 and 0.003 x 10^14 molecules cm⁻³, respectively, significant isotopic exchange would have affected only a small fraction of the CD₃CN while totally depleting the OH photolytic precursor. A very limited amount of data on reactions 3 and 4 in the presence of O₂ buffer gas was also obtained and is discussed below.

| TABLE IV: Summary of Arrhenius Parameters and 298 K Rate Constants for Reactions 1-4 |

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$</th>
<th>$E/R \cdot K$</th>
<th>$k(298 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + CH₃CN</td>
<td>1.17×10⁷</td>
<td>1104 ± 11</td>
<td>2.48 ± 0.38</td>
</tr>
<tr>
<td>OH + CD₃CN</td>
<td>0.96×10⁷</td>
<td>1175 ± 243</td>
<td>2.16 ± 0.11</td>
</tr>
<tr>
<td>OD + CH₃CN</td>
<td>3.18 ± 0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OD + CD₃CN</td>
<td>2.25 ± 0.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Errors are ± 2σ. Units are $10^{-15}$ cm³ molecule⁻¹ s⁻¹. "Units are $10^{-14}$ cm³ molecule⁻¹ s⁻¹. "At 680 Torr.

| TABLE V: On-Line and Off-Line Signals Observed during OH Regeneration |

<table>
<thead>
<tr>
<th>Signal + background, mV</th>
<th>background, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>on OH line</td>
<td>2372 ± 490</td>
</tr>
<tr>
<td>off OH line</td>
<td>903 ± 78</td>
</tr>
</tbody>
</table>

The voltages are the means ± standard error of 5 x 100 shot averages.

Figure 7. OH(D) temporal profiles in N₂/O₂ mixtures. (a) OD + CD₃CN, 296 K, 50 Torr total pressure, 50/50 N₂/O₂; (b) OD + CD₃CN, 296 K, 110 Torr total pressure, air; (c) OD + CH₃CN, 298 K, 270 Torr total pressure, 50/50 N₂/O₂. Solid lines are obtained from the simulations described in the text. Dashed lines represent behavior observed in N₂. The plots have been displaced vertically for clarity.

In order to attempt to distinguish between regeneration from the products of (1a) or (1b), we examined reaction 2 in the presence of O₂. Trace b in Figure 7 shows an OH temporal profile for reaction 2 in 100 Torr of air at 256 K together with the temporal profile which would be expected from the rate constant measured in N₂. Again the deviation from exponential behavior and the presence of OH regeneration is clear. Similar results were obtained in a number of experiments at 300 K. In this case the interpretation of the data is relatively unambiguous since any CD₃CN formed in reaction 2 cannot react with O₂ to regenerate OH. Either massive isotope exchange between CD₃CN and H₂O₂ must have taken place or OH regeneration must have occurred via a process which involves an OH adduct. The former explanation can be rejected on two counts. First, as noted above, IR spectra of mixtures of CD₃CN and H₂O₂ showed no indications of isotopic exchange taking place. Second, since the concentrations of CD₃CN and H₂O₂ were 7.1 and 0.003 x 10^14 molecules cm⁻³, respectively, significant isotopic exchange would have affected only a small fraction of the CD₃CN while totally depleting the OH photolytic precursor. A very limited amount of data on reactions 3 and 4 in the presence of O₂ buffer gas was also obtained and is discussed below.
TABLE VI: Best-Fit Parameters in OH Regeneration Simulations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>simulation parameters</th>
<th>measured rate in N₂</th>
<th>[CH₃CN]</th>
<th>[O₃] Torr</th>
<th>press. Torr</th>
<th>T. K</th>
<th>no. of exps</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ + CH₃CN (ι = 1)</td>
<td>k₁ = 1.25</td>
<td>k₂ = 1.25</td>
<td>k₃ = 4</td>
<td>k₄</td>
<td>4.9 - 11.2</td>
<td>120</td>
<td>600</td>
</tr>
<tr>
<td>O₃ + CD₃CN (ι = 2)</td>
<td>k₁ = 0.85</td>
<td>k₂ = 1.0</td>
<td>1.38</td>
<td>1.7 - 7.3</td>
<td>28</td>
<td>140</td>
<td>298</td>
</tr>
<tr>
<td>O₃ + CH₃CN (ι = 3)</td>
<td>k₁ = 2.25</td>
<td>k₂ = 1.15</td>
<td>2.2</td>
<td>2.5</td>
<td>135</td>
<td>270</td>
<td>298</td>
</tr>
<tr>
<td>O₃ + CD₃CN (ι = 4)</td>
<td>k₁ = 1.1</td>
<td>k₂ = 1.1</td>
<td>2.2</td>
<td>1.6</td>
<td>0.65</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

*Best fits were obtained by visual comparison of experimental and simulated decay profiles. Errors were estimated from the scatter in the experimental data and simulation parameters. 'Units are 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹. 'Units are 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹. *Models with

Modeling the Regeneration Process. In order to examine the plausibility of the above mechanism, we have modeled some of our O₃ data using a GEAR program[20] to numerically integrate the rate equations.

The simulations of reaction 1 in the presence of O₃ involved a simple four-reaction kinetic scheme which consisted of two reactive channels, (1c) and (1d), background losses, (6), and a regeneration step, (7), which involves the reaction of a product of (1d) with O₂ to produce OH.

The simulations arc able to reproduce the observed OH decay profiles at 256 K in 140 Torr total pressure. Table VI shows the values measured in N₂. Again the data is consistent with the reaction proceeding via two channels one of which leads to OH regeneration, and again the rate-determining step in the regeneration process proceeds with a bimolecular rate coefficient of (5 ± 4) × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹.

Four experiments at 298 K in 140 Torr of air and one experiment at 256 K in 100 Torr of air were analyzed and the results are summarized in Table VI. The fit to the 256 K experiment with k₃ = 5.5 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, k₄ = 3.5 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹, and k = 5 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ is shown in Figure 7 together with the decay profile which would be expected in N₂. Again the data is consistent with the reaction proceeding via two channels one of which leads to OH regeneration, and again the rate-determining step in the regeneration process proceeds with a bimolecular rate coefficient of (5 ± 4) × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹.

OD regeneration was observed for reactions 3 and 4 in the presence of O₃. Two observed decay profiles along with simulated profiles and decays which would be expected based on rates measured in N₂ are shown in Figure 7; the rate constants used in the simulation are included in Table VI.

Reactions 9 and 10 are the analogous OD regeneration steps. Reaction 4 shows similar behavior to reactions 1 and 2; however, for reaction 3 the degree of OD regeneration is less pronounced although still evident when compared with the decay profile expected from the rate constant measured in N₂. Overall, the above simulations indicate that the observed OH(D) regeneration profiles obtained under a variety of conditions can be simulated by using a simple four-step kinetic scheme. One channel leads to OH(D) regeneration and the initial step in the regeneration process appears to involve an addition step to produce...
an OH(D)/acetone nitrite adduct. The adduct, or one of its decomposition products, reacts with O$_3$ to regenerate OH(D) at a rate of $(5 \pm 4) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. A second channel or channels lead to the formation of products other than OH. By themselves the simulations give no added information on this channel since, in terms of the generated OH profiles, all of the possible mechanisms are kinetically equivalent. The observed kinetic effects and pressure dependences, however, have considerable mechanistic implications for this channel and these are discussed below.

**Reversible Adduct Formation.** Since the observed pressure dependence of reaction 2 and the observation of OH regeneration in reaction 2 and OD regeneration in reaction 3 provide strong evidence for an adduct channel, we investigated the possibility that reversible adduct formation was occurring. Such behavior might manifest itself in several ways. If the forward addition step is proceeding at a rate that is faster than the overall rate of reaction, but sufficiently slow that it is resolvable by the $(\approx 100$ ns) time resolution of this experiment, then nonexponential decays would be observed. An initial fast decay into equilibrium would be followed by a slower decay due to chemical reaction. In cases in which the adduct reacts with oxygen, the presence of oxygen results in an increase in the observed rate of reaction and a tendency toward exponential decay with increasing [O$_2$]. At the highest CH$_3$CN concentrations used, we saw no deviation from exponential behavior in N$_2$. In O$_2$, although we saw OH regeneration, the initial slopes of the decays were consistent with the reaction rate measured by N$_2$.

If reversible adduct formation took place on a very fast time scale (i.e. $<100$ ns), then although we would be unable to temporally resolve the decay into equilibrium, we should be able to detect its presence by monitoring the OH fluorescence signal immediately after photolysis in the presence and absence of CH$_3$CN. Since decay due to reaction is negligible, any decrease in the OH signal must be due to the fact that some OH has been tied up in adduct formation. We performed such experiments for reactions 1 and 2 in 600–700 Torr of N$_2$ buffer. Under these conditions the only significant deactivation processes for OH A$^2S^+$ are fluorescence and collisional quenching by N$_2$ and CH$_3$CN; the rates of these processes have the following magnitudes for a mixture of 5 Torr of CH$_3$CN in 600 Torr of N$_2$.

$$k_0(N_2) = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_f = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The quenching rate for CH$_3$CN does not appear to have been determined directly so the CH$_3$CN deviation rate was calculated assuming $k_0 = 3 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from comparison with known quenching rates. It can be seen that quenching by N$_2$ is the dominant deactivation process for OH A$^2S^+$ even assuming the very fast quenching rate for CH$_3$CN. Under these conditions the Stern-Volmer equation for fluorescence quenching

$$I_f/I_{f0} = k_f/(k_f + k_0[M])$$

reduces to

$$I_f(P_1)/I_f(P_2) = P_2/P_1$$

where $I_f(P_i)$ is the fluorescence intensity at pressure $P_i$.

In these experiments the OH signal was measured in the absence of CH$_3$CN and then a CH$_3$CN/N$_2$ mixture was added without adjusting the throttle valve. Hence the pressure increased, but the concentration of the OH precursor and the photolytically generated OH remained approximately the same. In the absence of any adduct formation we would therefore expect the OH signal to decrease in inverse proportion to the pressure increase. Table

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$P_{N_2}$/ Torr</th>
<th>$P_{CH_3CN}$/ Torr</th>
<th>$I_f$/ Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + CH$_3$CN</td>
<td>1.15</td>
<td>1.56 $\times 10^{-11}$</td>
<td>720</td>
</tr>
<tr>
<td>OH + CD$_3$CN</td>
<td>1.08</td>
<td>1.25 $\times 10^{-11}$</td>
<td>680</td>
</tr>
</tbody>
</table>

VII shows the OH signal and total pressure ratios for reactions 1 and 2 taken 300 ns after the photolysis pulse. The OH signal is seen to be inversely proportional to the total pressure, demonstrating the absence of any rapid reversible adduct formation.

**Mechanistic Implications.** While the consensus view of reaction 1 is that it proceeds via a direct abstraction mechanism, two aspects of our data are clearly inconsistent with such a mechanism being the dominant reaction pathway. First, if the reaction proceeded only via direct abstraction we would expect the observed pressure dependences to be quite different. The rates of reactions 1 and 3 would be similar, as would the rates of reactions 2 and 4, with small differences being due to a secondary isotope effect. The primary isotope effect would result in reactions 2 and 4, which break C-D bonds, being slower than reactions 1 and 3, which break C-H bonds. In fact, the rates of (1) and (4) are similar with those of (2) and (3) showing deviations. Second, we would not expect to see a pressure dependence for any of the reactions. Third, we would expect to see identical kinetic behavior in N$_2$ and oxygen-containing buffer gases for reactions 2 and 4, since in these cases any secondary chemistry involving the methylcyano radical and O$_3$ could not regenerate the radical which is being monitored.

The observed behavior can be reconciled with a complex reaction mechanism which proceeds via the formation of an energized intermediate, i.e.

$$A + B \rightarrow AB \rightarrow C + D$$

Such an energized intermediate could decompose to produce CH$_3$CN and H$_2$O, decompose back to reactants, or at sufficiently high pressures be collisionally stabilized. Hence the reaction proceeds at a finite rate at low pressure but shows an enhancement in the rate as the pressure is increased. Such mechanisms have been invoked to explain observations on reactions such as OH + CO and OH + HN$_2$O, which display complex kinetic behavior such as negative temperature dependencies, pressure effects, and curved Arrhenius plots.


directly measured the formation rates of the HOCO and DCCO complexes in reactions 11 and 12. They have constructed a detailed model which is able to reproduce the observed pressure, temperature, and isotope effects. Among the points noted in their study was the importance of including angular momentum effects since the rate of dissociation of the HOCO complex to H + CO, decreases with increasing J. Calculations on reaction 13 predict that it should show a small pressure dependence, while the rate of reaction 14 is predicted to be faster and to show a much larger pressure dependence. Recent careful experimental work indicates that k13 is weakly pressure dependent. Reaction 14 also appears to show a pressure dependence at room temperature; interestingly, k14 is found to be a factor of 14 slower than k13 in contradiction to the theoretical prediction that k14 > k13.

There are interesting parallels in some aspects of the behavior of reactions 1–4 and 11–14. Perhaps the most important point is that the behavior of reactions which proceed via such complexes is very different from third-order reactions. Detailed models with accurate structures for the complex and the transition states leading to complex and product formation are required in order to understand observed pressure, temperature, and isotope dependencies. While our data set is too limited to allow firm conclusions, the observed pressure and isotope effects are consistent with a complex mechanism. As we noted above, a direct abstraction channel should exhibit a significant isotope effect and no pressure dependence. In a study of the reaction of OH with dimethyl sulhide, (CH3)2S, we observed this type of behavior. An abstraction channel is observed which is pressure independent, shows a positive activation energy, and shows a significant isotope effect. A reversible addition channel becomes evident when oxygen is added to the system because the adduct reacts with oxygen rather than decomposing back to reactants; hence, the observed reaction rate increases. This increase shows no isotope dependence, implying that both the adduct and the rate of the adduct reaction with oxygen show no isotope dependence. The similarities between the rates of reactions 1, 4, and 2 at high pressure would argue against the presence of a major direct abstraction channel. Clearly, the definitive establishment of such a mechanism requires much further work including studies of the rate at low pressure and over a much wider temperature range, and also product identification studies.

Our data provides a limited amount of information on the mechanism of OH regeneration. As we have noted above, the initial step must involve the formation of an adduct followed by reaction of the adduct, or one of its decomposition products, with O2. While it is not possible to directly distinguish between these processes, it is possible to place a lower limit on the adduct decomposition rate which would be necessary if reaction of an adduct decomposition product with O2 were the rate-determining step in OH regeneration. This rate will be pressure dependent. However, for the 298 K, 450 Torr data for reaction 1, simulations of the experimentally observed decay profiles indicate that the adduct decomposition rate would have to be greater than 104 s–1 for reaction of an adduct decomposition product with O2 to be the rate-determining step. Considering the likely strength of chemical bonds in the adduct, it seems unlikely that it would decompose to products other than OH + CH3CN on such a fast time scale. Hence direct reaction of the adduct with O2 is probably the rate-determining step in reaction 1.

One possible reaction path (written for reaction 2) which is energetically feasible and results in OH regeneration via an adduct + O2 reaction is

\[
\text{OH} + \text{CD}_2\text{CN} + \text{O}_2 \rightarrow \text{DCCO} + \text{DOCN} + \text{OH} \quad \Delta H \sim -62 - \Delta H_{\text{add,OH}} \text{ kcal mol}^{-1} \quad (15)
\]

reported non-Arrhenius behavior over the range 296–520 K and expressed their data in terms of a two-parameter fit. However, over most of the temperature range of their study, Rhasa and Zellner’s results agree, within the combined uncertainties, with this work and that of Kurylo and Knable. Poulet et al. measured \( k_r \) at room temperature and at 393 K using the discharge-flow technique in 1 Torr of He; their room temperature results are in good agreement with the flash photolysis results, excluding those of Harris et al.\(^9\). However, their 393 K result is in good agreement with that of Harris et al. Poulet et al.’s data, if fit to a simple Arrhenius expression, would result in an activation energy that is considerably higher than was measured in other studies.

Of the studies of reaction 1 at room temperature only Zeitzsch\(^11\) has observed a significant pressure effect. In Ar buffer he observed a decrease from \( 2 \times 10^{-14} \) to \( 0.8 \times 10^{-14} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) over the pressure range 100–5 Torr. Rhasa and Zellner saw a small decrease in \( k_r \) at 10 Torr in He\(^13\) and Kurylo and Knable saw no pressure dependence over the range 20–50 Torr in Ar and SF\(_6\) buffers. Finally, as noted above, Poulet et al.\(^14\) measured a room temperature value of \( k_r \), in agreement with the average of the lower room temperature flash photolysis results and concluded that there is no pressure dependence. In a recent evaluation of reaction 1, Atkinson\(^23\) also concludes that the reaction proceeds mainly via abstraction, citing the lack of a pressure dependence and the fact that the OH + R-CN rate constant increases by a factor of 4–10 in going from acetonitrile to propionitrile.

Our results appear to be incompatible with reaction 1 proceeding primarily by simple abstraction, and our analysis of the OH regeneration data is consistent with the pressure-dependent channel accounting for 50% of the branching ratio, in good agreement with the results of Zeitzsch. The majority of the other available data would appear to contradict this view. However, a number of possible problems can be identified in the other studies. The 1 Torr discharge-flow study of Poulet et al.,\(^14\) while in apparent agreement with the room temperature high-pressure limits obtained in the flash photolysis studies (excluding that of Harris et al.), is a factor of 1.8 greater at 393 K. Atkinson\(^23\) cites the increase in the rate of reaction in going from acetonitrile to propionitrile as evidence of the reaction proceeding by abstraction, since such an enhancement might be expected due to the presence of more weakly bound secondary hydrogens. However, this rate increase is based on the study of Harris et al.\(^8\) and, since their measurement of \( k_r \) appears to be too high, it seems questionable to rely on other data from the same study for mechanistic interpretation without an independent verification. The failure of both Kurylo and Knable and Rhasa and Zellner to observe a pressure dependence is rather more difficult to explain. Rhasa and Zellner were attempting to reproduce the results of Zeitzsch and rationalize their failure to observe a pressure effect as being possibly due to impurities. This would require an impurity reaction which shows an inverse pressure dependence which exactly cancels the pressure dependence of reaction 1—an unlikely possibility.

Implications for Atmospheric Chemistry. The agreement between this work and that of Kurylo and Knable over an extended temperature range greatly decreases the uncertainty in \( k_r \), over the temperature and pressure range appropriate for most of the troposphere. Additionally, our results in N\(_2\) and N\(_2\)/O\(_2\) buffer gases indicate that while the mechanism of reaction 1 is the subject of considerable uncertainty, its effective rate under lower atmospheric conditions is well established. However, the unresolved question of the pressure dependence and reaction mechanism has important implications for modeling the upper troposphere and stratosphere. If reaction 1 proceeds via a pressure-dependent, complex mechanism, then a simple Arrhenius expression may not be appropriate for extrapolation to lower stratospheric temperatures. The most recent modeling calculations of CH\(_2\)CN profiles\(^7\) considered the effects of both the Harris et al. and Kurylo and Knable Arrhenius expressions for the rate of reaction 1. The Kurylo and Knable expression gives the best fit to the observed profiles above 20 km but predicts rather lower ground level mixing ratios than reported observations.\(^3\) The model also predicts that the only significant loss mechanism for CH\(_2\)CN below 40 km is reaction 1. Since a large body of data on CH\(_2\)CN concentration profiles above 20 km exists, the establishment of accurate ground level mixing ratios should place significant constraints on model calculations; it also potentially offers an alternate approach for calculation of OH profiles.

Summary

We have employed the PLP-PLIF technique to study the kinetics of reaction 1 over the temperature range 256–379 K and pressure range 50–700 Torr in N\(_2\), N\(_2\)/O\(_2\), Ar, and He buffer gases. Our results, which are in good agreement with a previous flash photolysis–resonance fluorescence study in 50 Torr of Ar,\(^12\) greatly decrease the uncertainty in the rate of reaction 1 for use in atmospheric modeling calculations. Our studies of the isotopic variants of reaction 1 together with the observation of complex kinetics in the presence of O\(_2\) indicate that the reaction cannot proceed only via a direct hydrogen abstraction mechanism. Our results are consistent with reaction proceeding via the formation of a complex intermediate which can dissociate to reactants or products, or be collisionally stabilized. The thermalized adduct does not appear to redissociate to OH; however, it, or one of its dissociation products, reacts with O\(_2\) to regenerate OH with a rate constant of \( (5 \pm 4) \times 10^{-14} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The unresolved question of the pressure dependence of reaction 1 at low temperature could be important for constraining models of stratospheric CH\(_2\)CN profiles and also for using these measured profiles to determine OH profiles.

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A competitive kinetics study of the reaction of Cl with CS$_2$ in air at 298 K

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The relative rate technique has been used to investigate the kinetics of the reaction of Cl atoms with carbon disulfide, CS$_2$, at 700 Torr total pressure of air at 298 K. The decay rate of CS$_2$ was measured relative to CH$_4$, CH$_3$Cl and CHF$_3$Cl. For experiments using CH$_4$ and CH$_3$Cl references, the decay rate of CS$_2$ was dependent on the ratio of the concentration of the reference to that of CS$_2$. We ascribe this behavior to the generation of OH radicals in the system leading to complicated secondary chemistry. From experiments using CHF$_3$Cl we are able to assign an upper limit of $4 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the overall reaction, Cl+CS$_2$→products.

1. Introduction

The gas-phase reaction of Cl atoms with organic species represents an important loss process for Cl atoms and organic compounds in the upper atmosphere [1,2]. Additionally, Cl atom attack provides a useful laboratory method for studying the kinetics and mechanisms by which organics are oxidized (see for example refs. [3,4]). Despite the importance of such reactions, there are significant uncertainties and inconsistencies in the kinetic data base for Cl atom reactions.

Carbon disulfide, CS$_2$, is an important biogenic sulfur compound which has been identified as a trace component of the atmosphere [5]. The reaction of Cl atoms with CS$_2$ has been the subject of two recent studies. In the first study of this reaction, Martin et al. [6] used a relative rate technique at 150-760 Torr total pressure of N$_2$/O$_2$ mixtures at 293 K. In their study, Martin et al. [6] monitored the decay of CS$_2$ relative to CH$_4$ and CH$_3$Cl in the presence of Cl atoms, and observed that the kinetics of this reaction varied as a function of both pressure and molecular oxygen concentration. These observations were interpreted in terms of a three-step mechanism with Cl atoms adding to CS$_2$ to form a weakly bound adduct which either dissociates to reform the reactants, or reacts with O$_2$ to form products:

$$\text{Cl} + \text{CS}_2 + \text{M} \rightarrow \text{CS}_2\text{Cl} + \text{M}, \quad (a)$$

$$\text{CS}_2\text{Cl} + \text{M} \rightarrow \text{CS}_2 + \text{Cl} + \text{M}, \quad (b)$$

$$\text{CS}_2\text{Cl} + \text{O}_2 \rightarrow \text{products}, \quad (c)$$

In 760 Torr of synthetic air, Martin et al. [6] report an effective rate constant for the reaction of Cl with CS$_2$,

$$k_1 = 8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (1)$$

In the second study of the Cl+CS$_2$ reaction, Nicovich et al. [7] employed an absolute technique (pulsed laser photolysis time-resolved fluorescence) to study the kinetics of Cl atom loss in the presence of CS$_2$. Experiments were performed over the temperature range 193-293 K and pressures up to 300 Torr of air. Nicovich et al. [7] confirmed that the
reaction of Cl with CS$_2$ proceeds via reversible adduct formation as proposed by Martin et al. [6]. Although no evidence for the occurrence of reaction (c) was observed by Nicovich et al. [7], their data do not preclude the occurrence of reaction (1) with an overall rate, $k_1 = 8 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in 760 Torr of air at 298 K (as reported by Martin et al. [6]), provided that the CS$_2$Cl+O$_2$ reaction occurs via a channel which regenerates chlorine atoms.

To further our understanding of the kinetics and mechanism of reaction (1) in particular, and of chlorine atmospheric chemistry in general, we have reinvestigated the kinetics of the reaction of Cl atoms with CS$_2$. Experiments were conducted using the relative rate technique at 700 Torr total pressure of synthetic air and 295 $\pm$ 2 K.

2. Experimental

The apparatus and experimental techniques employed in this work have been described previously [8,9], and are only briefly discussed here. The apparatus consists of a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer interfaced to a 2 m long evacuable pyrex chamber ($S/V = 0.14$ cm$^{-1}$). The pyrex chamber was surrounded by 22 UV fluorescent lamps which were used to generate chlorine atoms by the photolysis of molecular chlorine.

$$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}.$$ 

White type multiple reflection optics were mounted in the reaction chamber; the path length used in the present study was 26.6 m. The spectrometer was operated at a resolution of 0.25 cm$^{-1}$. Infrared spectra were derived from 16 co-added interferograms.

Reaction mixtures consisting of CS$_2$, a reference organic (CH$_4$, CH$_3$Cl, or CHF$_2$Cl) and chlorine, diluted in synthetic air, were admitted to the reaction chamber. In the presence of atomic chlorine, CS$_2$ and the reference organic decay via

$$\text{Cl} + \text{CS}_2 \rightarrow \text{products}$$

and

$$\text{Cl} + \text{reference organic} \rightarrow \text{products}.$$  

Providing that the CS$_2$ and reference organic are lost solely by reactions (1) and (2), and that neither is reformed in any process, it can be shown that

$$\ln \frac{[\text{CS}_2]_0}{[\text{CS}_2]_t} = k_1 \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} = k_2 \ln \frac{[\text{reference}]_0}{[\text{reference}]_t}$$  

(1)

where $[\text{CS}_2]_0$ and $[\text{reference}]_0$, and $[\text{CS}_2]_t$ and $[\text{reference}]_t$, are the concentrations of CS$_2$ and reference organic at times $t_0$ and $t$, respectively, and $k_1$ and $k_2$ are the rate constants of reactions (1) and (2), respectively.

To test for loss processes in addition to reactions (1) and (2), mixtures of chlorine with both organics were prepared and allowed to stand in the dark. In all cases, the reaction of the organic species with chlorine, in the absence of ultraviolet light, was of negligible importance over the time periods used in this work. Additionally, to test for the possible photolysis of the organics used in the present work, mixtures of the reactants in synthetic air in the absence of molecular chlorine were irradiated using the output of all the blacklamps surrounding the chamber for 10 min. No photolysis ($< 2\%$) of any of the reactants was observed. This observation is consistent with the fact that CH$_4$, CH$_3$Cl and CHF$_2$Cl do not absorb in the spectral region where the blacklamp emission is most intense (350–390 nm) and CS$_2$ absorption in this region is weak [10,11].

The decay of the CS$_2$ and reference organics were measured using their characteristic absorptions in the infrared over the following wavelength ranges (in cm$^{-1}$): CS$_2$, 1500–1575; CH$_4$, 1225–1400 and 2900–3100; CH$_3$Cl, 1300–1400; CHF$_2$Cl, 1000–1200. Initial concentrations of the gas mixtures were: CS$_2$, 1.5–4.4 mTorr; CH$_4$, 6.7–28 mTorr; CH$_3$Cl, 14–66 mTorr; CHF$_2$Cl, 3.4–4.4 mTorr; Cl$_2$, 70–110 mTorr. All reagents were purchased from commercial vendors at purities of > 99% and used without further purification. Experiments were performed at room temperature, 298 $\pm$ 2 K, and 700 Torr total pressure of synthetic air.

3. Results

Figs. 1 and 2 show plots of $\ln ([\text{CS}_2]_0/\text{CS}_2]_t)$ versus $\ln ([\text{reference}]_0/\text{reference}]_t)$ for the references CH$_4$ and CH$_3$Cl, respectively. As seen from figs. 1 and 2, we observe nonlinear decay plots for experiments using either CH$_4$ or CH$_3$Cl as references.
Fig. 1. Plot of $\ln\left(\frac{[\text{CS}_2]}{[\text{CS}_2]}\right)$ versus $\ln\left(\frac{[\text{CH}_4]}{[\text{CH}_4]}\right)$ for initial concentration ratios $[\text{CH}_4]/[\text{CS}_2]$: 1.7, (●); 3.5, (▲); 19, (△). Solid lines represent second- or third-order fit to the data to aid in visual inspection of the data trend. Dotted lines represent predicted behavior using chemical mechanism given in Table 1, corresponding to each data set.

Fig. 2. Plot of $\ln\left(\frac{[\text{CS}_2]}{[\text{CS}_2]}\right)$ versus $\ln\left(\frac{[\text{CH}_3\text{Cl}]}{[\text{CH}_3\text{Cl}]}\right)$ for initial concentration ratios $[\text{CH}_3\text{Cl}]/[\text{CS}_2]$: 24, (○) and 5.0, (●). Solid lines represent a second-order fit to the data to aid in visual inspection of the data trend.

with the initial values of the slope $k_1/k_2$ being dependent upon the initial concentration ratio $[\text{reference}]_0/[\text{CS}_2]$, where $[\text{reference}]_0 = [\text{CH}_4]$ or $[\text{CH}_3\text{Cl}]$.

The curvature shown in Figs. 1 and 2 indicates that the assumptions implicit in the derivation of eq. (1) are not valid, i.e. either there are processes which reform the reactants in our chamber, or there are loss processes for the reactants in addition to reaction with CI atoms, or both. With the exception of decomposition of the $\text{CS}_2\text{Cl}$ adduct, there are no processes that could regenerate either $\text{CS}_2$, $\text{CH}_4$ or $\text{CH}_3\text{Cl}$ in our system. Under our experimental conditions, the lifetime of the $\text{CS}_2\text{Cl}$ adduct is less than $1 \mu\text{s}$ [7] compared to the typical time scale of $10-100 \mu\text{s}$ for our experiments. Thus, decomposition of the $\text{CS}_2\text{Cl}$ adduct will not affect our kinetic plots. It seems likely that the origin of the curvature observed in Figs. 1 and 2 lies in the existence of significant loss processes for the reactants other than reaction with CI atoms. It is our hypothesis that these loss processes involve reactions with OH radicals.

The reaction of CI atoms with methane in air yields methyl peroxy radicals, $\text{CH}_3\text{O}_2$, which in turn are known to undergo self reaction to produce a variety of products ($\text{CH}_3\text{O}$, HCHO and $\text{CH}_3\text{OH}$). Methoxy radicals, $\text{CH}_3\text{O}$, formed from the self reaction of $\text{CH}_3\text{O}_2$, react with O$_2$ to produce HO$_2$ radicals which in turn are known to react rapidly with $\text{CH}_3\text{O}_2$ radicals to yield methyl hydroperoxide [12]. It has recently been demonstrated that CI atoms react rapidly with methyl hydroperoxide with a rate constant of $k = 5.7 \times 10^{-11} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [13]. This rate constant is some 570 times greater than that of reaction of CI atoms with $\text{CH}_4$. Hence, methyl hydroperoxide formed in our chamber will rapidly be consumed by CI atoms. By analogy to the reaction of OH radicals with CH$_3$OOH, the reaction of CI atoms with CH$_3$OOH is expected to lead to the generation of OH radicals [14,15]. Hydroxyl radicals may also be produced by the reaction of CI atoms with HO$_2$ radicals [16].

Hydroxyl radicals, if generated in a mixture of CH$_4$ and CS$_2$ will preferentially react with the CS$_2$ as the rate constant for the reaction of OH with CS$_2$ is 180 times larger than that with CH$_4$. As CS$_2$ and CH$_4$ are consumed a number of products, such as HCHO, SO$_2$, and HCl, build up and compete with CS$_2$ for the available OH radicals. The result of hydroxyl radical formation in our chamber will be a fast initial CS$_2$ decay rate followed by a slow CS$_2$ loss rate at high conversions, consistent with the nonlinear decay plots observed.

To test the above hypothesis, we have modelled the chemistry occurring in the chamber following irradiation of $\text{CH}_4/\text{CS}_2/\text{Cl}_2/\text{air}$ mixtures using the Acuchem [17] kinetic modelling program and the chemical mechanism given in Table 1.

The results of the modelling calculations are shown by the dotted lines in Fig. 1. It should be noted that...
the chemical mechanism shown in table 1 does not include any reaction of Cl with CS₂. The sole loss process of CS₂ in this chemical model is via reaction with OH radicals which are produced from the reaction of Cl atoms with methyl hydroperoxide and/or HO₂ radicals as discussed above. There is no available data concerning the branching ratio of the reaction of Cl with CH₃OOH, and thus we have arbitrarily assigned equal importance to the two possible channels. The kinetic data given in table 1 has been taken from the literature. No attempt has been made to fit the experimental data points by adjustment of any of the kinetic parameters. Instead, we have simply used our starting conditions in the model. From fig. 1, it can be seen that the model predictions are in qualitative agreement with our observations with large initial slopes which decrease with increasing consumption of the reactants. Quantitatively, the model predicts initial slopes, $k_1/k_2$, which are within 20% of those observed. As seen from fig. 1, at reactant conversions greater than 50%, the model prediction deviates significantly from our observations. At such high conversions, the chemistry in the chamber is complicated by the presence of large amounts of products. The qualitative agreement between the model given in table 1 and our experimental observations shows that it is possible to explain a large fraction, if not all, of the observed CS₂ loss in the CS₂/CH₄/Cl₂/air experiments as caused by OH attack.

As seen from table 1, in addition to hydroxyl radicals, there are a number of other transient radical species formed following the irradiation of CS₂/CH₄/Cl₂/air mixtures. These species include CH₃, CH₃O₂, CH₃O, HO₂ and HCO. None of these radicals are expected to react significantly with either CH₃ or CS₂. Reaction with molecular oxygen (present at a concentration of 140 Torr) is the exclusive fate of CH₃, CH₃O and HCO. Neither CH₃O₂ nor HO₂ radicals react with methane. No evidence for the reaction of HO₂ with CS₂ was observed in the recent study by Lovejoy et al. [22] enabling calculation of an upper limit of $k<4 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ for the rate constant of this reaction. Finally we are not aware of any literature data to suggest that there is any reaction between CH₃O₂ and CS₂.

The major source of OH radicals in our model was reaction of chlorine atoms with CH₃OOH. Reaction of chlorine with HO₂ was of minor importance accounting for less than 25% of the OH radical source.

We have not modelled the CH₃Cl/CS₂/Cl₂/air system as there is insufficient kinetic and mechanistic data available. However, in the light of the curved plots, and dependence of the initial rate on the CH₃Cl concentration shown in fig. 2, it seems likely that analogous effects are present in this system also.

Given the complexity of the CH₄/CS₂ and CH₃Cl/CS₂ systems, we decided to conduct relative rate experiments of the reaction of Cl atoms with CS₂ using a reference organic which possessed only one hydrogen atom thereby precluding generation of OH rad-
icals in the system. We chose to use freon-22 (CHF$_2$Cl) as the reference. Results are shown in fig. 3. Within our experimental uncertainties, there is no evidence for curvature of this data plot. Linear least squares analysis of the data given in fig. 3 yields a value of 1.05±0.05 for the rate constant ratio $k(\text{Cl} + \text{CS}_2)/k(\text{Cl} + \text{CHF}_2\text{Cl})$. Additionally, we measured the reactivity of Cl atoms towards CHF$_2$Cl relative to CH$_4$ in 700 Torr of nitrogen diluent; these results are also displayed in fig. 3. From these latter experiments we are able to define an upper limit of $k(\text{Cl} + \text{CHF}_2\text{Cl})/k(\text{Cl} + \text{CH}_4) < 0.04$. Using the literature value of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [16], we are then able to calculate an upper limit to the rate constant of the overall reaction of Cl with CS$_2$ in 700 Torr of air at 295 K of $4 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

To further compare the present work with that of Martin et al., we conducted a study of the products of the Cl atom initiated oxidation of CS$_2$. In our experiments, 3 mTorr of CS$_2$ together with 30 mTorr of Cl$_2$ were admitted into the chamber and diluted with N$_2$/O$_2$ mixtures to a total pressure of 700 Torr. The O$_2$ partial pressures used were 10, 150, and 700 Torr. Upon irradiation, CS$_2$ was observed to decay slowly. The observed products were, in order of importance, HCl, CO, CO$_2$, SO$_2$, and COS. Additionally, at the lowest oxygen concentration used, COCl$_2$ and SOCl$_2$ were detected as minor products. The major sulfur containing product observed was SO$_2$ with a yield (in terms of sulfur balance) of 50±20% (somewhat lower than the 70–82% yield reported by Martin et al.). Within our experimental errors, we observed no dependence of the SO$_2$ yield on O$_2$ partial pressure. Consistent with the observation of Martin et al., we observed the COS yield to increase by a factor of 4 on increasing the O$_2$ partial pressure from 10 to 700 Torr.

In terms of understanding the mechanism by which CS$_2$ is oxidized following the irradiation of CS$_2$/Cl$_2$/O$_2$ mixtures, the most significant observation in our product study was that of large amounts of HCl, CO and CO$_2$ products. In the present work the HCl yield and the sum of the CO and CO$_2$ yields were larger than the observed loss of CS$_2$ by factors of 9–15 and 3–8, respectively. Martin et al. observed HCl as a product in their system but, in marked contrast to our observations, did not report any CO or CO$_2$.

The HCl product in our experiments results from the reaction of Cl atoms with hydrogen containing compounds present either as impurities in the diluent gases used or on the walls of our reactor. In either case, a likely result of such reactions is the generation of OH radicals. Clearly, a detailed comparison between our product yields and those reported by Martin et al. is not justified at the present time.

4. Discussion

We have established an upper limit to the rate constant of the overall reaction of Cl with CS$_2$ in 700 Torr of air at 295 K of $k_1 < 4 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, reaction (1).

This value is consistent with the upper limit of $k^*_1 < 5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, reported by Nicovich et al. [7] for 300 Torr of air, where $k^*_1$ is defined as the overall rate constant for reaction (1) via all channels for which the adduct reaction with O$_2$ does not regenerate chlorine atoms. In contrast, our value is at least 20 times lower than that reported by Martin et al. [6] who used a relative technique almost identical to our own. As discussed above, we observe nonlinear decay plots when using CH$_4$ or CHF$_2$Cl as references. It is interesting to note that Martin et al. [6] did not also observe such nonlinear behavior. Instead, these workers report linear behavior. It is of interest to compare the initial slope, $k_1/k_2$, from our data in fig. 1 using initial concen-
tration ratios, \([\text{CH}_4]/[\text{CS}_2]\), of 1.7 and 3.5, i.e. those which most closely match the ratio of approximately 2 used by Martin et al. Linear least squares analysis of our data corresponding to \(\text{CH}_4\) loss of less than 30\% yields a rate constant ratio of \(\approx 0.8\) which is indistinguishable, within the experimental errors, with the value of 0.9 reported by Martin et al.

Under the conditions of our experiments, the \(\text{CS}_2\) concentration was very small compared to the concentrations of Cl atoms and \(\text{CS}_2\); hence, the steady state approximation to the mechanism consisting of reactions (a), (b) and (c) leads to the expression

\[
k_i = k_9 X[O_2]/(1 + X[O_2])
\]  

(II)

where

\[
X = k_9/k_0 .
\]  

(III)

Nicovich et al. [7] have shown that at room temperature and atmospheric pressure, \(k_9 \approx 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(k_0 \approx 2 \times 10^6 \text{ s}^{-1}\). Substituting these values into eq. (II) along with the value \(k_1 < 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) determined in this study leads to the following upper limit for the ad-

duct + \(O_2\) rate constant: \(k_9 < 8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

From the viewpoint of atmospheric chemistry, the present work provides an upper limit to the overall rate constant for the reaction of Cl with \(\text{CS}_2\) measured under simulated atmospheric conditions. This upper limit is at least two orders of magnitude less than the corresponding rate constant for OH radical attack. As the atmospheric levels of Cl atoms are 1–2 orders of magnitude less than that of OH [23], reaction with Cl atoms represents a negligible sink for \(\text{CS}_2\) in the earth’s atmosphere.

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References

Kinetics of the Reactions of IO Radicals with NO and NO₂

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A laser flash photolysis-long path absorption technique has been employed to study the kinetics of the reactions of IO radicals with NO and NO₂ as a function of temperature and pressure. The IO + NO rate coefficient is independent of pressure over the range 40-200 Torr of N₂, and its temperature dependence over the range 242-359 K is adequately described by the Arrhenius expression

\[ k_1 = (6.9 \pm 1.7) \times 10^{-12} \exp\left[\frac{328 \pm 71}{T}\right] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \] (errors are 2σ, precision only).

These Arrhenius parameters are similar to those determined previously for the ClO + NO and BrO + NO reactions. The IO + NO₂ association reaction is found to be in the falloff regime over the temperature and pressure ranges investigated (254-354 K and 40-750 Torr of N₂). Assuming \( F_e = 0.4 \) independent of temperature, a physically reasonable set of falloff parameters which adequately describe the data are \( k_o = 7.7 \times 10^{-11} (T/300)^{-1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) and \( k_w = 1.55 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) independent of temperature. The IO + NO₂ rate coefficients determined in this study are about a factor of 2 faster than those reported in the only previous study of this reaction.

Introduction

The potential role of iodine in tropospheric photochemistry has received considerable attention in recent years. It has been suggested that IO₃ chemistry can result in catalytic destruction of tropospheric ozone as well as perturbation of the tropospheric cycles of H₂O₂, NOₓ, and sulfur.¹⁻³ Iodine can potentially play a more important role in tropospheric photochemistry than other halogens for two reasons. First, unlike a majority of fluorine, chlorine, and bromine atom precursors, most iodine atom precursors of atmospheric importance are photosensitive at wavelengths (>300 nm) which penetrate to the earth's surface. Second, reactions of hydrogen-containing species with iodine atoms to form the reservoir species HI are, in general, endothermic and do not occur at atmospheric temperatures. (The I + H₂O reaction is

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Reactions of IO Radicals with NO and NO$_2$

a potentially important exception.)

Volatilization of CH$_3$I from the oceans is thought to be an important source of tropospheric iodine.$^{3,4}$ The reaction of O$_3$ with iodide in surface ocean waters may also result in volatilization of significant fluxes of I$_2$ and HOI into the atmosphere.$^{7-9}$ In addition, radioactive iodine atoms, generated as a fission product of uranium fuels, represent a potentially harmful airborne emission from nuclear power installations.$^9$

In the atmosphere, photodissociation of precursor molecules such as CH$_3$I, I$_2$, and HOI produces I atoms, which react with O$_3$ on a time scale of approximately 1 s$^{-1}$ to produce the IO radical. Hence, IO is an important intermediate in tropospheric IO$_x$ chemistry. Recycling of IO back to I atoms occurs primarily by photodissociation and the reaction

$$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2 \quad (1)$$

Data have been presented in the literature$^1$ which suggest that the reaction of IO with CH$_3$SCH$_3$ (dimethyl sulfide) is an important mechanism for recycling IO back to I in the marine boundary layer as well as an important sink for CH$_3$SH$_2$. However, recent work in our laboratory suggests that the IO + CH$_3$SCH$_3$ reaction is much slower than previously thought.$^1$

In addition to undergoing reactions that regenerate iodine atoms, IO radicals can react to form reservoir species:

$$\text{IO} + \text{NO} + \text{N}_2 \rightarrow \text{I} + \text{NO}_2 + \text{N}_2 \quad (2)$$

$$\text{IO} + \text{HO}_2 \rightarrow \text{I} + \text{O}_2 + \text{H}_2 \quad (3a)$$

$$\text{I} + \text{O} \rightarrow \text{IO} + \text{H} \quad (3b)$$

Reaction 2 appears to be the more important of the reservoir-forming reactions except under conditions of extremely low NO.$^{2,12}$ Depending upon the (unknown) rates at which IO and NO$_2$ photodissociates and thermally dissociates, it is possible that IO is the predominant IO$_x$ species in the atmosphere.

It is clear from the above discussion that accurate kinetic data for reactions 1 and 2 are required in order to successfully model tropospheric IO chemistry. Two studies of the kinetics of reaction 1 have appeared in the literature,$^{14,15}$ both of which were restricted to 77 K. The reported values for $k_1$ (298 K) differ by a factor of 1.7. The only reported study of the kinetics of reaction 2$^1$ covered a limited range of temperature and pressure and was carried out under conditions where a significant fraction of IO removal was due to heterogeneous reaction on the reactor walls and to the IO self-reaction. Hence, additional studies of the kinetics of reactions 1 and 2 are needed.

We have employed a laser flash photolysis-long path absorption technique to investigate the kinetics of reactions 1 and 2 as a function of temperature and pressure. Our results are reported in this paper.

Experimental Section

The kinetics of reactions 1 and 2 were investigated by monitoring the temporal profile of IO following 351-nm laser flash photolysis of I$_2$/NO$_3$/NO/N$_2$ mixtures. The laser flash photolysis-long path absorption apparatus was similar to one we employed recently to investigate the reactions of F and Cl atoms with

HNO$_3$.$^6$ A schematic of the apparatus and descriptions of the reaction cell and temperature measurement techniques can be found elsewhere.$^8$ The major apparatus modification required for the present study was replacement of the CW tunable dye laser used for NO$_2$ detection with a broad-band IO probe. An Osram XBO150W/5 150-W xenon arc lamp was employed as the probe light source. The lamp was housed in a PTI A100 housing and powered by a PTI LPS200X power supply.

The XeF laser (Lambda Physik EMG 200) photolysis beam was expanded by means of cylindrical lenses to be 12 cm wide and 2 cm high as it traversed the reactor. The xenon arc lamp beam was multipass through the reactor at right angles to the photolysis beam by using modified White cell optics; 32-512 passes were employed, giving absorption path lengths in the range 500-750 cm. Output radiation from the multipass cell was focused onto the entrance slit of a 0.22-m monochromator (SPEX 1681I) adjusted to transmit radiation at 427 nm, the peak of the strong, diffuse (due to excited-state predissociation) 4-0 band of the IO A' $^3$II $\rightarrow$ X'II system.$^{19,10}$ Reflective losses in the multipass system were minimized by using White cell mirrors coated for high reflectivity around 427 nm (Virgo Optics, HR-440). The xenon arc lamp was replaced by a broadband pump laser designed to generate a spectrum around 427 nm (Virgo Optics, M-2-427-D). As a trade-off between light throughput and resolution, the monochromator slit widths were set at 200 µm (resolution 0.72 nm full width at half maximum). Radiation exiting the monochromator was detected by a photomultiplier (Hamamatsu R928), the signal from which was monitored by a signal averager with a 1.5-µs time resolution and 10-bit voltage resolution (Nicolet 370). The results of 32-512 laser shots were averaged to obtain data with suitable signal-to-noise ratio for quantitative kinetic analysis. Digitzed voltage versus time data were transferred to a small computer (Beitron Turbo/XT) for storage and analysis.

In order to avoid accumulation of reaction or photolysis products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reaction cell was typically 2 cm$^{-1}$, and the excimer laser repetition rate was 0.15 Hz. Hence, the gas mixture in the photolysis zone was replenished between laser shots. NO and NO$_2$ were flowed into the reaction cell from 12-L bulbs containing dilute mixtures in nitrogen (NO) or zero grade air (NO$_2$). Preparation of the NO$_2$ bulb with air as the diluent gas prevented conversion of NO$_2$ to NO during storage. An I$_2$/N$_2$ flow was generated by passing N$_2$ through a tube containing iodine crystals. To prevent condensation of IO$_x$ species on the antireflection coated reaction cell windows, a four-port gas input/output system was employed.$^{16}$ The NO mixture, NO$_2$ mixture, and 85-90% of the N$_2$ buffer gas entered the reactor through an outer port while the I$_2$/N$_2$ mixture entered through the corresponding inner port. The remaining 10-15% of the N$_2$ buffer gas entered the reactor through the opposite outer port. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. In addition, the concentrations of NO$_2$ and I$_2$ were measured in situ in the slow flow system by UV-vis photometry using separate absorption cells plumbed in series with the reaction cell. Three closely spaced mercury lines around 366 nm were employed for NO$_2$ detection. With the combination of an Hg pen-ray lamp light source and the band-pass filter employed to isolate the 366-nm lines, the effective NO$_2$ absorption cross section is known to be $5.75 \times 10^{-19}$ cm$^2$.$^{20}$ Determination of the I$_2$ concentration was accomplished using 488-nm radiation from an argon ion laser as the light source and correcting the measured absorbance for the NO$_2$ contribution. Absorption cross sections for I$_2$ and NO$_2$ at 488 nm were taken from literature sources.$^{36,37}$


to be $1.64 \times 10^{-14}$ cm$^2$ and $2.68 \times 10^{-15}$ cm$^2$, respectively. The fraction of NO in the NO/N$_2$ bulb was checked at the end of each set of experiments by diluting the bulb with O$_2$, allowing sufficient time for quantitative conversion of NO to NO$_2$, and then measuring the NO$_2$ photometrically.

The gases used in this study were obtained from Matheson and had the following stated minimum purities: N$_2$, 99.999%; O$_2$, 99.99%; NO, 99.0%. Air was ultra zero grade with total hydrocarbons less than 0.1 ppm. N$_2$, O$_2$, and air were used as supplied. Purification of NO involved passage over ascarite and degassing at 77 K. NO$_2$ was prepared by mixing 1 part with 3 parts O$_2$ at a total pressure of 1000 Torr and allowing the mixture to react overnight. The resulting NO$_2$/O$_2$ mixture was pumped through a liquid nitrogen trap where the NO$_2$ was frozen out and the O$_2$ pumped away. The lack of any blue color in the trapped white solid indicated complete conversion of NO to NO$_2$.

Iodine crystals were obtained from Aldrich and had a stated minimum purity of 99.999%; they were used without further purification. Iodine was admitted to the reactor by diverting a small stream of air into a Finnigan gas chopper which was driven by a flow meter and needle valve, then through the tube containing I$_2$ crystals, and finally into the reactor. An ice-water bath was employed to keep the I$_2$ crystals at a constant temperature of 273 K, thus avoiding drifts in the I$_2$ concentration during the course of experiments.

**Results and Discussion**

The following scheme was employed to generate IO radicals:

1. $\text{NO}_2 + h\nu$ (351 nm) $\rightarrow$ NO + O (4)
2. $\text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I}_2$ (5a)
3. $\text{IO} \rightarrow \text{IO}^*$ + I (5b)
4. $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ (6)
5. $\text{IO}^* + \text{M} \rightarrow \text{IO} + \text{M}$ (7)

In the above reaction scheme, IO$^*$ represents vibrationally excited IO: our detection method is not sensitive to IO$^*$. In preliminary experiments, a mixture containing 1 x 10$^{-13}$ NO$_2$ cm$^{-1}$, 1 x 10$^{-13}$ I$_2$ cm$^{-1}$, and 20 Torr of N$_2$ was photolyzed and the appearance rate of 427-nm absorption was observed. Based on the literature value for $k_2$ and an IO concentration of about 10$^{-13}$ cm$^{-1}$, the observed photolysis rate was about 30 s$^{-1}$. However, the IO appearance rate increased with increasing pressure, suggesting that reaction 7 was the rate-limiting IO production step. In all experiments used to determine $k_1$ and $k_2$, the IO appearance rate was at least a factor of 5 faster than the IO decay rate. Reaction 5 is known to be 14 times faster than reaction 6, so it was not difficult to establish experimental conditions where most photolytically generated oxygen atoms reacted with I$_2$ rather than with NO$_2$.

For the optical path lengths (13-20 m) traversed by the probe beam through the reaction cell and the NO$_2$ concentrations employed (up to 3.05 x 10$^{13}$ molecules cm$^{-2}$), a large fraction of the probe radiation was absorbed by NO$_2$. Hence, destruction of NO$_2$ by reactions 4 and 6 led to a noticeable difference between the (base line) signal levels before and after the laser fired in experiments where NO$_2$ was photolyzed in the absence of I$_2$. In the presence of I$_2$, the magnitude of the rapid base-line shift upon firing the laser was reduced somewhat due to the occurrence of reaction 5 in competition with reaction 6. However, the IO generated by reaction 5 decayed via processes that either generated NO$_2$ (IO + NO) or converted NO$_2$ to IONO$_2$, a species whose absorption cross section at 427 nm is not known. Sander and Watson have shown that if an elementary reaction results in an absorbance change due to removal of an absorbing excess reactant and/or formation of an absorbing product, the correct decay rate is obtained from the first-order decay of the overall absorbance by using the signal level at t = $\infty$ as the base line. All of our kinetic data were analyzed in this manner. The only potential complication due to absorption of probe radiation by species other than IO which may have caused a problem in our kinetic analysis is the reaction of iodine atoms generated via reaction 5 with NO$_2$, i.e.

$$\text{I} + \text{NO}_2 + \text{M} \rightarrow \text{INO}_2 + \text{M}$$ (8)

The kinetics of reaction 8 have been characterized and an INO$_2$ absorption spectrum has been searched for unsuccessfully, leading van den Bergh and Troe to conclude that $e(\text{INO}_2) < e(\text{NO}_2)$ over the wavelength range 250-600 nm; their results suggest that absorption by INO$_2$ had a negligible effect on our experiments. We did notice, however, that the difference between the base line before the laser fired and the base line after IO had decayed away was typically smaller than predicted based on calculation of the amount of NO$_2$ destroyed. Apparently, INO$_2$ has a significant absorption cross section at 427 nm.

To ensure that we were detecting the IO radical, the spectrum of the absorbing species was mapped out over the wavelength range transmitted through the White cell (414-446 nm). The 5-0, 4-0, 3-0, and 2-0 bands of 10$^{14.19}$ were observed; no transient absorption was observed at wavelengths between the IO bands although, as discussed above, small base-line shifts do occur due to NO$_2$ removal and (probably) due to NO$_2$ formation. The apparent IO absorption cross section at the peak of the 4-0 band was estimated based on the measured laser fluence, the measured NO$_2$ and I$_2$ concentrations, and the known rate coefficients for reactions 5 and 6. A cross section of $(1.8 \pm 0.3) \times 10^{-19}$ cm$^2$ was obtained. At high resolution, the peak absorption cross section for the 4-0 band is $3.1 \times 10^{-17}$ cm$^2$. Our measured cross section is in the range expected based on the known high-resolution cross section, the known bandwidth, and our monochromator resolution of 0.72 nm.

Results obtained for reactions 1 and 2 are discussed separately below.

**The IO + NO Reaction.** Reaction mixtures employed to study reaction 1 contained 35 mTorr of NO$_2$, 0-14 mTorr of NO, 30-63 mTorr of I$_2$, and 40-200 Torr of N$_2$ buffer gas. As mentioned above, a small amount of O$_2$ (typically about 0.5 Torr) was also present in the reaction mixture because the NO$_2$ storage bulb contained air rather than N$_2$ as the diluent gas. Concentrations of IO radicals generated via reaction 7 were in the range of $(1.7-4.3) \times 10^{12}$ molecules cm$^{-3}$. In nearly all experiments, IO removal was dominated by reactions 1 and 2, so the data could be analyzed assuming pseudo-first-order kinetics:

$$\ln \left[ \frac{[\text{IO}]_0}{[\text{IO}]} \right] = \ln \left[ \frac{[\text{S}]/[\text{S}_0]}{[\text{S}]/[\text{S}_0]} \right] = (k_1[\text{NO}] + k_2[\text{NO}_2] + k_4)t = k't$$ (1)

In eq 1, $t'$ represents a time shortly after the laser fired when IO production was complete but little or no IO decay had occurred, $t$ represents a time after IO removal had gone to completion but before NO$_2$, INO$_2$, and IONO$_2$ destroyed or produced as a result of the laser flash diffused or flowed out of the detection volume. $S$ represents the signal level at time $t$, and $k_t$ represents the first-order rate coefficient for the process IO $\rightarrow$ loss by reaction with background impurities and diffusion out of the detection zone (9)

Under the conditions of our experiments $k_2[\text{NO}_2] \gg k_4$. The only significant interference in the study of reaction 1 was from the fast reaction

$$\text{IO} + \text{NO} \rightarrow \text{products}$$ (10)
Reactions of IO Radicals with NO and NO₂

While the contribution of reaction 10 was negligible in most experiments, it was significant at short times after the laser flash in experiments where NO levels were low. Temporal profiles measured under such conditions were corrected for the contribution from reaction 10 as follows: The experimental temporal profile was analyzed under the (incorrect) assumption that the decay was exponential to obtain a best-fit first-order decay rate, \( k' \). The temporal profile was also simulated by numerical integration of the rate equations assuming that the only important IO loss reaction is reaction 10. Experimental conditions: \( T = 273 \text{ K} \); \( P = 40 \text{ Torr of N}_2 \); electronic time constant = 16 μs; absorption path length ~ 552 cm; \( [\text{I} \text{O}] = 1.2 \times 10^3 \text{ molecules cm}^{-3} \); \( [\text{NO}] = 9.5 \times 10^4 \text{ molecules cm}^{-3} \); \( [\text{NO}] \text{ in units of } 10^4 \text{ molecules cm}^{-3} = (a) 0.028, (b) 1.30, (c) 2.47, and (d) 4.80. Number of laser shots averaged = (a) 128, (b) 320, (c) 384, and (d) 320. Solid lines are obtained from linear least-squares analyses and give the following pseudo-first-order decay rates (units are s⁻¹): (a) 992, (b) 3900, (c) 6610, (d) 11800. For the sake of clarity, temporal profiles are shifted on the absorbance scale; peak percent absorption was (a) 2.7, (b) 2.0, (c) 1.8, and (d) 1.7.

To measure \( k_i(T) \), pseudo-first-order IO decay rates were measured as a function of \( [\text{NO}] \) at constant \( [\text{NO}_2] \). Typical results are shown in Figures 1 and 2. As predicted by eq 1, observed IO decays were exponential and plots of \( k' \) versus \([\text{NO}]\) were linear; the desired bimolecular rate coefficients, \( k_{i(T)} \), were obtained from the slopes of the \( k' \) versus \([\text{NO}]\) plots. Measured rate coefficients are given along with other pertinent information in Table I. Uncertainties given in Table I for \( k_i(T) \) values are 2σ and represent precision only. Taking into account possible systematic errors (primarily in the determination of the NO concentration), we estimate the absolute uncertainty in any measured \( k_i(T) \) to be ±20% except at 328 K where unusually poor precision limits the absolute accuracy to ±25%.

Our results demonstrate that \( k_i(298 \text{ K}) \) is independent of pressure over the range 40–200 Torr and that \( k_i(T) \) increases with decreasing temperature. An Arrhenius plot for reaction 1 is shown in Figure 3. A weighted linear least-squares analysis of the ln \( k_i \) versus \( T^{-1} \) data gives the Arrhenius expression

\[
k_i(T) = \frac{(6.9 \pm 1.7) \times 10^{-12} \exp[(328 \pm 71)/T]}{\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}
\]

where uncertainties are 2σ and represent precision only.

![Figure 1](image1.png)

**Figure 1.** Typical IO temporal profiles observed in the study of the IO + NO reaction. Experimental conditions: \( T = 273 \text{ K} \); \( P = 40 \text{ Torr of N}_2 \); electronic time constant = 16 μs; absorption path length ~ 552 cm; \( [\text{I} \text{O}] = 1.2 \times 10^3 \text{ molecules cm}^{-3} \); \( [\text{NO}] = 9.5 \times 10^4 \text{ molecules cm}^{-3} \). Exponential to obtain a best-fit first-order decay rate, \( k' \). The temporal profile was also simulated by numerical integration of the rate equations assuming that the only important 10 loss reaction is reaction 10. Experimental conditions: \( T = 273 \text{ K} \); \( P = 40 \text{ Torr of N}_2 \); electronic time constant = 16 μs; absorption path length ~ 552 cm; \( [\text{I} \text{O}] = 1.2 \times 10^3 \text{ molecules cm}^{-3} \); \( [\text{NO}] = 9.5 \times 10^4 \text{ molecules cm}^{-3} \); \( [\text{NO}] \text{ in units of } 10^4 \text{ molecules cm}^{-3} = (a) 0.028, (b) 1.30, (c) 2.47, and (d) 4.80. Number of laser shots averaged = (a) 128, (b) 320, (c) 384, and (d) 320. Solid lines are obtained from linear least-squares analyses and give the following pseudo-first-order decay rates (units are s⁻¹): (a) 992, (b) 3900, (c) 6610, (d) 11800. For the sake of clarity, temporal profiles are shifted on the absorbance scale; peak percent absorption was (a) 2.7, (b) 2.0, (c) 1.8, and (d) 1.7.

**Figure 2.** Plots of \( k' \) versus \([\text{NO}]\) for data obtained at the temperature extremes of the IO + NO study. Solid lines are obtained from linear least-squares analyses and give the rate coefficients shown in the figure (units are cm³ molecule⁻¹ s⁻¹).

**TABLE I: Kinetic Data for the Reaction IO + NO → I + NO₂**

<table>
<thead>
<tr>
<th>( T, K )</th>
<th>( P, \text{Torr} )</th>
<th>( [\text{I} \text{O}] )</th>
<th>( [\text{NO}] )</th>
<th>( [\text{NO}_2] )</th>
<th>( k' ), s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>242</td>
<td>40</td>
<td>900</td>
<td>1130</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>273</td>
<td>40</td>
<td>1200</td>
<td>950</td>
<td>2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>298</td>
<td>40</td>
<td>1100</td>
<td>940</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>328</td>
<td>40</td>
<td>900</td>
<td>1020</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>359</td>
<td>40</td>
<td>1700</td>
<td>1100</td>
<td>3.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*Errors are 2σ and represent precision only.*

*Corrected downward by ±2% to account for contribution from the IO + IO reaction.*
The kinetics of reaction 1 have been studied previously only at 298 K. For the sake of comparison, the two previous determinations of $k_1(298 \text{ K})$ are plotted along with our data in Figure 3. Ray and Watson employed the discharge flow-mass spectrometry technique to study reaction 1 using the O$^+$ + I$_2$ reaction as the IO source; they obtained the result $k_1(298 \text{ K}) = (1.67 \pm 0.16) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The value for $k_1(298 \text{ K})$ determined in this study is intermediate between those reported previously. The small negative activation energy observed for reaction 1 (Figure 3) is consistent with the temperature dependence observed previously for the CIO + NO reaction and is typical of radical-radical reactions that proceed on a potential energy surface with a minimum along the reaction coordinate (corresponding in this case to IO NO which, to our knowledge, has never been observed but should be a bound species).

**The I0 + NO 2 Reaction.** Reaction mixtures employed to study reaction 2 contained 22-68 mTorr of I$_2$, 6-94 mTorr of NO$_2$, and 40-750 Torr of N$_2$ buffer gas. As mentioned above, a small amount of O$_3$ was also present in the reaction mixture because the NO$_2$ storage bulb contained air rather than N$_2$ as the diluent gas; typically [O$_3$] $\sim$ 10$^{-15}$ molecules cm$^{-3}$. Concentrations of IO radicals generated via reactions 4-7 were in the range (0.6-5.0) x 10$^{12}$ molecules cm$^{-3}$. The method of data analysis was similar to that described above for the I0 + NO reaction except, in the case of reaction 2, all measured IO temporal profiles were corrected for contributions from IO reaction with itself (usually very minor) and with flash-generated NO. The magnitude of the required corrections increased with increasing laser fluence. For a constant laser fluence, the corrections were largest at low pressure since the I0 + NO$_2$ reaction rate is pressure dependent while the I0 + NO reaction rate is pressure independent. A typical I0 temporal profile observed in 40 Torr of N$_2$ at 298 K is shown in Figure 4 while uncorrected and corrected $k'$ versus [NO$_2$] plots for the 40 Torr (N$_2$)$_2$ 298 K data are shown in Figure 5. At 254 K, the low-temperature extreme of our study, a small fraction of NO$_2$ was tied up as NO$_3$ ([NO$_3$] $\geq$ 37 [NO$_2$] in all experiments).

**Figure 3.** Arrhenius plot for the reaction IO + NO $\rightarrow$ I + NO$_2$. Filled circles are our data at $P = 40$ Torr, and open circle is our data at $P = 200$ Torr. The solid line is obtained from a weighted linear least-squares analysis and gives the Arrhenius expression shown in the figure (units are cm$^3$ molecule$^{-1}$ s$^{-1}$).

**Figure 4.** Typical I0 temporal profile observed in the study of the I0 + NO$_2$ reaction at $P = 40$ Torr and $T = 298$ K. [NO$_2$] $= 1.59 \times 10^{15}$ molecules cm$^{-3}$; [I$_2$] $= 1.6 \times 10^{13}$ molecules cm$^{-3}$; electronic time constant $= 16 \mu$s; absorption path length $\sim$ 552 cm; 256 laser shots averaged. Note that the base line after I0 decay is higher than the pretrigger base line by 0.00072 V, the equivalent of 0.13% absorption. The inset is a plot of ln(absorbance) versus time for the same data with absorbances calculated by using the base line obtained after I0 decayed away. The solid line in the inset is obtained from a linear least-squares analysis and gives the decay rate $k'$ $= 1100$ s$^{-1}$. The dashed line in the inset is the decay rate corrected for I0 reaction with itself and with flash-generated NO ($k'_{\text{corr}} = 950$ s$^{-1}$).

**Figure 5.** Plot of $k'$ versus [NO$_2$] for data obtained at 298 K in 40 Torr of N$_2$. Open circles are uncorrected for IO reaction with itself and with flash-generated NO while filled circles are corrected for these processes. Solid and dashed lines are obtained from linear least-squares analyses and give the rate coefficients shown in the figure (units are cm$^3$ mole- cule$^{-1}$ s$^{-1}$).

Kinetic analyses employed the reasonable assumption that N$_2$O$_4$ is much less reactive toward IO than NO$_2$.

Measured bimolecular rate coefficients $k_2([M], T)$ are summarized along with other pertinent information in Table II. Uncertainties given in Table II for $k_2([M], T)$ values are 2σ and represent precision only. Small systematic errors are possible in the NO$_2$ concentration determination and due to the assumption that absorption of 427-nm radiation by INO$_2$ had a totally negligible effect on the $k_2([M], T)$ determinations. We estimate the accuracy of any measured $k_2([M], T)$ to be ±20%.

Our results demonstrate that reaction 2 is in the "fallloff" regime between third- and second-order kinetics over the temperature and pressure ranges investigated. Troc and co-workers have

shown that bimolecular rate coefficient versus pressure curves (i.e., falloff curves) for association reactions can be approximated by the three-parameter equation

\[ k([M], T) = k_0(T)F_{\text{LH}}F([M], T) \]  

(IV)

where \( F_{\text{LH}} \) is the Lindeman-Hinshelwood factor

\[ F_{\text{LH}} = \frac{\text{X}}{\text{X}} \]  

(V)

\[ \text{X} = k_0([M], T)[M]/k_0(T) \]  

(VI)

In the above equations, \( k_0([M], T) \) is the rate coefficient in the low-pressure third-order limit, \( k_0(T) \) is the rate coefficient in the high-pressure second-order limit, and \( F([M], T) \) is the parameter which characterizes the broadening of the falloff curve due to the energy dependence of the rate coefficient for decomposition of the energized adduct. \( F([M], T) \) can be calculated from the spectroscopic and thermodynamic properties of the adduct. Examples of studies where detailed analyses of falloff behavior have been carried out include our study of the \( \text{OH} + \text{SO}_2 \) reaction\(^{34} \) and Sander et al.'s study of the \( \text{BrO} + \text{NO}_2 \) reaction.\(^{39} \) Hence, we take the temperature and pressure dependences of atmospheric association reactions independent of temperature (see text for rationale). A: \( k_0(298 \text{K}) \) and \( k_0(300 \text{K}) \) obtained by fitting 298 K data only; \( n \) and \( m \) obtained by fitting all data with \( m \) independent of temperature (see text for rationale). B: \( k_0(298 \text{K}) \) and \( k_0(300 \text{K}) \) obtained by fitting 298 K data only; \( n \) and \( m \) obtained by fitting all data with \( m \) independent of temperature (see text for rationale). C: \( k_0(300 \text{K}) \) and \( k_0(T) \) obtained by fitting all data with \( m \) independent of temperature (see text for rationale). The table below summarizes the rate coefficients obtained from the best-fit falloff parameters.

**TABLE II: Summary of Kinetic Data for the Reaction \( \text{IO} + \text{NO}_3 \rightarrow \text{IONO}_2 + \text{N}_2 \)**

<table>
<thead>
<tr>
<th>T, K</th>
<th>no. of expts</th>
<th>( N_2 )</th>
<th>( I_2 )</th>
<th>( \text{NO}_3^-/\text{IO}_3^- )</th>
<th>range of ( k', \text{s}^{-1} )</th>
<th>10(^{13}k_0, \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>7</td>
<td>3.240</td>
<td>0.8</td>
<td>0.23 - 1.54</td>
<td>290 - 880</td>
<td>406 - 2700</td>
</tr>
<tr>
<td>298</td>
<td>4</td>
<td>19.400</td>
<td>0.0</td>
<td>0.50 - 3.18</td>
<td>2120 - 1200</td>
<td>2230 - 6900</td>
</tr>
<tr>
<td>275</td>
<td>4</td>
<td>3.240</td>
<td>1.3</td>
<td>0.52 - 2.51</td>
<td>280 - 1200</td>
<td>782 - 3840</td>
</tr>
<tr>
<td>275</td>
<td>4</td>
<td>19.400</td>
<td>1.3</td>
<td>0.58 - 2.15</td>
<td>310</td>
<td>2060 - 8050</td>
</tr>
<tr>
<td>298</td>
<td>5</td>
<td>1.300</td>
<td>1.6</td>
<td>0.29 - 1.15</td>
<td>340</td>
<td>250 - 1470</td>
</tr>
<tr>
<td>298</td>
<td>6</td>
<td>3.240</td>
<td>2.0</td>
<td>0.35 - 1.15</td>
<td>410</td>
<td>434 - 2620</td>
</tr>
<tr>
<td>298</td>
<td>7</td>
<td>13.000</td>
<td>2.0</td>
<td>0.26 - 1.05</td>
<td>260 - 3400</td>
<td>719 - 4110</td>
</tr>
<tr>
<td>298</td>
<td>7</td>
<td>24.300</td>
<td>0.7</td>
<td>0.35 - 1.89</td>
<td>390</td>
<td>1170 - 6910</td>
</tr>
<tr>
<td>320</td>
<td>4</td>
<td>3.240</td>
<td>1.0</td>
<td>0.25 - 1.84</td>
<td>692 - 8080</td>
<td>692 - 8080</td>
</tr>
<tr>
<td>345</td>
<td>4</td>
<td>3.240</td>
<td>0.6</td>
<td>0.45 - 1.74</td>
<td>250</td>
<td>963 - 3700</td>
</tr>
<tr>
<td>354</td>
<td>4</td>
<td>3.240</td>
<td>0.7</td>
<td>0.72 - 2.09</td>
<td>390</td>
<td>1450 - 3980</td>
</tr>
</tbody>
</table>

**TABLE III: Comparison of Measured \( \text{IO} + \text{NO}_3 \rightarrow \text{IONO}_2 + \text{N}_2 \) Rate Coefficients with Those Obtained from "Best Fit" Falloff Parameters**

<table>
<thead>
<tr>
<th>T, K</th>
<th>( 10^{-11}[\text{M}] )</th>
<th>( 10^{13}k_2, \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>254</td>
<td>3.24</td>
</tr>
<tr>
<td>298</td>
<td>298</td>
<td>1.30</td>
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<td>298</td>
<td>3.24</td>
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<tr>
<td>320</td>
<td>320</td>
<td>2.34</td>
</tr>
<tr>
<td>354</td>
<td>354</td>
<td>2.34</td>
</tr>
<tr>
<td>354</td>
<td>354</td>
<td>2.34</td>
</tr>
</tbody>
</table>

**Errors are 2a and represent a measurement of one 10% temporal profile. a Units are \( 10^{13} \) molecules cm\(^{-3} \). b Corrected for contributions from the \( \text{IO} + \text{IO} + \text{NO} \) reactions. c Errors are 2a and represent precision only.
dramatically changes the best-fit $k_0$ derived from our data is rather large. The current NASA panel evaluation, for example, considers 36 association reactions of atmospheric importance (but no IO reactions); recommended values for $n$ range from 0 to 4.3. Two points should be made regarding the value $n \approx 5$ obtained in this study. First, no data were obtained at pressures close to the low-pressure limit, so the uncertainties in derived values for $k_0(300 \text{ K})$ and $n$ are significant. Second, IO may be a species which exhibits large temperature coefficients for association reactions. For example, the association channel for the IO self-reaction is known to have an unusually large negative activation energy. 

As can be seen from examination of Figure 6, the rate coefficients $k_0([M],T)$ reported in this study are about a factor of 2 faster than those reported previously by Jenkin and Cox, who employed a molecular modulation technique to study reaction 2 over the pressure ranges 35–404 Torr at 277 K and 24–101 Torr at 303 K. The study of Jenkin and Cox had two problems which may have resulted in inaccurate values for $k_0([M],T)$. Firstly, even at the highest NO$_2$ levels employed, extrapolated background IO removal rates (presumably due to heterogeneous processes) were about as fast as the apparent rate of IO removal by NO$_2$. Secondly, a second-order component was observed in their IO decay which increased markedly in importance with increasing pressure. Jenkin and Cox attributed the second-order component to the IO self-reaction. The recent study of the IO self-reaction by Sander found a much smaller pressure-dependent component and much larger pressure-independent component to $k_0$ than reported by Jenkin and Cox. Thus, the procedure used by Jenkin and Cox to extract values for $k_0([M],T)$ from their observed mixed first- and second-order decays must be considered suspect. It is of interest to compare the IO + NO$_2$ rate coefficients obtained in this study with reported measurements of $k_1$, $k_2([M],T)$, and $k_12([M],T)$. 

At 298 K, the high-pressure-limit rate coefficients are roughly equal for all three reactions, but the low-pressure-limit rate coefficients increase in the order $\text{IO} < \text{BrO} < \text{IO}$. Hence, at atmospheric pressures $k_3 > k_4 > k_1$. It is now generally accepted that the yields of products other than ClONO$_2$ from reaction 1 are negligible. However, DeMore et al. point out that "even though isomer formation seems to have been ruled out for the ClO + NO$_2$ reaction (i.e. the isomer stability is too low to make a significant contribution to the measured rate constant), this does not eliminate the possibility that BrO + NO$_2$ leads to more than one stable compound. In fact, if the measured low pressure limit rate constant for BrO + NO$_2$ is accepted, it can only be theoretically reconciled with reaction..."
A single isomer, BrONO$_2$, which would have a 6–7 kcal mole$^{-1}$ stronger bond than ClONO$_2$. This would fix the heat of formation of BrONO$_2$ to be the same as ClONO$_2$, an unlikely possibility." A similar situation exists when comparing the measured low-pressure limit rate coefficient for IO + NO$_2$ with that for ClO + NO$_2$. Clearly, the thermochemistry of XONO$_2$ (X = Br, I) requires further investigation, as does the possible formation of isomers such as OXNO$_2$, XOONO, or OXONO.

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Registry No. IO, 14696-98-1; NO, 10102-43-9; NO$_2$, 10102-44-0.
Kinetics of the Reactions of Cl(2P_d) and Br(2P_{3/2}) with O_3

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Abstract

A laser flash photolysis-resonance fluorescence technique has been employed to study the kinetics of the important stratospheric reactions Cl(2P_d) + O_3 \rightarrow ClO + O_2 and Br(2P_{3/2}) + O_3 \rightarrow BrO + O_2 as a function of temperature. The temperature dependence observed for the Cl(2P_d) + O_3 reaction is non-Arrhenius, but can be adequately described by the following two Arrhenius expressions (units are cm^3 molecule^{-1} s^{-1}, errors are 2\sigma and represent precision only): k_{1}(T) = (1.19 \pm 0.21) \times 10^{-13} \exp \left[(-33 \pm 37)/T\right] \text{ for } T = 189-269 \text{ K} and k_{1}(T) = (2.49 \pm 0.38) \times 10^{-13} \exp\left[(-233 \pm 46)/T\right] \text{ for } T = 269-385 \text{ K}. At temperatures below 230 K, the rate coefficients determined in this study are faster than any reported previously. Incorporation of our values for k_{1}(T) into stratospheric models would increase calculated ClO levels and decrease calculated HCl levels, hence the calculated efficiency of ClO, catalyzed ozone destruction would increase. The temperature dependence observed for the Br(2P_{3/2}) + O_3 reaction is adequately described by the following Arrhenius expression (units are cm^3 molecule^{-1} s^{-1}, errors are 2\sigma and represent precision only): k_{2}(T) = (1.50 \pm 0.16) \times 10^{-13} \exp\left[(-775 \pm 30)/T\right] \text{ for } T = 195-392 \text{ K}. While not in quantitative agreement with Arrhenius parameters reported in most previous studies, our results almost exactly reproduce the average of all earlier studies and, therefore, will not affect the choice of k_{2}(T) for use in modeling stratospheric BrO, chemistry.

Catalytic cycles involving ClO_2 and BrO_2 species play an important role in stratospheric chemistry [1,2]. In most catalytic destruction cycles involving ClO_2 and BrO_2, ozone is destroyed by the reactions

\begin{align*}
(1) \quad \text{Cl}(2P_d) + O_3 & \rightarrow \text{ClO} + O_2 \\
(2) \quad \text{Br}(2P_{3/2}) + O_3 & \rightarrow \text{BrO} + O_2.
\end{align*}

Although recycling of halogen monoxide radicals back to halogen atoms is rate-limiting under conditions which typically exist in the stratosphere, quantitative characterization of the kinetics of reactions (1) and (2) is nonetheless important because catalytic efficiencies are influenced by the competition between reactions (1) and (2) and reservoir-forming reactions such as

\begin{align*}
(3) \quad \text{Cl}(2P_d) + CH_4 & \rightarrow CH_3 + HCl \\
(4) \quad \text{Br}(2P_{3/2}) + HO_2 & \rightarrow O_2 + HBr.
\end{align*}

In recent years, two catalytic cycles involving ClO_2 and BrO_2 species have been implicated in the formation of the antarctic ozone hole [3,4]:

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In the wintertime antarctic lower stratosphere, heterogeneous reactions in polar stratospheric clouds (PSCs) can convert the reservoir species HCl and ClONO$_2$ into the photolytically labile species Cl$_2$ and HOCl [5,6], which photolyze rapidly in springtime to generate chlorine atoms. In this manner, high levels of ClO are produced at the expense of HCl and ClONO$_2$. Reactions on PSCs may also result in production of BrO from HBr and BrONO$_2$, although, since BrO is thought to predominate over the reservoir species in the "normal" stratosphere [7], the effect of heterogeneous reactions on BrO chemistry is expected to be much smaller than the effect on ClO chemistry. Under the NO$_x$ free conditions typical of the antarctic ozone hole, conversion of XO to X (X = Cl or Br) via reaction with NO ceases to occur, so reactions (5) and (8) become the principal mechanisms for cycling XO back to X. Hence, a photochemical steady state is established where the rates of reactions (1) and (2) become comparable to the rates of reactions (5) and (8).

A number of kinetics studies of both reaction (1) [8–14] and reaction (2) [14–19] are reported in the literature. At 298 K, there is excellent agreement between the various studies, such that the estimated uncertainties in $k_1(298 \text{ K})$ and $k_2(298 \text{ K})$ are only $\pm 15\%$ and $\pm 20\%$, respectively [20]. However, there is considerable scatter in reported activation energies for both reactions, leading to substantial uncertainties in both $k_1$ and $k_2$ at temperatures typical of the lower stratosphere. In this article we report the results of temperature dependent kinetics studies of reactions (1) and (2) over the temperature ranges 189–385 K and 195–392 K, respectively; particular attention was focused on obtaining accurate kinetic data near the low temperature end of the ranges studied. We find that extrapolation of previously reported Arrhenius expressions for $k_1(T)$ to lower temperature predicts rate coefficients in reasonable agreement with our measurements. However, the temperature dependence for $k_1$ observed in our study is quite different from any reported previously. Our measured value for $k_1(190 \text{ K})$ is significantly faster than would be predicted based on extrapolation of earlier measurements of $k_1(T)$.

**Experimental Technique**

The laser flash photolysis-resonance fluorescence apparatus used in this study was similar to one which we have employed previously in a number
of studies of chlorine atom kinetics [21–25] and one study of bromine atom kinetics [26]. Important features of the apparatus are described below.

A pyrex, jacketed reaction cell with an internal volume of 150 cm$^3$ was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol or a 1:1 methanol-ethanol mixture from a thermostated bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket could be injected into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment. Temperature variation within the reaction volume (i.e., the volume from which fluorescence could be detected) was less than 1 K at both the high and low temperature extremes of the study.

In most experiments halogen atoms ($X$) were produced by 355 nm pulsed laser photolysis of $X_2$. Third harmonic radiation from either a Quanta Ray model DCR-2 or a Quantel model 481-A Nd:YAG laser provided the photolytic light source. These lasers could deliver up to $1 \times 10^{17}$ photons per pulse at a repetition rate of up to 10 Hz; pulsewidths were about 6 ns. In some experiments chlorine atoms were produced by 193 nm pulsed laser photolysis of CF$\text{Cl}_2$. A Lambda Physik model EMG-200 ArF excimer laser was used as the photolytic light source. The excimer laser could deliver up to $4 \times 10^{17}$ 193 nm photons per pulse at a repetition rate of up to 10 Hz; the laser pulsewidth was about 15 ns.

An atomic resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the photolytically produced atoms. The resonance lamp consisted of an electrodeless microwave discharge through about one torr of a flowing mixture containing a trace of $X_2$ in He. The flows of a 0.1% $X_2$ in He mixture and pure He into the lamp were controlled by separate needle valves, thus allowing the total pressure and $X_2$ concentration to be adjusted for optimum signal-to-noise. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell the lamp output passed through a flowing gas filter. For detection of bromine atoms, the filter gas was 50 torr-cm CH$_4$ in N$_2$; this filter prevented radiation at wavelengths shorter than 139 nm (including impurity emissions from excited O, H, Cl, and N atoms) from entering the reaction cell, but transmitted the strong Br lines in the 140–160 nm region. For detection of chlorine atoms, the filter gas was normally 3 torr-cm N$_2$O in N$_2$; this filter blocked virtually all O atom impurity emissions at 130–131 nm while transmitting the chlorine lines in the 135–140 nm wavelength region. In some experiments, N$_2$ or dry air were used as the chlorine lamp filter. The only chlorine atom resonance lines transmitted through 760 torr-cm of air are the $^2D_{5/2, 7/2} - ^2P_{3/2}$ doublet at 118.9 nm [27]. For both chlorine and bromine, fluorescence intensities were found to vary linearly with atom concentration up to levels several times higher than any employed in kinetics experiments ([Br]$_0 \leq 6 \times 10^{11}$ per cm$^3$ and [Cl]$_0 \leq 8 \times 10^{11}$ per cm$^3$ in all experiments).

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and the resonance lamp beam, and imaged onto the photocathode of a solar blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with N$_2$. For detection of chlorine atoms in conjunction with N$_2$O/N$_2$ or pure N$_2$
lamp filters, a calcium fluoride window was placed between the reaction cell and the photomultiplier to prevent detection of emissions at wavelengths shorter than 125 nm (Lyman-α emission, for example). Signals were processed using photon counting techniques in conjunction with multi-channel scaling. For each halogen atom decay measured, signals from a large number of laser shots were averaged in order to obtain a well-defined temporal profile over (typically) three 1/e lifetimes of decay. The multi-channel analyzer sweep was triggered prior to the photolysis laser in order to allow a pre-trigger baseline to be obtained.

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was 2–3 cm s⁻¹ while the laser repetition rate was varied over the range 1–10 Hz. Even at the highest repetition rate employed, no volume element of the reaction mixture was subjected to more than a few laser shots. Cl₂, CF₂Cl₂, Br₂, and O₃ were flowed into the reaction cell from 12 liter bulbs containing dilute mixtures in nitrogen buffer gas. Hydrogen and nitrogen were flowed directly from their high pressure storage tanks. In most experiments, all components of the reaction mixtures were premixed before entering the reaction cell. As a check for the possible occurrence of heterogeneous reactions between X₂ and O₃, some experiments were carried out in a configuration where X₂ was injected into the reaction cell through a 1/8 inch O.D. teflon tube positioned such that X₂ mixed with other components in the reaction mixture about 2 cm upstream from the reaction zone. Concentrations of each component in the reaction mixtures were determined from measurements of the appropriate mass flow rates and the total pressure. The O₃ concentration was also measured in situ in the slow flow system by UV photometry at 253.7 nm using a 2-meter long absorption cell; the O₃ absorption cross section required to convert measured absorbances to concentrations was taken to be 1.146 × 10⁻¹⁷ cm² [28–31]. In most Cl + O₃ experiments the absorption cell was positioned downstream from the reaction cell. However, to check for O₃ loss in the flow system, some experiments were carried out with the absorption cell positioned upstream from the reactor. The Br + O₃ experiments employed two absorption cells, one upstream and one downstream from the reactor.

The stable, pure gases used in this study had the following stated minimum purities: N₂, 99.999%; Cl₂, 99.99%; CF₂Cl₂, 99.0%; O₂, 99.99%; H₂, 99.999%. Nitrogen, oxygen, and hydrogen were used as supplied while chlorine and CF₂Cl₂ were degased repeatedly at 77 K before use. Bromine was Fisher ACS reagent grade with a maximum impurity level of 0.06%; it was transferred into a vial fitted with a high vacuum stopcock, then degased repeatedly at 77 K before use. Ozone was prepared in a commercial ozonator using UHP oxyen. It was collected and stored on silica gel at 195 K, and degased at 77 K before use.

**Results and Discussion**

To study the kinetics of reactions (1) and (2) it is desirable to establish experimental conditions where the X(^3P₂) temporal profile is governed entirely by the following processes:
KINETICS OF REACTIONS

(9) \[ RX + h\nu \rightarrow R + X(2P_j) \]

(i) \[ X(2P_j) + O_3 \rightarrow XO + O_2 \quad i = 1 \text{ or } 2 \]

(10) \[ X(2P_j) \rightarrow \text{first order loss by diffusion from the detector field of view or reaction with background impurities} \]

Then, since \([O_3] \gg [X(2P_j)]\), simple first-order kinetics are obeyed:

(1) \[ \ln\left[\frac{[X(2P_j)]_0}{[X(2P_j)]_t}\right] = (k[O_3] + k_{i0})t = k't. \]

The bimolecular rate coefficients, \(k_i(T)\), are determined from the slopes of \(k'\) vs. \([O_3]\) plots. Observations of \(X(2P_j)\) temporal profiles which are exponential (i.e., obey equation 1), a linear dependence of \(k'\) on \([O_3]\), and invariance of \(k'\) to variations in laser photon fluence and \(RX\) concentration strongly suggests that reactions (i), (9), and (10) are the only processes which affect the \(X(2P_j)\) time history. Typical \([Br(2P_j)]\) temporal profiles and \(k'\) vs. \([O_3]\) plots for data from our study of reaction (2) are shown in Figures 1 and 2. Results for reactions (1) and (2) are discussed separately below.

![Figure 1](image_url)

Figure 1. Typical halogen atom temporal profiles. Reaction: \(Br(2P_{3/2}) + O_3 \rightarrow BrO + O_2\). Experimental conditions: \(T = 201\) K; \(P = 150\) torr; \([Br_{i0}] = 3.8 \times 10^{12}\) molecules per cm\(^2\); laser fluence \(= 11\) mJ/cm\(^2\); \([O_3]\) in units of \(10^{16}\) molecules per cm\(^2\) = (a) 0, (b) 1.04, (c) 3.29, (d) 5.43; number of laser shots averaged = (a) 64, (b) 128, (c) 926, (d) 1100. Solid lines are obtained from least squares analyses and give the following pseudo-first order decay rates in units of s\(^{-1}\): (a) 25, (b) 376, (c) 979, (d) 1700.
Figure 2. Typical plots of \( k' \), the pseudo-first order halogen atom decay rate, as a function of ozone concentration. Reaction: \( \text{Br}^\left(2\text{P}_{3/2}\right) + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \). For the sake of clarity, data points obtained with \( [\text{O}_3] = 0 \) are not shown. Solid lines are obtained from linear least squares analyses and give the following bimolecular rate coefficients in units of \( 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (errors are \( 2\sigma \), precision only): 195 K, 2.89 \( \pm \) 0.19; 234 K, 5.41 \( \pm \) 0.18; 283 K, 8.64 \( \pm \) 0.93; 376 K, 18.1 \( \pm \) 1.2.

A. The \( \text{Cl} + \text{O}_3 \) Reaction

Most experiments in our study of reaction (1) employed 355 nm photolysis of \( \text{Cl}_2 \) as the \( \text{Cl}^\left(2\text{P}_j\right) \) source. Ozone in its ground vibrational state is totally transparent at 355 nm [32]. The \( \text{N}_2 \) levels employed were sufficiently high that relaxation of atoms in the \( 2\text{P}_{1/2} \) spin-orbit excited state was expected to be much more rapid than the rate of chemical removal of \( \text{Cl}^\left(2\text{P}_j\right) \) [33, 34]. Hence, all measured chlorine atom temporal profiles should be considered as representative of the removal of an equilibrium mixture of \( \text{Cl}^\left(2\text{P}_{3/2}\right) \) and \( \text{Cl}^\left(2\text{P}_{1/2}\right) \). As an experimental check on the above argument, some experiments were carried out with \( \text{CF}_2\text{Cl}_2 \), a species which deactivates \( \text{Cl}^\left(2\text{P}_{1/2}\right) \) at a gas kinetic rate [35], added to the \( \text{Cl}_2/\text{O}_3/\text{N}_2 \) photolysis mixtures. Addition of \( 2 \times 10^{13} \text{ CF}_2\text{Cl}_2 \) per cm\(^3\) had no effect on the observed kinetics of reaction (1). Over the temperature range investigated (189–385 K), the equilibrium fraction of chlorine atoms in the \( 3\text{P}_{1/2} \) state ranges from 0.0012 to 0.037.

A total of about 300 \( \text{Cl}^\left(2\text{P}_j\right) \) temporal profiles were measured under a wide variety of experimental conditions. The results used to obtain values for \( k_1(T) \) are summarized in Table I. All experiments were consistent with equation 1, i.e., all decays were exponential and, in a given set of experiments, \( k' \) increased linearly with increasing ozone concentration. The observed kinetics were unaffected by significant variations in laser repetition rate, \( \text{Cl}_2 \) concentration, the concentration of photolytically produced atoms, and the distance in the flow system over which \( \text{Cl}_2 \) and \( \text{O}_3 \) were allowed to interact before entering the reaction zone. In preliminary experiments (not summarized in Table I) it was established that ozone was not lost during
**Kinetics of Reactions**

**Table I. Summary of kinetic data for the reaction Cl($^3P_J$) + O$_3$ → ClO + O$_2$**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (Torr)</th>
<th>Cl($^2P_J$) [10$^{-18}$ cm$^{-3}$]</th>
<th>[Cl] [10$^{-15}$ cm$^{-3}$]</th>
<th>N</th>
<th>k ($10^{-6}$ cm$^{-3}$ mol$^{-1}$ s$^{-1}$)</th>
<th>10$^{-9}$ cm$^2$ (mol molecule$^{-1}$)$^{-1}$</th>
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</tr>
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<td>180</td>
<td>100</td>
<td>Cl$_2$, 7</td>
<td>5</td>
<td>5</td>
<td>2440</td>
<td>9.66 ± 0.29</td>
<td>d</td>
</tr>
<tr>
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<td>Cl$_2$, 7</td>
<td>5</td>
<td>9</td>
<td>2600</td>
<td>9.82 ± 0.28</td>
<td>d</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<td>9.90 ± 0.20</td>
<td>d</td>
</tr>
<tr>
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<td>ClF, 5</td>
<td>5</td>
<td>4</td>
<td>2280</td>
<td>9.90 ± 0.20</td>
<td>d</td>
</tr>
<tr>
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<td>4</td>
<td>2730</td>
<td>10.3 ± 0.2</td>
<td>d</td>
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<td>6</td>
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<td>1690</td>
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<td>d</td>
</tr>
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<td>Cl, 15</td>
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<td>10.0 ± 0.4</td>
<td>d</td>
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<td>Cl, 15</td>
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<td>10.6 ± 1.0</td>
<td>d</td>
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<td>Cl, 15</td>
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<td>7</td>
<td>1860</td>
<td>10.3 ± 0.7</td>
<td>d</td>
</tr>
<tr>
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<td>Cl, 2, 7</td>
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<td>10.3 ± 0.7</td>
<td>d</td>
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<td>Cl, 2, 7</td>
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<td>1960</td>
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<td>Cl, 11</td>
<td>2</td>
<td>8</td>
<td>2360</td>
<td>10.3 ± 0.7</td>
<td>d</td>
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<td>4</td>
<td>4</td>
<td>1430</td>
<td>10.9 ± 0.8</td>
<td>d</td>
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<td>11.4 ± 0.5</td>
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<td>d</td>
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<td>Cl$_2$, 2</td>
<td>3</td>
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<td>1960</td>
<td>12.9 ± 0.6</td>
<td>d</td>
</tr>
<tr>
<td>220</td>
<td>2000</td>
<td>Cl$_2$, 2</td>
<td>4</td>
<td>7</td>
<td>1520</td>
<td>13.7 ± 0.6</td>
<td>d</td>
</tr>
</tbody>
</table>

* Unless otherwise indicated, the purge gas between the resonance lamp and reactor was a dilute N$_2$/O$_2$ mixture and the gas flows were combined in a mixing chamber upstream from the reactor. The linear flow rate through the reactor was 2-3 cm s$^{-1}$ in all experiments and the laser repetition rate was varied over the range 1-10 Hz. Nitrogen was used as the buffer gas in all experiments. The background Cl($^3P_J$) decay rate was typically 35 s$^{-1}$.

* Photolysis wavelengths were 355 nm for Cl$_2$ and 193 nm for CF$_2$Cl$_2$.

* $N$ = number of individual pseudo-first order decay rates measured.

* $2 \times 10^{18}$ CF$_2$Cl$_2$ per cm$^2$ added to reaction mixture to facilitate equilibration of the Cl($^3P_J$) spin-orbit states.

* Volume between resonance lamp and reactor purged with dry air.

* Cl$_2$ injected into O$_3$/N$_2$ flow just upstream from the reaction zone.

* Volume between resonance lamp and reactor purged with N$_2$.

---

traversal through the flow system, i.e., ozone concentrations measured upstream and downstream from the reaction zone were identical. The observed kinetics were also found to be independent of the Cl($^3P_J$) photolytic source reaction (355 nm photolysis of Cl$_2$ or 193 nm photolysis CF$_2$Cl$_2$) and independent of whether N$_2$O/N$_2$, N$_2$, or dry air was purged through the
volume between the resonance lamp and the reactor; these variations suggest that reactions and/or inadvertent detection of interfering radicals, such as $O(^3P_u)$ for example, did not result in systematic errors in our measurements.

The results in Table I show that $k_1$ is independent of pressure and only weakly dependent on temperature. An Arrhenius plot for reaction (1) is shown in Figure 3. Despite the rather small variation of $k_1$ as a function of temperature, the ln $k_1$ vs. $T^{-1}$ plot is clearly nonlinear, i.e., the activation energy for reaction (1) is larger at higher temperature. Arrhenius parameters can be used to describe the temperature dependence of $k_1$ if two separate temperature regimes are considered:

$$k_1(T) = (1.19 \pm 0.21) \times 10^{-11} \exp\left[(-33 \pm 37)/T\right] \quad 189 \text{ K} \leq T \leq 263 \text{ K}$$

$$k_1(T) = (2.49 \pm 0.38) \times 10^{-11} \exp\left[(-233 \pm 46)/T\right] \quad 262 \text{ K} \leq T \leq 385 \text{ K}$$

Units in the above expressions are cm$^3$ molecule$^{-1}$ s$^{-1}$ and errors are 2σ, precision only. The absolute uncertainty (2σ) in $k_1(T)$ calculated from the above expressions is estimated to be ±15% independent of temperature. This error estimate is based on the precision of our rate coefficients (Table I), estimates of possible systematic errors (primarily in the ozone concentration determination), and the ability of the above Arrhenius expressions to reproduce the experimental data; the precision of the derived A-factors and activation energies suggest uncertainties in $k_1(T)$ values which we believe to be unrealistically high. It should be noted that data at $T = 262$ K and

![Figure 3. Arrhenius plot for the reaction Cl($^2P_u$) + O$_2$ → ClO + O$_2$. Solid lines are obtained from unweighted least squares analyses of data over the temperature ranges 189–263 K and 262–385 K.](image-url)
263 K were used to obtain both of the above Arrhenius expressions; the values of $k_1$ (262.5 K) predicted by the two expressions differ by 2.5%. The two expressions give exactly equal rate coefficients at $T = 269$ K, so this would be the best temperature to switch from use of one expression to the other.

Our rate coefficient determinations for reaction (1) are compared with those reported by other investigators in Table II. Error estimates are not included in the Table because comparing reported errors from different labs can often be misleading. For a majority of the studies summarized in Table I, 2σ error limits appear to be around 15–20% for $k_1(T)$ at any temperature within the range investigated. The discharge flow-mass spectrometry studies of Clyne and Watson [8] and Leu and DeMore [12] required an absolute calibration for the unstable species Cl($^3P_j$); the error limits in these studies are about ±30%. The rate coefficients reported by Clyne and Nip [9] also have error limits of about ±30% due to somewhat larger scatter in the data than was observed in other studies. With the exception of the faster rate coefficient reported by Clyne and Watson [8] and the somewhat slower rate coefficient reported by Kurylo and Braun [11], reported values for $k_1(298 \text{ K})$ fall within the narrow range $(1.22 \pm 0.08) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. It is interesting to note, however, that the three studies which employed flash photolysis techniques (this work along with refs. [11] and [13]) obtained the three lowest reported values for $k_1(298 \text{ K})$, suggesting the presence of a small but significant systematic error in either the flash photolysis method or the discharge flow method. The source of such an error is not readily identifiable, although it is possible that some studies could have been affected by Cl($^3P_j$) or O$_3$ removal and/or re-
generation resulting from reactions of the vibrationally excited ClO (ClO*) produced in reaction (1) [36]:

\[
\begin{align*}
(1) & \quad \text{Cl}(^{2}P_{J}) + \text{O}_3 \rightarrow \text{ClO}^* + \text{O}_2 \\
(11) & \quad \text{ClO}^* + \text{Cl}(^{2}P_{J}) \rightarrow \text{O}(^{3}P_{J}) + \text{Cl}_2 \\
(12a) & \quad \text{ClO}^* + \text{O}_2 \rightarrow \text{ClO} + \text{O}_2 + \text{O}(^{3}P_{J}) \\
(12b) & \quad \rightarrow \text{Cl}(^{2}P_{J}) + 2\text{O}_2 \\
(13) & \quad \text{ClO}^* + \text{M} \rightarrow \text{ClO} + \text{M} \\
(14) & \quad \text{O}(^{3}P_{J}) + \text{ClO} \rightarrow \text{Cl}(^{2}P_{J}) + \text{O}_2 \\
(15) & \quad \text{O}(^{3}P_{J}) + \text{Cl}_2 \rightarrow \text{Cl}(^{2}P_{J}) + \text{ClO}_2
\end{align*}
\]

It has been observed experimentally that reaction (1) can lead to production of O(\(^{3}P_{J}\)) [37-40], and reaction (11) has been identified as a probable O(\(^{3}P_{J}\)) source under conditions of high [Cl(\(^{2}P_{J}\))] [38-40]. We have shown previously [39] that O(\(^{3}P_{J}\)) production via the above chemistry is greatly suppressed at high N\(_2\) pressures, presumably because reaction (13) becomes dominant over reactions (11) and (12). Hence, our observation that \(k_1(T)\) is independent of pressure over the range 30-300 torr N\(_2\) strongly suggests that the above chemistry did not affect our measurements.

While reported values for \(k_1(298 \text{ K})\) are in quite good agreement, the scatter in reported and/or extrapolated rate coefficients increases with decreasing temperature. At temperatures below 230 K, the values for \(k_1(T)\) reported in this study are higher than any reported previously. As shown in Table I, our measured value of \(10.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for \(k_1(190 \text{ K})\) is a factor of 1.4 faster than current "recommendations" [20,41], and agrees within combined error limits only with the (extrapolated) result of the discharge flow study of Zahniser et al. [10].

Incorporation of our results into models of stratospheric chemistry would increase the steady state fraction of ClO, existing as ClO and reduce the fraction existing as the unreactive reservoir HCl, hence, model calculations aimed at reproducing ClO measurement data would predict higher ClO levels if our values for \(k_1(T)\) were used in place of currently recommended values [20,41]. Our values for \(k_1(T)\) would increase the calculated efficiency of chlorine catalyzed ozone destruction in modeling studies where ClO levels are calculated from analysis of production and loss terms. However, in some calculations of chlorine catalyzed ozone depletion, attempts are made to reproduce observed ClO levels by adjusting the total available inorganic chlorine; predictions from these models should be relatively insensitive to changes in \(k_1(T)\).

Toohey et al. [14] have recently shown that rate coefficients for the reactions of O\(_3\) with Br, Cl, F, O, and N atoms and OH radicals correlate with the electron affinities of the radicals, a correlation which leads these authors to suggest that \(X + \text{O}_3\) reactions proceed through early transition states dominated by transfer of electron density from the highest occupied molecular orbital of ozone to the singly occupied molecular orbital of the radical. A semi-empirical ClO\(_3\) potential energy surface has been constructed by Farantos and Murrell [42] which also suggests an early transition state for the collinear collision (Cl—O bond distance about 2.5 Å).
Farantos and Murrell [42] found no evidence for long-lived complex formation along the collinear pathway, but it does not appear that the possibility of energetically favorable insertion pathways was examined in detail by these authors. One possible explanation for the non-Arrhenius temperature dependence observed in our study of reaction (1) is that a weak minimum exists in the potential energy surface for Cl(2Pg) insertion into an O—O bond of ozone, thus permitting formation of a long-lived OClO0 complex whose decomposition to ClO + O2 makes a significant contribution to the overall reaction rate at low temperatures. However, a matrix isolation study of reaction (1) failed to observe evidence for any ClO3 isomers [43]. As suggested by Toohey et al. [14], ab-initio studies of X + O3 reaction dynamics would certainly be a worthwhile endeavor.

B. The Br + O3 Reaction

In our study of reaction (2), 355 nm photolysis of Br2 was employed as the Br(2Pg) source. Both theoretical [44] and experimental [45] information suggest that virtually all bromine atoms are produced in the 2P3/2 ground state. To insure rapid relaxation of any photolytically generated Br(2P1/2), about 2 torr of H2 was added to the reaction mixture. The reaction

\[ \text{Br}(2P_{1/2}) + \text{H}_2(u = 0) \rightarrow \text{Br}(2P_{3/2}) + \text{H}_2(u = 1) \]

is known to be fast, with \( k_{16} = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [46]. Since the equilibrium concentration of Br(2P1/2) is negligible over the temperature regime of our study, all measured bromine atom temporal profiles should be considered as representative of removal of ground state atoms, Br(2P3/2).

A total of about 250 Br(2P3/2) temporal profiles were measured under a wide variety of experimental conditions. The results used to determine values for \( k_2(T) \) are summarized in Table III. All experiments summarized in Table III were consistent with equation I, i.e., all decays were exponential and, in a given set of experiments, \( k' \) increased linearly with increasing ozone concentration. The observed kinetics were unaffected by significant variations in Br2 concentration, the concentration of photolytically produced atoms, and the distance in the flow system over which Br2 and O3 were allowed to interact before entering the reaction zone. In all experiments summarized in Table III, ozone concentrations were measured both upstream and downstream of the reaction cell; no evidence for ozone loss in the flow system was observed except at 392 K where the downstream ozone concentration was typically 10% lower than the upstream concentration, even when O(3P) production was minimized (see below). At 392 K, the ozone concentration in the reaction zone was taken to be the average of the upstream and downstream concentrations.

In preliminary experiments (not summarized in Table III), nonexponential decays were observed at high temperatures and under conditions where the ratio \([O_3]/[Br_2]\) was relatively high. The observed deviation from the prediction of equation I is attributed to Br(2P3/2) regeneration via the following mechanism:

\[ O_3^* + \text{hv}(355 \text{ nm}) \rightarrow O(3P) + O_2 \]

\[ O(3P) + \text{Br}_2 \rightarrow \text{Br}(2P_{3/2}) + \text{BrO} \]
TABLE III. Summary of kinetic data for the reaction $\text{Br}^3P_{3/2} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$P$(Torr)</th>
<th>[Br$_2$]$10^{16}$ cm$^{-3}$</th>
<th>[Br$_3$]$10^{16}$ cm$^{-3}$</th>
<th>$N$</th>
<th>$k_2$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>In $k_2$ vs. T</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>150</td>
<td>2.7</td>
<td>0.6 - 2</td>
<td>9</td>
<td>1830</td>
<td>$2.79 \pm 0.19$</td>
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<tr>
<td>201</td>
<td>150</td>
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<td>1410</td>
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<td>223</td>
<td>150</td>
<td>2.4</td>
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<td>6</td>
<td>1290</td>
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<td>150</td>
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<td>9</td>
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<td>150</td>
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<td>6</td>
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<tr>
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<td>150</td>
<td>4</td>
<td>1.4</td>
<td>6</td>
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<td>$5.41 \pm 0.18$</td>
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<tr>
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<td>150</td>
<td>2.6</td>
<td>0.8 - 2</td>
<td>8</td>
<td>999</td>
<td>$5.95 \pm 0.36$</td>
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<tr>
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<td>150</td>
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<td>5</td>
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<td>283</td>
<td>150</td>
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<td>0.9 - 2</td>
<td>8</td>
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<td>$8.64 \times 10^{-2}$</td>
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<td>30</td>
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<td>1080</td>
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<td>298</td>
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<td>300</td>
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<td>1.6</td>
<td>6</td>
<td>888</td>
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<tr>
<td>328</td>
<td>150</td>
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<td>0.6 - 2</td>
<td>13</td>
<td>2150</td>
<td>$14.4 \pm 0.5$</td>
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<td>1.3</td>
<td>8</td>
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<td>$14.7 \pm 0.7$</td>
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<tr>
<td>352</td>
<td>150</td>
<td>4.9</td>
<td>1.3 - 3</td>
<td>6</td>
<td>1440</td>
<td>$17.8 \pm 1.1$</td>
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<tr>
<td>365</td>
<td>150</td>
<td>4</td>
<td>1.6</td>
<td>7</td>
<td>2460</td>
<td>$18.0 \pm 1.0$</td>
</tr>
<tr>
<td>376</td>
<td>150</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td>1680</td>
<td>$18.1 \pm 1.2$</td>
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<tr>
<td>386</td>
<td>150</td>
<td>14</td>
<td>4</td>
<td>7</td>
<td>1920</td>
<td>$20.8 \pm 0.9$</td>
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<tr>
<td>392</td>
<td>150</td>
<td>13 - 39</td>
<td>4</td>
<td>6</td>
<td>1670</td>
<td>$22.6 \pm 0.9$</td>
</tr>
</tbody>
</table>

$^a$The purge gas between the resonance lamp and reactor was 5% CH$_4$ in N$_2$. The linear flow rate through the reactor was 2–3 cm s$^{-1}$ and the laser repetition rate was 1 Hz in all experiments. Nitrogen was used as the buffer gas in all experiments. The background Br$_2$ decay rate was typically 30 s$^{-1}$. The photolysis wavelength was 355 nm.

$^b$N = number of individual pseudo-first order decay rates measured.

Reaction (18) is quite fast, i.e., $k_2$ ca. $2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, with little or no temperature dependence [19,47,48]. As mentioned above, ozone in its ground vibrational level is totally transparent at 355 nm [32]. However, near the high temperature extreme of our study (i.e., $T > 380$ K), excited vibrational levels from which 355 nm absorption can occur [32] become sufficiently populated to cause the above interference. To avoid Br$_2$ regeneration, our experiments at 386 K and 392 K employed much higher Br$_2$ levels than normal but relatively low laser powers, such that the concentration of photolytically generated Br$_3$ was much greater than the concentration of photolytically generated O$_2$($^3P$). The only deleterious effect of these experimental conditions was to increase the background count rate due to photodissociation of Br$_2$ by the resonance lamp and detection of the resultant Br$_3$($^3P_{3/2}$); this two-photon process could be minimized by operating the resonance lamp at a relatively lower power level, though some signal counts were sacrificed in the process.

An Arrhenius plot for reaction (2) is shown in Figure 4. A linear least squares analysis of the In $k_2$ vs. $T^{-1}$ plot gives the following Arrhenius expression in units of cm$^3$ molecule$^{-1}$ s$^{-1}$:

$$k_2(T) = (1.50 \pm 0.16) \times 10^{-11} \exp[-(775 \pm 30)/T].$$
Uncertainties in the above expression are 2σ and represent precision only. The absolute uncertainty in \( k_2(T) \) calculated from the above expression is estimated to be ±15% except at 392 K where a small potential contribution from reactions (17) and (18) along with greater uncertainty in the \( O_3 \) concentration raise the estimated uncertainty in \( k_2(392 \text{ K}) \) to ±25%.

Our rate coefficient determinations for reaction (2) are compared with those reported by other investigators in Table IV. As was the case for reaction (1), 2σ error limits in most previous determinations of \( k_2(T) \) appear to be in the 20–30% range, although Leu and DeMore [16] report an uncertainty of ±40% for their lowest temperature (224 K) rate coefficient. Activation energies determined from the six temperature dependent studies of reaction (2) span the range 1.20–1.94 kcal mol\(^{-1}\) with the discharge flow studies of Leu and DeMore [16] and Toohey et al. [14] at the high end, the flash photolysis and discharge flow studies of Michael and co-workers [17,18] at the low end, and our study along with the study of Dodonov et al. [19] in the middle. While our results are in quantitative agreement only with those of Dodonov et al., they rather fortuitously are in almost exact agreement with current panel recommendations for \( k_2(T) \), which are obtained by averaging all previous results except the results of Dodonov et al. [20,41]. Hence, the values for \( k_2(T) \) currently being employed to model stratospheric chemistry are in exact agreement with our measurements. It should be noted that the excellent agreement of our Arrhenius parameters with those reported by Dodonov et al., may be somewhat fortuitous since our study spans a range of \( 1/T \) more than four times larger than the range spanned by Dodonov et al.’s study.
TABLE IV. Comparison of our results for the reaction Br(\(^2P_{3/2}\)) + O\(_3\) → BrO + O\(_2\) with results reported by other investigators.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Technique</th>
<th>Range of T (K)</th>
<th>298K</th>
<th>230K</th>
<th>190K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clyne &amp; Watson [15]</td>
<td>DF-MS</td>
<td>298</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leu &amp; DeMore [16]</td>
<td>DF-MS</td>
<td>224-422</td>
<td>12.5</td>
<td>4.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Michael et al. [17]</td>
<td>FP-RF</td>
<td>200-360</td>
<td>10.2</td>
<td>5.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Michael &amp; Payne [18]</td>
<td>DF-RF</td>
<td>234-360</td>
<td>10.4</td>
<td>5.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Dodonov et al. [19]</td>
<td>DFL-MS</td>
<td>281-337</td>
<td>10.9</td>
<td>4.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Toohey et al. [14]</td>
<td>DF-RF</td>
<td>248-418</td>
<td>13.8</td>
<td>5.4</td>
<td>2.3</td>
</tr>
<tr>
<td>This Work</td>
<td>LFP-RF</td>
<td>195-392</td>
<td>11.1</td>
<td>5.2</td>
<td>2.5</td>
</tr>
<tr>
<td>NASA Panel [20]</td>
<td></td>
<td></td>
<td>11.6</td>
<td>5.2</td>
<td>2.5</td>
</tr>
<tr>
<td>I. PA Panel [41]</td>
<td></td>
<td></td>
<td>11.6</td>
<td>5.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\(k_2: 10^{13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) at 1 bar.

- **DF**: discharge flow; **FP**: flash photolysis; **DFL**: diffusion flame; **LFP**: laser flash photolysis; **MS**: mass spectrometry; **RF**: resonance fluorescence.
- *Where \(T\)-dependent data is reported, rate coefficients are calculated from Arrhenius expressions.
- Error estimates are discussed in the text.
- * Obtained by extrapolation of more than a factor of 1.1 in \(1/T\).

Examination of Table IV shows that values for \(k_2(230 \text{ K})\) and \(k_2(190 \text{ K})\) calculated using various reported Arrhenius expressions agree quite well; the differences between the results of various studies are greatest at higher temperatures. Both studies of Michael and co-workers were carried out under less than ideal conditions and could be subject to systematic errors. Their flash photolysis study [17] was hampered by Br(\(^2P_{3/2}\)) regeneration which was attributed to the reaction of photolytically generated O(\(^3P_2\)) with BrO, while their discharge flow study [18] was hampered by a severe wall loss problem. The studies where relatively large activation energies were measured [14,16] are harder to find fault with, particularly the study of Toohey et al. [14] which appears to have been done very carefully.

**Summary**

A laser flash photolysis-resonance fluorescence technique has been employed to study the kinetics of the reactions of Cl(\(^2P_j\)) and Br(\(^2P_{3/2}\)) with O\(_3\), with particular emphasis on characterization of the rate coefficients at low temperature. Our observed temperature dependence for the Cl(\(^2P_j\)) + O\(_3\) rate coefficient is non-Arrhenius, but can be adequately described by the following two Arrhenius expressions (units are \(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)): \(k_2(T) = 1.19 \times 10^{-11} \exp(-33/T)\) for \(T = 189-269 \text{ K}\) and \(k_2(T) = 2.49 \times 10^{-11} \exp(-233/T)\) for \(T = 269-385 \text{ K}\). At lower stratospheric temperatures, the rate coefficients determined in this study are faster than any reported previously. Incorporation of our results into stratospheric models would lead to an increase in calculated ClO levels and a decrease in calculated HCl levels; hence, the calculated efficiency of ClO catalyzed ozone...
destruction would increase. For the \( \text{Br}^2P_{3/2} + \text{O}_3 \) reaction, we obtain the result \( k_2(T) = 1.50 \times 10^{-11} \exp(-775/T) \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for \( T = 195-392 \) K. While not in quantitative agreement with Arrhenius parameters reported in most previous studies, our results almost exactly reproduce the average of all earlier studies and, therefore, will not affect the choice of \( k_2(T) \) for use in modeling stratospheric BrO\(_3\) chemistry.

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Bibliography


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Kinetics of the Reactions of \( \text{O}^3\text{P} \) and \( \text{Cl}^2\text{P} \) with HBr and Br\(_2\)

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Abstract

A laser flash photolysis-resonance fluorescence technique has been employed to study the kinetics of reactions (1)–(4) as a function of temperature.

(1) \( \text{O}^3\text{P} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br}^2\text{P}_3 \) (255–350 K)
(2) \( \text{Cl}^2\text{P} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}^2\text{P}_3 \) (298–401 K)
(3) \( \text{O}^3\text{P} + \text{HBr} \rightarrow \text{OH} + \text{Br}^2\text{P}_3 \) (250–402 K)
(4) \( \text{Cl}^2\text{P} + \text{HBr} \rightarrow \text{HCl} + \text{Br}^2\text{P}_3 \) (257–404 K)

In all cases, the concentration of the excess reagent, i.e., HBr or Br\(_2\), was measured in situ in the slow flow system by UV-visible photometry. Heterogeneous dark reactions between \( \text{XBr} (\text{X} = \text{H} \text{or} \text{Br}) \) and the photolytic precursors for \( \text{Cl}^2\text{P} \) and \( \text{O}^3\text{P} \) (\( \text{Cl}_2 \) and \( \text{O}_3 \), respectively) were avoided by injecting minimal amounts of precursor into the reaction mixture immediately upstream from the reaction zone. The following Arrhenius expressions summarize our results (errors are \( 2\sigma \) and represent precision only, units are \( \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)): 

\[ k_1 = (1.76 \pm 0.80) \times 10^{-11} \exp[-(144 \pm 176)/T]; \]

\[ k_2 = (2.40 \pm 1.25) \times 10^{-10} \exp[-(144 \pm 176)/T]; \]

\[ k_3 = (5.11 \pm 2.82) \times 10^{-12} \exp[-(1450 \pm 160)/T]; \]

\[ k_4 = (2.25 \pm 0.56) \times 10^{-11} \exp[-(400 \pm 80)/T]. \]

The consistency (or lack thereof) of our results with those reported in previous kinetics and dynamics studies of reactions (1)–(4) is discussed.

Introduction

The increasing levels of anthropogenic bromine compounds in the earth's atmosphere has led to concerns over the contribution of these species to the catalytic destruction of stratospheric ozone [1]. To support studies of bromine chemistry directly relevant to the chemistry of the atmosphere, the kinetics of reactions (1)–(4) have been studied as a function of temperature.

(1) \( \text{O}^3\text{P} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br}^2\text{P}_3 \)
(2) \( \text{Cl}^2\text{P} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}^2\text{P}_3 \)
(3) \( \text{O}^3\text{P} + \text{HBr} \rightarrow \text{OH} + \text{Br}^2\text{P}_3 \)
(4) \( \text{Cl}^2\text{P} + \text{HBr} \rightarrow \text{HCl} + \text{Br}^2\text{P}_3 \)

While not of direct atmospheric importance, reactions (1)–(4) often occur in laboratory systems designed to obtain kinetic data for other reactions of atmospheric interest. For example, reaction (1) is a commonly employed laboratory source of BrO, the predominant BrO\(_2\) species in the stratosphere [2].

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Interest in reactions (1)–(4) also derives from the fact that a large number of theoretical and experimental studies of the dynamics of these reactions have been reported [3–37], and accurate kinetic data as a function of temperature provides a useful check on some of the conclusions from these studies.

Available kinetic data for reactions (1) and (2) is rather limited [38–44] and, in fact, reaction (2) has been studied only at 298 K [43,44]. Although reaction (4) has been studied by several groups [33–37,45,46], the results are somewhat contradictory. Of the four reactions, only reaction (3) has a large, self-consistent data base [47–50]; even in this case, however, a recent theoretical prediction of a non-Arrhenius temperature dependence in the 200–500 K regime [17] requires verification.

**Experimental Technique**

The laser flash photolysis–resonance fluorescence apparatus used in this study was similar to one which we have employed previously to study a number of atom–molecule reactions of Cl [51–55] and O [56–62]. Important features of the apparatus are described below.

A pyrex, jacketed reaction cell with an internal volume of 150 cm$^3$ was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol or methanol from a thermostated bath through the outer jacket. A copper-constantan thermocouple with a stainless steel jacket could be injected into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment.

For studies of reactions (1) and (3), ground state oxygen atoms were produced by 266 nm pulsed laser photolysis of O$_3$ in the presence of (typically) 100 torr N$_2$.

\[
(5(a)) \quad \text{O}_3 + h\nu(266 \text{ nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_u) \\
(5(b)) \quad \rightarrow \text{O}(^3\text{P}) + \text{O}_2(X^3\Sigma^-) \\
(6) \quad \text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2
\]

About 88% of the photolytically produced atoms are initially in the electronically excited $^1$D state [63], but experimental conditions were always such that \( k_6[N_2] \gg k_1[Br_2] \) or \( k_3[HBr] \) \((k_6 \approx 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\) [56,64,65]. Fourth harmonic radiation from a Nd:YAG laser served as the photolytic light source for oxygen atom production. The laser could deliver up to \( 3 \times 10^{14} \) photons per pulse at a repetition rate of up to 10 Hz; the pulsewidth was 5 ns. The three fine structure levels of O($^3P$) have splittings which are much smaller than thermal collision energies; hence, it is safe to assume that our kinetics experiments probed a thermally equilibrated mixture of O($^3P_0$), O($^3P_1$), and O($^3P_2$).

For studies of reactions (2) and (4), chlorine atoms were produced by 355 nm pulsed laser photolysis of Cl$_2$ in the presence of (typically) 100 torr N$_2$.

\[
(7) \quad \text{Cl}_2 + h\nu(355 \text{ nm}) \rightarrow n\text{Cl}(^2\text{P}_{3/2}) + (2 - n)\text{Cl}(^2\text{P}_{1/2}) \\
(8) \quad \text{Cl}(^2\text{P}_{1/2}) + \text{N}_2 \rightarrow \text{Cl}(^2\text{P}_{3/2}) + \text{N}_2
\]
Based on literature values for deactivation of spin-orbit excited Cl($^2P_{1/2}$) by N$_2$ ($k_1$, ca. $5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ ([66,67]), it appears that experimental conditions were always such that $k_3$[N$_2$] $>$ $k_3$[Br$_2$] or $k_4$[HBr]. Hence, all measured chlorine atom temporal profiles should be considered as representative of the removal of an equilibrium mixture of Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$).

Third harmonic radiation from a Nd:YAG laser served as the photolytic light source for chlorine atom production. The laser could deliver up to $1 \times 10^{17}$ photons per pulse at a repetition rate of up to 10 Hz; the pulse-width was 6 ns.

An atomic resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the photolytically produced atoms. The resonance lamp consisted of an electrodeless microwave discharge through about one torr of a flowing mixture containing a trace of O$_2$ or Cl$_2$ in He. The flows of a 0.1% O$_2$ or Cl$_2$ in He mixture and pure He into the lamp were controlled by separate needle valves, thus allowing the total pressure and O$_2$ or Cl$_2$ concentration to be adjusted for optimum signal-to-noise. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell, the lamp output passed through a flowing gas filter. For O($^3P$) detection, the gas filter was 0.1 cm-atm O$_2$ in N$_2$; this filter prevented lamp emissions in the 135–165 nm region from entering the reactor. For Cl($^2P$) detection, the gas filter was 0.004 cm-atm N$_2$O in N$_2$; this filter absorbed all impurity emissions from the oxygen triplet at 130–131 nm while only slightly attenuating the chlorine lines in the 135–140 nm region, and also provided some attenuation of impurity emissions in the 140–150 nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and the resonance lamp beam, and imaged onto the photocathode of a solar blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with N$_2$. A calcium fluoride window was placed between the reaction cell and the photomultiplier to prevent detection of emissions at wavelengths shorter than 125 nm (Lyman-$\alpha$ emission, for example). Signals were processed using photon counting techniques in conjunction with multichannel scaling. For each atom decay measured, signals from a large number of laser shots were averaged to obtain a well-defined temporal profile over (typically) three 1/e lifetimes of decay. The multichannel analyzer sweep was triggered prior to the photolysis laser in order to allow a pre-trigger baseline to be obtained.

In order to avoid accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was typically 5 cm s$^{-1}$ and the laser repetition rate was 5 Hz. Hence, no volume element of the reaction mixture was subjected to more than one or two laser shots. The photolytic precursors O$_3$ and Cl$_2$ and the stable reactants Br$_2$ and HBr were flowed into the reaction cell from 12 liter bulbs containing dilute mixtures in nitrogen buffer gas. The stable reactant flow was pre-mixed with additional nitrogen before entering the reaction cell. Since heterogeneous reactions of the photolytic precursors with the stable reactants were a problem in these studies, in
most experiments the photolytic precursors were not pre-mixed with other components of the reaction mixture upstream from the reaction cell; instead, they were injected into the reaction cell through a \( \frac{1}{8} \) inch O.D. teflon tube positioned such that the photolyte mixed with other components about 1 to 5 cm upstream from the reaction zone.

Concentrations of each component in the reaction mixtures were determined from measurements of the appropriate mass flow rates and the total pressure. The concentrations of HBr and Br\(_2\) were also measured \textit{in situ} in the slow flow system by UV photometry. The 184.9 nm emission from an Hg pen ray lamp was employed as the light source for monitoring HBr. Absorption cells were 20 cm long in the study of reaction (3) and 216 cm long in the study of reaction (4). After passing through the absorption cell, the 184.9 nm radiation was isolated for detection using a \( \frac{1}{4} \) meter monochromator-bandpass filter combination. The HBr absorption cross section at 184.9 nm was taken to be \( 2.36 \times 10^{-18} \text{ cm}^2 \) [68,69]. A multipass White cell arrangement was employed to monitor Br\(_2\). Radiation from a xenon arc lamp was multipassed through a 35 cm absorption cell 42 times giving an absorption pathlength of 14.7 meters. A \( \frac{1}{4} \) meter monochromator in conjunction with dielectric coated White cell mirrors and narrow-band anti-reflection coated absorption cell windows isolated radiation at the monitoring wavelength, 415.8 nm. The Br\(_2\) absorption cross section at 415.8 nm was taken to be \( 5.87 \times 10^{-19} \text{ cm}^2 \) [70]; measurements carried out during the course of our study confirmed that this cross section is correct. To ensure that the reactant concentration was not changing during transit through the flow system, all four reactions were studied with the absorption cell positioned both upstream and downstream from the reaction cell; in the upstream position, of course, a small correction was required for dilution upon injection of the photolyte into the mixture.

The gases used in this study had the following stated minimum purities: N\(_2\), 99.9999%; He, 99.999%; Cl\(_2\), 99.99%; HBr, 99.8%. Nitrogen and helium were used as supplied while Cl\(_2\) and HBr were degassed repeatedly at 77 K before use. Bromine was Fischer ACS reagent grade with a maximum impurity level of 0.06%; it was transferred into a vial fitted with a high vacuum stopcock, then degassed repeatedly at 77 K before use. Ozone was prepared in a commercial ozonator using UHP oxygen (99.99%). It was collected and stored on silica gel at 195 K, and degassed at 77 K before use.

\section*{Results and Discussion}

All experiments were carried out under pseudo-first order conditions with HBr or Br\(_2\) in large excess over O\(^{(3P)}\) or Cl\(^{(3P)}\). Hence, in the absence of secondary reactions which enhance or deplete the atom concentration, the atom temporal profile is dominated by the reactions

\begin{equation}
A + XBr \rightarrow AX + Br, \quad i = 1-4
\end{equation}

\begin{equation}
A \rightarrow \text{loss by diffusion from the detector field of view and/or reaction with background impurities}
\end{equation}

where \( A = \text{O or Cl} \) and \( X = \text{Br or H} \). Integration of the rate equations for the above scheme yields the simple relationship
The bimolecular rate coefficients, $k_\text{b}$, are determined from the slopes of $k'$ vs. $[\text{XBr}]$ plots.

For all four reactions studied, atom temporal profiles were found to be exponential (i.e., obeyed eq. (I)) and to increase linearly with increasing XBr concentration. Observed pseudo-first order decay rates were found to be independent of laser photon fluence and photolytic precursor concentration in all cases. The above set of observations strongly supports the contention that reactions (i) and (9) are the only processes which affected the post-flash atom time histories in our studies of reactions (1)–(4). Results for reactions (1)–(4) are discussed separately below.

$O(3P) + \text{Br}_2$

Results from our study of reaction (1) are summarized in Table I. The rate coefficient $k_1$ is found to be virtually independent of temperature over the range 255–350 K. Typical $O(3P)$ temporal profiles are shown in Figure 1 while $k'$ vs. $[\text{Br}_2]$ plots for data taken at 255 K and 350 K are shown in Figure 2. A linear least squares analysis of the $\ln k_1$ vs. $T^{-1}$ data gives the Arrhenius expression.

$$k_1(T) = (1.76 \pm 0.80) \times 10^{-11} \exp[(40 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

The temperature independent rate coefficient $k_1 = (2.03 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an equally good representation of our results. Errors in the above expressions are $2\sigma$ and represent precision only. We estimate the absolute uncertainty ($2\sigma$) in $k_1(T)$ at any temperature within the range of our study to be $\pm 15\%$.

There have been a limited number of previous studies of the thermal rate coefficient for reaction (1). In a study by Clyne and coworkers [40], $k_1$ was measured at room temperature in a discharge flow system using resonance fluorescence to follow oxygen atom loss and, in separate experiments, bromine atom production. At lower stoichiometries these workers found

<table>
<thead>
<tr>
<th>$T$</th>
<th>$P$</th>
<th>$[O_3]$</th>
<th>$[O(3P)]_0$</th>
<th>$N'$</th>
<th>$k_{\text{max}}$</th>
<th>$k_1^{\circ}$</th>
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<td>255</td>
<td>100</td>
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<td>2.01 ± 0.07</td>
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<td>6</td>
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<td>1.97 ± 0.05</td>
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<tr>
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<td>8</td>
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<td>2.14 ± 0.10</td>
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<td>0.7–3.4</td>
<td>19</td>
<td>10300</td>
<td>2.11 ± 0.07</td>
</tr>
<tr>
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<td>900</td>
<td>10</td>
<td>6</td>
<td>10000</td>
<td>2.08 ± 0.09</td>
</tr>
<tr>
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<td>100</td>
<td>160</td>
<td>2.0</td>
<td>7</td>
<td>8550</td>
<td>1.91 ± 0.07</td>
</tr>
</tbody>
</table>

**Table I. Kinetic data for the reaction of $O(3P)$ with $\text{Br}_2$.**

- Units are as follows: $T$ (K); $P$ (torr); $[O_3]$; $[O(3P)]_0$ ($10^{11}$ per cm$^3$); $k_{\text{max}}$ (s$^{-1}$); $k_1$ ($10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).
- All experiments were done with $N_2$ buffer gas. The linear flow rate was varied from 3 cm s$^{-1}$ to 15 cm s$^{-1}$ (6 cm s$^{-1}$ typical). The laser repetition rate was varied from 1 Hz (typical) to 2.5 Hz. The $O(3P)$ loss rate in the absence of $\text{Br}_2$ was typically 100 s$^{-1}$.
- $N' =$ number of pseudo first order decays measured.
- $^\circ$ Error is $2\sigma$ and represents precision only.
Figure 1. Typical $O(^3P)$ temporal profiles obtained in our study of the $O(^3P) + Br_2$ reaction. Experimental conditions: $T = 298$ K, $P = 300$ torr; $[O_3] = 9.0 \times 10^{13}$ molecules per cm$^3$; $[O(^3P)]_0 = 5 \times 10^{11}$ atoms per cm$^3$; $[Br_2]$ in units of $10^{14}$ molecules per cm$^3$ = (a) 1.04, (b) 2.05, (c) 4.86; number of laser shots averaged = (a) 150, (b) 250, (c) 500. Solid lines are obtained from least squares analyses and give the following pseudo-first order decay rates in units of s$^{-1}$: (a) 1930, (b) 4400, (c) 10000.

that secondary chemistry due to the BrO produced from reaction (1) (i.e., the BrO + O reaction) was suppressed by adding excess NO. A value of $(1.4 \pm 0.2) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was reported; the currently recommended value for $k_1$ [71] is based on this result. Clyne et al. [40] also discussed previous studies of reaction (1) carried out in Clyne’s laboratory [38,39]. The experiments of Clyne and Cruse [38], also performed in a discharge flow system with resonance fluorescence detection of $O(^3P)$, were carried out in excess NO but with $[Br_2]_0$ ca. $[O_3]$. Therefore, Clyne et al. concluded that the reaction

$$O(^3P) + NO_2 \rightarrow O_2 + NO$$

was a complication in the Clyne and Cruse study and proposed that the earlier result should be lowered to $(1.2 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from the originally reported $1.74 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Also discussed by Clyne et al. is the work of Cruse [39]. Using techniques similar to Clyne et al., the study of Cruse apparently yielded a value of $(2.1 \pm 0.4) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $k_1$. This is again the composite result of both $O(^3P)$ disappearance and $Br(^3P)$ appearance measurements. As a weighted
average of all three studies, Clyne et al. [40] offer $k_1 = (1.65 \pm 0.30) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.

There have been two studies of the temperature dependence of $k_1$ reported in the literature. Moin et al. [41] measured $k_1(T)$ relative to $k_{11}(T)$

\[
O(^3P) + Cl_2 \rightarrow ClO + Cl(^2P)
\]

over the temperature range 306 K to 425 K. These investigators report $k_1(T)/k_{11}(T) = (3.98 \pm 2.81) \exp[(1300 \pm 45)/T]$. Using our recently reported [60] Arrhenius expression for reaction (11), $k_{11}(T) = (7.4 \pm 2.4) \times 10^{-12} \exp[-(1650 \pm 100)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$, in conjunction with the $k_1(T)/k_{11}(T)$ ratios reported by Moin et al. [41] leads to the result $k_1(T) = (3.0 \pm 2.3 \times 10^{-11}) \exp[-(350 \pm 150)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Dodonov et al. [42], have also measured $k_1(T)$ over the temperature range 246–431 K using a diffusional flame method. These investigators obtained the result $k_1(T) = 4.6 \times 10^{-11} \exp[-(210 \pm 75)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The results of Dodonov et al. are in fair agreement with our results particularly at temperatures below 298 K. The error limits reported by Moin et al. are so large that quantitative comparison with their study is a pointless exercise; their results do suggest values for $k_1(T)$ of the same order of magnitude as do our results.
Both experimental and theoretical studies of the dynamics of reaction (1) have appeared in the literature. Reactive scattering experiments at low translational energies (1–3 kcal mol\(^{-1}\)) [3,4] indicate a long lived collision complex while higher energy (15–40 kcal mol\(^{-1}\)) scattering experiments [5,6] are more compatible with a complex that is short lived compared to a rotational period. An RRKM model [7] suggests that the long lived complex mechanism may adequately describe the scattering experiments. The same RRKM model has been used to calculate a thermal rate coefficient for reaction (1) [8]. Good agreement is obtained only when a barrier of approximately 1 kcal mol\(^{-1}\) is introduced into the entrance channel. While this activation energy is consistent with a roughly estimated value that has appeared in the literature [72], and is reasonably close to that observed by Moin et al. [41], it is not compatible with the lack of a significant temperature dependence observed in our study.

\[
\text{Cl}(^2P) + Br_2
\]

In order to study reaction (2) with in situ measurement of the Br\(_2\) concentration, it was necessary to observe pseudo-first order decay rates approaching \(10^5\) s\(^{-1}\), i.e., more than an order of magnitude faster than is customarily employed in flash photolysis-resonance fluorescence studies. Typical Cl\((^2P)\) temporal profiles observed in our study of reaction (2) are shown in Figure 3, while a summary of the data is compiled in Table II. The rate coefficient \(k_2\) is found to be virtually independent of temperature over the range 298–401 K. A linear least squares analysis of the \(\ln k_2\) vs. \(T^{-1}\) data gives the Arrhenius expression

\[
k_2(T) = (2.40 \pm 1.25) \times 10^{-10} \exp[-(144 \pm 176)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

The temperature independent rate coefficient \(k_2 = (1.58 \pm 0.22) \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) is an equally good representation of our results. Errors in the above expressions are 2\(\sigma\) and represent precision only. We estimate the absolute uncertainty (2\(\sigma\)) in \(k_2(T)\) at any temperature within the range of our study to be \(\pm 20\%\).

There have been two previous studies of \(k_2\). Both studies were performed in the same laboratory using a discharge flow-resonance fluorescence system at low pressures. In the earlier study Clyne and Cruse [43] reported \(k_2(298\text{ K}) = (1.20 \pm 0.15) \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). In the later work Bemand and Clyne [44] measured \(k_2(298\text{ K}) = (1.9 \pm 0.2) \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The average of these two studies is in good agreement with our result. Given the rapidity of reaction (2) it is not surprising that there is no significant activation energy.

There have been several molecular beam studies of the dynamics of reaction (2). As summarized by Valentini et al. [9] the lack of a significant dependence of the total cross section on collision energy indicates a lack of any energy barrier. This conclusion is also supported by the forwardly peaked center of mass angular distributions of the product BrCl which are independent of total collision energy. The total cross sections quoted in the molecular beam studies, 1–20 Å\(^2\) for \(E_{\text{trans}} = 2.0\) kcal/mol\(^{-1}\) [10–12], 4–33 Å\(^2\) for \(E_{\text{trans}} = 6.8\) kcal/mol\(^{-1}\) [9], and 5–42 Å\(^2\) for \(E_{\text{trans}} = 14.7\) kcal/mol\(^{-1}\) [9] are less than an estimated hard sphere cross section (ca. 48 Å\(^2\)) [73]. For the
Figure 3. Typical Cl(2P) temporal profiles obtained in our study of the Cl(2P) + Br2 reaction. Experimental conditions: T = 327 K; P = 100 torr; [Cl2] = 1.9 x 10^13 molecules per cm^3; [Cl(2P)]_0 ca. 3 x 10^11 atoms per cm^3; [Br2] in units of 10^14 molecules per cm^3 = (a) 1.04, (b) 2.58, (c) 3.65; number of laser shots averaged = (a) 1024, (b) 2048, (c) 8192. Solid lines are obtained from least squares analyses and give the following pseudo-first order decay rates in units of s^{-1}: (a) 18400, (b) 41600, (c) 59400.

In order to compare, if our value for the thermal rate coefficient is divided by the mean relative velocity at 298 K a "cross section" of 34 Å² is derived.

Cl(2P) + Br2

Results from our study of reaction (3) are summarized in Table III and plots of k' vs. [HBr] at a series of temperatures are shown in Figure 4. An

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (torr)</th>
<th>[Cl2] (10^13 per cm^3)</th>
<th>[Cl(2P)]_0 (10^11 per cm^3)</th>
<th>N'</th>
<th>k'_{max} (s^{-1})</th>
<th>k_2 (10^{-10} cm^3 molecule^{-1} s^{-1})</th>
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<tr>
<td>298</td>
<td>100</td>
<td>130–630</td>
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<td>3.0</td>
<td>6</td>
<td>59200</td>
<td>1.60 ± 0.05</td>
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<tr>
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<td>5</td>
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<tr>
<td>401</td>
<td>100</td>
<td>220</td>
<td>3.4</td>
<td>6</td>
<td>59900</td>
<td>1.72 ± 0.11</td>
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</table>

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (torr)</th>
<th>[Cl2] (10^13 per cm^3)</th>
<th>[Cl(2P)]_0 (10^11 per cm^3)</th>
<th>N'</th>
<th>k'_{max} (s^{-1})</th>
<th>k_2 (10^{-10} cm^3 molecule^{-1} s^{-1})</th>
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<td>298</td>
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<td>130–630</td>
<td>1.3–5.3</td>
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<td>327</td>
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<td>100</td>
<td>200</td>
<td>1.5</td>
<td>5</td>
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<td>1.49 ± 0.17</td>
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<tr>
<td>401</td>
<td>100</td>
<td>220</td>
<td>3.4</td>
<td>6</td>
<td>59900</td>
<td>1.72 ± 0.11</td>
</tr>
</tbody>
</table>

Units are as follows: T (K); P (torr); [Cl2], [Cl(2P)]_0 (10^11 per cm^3); k'_{max} (s^{-1}); k_2 (10^{-10} cm^3 molecule^{-1} s^{-1}).

All experiments were done with N_2 buffer gas at ~5 cm s^{-1} linear flow rate and 1 Hz laser repetition rate. The loss rate of Cl(2P) in the absence of Br2 was typically 120 s^{-1}.

N' = number of pseudo first order decays measured.

Error is 2σ and represents precision only.
TABLE III. Kinetic data for the reaction of O(3P) with HBr \(^{a,b}\)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (torr)</th>
<th>[O(3P)] (_0) (10(^{11}) per cm(^3))</th>
<th>N(^v)</th>
<th>(k_{\text{max}})</th>
<th>(k_3)</th>
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<td>250</td>
<td>100</td>
<td>76–130 6.0–10</td>
<td>7</td>
<td>1410</td>
<td>1.65 ± 0.09</td>
</tr>
<tr>
<td>272</td>
<td>100</td>
<td>38     2.0</td>
<td>7</td>
<td>1130</td>
<td>2.55 ± 0.09</td>
</tr>
<tr>
<td>298</td>
<td>30</td>
<td>40     3.0</td>
<td>5</td>
<td>1040</td>
<td>3.56 ± 0.15</td>
</tr>
<tr>
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<td>100</td>
<td>80–230 5.0–12</td>
<td>11</td>
<td>1710</td>
<td>3.65 ± 0.15</td>
</tr>
<tr>
<td>298</td>
<td>100</td>
<td>40     3.0</td>
<td>6</td>
<td>1040</td>
<td>3.51 ± 0.16</td>
</tr>
<tr>
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<td>340    20</td>
<td>6</td>
<td>1120</td>
<td>3.51 ± 0.26</td>
</tr>
<tr>
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<td>100</td>
<td>40–80  3.2–7.0</td>
<td>10</td>
<td>1340</td>
<td>7.12 ± 0.53</td>
</tr>
<tr>
<td>402</td>
<td>100</td>
<td>30–130 2.0–12</td>
<td>17</td>
<td>1660</td>
<td>15.2 ± 1.4</td>
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\(^a\)Units are as follows: T (K); P (torr); [O(3P)] \(_0\) (10\(^{11}\) per cm\(^3\)); \(k_{\text{max}}\) (s\(^{-1}\)); \(k_3\) (10\(^{-14}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)).

\(^b\)All experiments were done with N\(_2\) buffer gas at 5 cm s\(^{-1}\) linear flow rate. The laser repetition rate was varied from 1 Hz (typical) to 5 Hz. The typical O(3P) loss rate in the absence of HBr was 80 s\(^{-1}\).

\(^v\)N = number of pseudo first order decays measured.

\(^\circ\)Error is 2\(\sigma\) and represents precision only.

Arrhenius plot for reaction (3) is shown in Figure 5. A linear least squares analysis of the ln \(k_3\) vs. \(T^{-1}\) data gives the Arrhenius expression

\[
k_3(T) = (5.11 ± 2.82) \times 10^{-12} \exp[-(1450 ± 160)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

Errors in the above expression are 2\(\sigma\) and represent precision only. We estimate the absolute uncertainty (2\(\sigma\)) in \(k_3(T)\) at any temperature within the range of our study (250–402 K) to be ±15%.

![Figure 4](image_url)
The kinetics of reaction (3) have been studied by four other groups over the combined temperature range 221–554 K [47–50]; their results are compared with ours in Table IV. The agreement among all studies is excellent, especially considering the diversity of experimental methods employed. Broida et al. [17] recently reported very good agreement between the experi-

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Technique*</th>
<th>Range of T</th>
<th>$A^a$</th>
<th>$E/R^b$</th>
<th>$k_3$(298 K)$^c$</th>
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<tbody>
<tr>
<td>Takacs &amp; Glass [47]</td>
<td>DF-ESR</td>
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<tr>
<td>Brown &amp; Smith [48]</td>
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<td>400</td>
<td>1360</td>
<td>4.2</td>
</tr>
<tr>
<td>Singleton &amp; Cvetanovic [49]</td>
<td>MM-CL</td>
<td>298–554</td>
<td>1340</td>
<td>1810</td>
<td>3.52</td>
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<td>1540</td>
<td>3.37</td>
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<tr>
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<td>200–550</td>
<td>530</td>
<td>1410</td>
<td>3.9</td>
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<tr>
<td>This Work</td>
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<td>250–402</td>
<td>511</td>
<td>1450</td>
<td>3.55</td>
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</table>

*DF = discharge flow; ESR = electron spin resonance; CL = chemiluminescence; MM = molecular modulation; FP = flash photolysis; RF = resonance fluorescence; QTC = quasi-classical trajectory calculation; LFP = laser flash photolysis.

Units are degrees Kelvin.

$^c$Units are $10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. 

Figure 5. Arrhenius plot for the reaction of O($^3P$) with HBr. Solid line is obtained from a least squares analysis of all data. Dashed line is obtained from a least squares analysis of all data at $T \geq 298$ K. Dotted line is obtained from a least squares analysis of all data at $T < 298$ K. The data point at 298 K (open circle) actually represents the average of four separate $k_3$(298 K) determinations (see Table III for individual rate coefficients).
mental results [47–50] and their own quasiclassical trajectory calculations which were carried out on a London-Eyring-Polanyi-Sato semiempirical potential energy surface. McKendrick et al. [15] have used the same potential energy surface to calculate the energy partitioning in the products of reaction (4), and have obtained good agreement with their experimental product state distributions. It is interesting to note that the theoretical results of Broida et al. predict slightly non-Arrhenius behavior for reaction (3) over the temperature range of our study. Both our results and the results of Nava et al. [50] seem to show a slight trend toward increasing activation energy with increasing temperature, as predicted by Broida et al.’s calculations. For example, the rate coefficients we have measured at \( T \leq 298 \text{K} \) suggest an activation energy of 2.36 ± 0.36 kcal mol\(^{-1}\), while the rate coefficients we have measured at \( T \geq 298 \text{K} \) suggest an activation energy of 3.32 ± 0.37 kcal mol\(^{-1}\) (errors are 2\(\sigma\) and represent precision only).

\[ \text{Cl(}^{2}\text{P}) + \text{HBr} \]

Results from our study of reaction (4) are summarized in Table V and plots of \( k^* \) vs. [HBr] at the temperature extremes of our study are shown in Figure 6. An Arrhenius plot for reaction (4) is shown in Figure 7. A linear least squares analysis of the ln \( k^* \) vs. \( T^{-1} \) data gives the Arrhenius expression

\[ k^*(T) = (2.25 \pm 0.56) \times 10^{-11} \exp\left[-(400 \pm 80)/T\right] \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}. \]

| \( \text{T K} \) | \( P \text{ (torr)} \) | \( |\text{Cl}_2| \) | \( |\text{Cl}(^{2}\text{P})|_0 \) | \( N^* \) | \( k_{\text{max}} \) | \( k^*_4 \) |
|---|---|---|---|---|---|---|
| 257 | 100 | 110–470 | 0.6–2.7 | 10 | 9600 | 5.06 ± 0.35 |
| 260 | 100 | 120 | 1.2 | 7 | 8160 | 4.96 ± 0.19 |
| 272 | 100 | 160 | 1.1 | 6 | 8290 | 5.15 ± 0.13 |
| 294 | 100 | 100 | 1.1 | 11 | 7960 | 5.39 ± 0.34 |
| 298 | 30 | 170 | 1.6 | 5 | 6780 | 5.37 ± 0.31 |
| 298 | 100 | 60–230 | 0.3–3.6 | 13 | 8230 | 5.55 ± 0.28 |
| 298 | 100 | 170 | 2.7 | 6 | 11400 | 5.64 ± 0.23 |
| 298 | 100 | 200 | 1.6 | 7 | 7600 | 5.63 ± 0.23 |
| 298 | 300 | 200 | 2.0 | 6 | 7550 | 5.84 ± 0.20 |
| 304 | 100 | 100 | 1.0 | 8 | 8710 | 5.90 ± 0.34 |
| 319 | 100 | 190 | 1.9 | 6 | 7280 | 5.94 ± 0.37 |
| 320 | 100 | 90 | 1.0 | 7 | 7580 | 6.12 ± 0.20 |
| 347 | 100 | 200 | 1.7 | 6 | 7760 | 7.14 ± 0.36 |
| 372 | 100 | 180 | 1.5 | 6 | 10900 | 8.27 ± 0.43 |
| 404 | 100 | 210 | 2.0 | 14 | 8720 | 8.56 ± 0.46 |

*Units are as follows: \( T \) (K); \( P \) (torr); \( |\text{Cl}_2| \); \( |\text{Cl}(^{2}\text{P})|_0 \) (10\(^{11}\) per cm\(^3\)); \( k_{\text{max}} \) (s\(^{-1}\)); \( k^*_4 \) (10\(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)).

*All experiments were done with \( \text{N}_2 \) buffer gas at a flow rate of \( \approx 5 \text{ cm s}^{-1} \). The laser repetition rate was typically 1 Hz, although this was varied up to 5 Hz. The typical \( \text{Cl}(^{2}\text{P}) \) loss rate in the absence of HBr was \( 180 \text{ s}^{-1} \).

*N is number of pseudo first order decays measured.

*Error is \( 2\sigma \) and represents precision only.
Figure 6. Plots of $k'$ vs. [HBr] for data obtained at the temperature extremes of our Cl($^2P$) + HBr study. Lines are obtained from linear least squares analyses and give the rate coefficients $5.04 \pm 0.35$ at 257 K and $8.56 \pm 0.47$ at 404 K in units of $10^{-12}$ cm$^3$ molecule$^{-1}$s$^{-1}$; errors are $2\sigma$ and represent precision only. Errors in the above expression are $2\sigma$ and represent precision only. As we discuss below, heterogeneous dark reaction between Cl$_2$ and HBr was a problem in this study. For this reason, the absolute uncertainty ($2\sigma$) in $k'_4(T)$ at any temperature within the range of our study (257–404 K) is relatively large, and is estimated to be $\pm 25\%$.

Systematic variations in experimental parameters during the course of our investigation demonstrated that it was imperative to inject the Cl($^2P$)...

Figure 7. Arrhenius plot for the reaction of Cl($^2P$) with HBr. The solid line is obtained from a linear least squares analysis.
precursor (Cl₂) into the reaction mixture close to the reaction zone. As the contact time between Cl₂ and HBr in the flow system was increased, the observed Cl²(P) decay rate increased. When relatively large Cl₂ concentrations were employed, a decrease in the HBr concentration (measured downstream from the mixing point) was observed. This phenomenon has been observed previously [35] and appears to be attributable to the reactions

\begin{align*}
(12) & \quad \text{HBr} + \text{Cl}_2 \longrightarrow \text{BrCl} + \text{HCl} \\
(13) & \quad \text{HBr} + \text{BrCl} \longrightarrow \text{Br}_2 + \text{HCl}
\end{align*}

Wen and Noyes [74] have estimated upper limits for the homogeneous gas phase rate coefficients \( k_{12} \) and \( k_{13} \) to be \( 1.3 \times 10^{-21} \ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) and \( 2.5 \times 10^{-20} \ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) respectively, but have observed that reactions (12) and (13) are surface catalyzed. As shown in this study, the reaction of Cl²(P) with Br₂ is very fast. The reaction

\begin{align*}
(14) & \quad \text{Cl}(^2\text{P}) + \text{BrCl} \longrightarrow \text{Cl}_2 + \text{Br}(^3\text{P})_2
\end{align*}

is also quite fast, with \( k_{14} \) ca. \( 1.5 \times 10^{-11} \ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) [43].

The results reported in Table V were all obtained under experimental conditions where we believe the interference from reactions (12) and (13) was negligible. The following observations support this contention:

1. For Cl₂ concentrations of \( 1-7 \times 10^{13} \ \text{molecules per cm}^3 \), \( k' \) was found to increase linearly as a function of HBr concentration (over the range 0 to \( 1.5 \times 10^{15} \ \text{molecules per cm}^3 \)) while the resonance fluorescence signal strength was independent of the quantity \( [\text{HBr}] / f [\text{Cl}_2]_0 \) \((f = \text{laser fluence} \quad \text{and} \quad [\text{Cl}_2]_0 = \text{molecular chlorine concentration calculated assuming no loss due to dark reaction}); this suggests negligible loss of Cl₂ via dark reaction.

2. The average of \( k' \) values at \( [\text{HBr}] = 0 \) calculated from linear least squares analyses of the \( k' \) vs. \( [\text{HBr}] \) data was ca. \( 60 \text{s}^{-1} \) higher than the directly measured background Cl²(P) decay rate. If the observed increase is attributed entirely to production of Br₂ via reactions (12) and (13) then, based on our measured values for \( k_2(T) \), about \( 3 \times 10^{11} \ \text{Br}_2 \text{per cm}^3 \) are generated (apparently) by a dark reaction which occurs when small amounts of HBr are added to the reaction cell but “saturates” and does not become faster with increasing [HBr]. For the range of Cl₂ and HBr concentrations used to obtain the data in Table V, production of \( 3 \times 10^{11} \ \text{Br}_2 \text{per cm}^3 \) would be accompanied by a drop in [Cl₂] of ca. 1% and a negligible change in [HBr].

3. For \( [\text{Cl}_2] \leq 7 \times 10^{13} \ \text{molecules per cm}^3 \) and for Cl₂ injection into the flow near the reaction zone, measured rate coefficients, \( k_4(T) \), were found to be independent of Cl₂ concentration and injector position. In these experiments the injector position was varied over the range 1 to 5 cm upstream from the reaction zone, corresponding to a pre-flash contact time between Cl₂ and HBr of 0.2 to 1.0 seconds.

There have been several previous investigations of the kinetics of reaction (4). Moore and coworkers [33–35] studied reaction (4) by observing the time-resolved infrared emission from vibrationally excited HCl product. Rubin and Persky [45] measured \( k_4(T) \) relative to reaction (14) in a discharge flow system.

\begin{align*}
(14) & \quad \text{Cl}(^2\text{P}) + \text{C}_2\text{H}_6 \longrightarrow \text{HCl} + \text{C}_2\text{H}_4
\end{align*}
Lamb et al. [46] studied reaction (4) using the very low pressure reactor (VLPR) technique. Using an apparatus similar to that employed by Moore and coworkers [33–35], Nesbitt and Leone [36] reported a value for \( k_A \) (298K) from their study of the \( Cl/HBr \) laser initiated chain reaction. More recently, Dolson and Leone [37], also using an infrared chemiluminescence (IRCL) technique but with improved wavelength resolution, re-investigated the \( Cl/HBr \) laser-initiated chain reaction and, in the process, re-measured \( k_A(T) \). Several theoretical calculations of \( k_A \) are also reported in the literature [21–23,32]. Our results are compared with all previous studies of the kinetics of reaction (4) in Table VI.

It can be seen from inspection of Table VI that significant discrepancies exist in measured values for \( k_A(298 \text{ K}) \) and in measured activation energies for reaction (4). Dolson and Leone [37] suggest that in all earlier IRCL studies [33–36], where the infrared emission was poorly resolved, \( k_A(T) \) may have been underestimated due to vibrational cascading into the levels being detected. Dolson and Leone demonstrated that improper accounting for vibrational cascading could lead to the non-Arrhenius temperature dependence reported by Mei and Moore [35]. The relatively fast rate coefficient reported by Dolson and Leone agrees well with the competitive

<table>
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<td>Wodarsz &amp; Moore</td>
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<td>Nesbitt &amp; Leone</td>
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<td>QTC</td>
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<td>This Work</td>
<td>LFP-RF</td>
<td>257–404</td>
<td>22.5</td>
<td>400</td>
<td>4.9°</td>
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</table>

* LFP = laser flash photolysis; IRCL = infrared chemiluminescence; DF = discharge flow; MS = mass spectrometry; CK = competitive kinetics; VLPR = very low pressure reactor; RF = resonance fluorescence; QTC = quasi-classical trajectory calculation; CTC = classical trajectory calculation.

* Units are degrees Kelvin.

* Units are \( 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

* \( T = 295 \text{ K} \).

* For 218–298 K data only; non-Arrhenius behavior observed at \( T > 298 \text{ K} \).

* Calculated from Arrhenius parameters.

* Calculated assuming the following Arrhenius expression for the \( Cl + C_2H_4 \) reference reaction (71,75): \( k = 7.7 \times 10^{11} \text{ exp} \left(-90/T \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

* Activation energy reported but temperature range and absolute rate coefficients not given.

* Assuming units in ref. [23] were meant to be \( \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1} \).

* For 1000 K results, \( E = 8.9 \text{ K} / (300 \text{ K}) \).

* \( T = 300 \text{ K} \).

* Arrhenius fit to rate coefficients calculated at 220 K, 300 K, and 500 K. Slightly non-Arrhenius behavior actually computed with 220 K and 300 K results giving \( E/R \) ca. 300 K while 300 K and 500 K results give \( E/R \) ca. 500 K.
kinetics result of Rubin and Persky [45], when the currently recommended Arrhenius expression for \( k_4(T) \) [71,75] is used to put the Rubin and Persky result on an absolute scale. The VLPR study of Lamb et al. [36] employed much different experimental conditions than all other studies of reaction (4) (i.e., 5 mtorr total pressure, [CI] ca. [HBr] ca. \( 5 \times 10^{11} \) per cm\(^3\)); these investigators report a value for \( k_4(298 \text{ K}) \) which is about a factor of three lower than the values reported by Dolson and Leone and by Rubin and Persky, and observe no temperature dependence for \( k_4 \) over the range 267–333 K. Lamb et al. present mass balance data which suggests no problem with wall reactions. These authors also present an entropy calculation for reaction (4) which suggests an A-factor of \( 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), significantly smaller than other experimental determinations (including ours). It is well established that a significant fraction of the HCl product of reaction (4) is formed in the second excited vibrational level [19,37]. Under the conditions employed by Lamb et al., it is possible that occurrence of the slightly exothermic back reaction

\[
(15) \quad \text{Br}(^2P_{3/2}) + \text{HCl}(v = 2) \rightarrow \text{Cl}(^2P_{3/2}) + \text{HBr}(v = 0)
\]

could have resulted in underestimation of \( k_4 \). All other experimental studies employed conditions where [HBr] \( \gg \) [Cl(\(^2P\))] and, therefore, would not have been influenced by reaction (15).

The calculated rate coefficient reported by Brown et al. [23] appears to have been printed incorrectly in ref. [23] since the authors claim good agreement with the early experimental work of Wodarczyk and Moore [24] even though the value for \( k_4(298 \text{ K}) \) which appears in their article, \( 30.2 \times 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), is absurd. Rubin and Persky [34] suggest that Brown et al.'s rate coefficient is actually in units of cm\(^3\) mol\(^{-1}\) s\(^{-1}\); dividing Brown et al.'s reported value by Avogadro's number gives \( k_4(298 \text{ K}) = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), much faster than all experimental values. Smith [22] has carried out a classical trajectory study of reaction (4) and reports \( k_4(300 \text{ K}) = (4.7 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), in excellent agreement with our result. A quasi classical trajectory calculation of \( k_4(T) \) was recently reported by Broida and Persky [32]; their result, \( k_4(300 \text{ K}) = 8.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), is intermediate between our experimental value and the experimental values reported by Dolson and Leone [37] and by Rubin and Persky [45]. Comparison of experimental and theoretical values for \( k_4 \), at ambient temperature is probably not very meaningful since the potential energy surfaces used in the trajectory calculations [22,32] were adjusted to give reasonable agreement with experimental values for \( k_4(298 \text{ K}) \).

The activation energy for reaction (4) obtained in our study, 0.8 kcal mol\(^{-1}\), agrees well with the activation energy reported by Rubin and Persky [45] and with the low temperature activation energy reported by Mei and Moore [35], but is in poor agreement with the result \( E_{\text{ar}} \) ca. 0 reported by Lamb et al. [46]. Smith [22] has calculated \( k_4 \) at 300 K and 1000 K and finds that \( k_4 \) increases by a factor of 8.9 between these two temperatures. Assumption of a linear \( \ln k_4(T) \) vs. \( T^{-1} \) dependence between 300 K and 1000 K would lead to an activation energy of 1.9 kcal mol\(^{-1}\) from Smith's calculated rate coefficients, considerably larger than all experimental values (obtained from data at \( T < 504 \text{ K} \)). It is possible that \( E_{\text{ar}} \), in-
increases with increasing $T$ between 500 K and 1000 K. In fact, the rate coefficients calculated by Broida and Persky [32] at 220 K, 300 K, and 500 K suggest just such a trend, increasing $E_{act}$ with increasing $T$. Both the magnitude and the temperature dependence of $E_{act}$ calculated by Broida and Persky are consistent with our results. However, the scatter in our data prevents us from stating conclusively that we observe non-Arrhenius behavior.

Summary

The laser flash photolysis-resonance fluorescence technique has been employed along with in situ monitoring of the excess reactant to study the temperature dependence of the thermal rate coefficients for reactions (1)–(4). The rate coefficient for reaction (1) has been found to be $(2.03 \pm 0.30) \times 10^{-11}$ cm$^2$ molecule$^{-1}$ s$^{-1}$ independent of temperature over the range 255–350 K, in reasonable though not quantitative agreement with previous work [38–42] and about 40% faster than the currently recommended [71] value. The first temperature dependence study of the kinetics of reaction (2) is reported. We find that $k_2 = (1.58 \pm 0.36) \times 10^{-10}$ cm$^2$ molecule$^{-1}$ s$^{-1}$ independent of temperature; our value for $k_2(298 \text{ K})$ agrees reasonably well with the rate coefficients reported previously by Clyne and coworkers [43,44]. Reaction (3) was studied over the temperature range 250 K to 402 K. As predicted by a recent theoretical study [17], our data are suggestive of a slightly non-Arrhenius temperature dependence; best fit activation energies over various temperature ranges are $2.36 \pm 0.32$ kcal mol$^{-1}$ for 250 K $< T < 298$ K, $3.32 \pm 0.37$ kcal mol$^{-1}$ for 298 K $< T < 402$ K, and $2.88 \pm 0.32$ kcal mol$^{-1}$ for 250 K $< T < 402$ K. Values for $k_3(T)$ obtained in our study agree well with those reported previously [47–50]. Our results for reaction (4) are adequately described by the Arrhenius expression $k_4(T) = 2.25 \times 10^{-11} \exp(-400/T)$ for 257 K $\leq T \leq 404$ K although an activation energy which increases slightly with increasing temperature would also be consistent with our data. Due to problems with a heterogeneous dark reaction between HBr and Cl, the absolute uncertainty (2σ) in $k_4(T)$ at any temperature within the range studied is relatively high, and is estimated to be ±25%. The values for $k_4(T)$ reported in this study are in rather poor agreement with all previously reported experimental rate coefficients [33–37,45,46].

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Bibliography


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Kinetics and Thermochemistry of Reversible Adduct Formation In the Reaction of CI(3Pγ) with CS2

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Reversible adduct formation in the reaction of CI(3Pγ) with CS2 has been observed over the temperature range 193–258 K by use of time-resolved resonance fluorescence spectroscopy to follow the decay of pulsed-laser-generated CI(3Pγ) into equilibrium with CS2CI. Rate coefficients for CS2CI formation and decomposition have been determined as a function of temperature and pressure; hence, the equilibrium constant has been determined as a function of temperature. A second-law analysis of the temperature dependence of Kp and heat capacity corrections calculated with use of an assumed CS2CI structure yields the following thermodynamic parameters for the association reaction: ΔH° = -30.0 ± 0.5 kcal mol⁻¹, ΔS° = -26.8 ± 2.4 cal mol⁻¹ K⁻¹, and ΔG° = 46.4 ± 0.6 kcal mol⁻¹. The resonance fluorescence detection scheme has been adapted to allow detection of CI(3Pγ) in the presence of large concentrations of O2, thus allowing the CS2Cl + O2 reaction to be investigated. We find that the rate coefficient for CS2Cl + O2 reaction via all channels that do not generate CI(3Pγ) is <2.5 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ at 293 K and 300-Torr total pressure and that the total rate coefficient is <2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 230 K and 30-Torr total pressure. Evidence for reversible adduct formation in the reaction of CI(3Pγ) with COS was sought but not observed, even at temperatures as low as 194 K.

Introduction

It is now well established that the reaction of OH radicals with CS2 in air proceeds via a complex three-step mechanism involving formation of a weakly bound adduct that reacts with O2 to form products in competition with unimolecular decomposition back to reactants.1–5 Recently, Martin et al.6 reported results from a steady-state-photolysis-competitive-kinetics-and-product-analysis study that suggest that chlorine atoms react with CS2 via a similar mechanism

\[ \text{Cl}(^3\text{P}_\gamma) + \text{CS}_2 + \text{M} \rightarrow \text{CS}_2\text{Cl} + \text{M} \] (1)

\[ \text{CS}_2\text{Cl} + \text{M} \rightarrow \text{Cl}(^3\text{P}_\gamma) + \text{CS}_2 + \text{M} \] (2)

CS2Cl + O2 → products

In this study, we report direct kinetic observations that test the above mechanism and allow determination of rate coefficients for reactions 1, –1, and 2 as well as the CS2Cl heat of formation. A few experiments that examine the related reactions of CI(3Pγ) with COS are also reported.

Experimental Technique

The laser flash photolysis–resonance fluorescence apparatus used in this study was similar to one we have employed previously in a number of studies of chlorine atom kinetics.7–9 Some modifications were required in order to facilitate Cl(3Pγ) detection in the presence of relatively large concentrations of O2. Important features of the apparatus are described below.

A Pyrex-jacketed reaction cell with an internal volume of ~150 cm³ was used in most experiments,10 while a newly constructed Pyrex-jacketed cell with a similar internal volume was used in a few experiments with O2 buffer gas. The new reaction cell was specifically designed to minimize the path of fluorescence excitation radiation and emitted fluorescence through O2; a schematic of the new cell is shown in Figure 1. Both cells could be maintained at a constant temperature by circulating ethylene glycol or 50% methanol/50% ethanol from a thermostated bath through the outer jacket. A copper–constantan thermocouple with glycol or 50% methanol/50% ethanol from a thermostated bath maintained at a constant temperature by circulating ethylene glycol or 50% methanol/50% ethanol from a thermostated bath.

References

Reversible Adduct Formation in Cl(2P3) + CS2

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and the resonance lamp beam and imaged onto the photocathode of a solar-blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with N2. For detection of chlorine atoms in N2 buffer gas, a calcium fluoride window was placed between the reaction cell and photomultiplier to prevent lamp emissions at wavelengths shorter than 125 nm (Lyman-α emission for example) from reaching the photomultiplier. Signals were processed by photon-counting techniques in conjunction with multichannel scaling. The multichannel analyzer sweep was triggered prior to the laser Q switch to allow a pretrigger base line to be obtained.

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under "slow-flow" conditions. The linear flow rate through the reactor was (typically) 3 cm s\(^{-1}\), and the laser repetition rate was (typically) 2 Hz. Hence, no volume element of the reaction mixture was subjected to more than a few laser shots. CS2, COS, O3, and Cl2 were flowed into the reaction cell from 12-L bulbs containing dilute mixtures in nitrogen, air, or oxygen buffer gas. The reactant mixture, chlorine mixture, and additional buffer gas were premixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. Concentrations of CS2, COS, and O3 were also measured in situ in the slow-flow system by UV photometry. Monitoring wavelengths, light sources, absorption path lengths, and absorption cross sections relevant to the photometric measurements are summarized in Table I.

The pure gases used in this study had the following stated minimum purities: N2, 99.999%; O3, 99.99%; Cl2, 99.99%; COS, 97.5%. Air was ultra zero grade with total hydrocarbons less than 0.1 ppm. Oxygen, nitrogen, and air were used as supplied. Chlorine was degassed at 77 K before use. The COS sample was purified by degassing at 77 K after passage over ascarite. Cl2.

Carbon disulfide was Aldrich Gold Label with a stated purity of 97.5%.

Air was ultra zero grade with total hydrocarbons less than a few laser shots. CS2, COS, O3, and Cl2 were flowed into the reaction cell from 12-L bulbs containing dilute mixtures in nitrogen, air, or oxygen buffer gas. The reactant mixture, chlorine mixture, and additional buffer gas were premixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. Concentrations of CS2, COS, and O3 were also measured in situ in the slow-flow system by UV photometry. Monitoring wavelengths, light sources, absorption path lengths, and absorption cross sections relevant to the photometric measurements are summarized in Table I.

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Carbon disulfide was Aldrich Gold Label with a stated purity of 97.5%.
Figure 3. Plot of the pseudo-first-order chlorine atom decay rate, \(k_1\), as a function of the \(O_3\) concentration. Experimental conditions: \(T = 293\) K, \(P = 300\) Torr of air, \([CI]\) = 1.0 \times 10^{14} \text{ molecules/cm}^3, \([Cl(P2)] = 1.0 \times 10^{12} \text{ atoms/cm}^3\). The solid line is obtained from a linear least-squares analysis and gives the bimolecular rate coefficient \((1.12 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) where the uncertainty is 2\(\sigma\) and represents precision only.

first-order \(Cl(P2)\) decays observed in the CI + \(O_3\) experiment are shown in Figure 2; the photolytically produced chlorine atom concentration in all four experiments shown in Figure 2 was 1.0 \times 10^{12} \text{ atoms/cm}^3. A plot of the pseudo-first-order chlorine atom decay rate as a function of the ozone concentration is shown in Figure 3. The slope of this plot gives a bimolecular rate coefficient \((1.12 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) where the uncertainty is 2\(\sigma\) and represents precision only. Agreement with the literature value\(^{14}\) of \(1.16 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) is excellent. The results shown in Figures 2 and 3 clearly demonstrate that time-resolved resonance fluorescence spectroscopy is a viable detection scheme for flash photolysis studies of chlorine atom kinetics in the presence of large levels of \(O_2\).

Results and Discussion

As mentioned above, \(Cl(P2)\) was produced by 355-nm pulsed laser photolysis of \(Cl_2\).

\[ Cl_2 + h\nu (355 \text{ nm}) \rightarrow n Cl(Cl(P2)_{1/2}) + (2 - n) Cl(Cl(P1/2)) \]  

Reported rate coefficients for quenching of the spin-orbit excited state, \(Cl(Cl(P2)_{1/2})\), by \(N_2\) and \(O_2\) are in the range \((4.0 - 6.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \((3.3 - 230) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), respectively.\(^{14,15}\) Hence, for the \(N_2\), \(O_2\), and \(CS_2\) levels employed in this study (Table I), relaxation of \(Cl(Cl(P2)_{1/2})\) was greater than 10 times more rapid than chemical removal of \(Cl(Cl(P2))\), and all measured \(Cl(Cl(P2))\) temporal profiles can be considered as representative of the removal of an equilibrium mixture of \(Cl(Cl(P2))\) and \(Cl(Cl(P2))_{1/2}\). The equilibrium fraction of chlorine atoms in the \(Cl(2P, J = 1/2)\) state ranges from \(0.0013\) at 190 K to \(0.015\) at 300 K. The \(CS_2\) absorption cross section at 355 nm is very small \(<1 \times 10^{-21} \text{ cm}^2\).\(^{16}\) In the presence of \(O_2\) buffer gas, electronically excited \(CS_2\) can react with \(O_2\) to produce \(CS + SO_2\); the quantum yield for chemical reaction is thought to be a few percent.\(^{17}\) Under the conditions of our experiments with \(O_2\) buffer gas, \(CS_2\) produced via the above mechanism was about 100 times lower in concentration than \(Cl(Cl(P2))\) produced via \(Cl_2\) photolysis. Hence, side reactions involving \(CS_2\) that produce or destroy \(Cl(Cl(P2))\) could not have been a significant interference in any of our experiments. If the mechanism for the \(CI + CS_2\) reaction proposed by Martin et al.\(^{13}\) is correct, then, in the absence of \(O_2\), the \(Cl(Cl(P2))\) temporal profile should be controlled by the following reactions:

\[ Cl(Cl(P2)) + CS_2 + M \rightarrow CS_2Cl + M \]  

\(Cl(Cl(P2)) \rightarrow\) loss by diffusion from the detector field of view and reaction with background impurities

\[ Cl(Cl(P2)) \rightarrow\) loss by processes that do not regenerate \(Cl(Cl(P2))\)

There appear to be no energetically allowed bimolecular channels for the \(CI + CS_2\) reaction. The rate equations for the above scheme can be solved analytically as long as all \(Cl(Cl(P2))\) and \(CS_2Cl\) loss processes are first order:

\[ \frac{[Cl(Cl(P2))]}{[Cl(Cl(P2))]}_0 = \frac{(Q + \lambda_1) \exp(\lambda_1 t) - (Q + \lambda_2) \exp(\lambda_2 t)}{\lambda_1 - \lambda_2} \]  

where

\[ \lambda_1 = 0.5((a^2 - 4\theta)^{1/2} - a) \]  

\[ \lambda_2 = -0.5((a^2 - 4\theta)^{1/2} + a) \]  

\[ Q = k_2 + k_3 \]  

\[ \alpha = Q + k_4 + k_5[CS_2] = -(\lambda_1 + \lambda_2) \]  

\[ \beta = k_3Q + k_4[k_5[CS_2]] = \lambda_1\lambda_2 \]  

A double-exponential decay is predicted. Good-quality experimental data could be fit to eq I to obtain values for the three parameters \(\lambda_1, \lambda_2\), and \(Q\). Since \(k_5\) is directly measured, the other elementary rate coefficients can be obtained as follows:

\[ k_1 = -(\lambda_1 + \lambda_2 + k_4 + Q)/[CS_2] \]  

\[ k_3 = (\lambda_1\lambda_2 - k_4Q)/k_3[CS_2] \]  

\[ k_{21} = Q - k_3 \]  

It should be noted that the parameter \(Q\) represents the sum of all first-order \(CS_2Cl\) removal processes. Therefore, eqs IV and IX require the assumption that the only \(CS_2Cl\) removal process that regenerates chlorine atoms is reaction I. When \(Cl_2/CS_2/N_2\) mixtures at 298 K were subjected to 355-nm laser flash photolysis, the double-exponential decays predicted in the above analysis were not observed. However, at temperatures
Reversible Adduct Formation in Cl(2Pj) + CS2

Since there are no energetically feasible bimolecular channels for Cl(2Pj) + CS2 reaction, the apparent reactivity must be attributed to the observed depletion of Cl(2Pj) and CS2 levels. A likely explanation for the nonexponential decays observed in high-pressure conditions is proposed to result from the fact that Cl2S2 adduct can react with O2 in competition with reaction 1. However, in order to calculate the reaction rate, we need to know the relative rates of reaction 1 and -1. To investigate this possibility, we studied the kinetics of Cl(2Pj) removal in 300 Torr N2 and, to a lesser extent, in air, as shown in Figure 5. A van’t Hoff plot for the equilibrium Cl(2Pj) + CS2 = CS2-Cl, which is obtained from a linear least-squares analysis, gives the slope of $\Delta H = -10.34 \pm 0.23$ kcal mol$^{-1}$ and the intercept gives $\Delta S = -25.94 \pm 1.02$ cal mol$^{-1}$ deg$^{-1}$, where the uncertainties are 2$s$ and represent precision only.

The solid line is obtained from a linear least-squares analysis; its slope gives $\Delta H = -10.34 \pm 0.23$ kcal mol$^{-1}$, and its intercept gives $\Delta S = -25.94 \pm 1.02$ cal mol$^{-1}$ deg$^{-1}$, where the uncertainties are 2$s$ and represent precision only.

A van’t Hoff plot for the equilibrium defined by reactions 1 and -1 is shown in Figure 5. Since

$\ln K_P = \frac{\Delta S}{R} = \frac{(\Delta H - \Delta S)}{RT}$

the enthalpy change associated with reaction 1 is obtained from the intercept of the van’t Hoff plot while the entropy change is obtained from the slope of the van’t Hoff plot when the temperature is equal to 0 from the experimental parameters. Values for $k_1$, $k_{-1}$, and $K_P$ were then calculated.

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2599
TABLE II: Results of the Cl(2P_J) + CS₂ + N₂ → CS₂Cl + N₂ "Approach-to-Equilibrium" Experiments

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Nicosich et al.
observed in air reflect the fact that a larger fraction of chlorine atoms were removed by nonchain processes in the air experiments (due to the faster background chlorine atom decay rate in air). It is also possible that O atoms or an impurity in the air sample scavenged SH effectively in competition with reaction 7. It should be noted that the rate coefficient for the SH + O reaction is thought to be very slow.19

If, as suggested above, reactions 6 and 7 can influence observed Cl(2Pj) temporal profiles, then two assumptions made in analyzing the "approach-to-equilibrium" data (Table II) need to be reevaluated. First, it was assumed that $k_5$ was independent of CS$_2$ concentration. Also, the derivation of eq 1 assumes that radical species other than Cl(2Pj) and CS$_2$Cl (SH, for example) exert a negligible influence on observed chlorine atom temporal profiles. To test the validity of the above assumptions, we carried out computer simulations of a number of typical approach-to-equilibrium experiments with and without reactions 6 and 7 included in the mechanism. The rate coefficient $k_5$ was assumed to be independent of temperature while $k_5$ was assigned an $A$ factor of 1 $\times$ 10$^{11}$ cm$^{-1}$ molecule$^{-1}$ s$^{-1}$, leading to an assumed activation energy of 1.16 kcal mol$^{-1}$. Because Cl$_2$ concentrations in the approach-to-equilibrium experiments were generally rather low (Table II), and because large CS$_2$ concentrations were employed only in experiments where the approach to equilibrium was very fast, the influence of reactions 6 and 7 on the approach-to-equilibrium data was found to be negligible under all experimental conditions employed.

The results shown in Figure 6 would seem to suggest that the effective rate coefficient, $k_a$, for reaction of Cl(2Pj) with CS$_2$ via reactions 1, -1, and 2 in 300 Torr of air at 293 K is very slow. However, it should be kept in mind that our experiment is "blind" to channels for reaction 2 which result in Cl(2Pj) regeneration:

$$\text{CS}_2\text{Cl} + \text{O}_2 \rightarrow \text{SOCl} + \text{COS} \quad -\Delta H = 102 \text{ kcal mol}^{-1}$$ (2a)

$$\rightarrow \text{Cl}(2Pj) + \text{S}_2 + \text{CO}_2 \quad -\Delta H = 81 \text{ kcal mol}^{-1}$$ (2b)

$$\rightarrow \text{Cl}(2Pj) + \text{SO} + \text{CO} \quad -\Delta H = 50 \text{ kcal mol}^{-1}$$ (2c)

$$\rightarrow \text{S} + \text{SCI} + \text{CO}_2 \quad -\Delta H = 38 \text{ kcal mol}^{-1}$$ (2d)

$$\rightarrow \text{SO} + \text{SCI} + \text{CO} \quad -\Delta H = 35 \text{ kcal mol}^{-1}$$ (2e)

$$\rightarrow \text{CICS} + \text{SO}_2$$ (2f)

$$\rightarrow \text{ClP}_2 + \text{SO}_2 + \text{CS} \quad -\Delta H = 10 \text{ kcal mol}^{-1}$$ (2g)

With $k_a$ defined to be the effective rate coefficient for reaction of Cl(2Pj) with CS$_2$ via reactions 1, -1, and those channels of reaction 2 that do not produce Cl(2Pj), i.e., channels 2a, 2d, 2e, and 2f, the data in Figure 6 show that $k_a$ is $<5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. By comparison, Martin et al.2 whose experiment was sensitive to the total rate coefficient for reaction 2 independent of whether or not Cl(2Pj) is produced, report values for $k_a$ in units of $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ of $49 \pm 16, 68 \pm 12$, and $70 \pm 30$ in 50 Torr of O$_2 + 710$ Torr of N$_2$, 100 Torr of O$_2 + 660$ Torr of

\[(\text{18})\text{ Nesbitt, D. J.; Leone, S. R. J. Chem. Phys. 1960, 72, 1722.}

The CI(2P,) temporal profiles observed in 30 Torr of O2 at 230 K. CI(2P,) + O2 + O2 K CI + O2 + O2 and assume that k0 = 0, but rather that (a) k2 = 3 x 10^{-11} cm^3 molecule^{-1} s^{-1}, k2 = 0 or (b) k2 = k_{a2} = 3 x 10^{-13} cm^3 molecule^{-1} s^{-1}. Similarly, the dotted lines are obtained from simulations that assume that (a) k1 = 1 x 10^{-13} cm^3 molecule^{-1} s^{-1}, k3 = 0 or (b) k3 = k_{a3} = 1 x 10^{-14} cm^3 molecule^{-1} s^{-1}. N2, and 150 Torr of O2 + 150 Torr of N2, respectively (errors are 2e).

Clearly, one possible explanation for the fact that Martin et al.1 report values for K_{eff} that are much larger than our value for K_{eff} is that reaction 2 proceeds via channels that produce CI(2P,) + O2 + O2 K CI + O2 + O2 and/or CI(2P,) + O2 + O2 K CI + O2 + O2. To further investigate this possibility, we conducted some experiments using O2 buffer gas under experimental conditions (low temperature and pressure) where the double-exponential decays predicted by equation I would be observable unless the CS2Cl + O2 reaction was fast. A typical CI(2P,) temporal profile observed in these experiments is shown in Figure 7. The data were first analyzed with use of 1-1X, i.e., assuming k2 = 0. Both k1 and k3 were found to be about 25% faster at 230 K in 30 Torr of O2 than at 230 K in 30 Torr of N2, suggesting that O2 is a little more efficient than N2 as a third body. However, the equilibrium constant obtained from analysis of the O2 data, K_{eq} = 13 000 atm^{-1}, is in excellent agreement with the equilibrium constants determined from experiments in N2 at 229 and 231 K (see Table II)—a result that strongly suggests that the CS2Cl + O2 reaction is slow. If reaction 2 proceeds via a channel that does not produce CI(2P,), the slow component in the decay shown in Figure 7 would be much faster than was observed. On the other hand, if reaction 2 proceeded via a channel that regenerated CI(2P,), the steady-state CI(2P,) concentration at long times after the laser flash would be faster than the concentration expected from the equilibrium between reactions 1 and -1; hence, the above analysis would have given an erroneously small value for k1.

To put a quantitative upper limit on k2, we expand the mechanism used to derive equations I-VI to include reaction 2.

Equations I, II, III, and V remain unchanged while eqs IV and VI are modified as follows:

\[ Q = k_1 + k_3 + k_2[O_2] \quad \text{(IV')} \]
\[ \beta = k_2[Q + k_1[CS_2] + k_3[O_2]] \quad \text{(V')} \]

In the above equations, k_{a2} represents all channels of reaction 2 that do not produce CI(2P,).

\[ k_{a2} = k_{a2} + k_{a2} + k_{a2} = k_1 - k_{a2} - k_{a2} \quad \text{(XII)} \]

The CI(2P,) temporal profiles observed in 30 Torr of O2 at 230 K were simulated with equations I-VI modified as follows: I-VI'. Values assumed for k1, k3, and k3 were those obtained from a nonlinear least-squares analysis with k3, set equal to zero (solid line in Figure 7). The objective was to determine minimum values for k_{a2} and k_{a2} which were clearly inconsistent with our data. As shown in Figure 7, if either k_{a2} or k_{a2} is assumed to be 1 x 10^{-15} cm^3 molecule^{-1} s^{-1} or greater, a noticeably different CI(2P,) temporal profile is predicted. Further simulations showed that it is not possible to reproduce the experimental data by assuming values for k_{a2} and/or k_{a2} larger than 1 x 10^{-15} cm^3 molecule^{-1} s^{-1} and varying k1, k3, and/or k3 to optimize the fit. It appears that the slow CI(2P,) decay rate and "correct" equilibrium CI(2P,) concentration observed at long times after the laser flash can only be explained by postulating a very slow rate for reaction 2. We feel that our data support an upper limit of 1 x 10^{-15} cm^3 molecule^{-1} s^{-1} for k3 at 230 K in 30 Torr of O2.

Under the conditions of Martin et al.'s experiments (293 K, 760 Torr of air, 5 ppm CS2), the CS2Cl concentration was very small compared to the concentrations of CI(2P,) and CS2; hence, the steady-state approximation can be applied to CI(2P,). Application of the steady-state approximation to the mechanism consisting of reactions 1, -1, 4, 5, and 2 leads to the expression

\[ k_{eff} = k_2[Q][O_2]/(1 + [O_2]) \quad \text{(XIII)} \]

where \( X = k_2/k_1 \quad \text{(XIV)} \)

Although long extrapolations are required, our data can be used to estimate values for k1 and k2. At 293 K and 760-Torr total pressure, the conditions of most of Martin et al.'s competitive kinetics experiments\(^3\) with an accuracy of about a factor of 2, we estimate k1 \sim 2 x 10^{-11} cm^3 molecule^{-1} s^{-1} and k2 \sim 2 x 10^{-16} cm^3 molecule^{-1} s^{-1}—not inconsistent with our 230 K, 30 Torr of O2 upper limit of 2 x 10^{-12} cm^3 molecule^{-1} s^{-1} (it is, of course, possible that k2 increases with increasing temperature or pressure). Hence, although we observe no positive evidence for a reaction between CS2Cl and O2, our data do not preclude the occurrence of reaction 2 with a rate coefficient (on the order of 10^{-12} cm^3 molecule^{-1} s^{-1}) consistent with the steady-state-kinetics observations of Martin et al.,\(^3\) provided that reaction 2 occurs by a channel that regenerates CI(2P,).

As discussed above, the data in Figure 6 suggest that k_{a2} < 5 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 293 K and 300-Torr total pressure. Considering this result in conjunction with eq XIII leads to k_{a2} < 2.5 x 10^{-16} cm^3 molecule^{-1} s^{-1} at T = 293 K and P = 300 Torr.

Direct observation of the approach to equilibrium in O2 buffer gas at temperatures below 230 K could potentially allow very slow values for k_2 (i.e., <10^{-12} cm^3 molecule^{-1} s^{-1}) to be determined. However, interpretation of such experiments is complicated by the occurrence of another rapid equilibrium

\[ \text{Cl}(2P,)+O_2+O_2 K \text{ ClO} + O_2 + O_2 \quad (8-8) \]

Recent work in our laboratory\(^{20}\) has established that the equilibrium concentration of ClO in 30 Torr of O2 is negligible at temperatures of 230 K and above.

It is interesting to compare the kinetic and thermodynamic data reported in this paper for the CS2Cl adduct with analogous results reported elsewhere\(^3,4\) for the CS2OH adduct. The enthalpy changes for the CI + CS2 or OH + CS2 association reactions at 298 K are both around -10-11 kcal mol^{-1}, but the entropy change associated with the CI + CS2 reaction, ΔS^\text{deg}_\text{S}(298 K) = -26.8 cal mol^{-1} deg^{-1}, appears to be somewhat larger than the larger entropy change associated with the OH + CS2 reaction (analysis of our K_2 versus 1/T data gives ΔS^\text{deg}_\text{S} = -22 ± 3 cal mol^{-1} deg^{-1} while Murrells et al.\(^4\) report ΔS^\text{deg}_\text{S} = -24 ± 4 cal mol^{-1} deg^{-1}). Hence, at a given temperature, K_2 is about a factor of 3 larger for the OH + CS2 equilibrium than for the CI + CS2 equilibrium. At T = 256-258
Reversible Adduct Formation in Cl(2P_J) + CS2

Figure 8. Cl(2P_J) temporal profile observed following pulsed laser photolysis of 3.0 x 10⁻³ Cl2 molecules/cm² + 5.5 x 10⁻³ COS molecules/cm² in 30 Torr of N₂ at 194 K. [Cl(2P_J)]₀ = 2 x 10⁻¹ atoms/cm², 2500 laser shots averaged. The laser fired at time t = 0.

K and P = 75 Torr of N₂, a temperature and pressure regime where experimental kinetic data are available for both the Cl + CS2 and OH + CS2 reactions, we find that adduct formation proceeds about 2.5 times more rapidly for Cl + CS2 (k = 2.5 x 10⁻¹² cm³ molecule⁻¹ s⁻¹) than for OH + CS2 (k = 1.0 x 10⁻¹² cm³ molecule⁻¹ s⁻¹) while the adduct lifetime toward unimolecular decomposition back to reactants is about 7.5 times shorter for CS₂Cl (τ = 16 μs) than for CS₂OH (τ = 120 μs). CS₂OH is at least 1 order of magnitude more reactive with O₂ than is CS₂Cl, a reasonable finding considering that the CS₂OH reaction with O₂ appears to involve breaking of the O-H bond.

In addition to the studies of CS₂Cl formation and removal described above, we also searched for evidence of reversible adduct formation in the Cl + COS system. As typified by the Cl(2P_J) temporal profile shown in Figure 8, no evidence for formation of a COSCl adduct was observed. Each data point in Figure 8 represents 1 μs of time. Since the COS concentration was 5.5 x 10⁻³ molecules/cm², in order for a decay of Cl(2P_J) into equilibrium to be too rapid for observation, the Cl(2P_J) + COS rate coefficient would have to be unrealistically fast, i.e., close to 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at a pressure (30 Torr of N₂) expected to be far removed from the high-pressure limit. It seems safe to assume, therefore, that the absence of a fast component in the Cl(2P_J) decay implies that [COSCl]₀ < 0.1[Cl(2P_J)]₀ at 194 K and [COS] = 5.5 x 10⁻³ molecules/cm³. Hence, K_s < 1.8 x 10⁻¹⁷ cm³/molecule and K_p < 680 atm⁻¹. Our data suggest that either (a) a significant barrier exists in the entrance channel that prevents Cl(P_J) addition to COS or (b) the species COSCl is very weakly bound. Since no barrier to addition is observed for the similar Cl(P_J) + CS₂ reaction, the latter of the above possibilities seems more reasonable. In either case, COSCl should not be an important species in atmospheric chemistry. It is worth noting that Wahner and Ravishankara,²² in a study of the similar OH + COS reaction, also found no evidence for adduct formation.

Summary

Reversible adduct formation in the reaction of Cl(P_J) with CS₂ has been observed via direct monitoring of the decay of pulsed-laser-generated Cl(P_J) into equilibrium with time-resolved resonance fluorescence spectroscopy as the detection technique. Rate coefficients for CS₂Cl formation and decomposition have been determined as a function of temperature and pressure; hence, the equilibrium constant has been determined as a function of temperature. A second-law analysis of the temperature dependence of K_s and heat capacity corrections calculated with an assumed CS₂Cl structure yields the following thermodynamic parameters for the association reaction: ΔH°₂₉₈ = -10.5 ± 0.5 kcal mol⁻¹, ΔH°₂₉₈ = -9.5 ± 0.7 kcal mol⁻¹, ΔS°₂₉₈ = -26.8 ± 2.4 cal mol⁻¹ deg⁻¹, and ΔH°₂₉₈(CS₂Cl) = 46.4 ± 0.6 kcal mol⁻¹.

The resonance fluorescence detection scheme has been adapted to allow detection of Cl(P_J) in the presence of large concentrations of O₂, thus allowing the reaction of CS₂Cl with O₂ to be investigated. Our results demonstrate that k₂₃₃, the rate coefficient for the CS₂Cl + O₂ reaction via all channels that do not regenerate Cl(P_J), is less than 2.5 x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 293 K and 300-Torr total pressure. Another series of experiments places an upper limit of 2 x 10⁻¹³ cm³ molecule⁻¹ s⁻¹ on the total rate coefficient at 230 K and 30-Torr total pressure.

Evidence for reversible adduct formation in the reaction of Cl(P_J) with COS was sought but not observed, even at temperatures as low as 194 K, suggesting either that a barrier exists in the Cl + COS entrance channel or that COSCl is a very weakly bound species.

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Kinetics and thermochemistry of CICO formation from the Cl + CO association reaction

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Laser flash photolysis of Cl₂/CO/M mixtures (M = N₂, CO, Ar, CO₂) has been employed in conjunction with Cl(P, 2) detection by time-resolved resonance fluorescence spectroscopy to investigate equilibration kinetics in the reactions Cl(P, 2) + CO → CICO as a function of temperature (185–260 K) and pressure (14–200 Torr). The association and dissociation reactions are found to be in the low-pressure limit over the range of experimental conditions investigated. In N₂ and/or CO buffer gases, the temperature dependences of the CICO formation and dissociation reaction rate constants are described by the Arrhenius expressions

\[ k_+ = (1.05 ± 0.36) \times 10^{-14} \exp\left(\frac{810 ± 70}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \]  
\[ k_- = (4.1 ± 3.1) \times 10^{-10} \exp\left(\frac{— 2960 ± 160}{T}\right) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \]  

Second- and third-law analyses of the temperature dependence of the equilibrium constant \( k_+ / k_- \) lead to the following thermodynamic parameters for the association reaction:

\[ \Delta H^\circ_{298} = -7.7 ± 0.6 \text{ kcal mol}^{-1} \]  
\[ \Delta S^\circ_{298} = 23.8 ± 2.0 \text{ cal mole}^{-1} \text{K}^{-1} \]  
\[ \Delta G^\circ_{298} = 5.2 ± 0.6 \text{ kcal mol}^{-1} \]  

These results were reported in this study significantly reduce the uncertainties in all reported kinetic and thermodynamic parameters.

INTRODUCTION

The chloroformyl radical (CICO) has been of interest to photochemists for many years. Bodenstein, Lenher, and Wagner first postulated the existence of CICO as an intermediate in the photocatalyzed production of phosgene (Cl₂/CO) from Cl₂/CO mixtures. Models of the CO₂-rich atmosphere of Venus have included the chemistry of chloroformyl radicals. CICO may also play a role in the chemistry of the Earth’s atmosphere. For instance, photooxidation of CCICl₂ can lead to CICO production via a CICO reservoir. Information concerning the kinetics and thermochemistry of the Cl + CO association reaction is rather sparse:

\[ \text{Cl} + \text{CO} + M \rightarrow \text{CICO} + M. \]  

(R1)

The only study of the kinetics of reaction (R1) was carried out by Clark, Clyne, and Stedman over 20 years ago. These authors employed a discharge flow reactor to measure \( k_+ \) at 195 and 300 K in argon buffer gas. Reported values for the CICO bond dissociation energy are based on indirect experimental information and ab initio theory, and range from 3.5 to 7.1 kcal mol⁻¹.

In this paper we report direct observations of the decay of pulsed-laser-generated chlorine atoms into equilibrium with CICO. These experiments allow determination of \( k_+ \) and \( k_- \), as functions of temperature and pressure, and the equilibrium constant \( k_+ / k_- \) as a function of temperature. Second- and third-law methods are employed to evaluate the CICO entropy, heat of formation, and bond dissociation energy.

EXPERIMENTAL SECTION

The apparatus employed in this study was similar to those used in this laboratory in several previous studies of chlorine atom kinetics. The salient features of the apparatus and technique are described below.

A Pyrex reaction cell with an internal volume of 150 cm³ was used in all experiments. A 1:1 methanol/ethanol mixture from a thermostated bath was circulated through an outer jacket of the reactor to control the experimental temperature. The temperature of the gas mixture under the exact pressure and flow rate conditions of the experiment was measured with a retractable copper-Constantan thermocouple.

Chlorine atoms were produced by 355 nm pulsed laser photolysis of Cl₂ using third-harmonic radiation from a Quanta Ray model DCR-2 Nd:YAG laser. Cl atom fluorescence was excited by radiation from a cw atomic resonance lamp, which consisted of an electrodeless, microwave-powered discharge through a few Torr of flowing Cl₂/He mixture. Radiation was coupled out of the lamp through a MgF₂ window and into the cell through a MgF₂ lens. The resonance lamp radiation intersected the photolysis laser beam at 90° near the center of the reaction cell. A flowing gas filter between the resonance lamp radiation, and imaged onto the photocathode of a solar blind photomultiplier. The region between the reaction cell and the photomultiplier was purged with N₂. Whenever N₂O filtered the resonance lamp, a CaF₂ window was
placed between the reaction cell and the photomultiplier to prevent detection of radiation at wavelengths shorter than 125 nm (Lyman-α, for instance). Signals were processed using photon counting techniques in conjunction with multichannel scaling. For each chlorine atom decay profile measured, between 200 and 34,000 laser shots were averaged to obtain a well-defined temporal profile. The multichannel scaler sweep was triggered before the laser pulse to permit determination of the (constant) background signal level.

In order to avoid the accumulation of photolysis or reaction products, all experiments were carried out under slow flow conditions. The linear flow rate through the reactor was typically 3 cm s⁻¹ while the laser repetition rate was varied from 1 to 10 Hz (5 Hz typical). Hence, no volume element of the reaction mixture was subjected to more than two or three laser shots. Cl₂ was leaked from a 12 liter Pyrex bulb containing a dilute (≈10%) mixture of Cl, in N₂, while the other reagents flowed directly from high-pressure storage tanks. The CO was passed through a Pyrex trap maintained at 77 K before mixing with other gases immediately upstream of the reaction cell; this procedure removed reactive, photosensitive metal carbonyls from the CO flow. The concentrations of each component in the reaction mixtures were determined from measurement of individual flows using calibrated electronic mass flow meters. The reagent gases had the following stated minimum purities: N₂ 99.999%, Cl₂, 99.999%; O₂, 99.999%; CO₂, 99.999%; Ar, 99.999%; CO, 99.999%. The Cl₂ we repeatedly degased at 77 K before dilution. The other gases were used as supplied.

RESULTS AND DISCUSSION

All experiments were carried out under pseudo-first-order conditions with [CO] >> [Cl]₀ (the concentration of Cl atoms immediately following the laser pulse). Reaction mixtures contained (1.0–18) × 10¹³ molecules cm⁻³ Cl₂ while [Cl]₀ varied from (2.0–10) × 10¹¹ atoms cm⁻³. Experiments were performed over the temperature range 185–260 K, and the total pressure was varied from 14 to 200 Torr by diluting the gas mixture with the appropriate partial pressure of an unreactive buffer gas (N₂, CO₂, or Ar).

In these experiments the fate of Cl atoms is controlled by the following reactions:

\[
\begin{align*}
\text{Cl} + \text{CO} + \text{M} &\rightarrow \text{CICO} + \text{M}, \quad (R1) \\
\text{CICO} + \text{M} &\rightarrow \text{Cl} + \text{CO} + \text{M}, \quad (R-1) \\
\text{Cl} &\rightarrow \text{Cl} \text{-loss by diffusion from the detector field of view and reaction with background impurities, (R2)} \\
\text{CICO} &\rightarrow \text{Cl} \text{-loss by processes which do not regenerate Cl atoms. (R3)}
\end{align*}
\]

The rate equations for reactions (R1), (R-1), (R2), and (R3) can be solved analytically:

\[
\frac{[\text{Cl}]}{[\text{Cl}]_0} = \left(\frac{Q + \lambda_1}{Q + \lambda_2}\right) \exp\left(\lambda_1 t\right) - \left(\frac{Q + \lambda_2}{Q + \lambda_1}\right) \exp\left(\lambda_2 t\right),
\]

where

\[
\lambda_1 = 0.5\left\{\left(A^2 - 4B\right)^{1/2} - A\right\},
\]

\[
Q = k_{-1} + k_3,
\]

\[
A = Q + k_2 + k_1[\text{CO}],
\]

\[
B = k_3Q + k_1[\text{CO}].
\]

The observed temporal profiles for Cl atoms were fit to the double-exponential equation (1) using a nonlinear least-squares method to obtain values for \(\lambda_1, \lambda_2,\) and \(Q\) for each decay. The background Cl atom loss rate in the absence of CO (\(k_2\)) was directly measured at each temperature and pressure. \(k_3\) ranged from 10 to 40 s⁻¹ except for the experiments in CO₂ buffer gas, where \(k_3\) was approximately 600 s⁻¹ due to reaction of Cl(²P) with an impurity in the CO₂.

Using the identities

\[
\lambda_1 + \lambda_2 = -A,
\]

\[
\lambda_1\lambda_2 = B,
\]

and the fit parameters \(\lambda_1, \lambda_2,\) and \(Q\) can be directly related to the rate coefficients of interest via

\[
k_1 = \frac{Q + k_2 + \lambda_1 + \lambda_2}{[\text{CO}]},
\]

\[
k_2 = \frac{(\lambda_1 \lambda_2 - k_1 Q)/k_1[\text{CO}]}{Q - k_3},
\]

Typical observed Cl atom temporal profiles are shown in Fig. 1. The results for all experiments are presented in Table I. The results exhibit no systematic dependence upon

![FIG. 1. Cl(²P) temporal profiles in the presence of varying amounts of CO at 100 Torr total pressure (N₂, diluent) and 227 K. For all experiments [Cl₂] = 3.1 × 10¹⁸ molecules cm⁻³ and [Cl]₀ = 5.2 × 10¹¹ atoms cm⁻³. The carbon monoxide concentrations for each experiment to units of 10¹⁰ molecules cm⁻³ are A: 1.90, B: 3.72, and C: 8.08. The number of laser shots averaged for each experiment are A: 4400, B: 4000, and C: 10 000. The values for the birexponential parameters (see text) for A, B, and C, respectively, are \(-\lambda_1 = 67.1, 81.9,\) and \(107, -\lambda_2 = 5790, 9180,\) and 16 500, and \(Q = 3110, 3470,\) and 3590; units are s⁻¹. The inset shows decay C with the signal counts displayed on a linear scale.](image-url)
TABLE I. Summary of kinetic and equilibrium measurements.

<table>
<thead>
<tr>
<th>T(K)/M</th>
<th>([Cl]°)</th>
<th>([Cl]₀)</th>
<th>([CO])</th>
<th>([M])</th>
<th>k₁</th>
<th>k₋₁</th>
<th>k₁</th>
<th>Kₛ'</th>
</tr>
</thead>
<tbody>
<tr>
<td>260/N₂,CO</td>
<td>150</td>
<td>4.4</td>
<td>18.6</td>
<td>111</td>
<td>1.86</td>
<td>40.2</td>
<td>317</td>
<td>13.1</td>
</tr>
<tr>
<td>150</td>
<td>4.4</td>
<td>111</td>
<td>2.03</td>
<td>44.3</td>
<td>126</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>4.4</td>
<td>201</td>
<td>2.20</td>
<td>52.2</td>
<td>247</td>
<td>11.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

242/N₂,CO

| 220 | 5.5 | 79.4 | 79.4 | 3.11 | 25.1 | 101 | 37.6 |
| 1800 | 4.2 | 83.4 | 83.4 | 3.12 | 28.9 | 132 | 32.7 |
| 160 | 4.1 | 120 | 3.62 | 26.3 | 497 | 41.7 |
| 160 | 4.4 | 159 | 3.17 | 24.3 | 247 | 39.6 |
| 160 | 4.1 | 199 | 2.93 | 22.8 | 133 | 39.0 |

227/N₂,CO

| 310 | 5.2 | 19.0 | 425 | 3.39 | 7.01 | 129 | 156 |
| 310 | 5.2 | 79.4 | 79.4 | 3.11 | 25.1 | 101 | 37.6 |
| 310 | 5.2 | 37.2 | 3.63 | 7.84 | 123 | 150 |
| 310 | 5.2 | 80.8 | 3.79 | 8.14 | 133 | 151 |

226/N₂, CO

| 140 | 3.8 | 19.2 | 128 | 3.52 | 8.91 | 128 | 128 |
| 230 | 3.7 | 54.2 | 128 | 4.02 | 11.0 | 84.4 | 119 |
| 220 | 3.1 | 108 | 128 | 3.82 | 11.4 | 53.4 | 109 |

216/CO₂

| 140 | 3.0 | 13.9 | 67.2 | 17.8 | 6.51 | 191 | 929 |
| 180 | 4.6 | 6.70 | 61.2 | 14.7 | 8.74 | 21.4 | 576 |
| 180 | 4.6 | 9.73 | 63.5 | 14.6 | 7.90 | 43.7 | 632 |
| 180 | 4.6 | 13.5 | 66.5 | 16.1 | 7.02 | 139 | 785 |
| 180 | 4.6 | 15.9 | 69.3 | 16.4 | 8.14 | 59.7 | 689 |

215/CO₂

| 220 | 5.0 | 6.04 | 137 | 3.19 | 1.72 | 90.8 | 642 |
| 220 | 5.0 | 7.66 | 137 | 3.33 | 1.81 | 89.9 | 637 |
| 220 | 5.0 | 10.1 | 137 | 3.34 | 1.76 | 89.0 | 657 |
| 220 | 5.0 | 18.7 | 137 | 3.57 | 2.04 | 111 | 606 |

212/Ar

| 140 | 3.1 | 3.50 | 924 | 6.72 | 17.4 | 113 | 1350 |
| 100 | 3.1 | 5.27 | 924 | 5.93 | 18.5 | 184 | 1120 |
| 100 | 3.1 | 8.10 | 924 | 5.81 | 17.5 | 142 | 1170 |
| 100 | 3.1 | 8.24 | 924 | 6.14 | 17.7 | 128 | 1210 |

209/N₂

| 220 | 5.0 | 6.04 | 137 | 3.19 | 1.72 | 90.8 | 642 |
| 220 | 5.0 | 7.66 | 137 | 3.33 | 1.81 | 89.9 | 637 |
| 220 | 5.0 | 10.1 | 137 | 3.34 | 1.76 | 89.0 | 657 |
| 220 | 5.0 | 18.7 | 137 | 3.57 | 2.04 | 111 | 606 |

208/N₂

| 130 | 4.1 | 5.30 | 139 | 5.19 | 2.45 | 88.8 | 749 |
| 130 | 4.1 | 8.54 | 139 | 5.55 | 2.46 | 89.4 | 796 |
| 130 | 4.1 | 11.2 | 139 | 5.47 | 2.31 | 73.2 | 836 |
| 130 | 4.1 | 18.0 | 139 | 5.54 | 2.82 | 97.0 | 694 |

206/N₂

| 210 | 4.3 | 3.85 | 141 | 4.86 | 2.15 | 95.6 | 807 |
| 210 | 4.3 | 6.45 | 141 | 4.97 | 2.43 | 70.0 | 730 |
| 200 | 5.8 | 15.8 | 141 | 5.87 | 2.09 | 113 | 1000 |

197/N₂

| 140 | 5.9 | 3.34 | 147 | 6.86 | 1.06 | 64.1 | 2410 |
| 140 | 5.9 | 6.57 | 147 | 6.61 | 1.02 | 54.8 | 2410 |
| 140 | 5.9 | 9.85 | 147 | 6.43 | 1.19 | 93.9 | 2010 |
| 140 | 5.9 | 19.0 | 147 | 6.38 | 1.15 | 94.5 | 2060 |

187/N₂

| 110 | 3.2 | 16.7 | 155 | 7.16 | 0.789 | 81.6 | 3560 |
| 310 | 2.9 | 16.9 | 155 | 7.12 | 0.708 | 73.6 | 3940 |
| 1000 | 10 | 17.1 | 155 | 7.07 | 0.712 | 81.2 | 3890 |
| 1000 | 2.9 | 17.2 | 155 | 7.23 | 0.726 | 95.5 | 3910 |

185/N₂

| 110 | 4.4 | 5.55 | 130 | 7.41 | 0.554 | 96.7 | 5310 |
| 110 | 4.0 | 5.34 | 193 | 9.03 | 0.391 | 98.3 | 9160 |
| 110 | 4.0 | 10.5 | 193 | 8.92 | 0.647 | 175 | 5470 |
| 100 | 4.0 | 10.6 | 261 | 10.0 | 0.561 | 169 | 7070 |
| 130 | 4.4 | 6.64 | 397 | 9.52 | 0.430 | 190 | 8780 |
| 130 | 4.4 | 13.3 | 397 | 8.53 | 0.570 | 224 | 5940 |
| 170 | 5.2 | 8.20 | 522 | 8.54 | 0.448 | 89.1 | 7570 |
| 110 | 3.7 | 5.47 | 1040 | 6.32 | 0.331 | 179 | 7570 |
| 110 | 3.7 | 12.9 | 1040 | 7.27 | 0.411 | 9.5 | 7020 |

*Units are 10¹¹ molecules (atoms) cm⁻³.
*Units are 10¹⁰ molecules (atoms) cm⁻³.
*Units are 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹.
*Units are 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹.
*Units are s⁻¹.
*Units are atm⁻¹.

Variations in [CO], [Cl₂], [Cl]₀, or laser repetition rate. It was also found that measured values for the termolecular rate coefficient k₁ and the bimolecular rate coefficient k₋₁ were independent of total bath gas pressure over a wide range, indicating that reactions (R₁) and (R₋₁) are in the low-pressure limit up to approximately 200 Torr. An Arr-
henius plot for reaction (R1) is shown in Fig. 2. A linear least-squares analysis of ln $k_1$ vs $T^{-1}$ for all data taken in N$_2$ and/or CO buffer gases yields

$$k_1 = (1.05 \pm 0.36) \times 10^{-34} \exp \left[ \frac{(810 \pm 70)}{T} \right]$$

in units of cm$^3$ molecule$^{-2}$ s$^{-1}$. Similar analysis of the results for the reverse process ($k_{-1}$) gives

$$k_{-1} = (4.1 \pm 3.1) \times 10^{-10} \exp \left[ -\frac{(2960 \pm 160)}{T} \right]$$

cm$^3$ molecule$^{-1}$ s$^{-1}$. Panel recommendations of kinetic data for use in modeling atmospheric chemistry parametrize the temperature dependence of association rate constants using the relationship $k(T) = k(300 \text{ K})(T/300)^{-n}$. Analysis of our measurements of $k_1$ in this form yields the expression

$$k_1 = (1.31 \pm 0.15) \times 10^{-33}(T/300)^{-3.4 \pm 0.3}$$

cm$^6$ molecule$^{-2}$ s$^{-1}$. A van't Hoff plot for the equilibrium defined by reactions (R1) and (R-1) is shown in Fig. 3. A linear least-squares analysis of the ln $K_p$ vs $T^{-1}$ data yields the result

$$\ln K_p (\text{atm}^{-1}) = -\frac{\Delta H}{R \cdot T} + \frac{\Delta S}{R} = (7830 \pm 420)/RT - (24.5 \pm 2.0)/R,$$

where $R$ is the universal gas constant in units of cal mol$^{-1}$ K$^{-1}$. Errors in the above expressions are 2σ and represent precision only. We believe that systematic errors associated with, for example, the measurement of $T$, $P$, and [CO] are small and do not increase the above uncertainties significantly.

At higher temperatures relatively large concentrations of CO were necessary to drive the system into equilibrium. Therefore most of the experiments at 242 and 260 K were carried out in nearly pure CO. Over the entire temperature range studied, the fractional CO concentration ($X_{\text{CO}}$) varied from 0.005 to 1.0. At a given temperature, the invariance of $k_1$ and $k_{-1}$ with $X_{\text{CO}}$ indicates that N$_2$ and CO have essentially the same efficiencies as third-body colliders for these reactions. The experiments carried out in CO$_2$ and Ar result in values of $K_p$ very near the N$_2$/CO results but with different values for the individual rate constants. A comparison of $k_1$ and $k_{-1}$ for the various buffer gases at $T = 214 \pm 2$ K gives the following relative collision efficiencies for stabilization of the energized CICO adduct:

$$\beta(\text{CO}_2)/\beta(\text{CO}/\text{N}_2)/\beta(\text{Ar}) = 3.2:1.0:0.8.$$  

The relative collision efficiencies for two buffer gases $M_1$ and $M_2$ are computed from the relationship

$$\beta(M_1)/\beta(M_2) = k_1(M_1)/k_1(M_2)Z_{\text{LJ}}(M_2)/Z_{\text{LJ}}(M_1),$$

where $Z_{\text{LJ}}$ is the Lennard-Jones collision frequency for CICO-M collisions. It should be noted that the results given in Table I and Figs. 2 and 3 for experiments performed with CO$_2$ and Ar diluent gas have been corrected for the contribution of CO to the total bath gas concentration.

In Figs. 2 and 3 the results of this study are compared to previous kinetics and equilibrium studies of reactions (R1) and (R-1). From a photochemical study of the formation of CI.C0 from Cl$_2$/CO mixtures over the temperature range 298–328 K, Burns and Dainton report the following expression for the equilibrium constant: $K_p = 10^{-10} \exp \left( \frac{6310}{RT} \right)$ liter mol$^{-1}$. When extrapolated to near 300 K, our re-
results for $K_p$ agree quite well with the Burns and Dainton measurement. The narrow temperature range of the Burns and Dainton study makes comparison at lower temperatures risky. The measurements of the forward rate coefficient by Clark, Clyne, and Stedman were carried out at low pressure (< 3 Torr) in Ar at 195 and 300 K with CI atoms in excess over CO. At 195 K these authors report that the kinetics in their discharge flow system were controlled by reaction (R1) followed by the faster process

$$\text{CICO} + \text{Cl} \rightarrow \text{CO} + \text{Cl}_2.$$  \hspace{1cm} (R4)

At higher temperatures decomposition of the CICO apparently was a complication, competing with reaction (R4). Clark, Clyne, and Stedman report an activation energy for reaction (R1) of approximately $-2$ kcal mol$^{-1}$, which is in reasonable agreement with our observed activation energy in N$_2$/CO. In argon at 214 K our result is virtually identical to the value of $k_p$ derived by interpolation of the results of Clark, Clyne, and Stedman.

The infrared spectrum of CICO has been observed by Jacox and Milligan in an argon matrix at 14 K. They investigated assigned bands at 1830, 570, and 281 cm$^{-1}$ to the chloroformyl radical. The CICO radical has also been the subject of two theoretical investigations. Self-consistent-field, molecular-orbital calculations have been carried out by Hinchcliffe. An optimized geometry for an sp basis set gave a C1-C=O bond angle of 134° with $r_{C-C1} = 178$ pm and $r_{C-O} = 129$ pm. More recently, Francisco and Goldstein have reported the results of ab initio molecular-orbital calculations. These workers arrived at a slightly different equilibrium geometry with $r_{C-C1} = 179$ pm, $r_{C-O} = 118$ pm, and bond angle $= 128.9°$. The two geometries derived theoretically are quite similar to the configuration originally estimated by Jacox and Milligan ($r_{C-C1} = 175$ pm, $r_{C-O} = 118$ pm, and $120° <$ bond angle $< 134°$). The results of Francisco and Goldstein's calculations indicate that the bent $A^1$ electronic state is more stable than the linear $\Sigma^+$ electronic state by 1.0 kcal mol$^{-1}$. Francisco and Goldstein's results also allow comparison of calculated vibrational frequencies and intensities with the experimental results of Jacox and Milligan. The calculated frequency of the CICO bend is much larger, 384 cm$^{-1}$ compared to 281 cm$^{-1}$, and the calculated intensity relatively weaker than the frequency and intensity as assigned by Jacox and Milligan. Therefore, Francisco and Goldstein suggest reassignment of the lowest-energy fundamental vibration to a weaker absorption observed by Jacox and Milligan at 333 cm$^{-1}$.

Despite the above-mentioned uncertainties in the structure and properties of the CICO radical, it is possible to make a reasonably accurate calculation of the CICO entropy. A value for the entropy of CICO at 298 K of 63.4 ± 0.3 cal mol$^{-1}$ K$^{-1}$ has been derived using standard statistical mechanical methods. The vibrational frequency assignments of Jacox and Milligan were assumed along with a low-lying excited electronic state 1000 cal mol$^{-1}$ above the ground state. The uncertainty in the entropy is based upon variation in the calculated value of $S^0$ over the range of proposed geometries, choice of bending frequency, and allowance for a low-lying electronic state in the range 300-6000 cal mol$^{-1}$ above the ground state. The value of $\Delta S^0_{298}$ for reaction (1a) is therefore $-23.3 \pm 0.3$ cal mol$^{-1}$ K$^{-1}$. Using calculated entropies at each experimental temperature and our measured values of $K_p(T)$, the heat of reaction (1a) at each temperature was calculated. Each value of $\Delta H_F(rxn)$ was then adjusted to $\Delta H^0_{298}$ using calculated changes in heat capacity for the reaction. An average "third-law" value of $\Delta H^0_{298}$ (rxn) was thus derived. The third-law values of $\Delta H^0_{298}$ and $\Delta S^0_{298}$ can be compared to the same quantities given by the slope and intercept of the van't Hoff plot, i.e., the second-law method. Taking the slope of the van't Hoff plot (Fig. 3) and correcting to the standard temperature gives $\Delta H^0_{298}$ (rxn) $= -7.95 \pm 0.45$ kcal mol$^{-1}$. The intercept of the van't Hoff plot gives $\Delta S^0_{298}$ (rxn). Using known heats of formation for Cl and CO (Ref. 14) leads to a value of $-5.2 \pm 0.6$ kcal mol$^{-1}$ for $\Delta H^0_{298}$ (CICO); the currently recommended value for $\Delta H^0_{298}$ (CICO) is $-4.1$ kcal mol$^{-1}$. The calculated enthalpy functions were used to correct to absolute zero giving $\Delta H^0_0$ (rxn) = $-6.9 \pm 0.7$ kcal mol$^{-1}$ (identically equal to the Cl=CO bond dissociation energy) and $\Delta H^0_0$ (CICO) = $-5.6 \pm 0.7$ kcal mol$^{-1}$.

The previous measurement of the equilibrium constant by Burns and Dainton also yields an estimate of the heat of reaction (R1). After first converting the results of these workers from an equilibrium constant expression in concentration units to $K_p$ in units of atm$^{-1}$, a value of $\Delta H^0_{298}$ (rxn) = $-7.1$ kcal mol$^{-1}$ is derived. Due to the limited temperature range covered by Burns and Dainton's study, there should be a rather large error bar associated with the enthalpy value of these researchers. Our results agree quite well with those of Burns and Dainton but are more precise and are based on more direct experimental information. Additional information on the thermochemistry of CICO has been reported by Walker and Prophet. The heat of formation of gas phase CICO at 298 K was deduced from a measurement of the heat of formation of liquid oxalyl chloride ($\text{C}_2\text{Cl}_4\text{O}_2$, a stable dimeric form of CICO) and an estimate of the C=C bond strength in CICO. Our value for $\Delta H^0_{298}$ (CICO) agrees quite well with Walker and Prophet's estimate of $-4.0 \pm 3.0$ kcal mol$^{-1}$ although the precision of the value obtained in this study is considerably improved. In the theoretical study by Francisco and Goldstein a value for the bond dissociation energy of CICO at 298 K of 3.5 kcal mol$^{-1}$ (approximately one-half of our experimental value) is reported. Francisco and Goldstein's results also indicate that there should be no potential-energy barrier for the formation of CICO from reaction (1). The substantial "negative" activation energy observed in our study and in the study of Clark, Clyne, and Stedman confirm the lack of an energy barrier.

**SUMMARY**

Using time-resolved resonance fluorescence spectroscopy to detect pulsed-laser-generated CI($^2P$) in the presence of CO, the kinetics of the formation and decomposition of
CICO radicals have been directly measured over the temperature range 185–260 K and the pressure range 14–200 Torr. Both second- and third-law methods have been employed to evaluate the enthalpy and entropy of reaction, with good agreement obtained between the two methods. The results reported herein represent the first direct study of the kinetics and equilibrium of the Cl + CO reaction over a wide temperature range and, therefore, significantly improve the quality of the database for CICO kinetics and thermochemistry.

ACKNOWLEDGMENTS

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19See, for example, J. H. Knox, Molecular Thermodynamics (Wiley-Interscience, London, 1971).
KINETICS OF THE Br₂–CH₃CHO PHOTOCHEMICAL CHAIN REACTION

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Summary

Time-resolved resonance fluorescence spectroscopy was employed in conjunction with laser flash photolysis of Br₂ to study the kinetics of the two elementary steps in the photochemical chain reaction nBr₂ + nCH₃CHO + hv → nCH₃CBrO + nHBr. In the temperature range 255 - 400 K, the rate coefficient for the reaction Br(²P₃/₂) + CH₃CHO → CH₃CO + HBr is given by the Arrhenius expression k₂(T) = (1.51 ± 0.20) x 10⁻¹¹ exp{−(364 ± 41)/T} cm³ molecule⁻¹ s⁻¹. At 298 K, the reaction CH₃CO + Br₂ → CH₃CBrO + Br proceeds at a near gas kinetic rate, k₁ (298 K) = (1.08 ± 0.38) x 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹.

1. Introduction

The reaction of ground state halogen atoms with acetaldehyde is a useful laboratory source of the acetyl radical, a precursor to the important atmospheric species peroxyacetylnitrate (PAN)

\[ X₂ + hv \rightarrow 2X \quad (1) \]
\[ X + CH₃CHO \rightarrow CH₃CO + HX \quad (2) \]
\[ CH₃CO + O₂ + M \rightarrow CH₃C(O)OO + M \quad (3) \]
\[ CH₃C(O)OO + NO₂ + M \rightarrow CH₃C(O)OONO₂ + M \quad (4) \]

(PAN)

Niki et al. [1] have shown that quantitative conversion of acetaldehyde to PAN is facilitated when bromine is employed as the initiating halogen species instead of the more commonly used chlorine molecule. A major advantage of

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the bromine system is that Br₂ can be photolyzed at wavelengths where neither CH₃CHO nor NO₂ are photochemically active, thus avoiding numerous complicating side reactions involving CH₃CHO and NO₂ photofragments. Another advantage of the bromine system is that only abstraction of the aldehydic hydrogen is energetically allowed, whereas in the chlorine system abstraction of a methyl hydrogen is also possible.

In the absence of oxygen, photolysis of Br₂ is known to initiate a chain reaction [1]

\[ \text{Br}_2 + h\nu \rightarrow 2\text{Br} \]  \hspace{1cm} (5)

\[ \text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{HBr} \]  \hspace{1cm} (6)

\[ \text{CH}_3\text{CO} + \text{Br}_2 \rightarrow \text{CH}_3\text{CBrO} + \text{Br} \]  \hspace{1cm} (7)

Niki et al. [1] demonstrated the occurrence of reaction (7) through Fourier transform IR (FTIR) spectroscopic observation of CH₃CBrO production. They also measured the ratio \( k_6/k_8 \) at 298 K.

\[ \text{Br} + \text{HCHO} \rightarrow \text{HCO} + \text{HBr} \]  \hspace{1cm} (8)

Combining their result with the literature value \( k_8 (298 \text{ K}) = 1.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) [2], Niki et al. reported \( k_8 (298 \text{ K}) = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). One absolute measurement of \( k_6 (300 \text{ K}) \) has also been reported. Islam et al. [3], using the very low pressure reactor (VLPR) technique, obtained the result \( k_6 (300 \text{ K}) = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), in excellent agreement with the findings of Niki et al.

We have employed pulsed laser photolysis of Br₂ in conjunction with time-resolved detection of Br(2P₃/₂) by resonance fluorescence spectroscopy to carry out the first temperature-dependent study of reaction (6) and the first determination of \( k_7 \). Our results are reported in this paper.

2. Experimental technique

The experimental apparatus used was similar to that employed previously in our laboratory to study chlorine atom kinetics [4-6]. A schematic diagram of the apparatus is shown in Fig. 1 and a brief description is given below.

A Pyrex jacketed reaction cell with an internal volume of 150 cm³ was used in all experiments. The cell was maintained at a constant temperature by circulating ethylene glycol or methanol from a thermostatically controlled bath through the outer jacket. A copper–constantan thermocouple with a stainless steel jacket was injected into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow rate conditions of the experiment.

Br(2P₃/₂) was produced by 355 nm pulsed laser photolysis of Br₂. Third harmonic radiation from a Quanta Ray model DCR-2 Nd:YAG laser provided the photolytic light source. The laser could deliver up to \( 1 \times 10^{17} \) photons pulse⁻¹ at a repetition rate of up to 10 Hz; the pulse width was 6 ns.
A bromine resonance lamp, situated perpendicular to the photolysis laser, excited resonance fluorescence in the photolytically produced atoms. The resonance lamp consisted of an electrodeless microwave discharge through about 1 Torr of a flowing mixture containing a trace of Br₂ in helium. The flows of a 0.2% Br₂ in helium mixture and pure helium into the lamp were controlled by separate needle valves, thus allowing the total pressure and Br₂ concentration to be adjusted for optimum signal-to-noise ratio. Radiation was coupled out of the lamp through a magnesium fluoride window and into the reaction cell through a magnesium fluoride lens. Before entering the reaction cell the lamp output passed through a flowing gas filter containing 50 Torr cm of methane in nitrogen. The methane filter prevented radiation at wavelengths shorter than 140 nm (including impurity emissions from excited oxygen, hydrogen, chlorine and nitrogen atoms) from entering the reaction cell, but transmitted the strong bromine lines in the 140-160 nm region.

Fluorescence was collected by a magnesium fluoride lens on an axis orthogonal to both the photolysis laser beam and resonance lamp beam and was imaged onto the photocathode of a solar blind photomultiplier. Signals were processed using photon counting techniques conjunction with multichannel scaling. For each bromine atom decay measured, signals from a large number of laser shots were averaged in order to obtain a well-defined temporal profile over at least two 1/e times of decay.
To avoid the accumulation of photolysis or reaction products, all experiments were carried out under "slow flow" conditions. The linear flow rate through the reactor was (typically) 3 cm s\(^{-1}\) and the laser repetition rate was (typically) 5 Hz. Hence no volume element of the reaction mixture was subjected to more than a few laser shots. Acetaldehyde and bromine flowed into the reaction cell from bulbs (12 l) containing dilute mixtures in nitrogen. The acetaldehyde mixture, bromine mixture and additional nitrogen were pre-mixed before entering the reactor. The concentrations of each component in the reaction mixture were determined from measurements of the appropriate mass flow rates and the total pressure. The fractions of acetaldehyde and bromine in the bulb mixtures were checked frequently by UV photometry using atomic mercury lines as the absorption light sources. The monitoring wavelength for acetaldehyde was 253.7 nm and the monitoring wavelength for bromine was 404.7 nm. Absorption cross-sections were measured during the course of this investigation; they were found to be 1.46 \(\times\) \(10^{-20}\) cm\(^2\) for acetaldehyde at 253.7 nm and 5.85 \(\times\) \(10^{-19}\) cm\(^2\) for bromine at 404.7 nm, in good agreement with literature values [7].

The nitrogen used in this study had a stated minimum purity of 99.9999% (UHP grade). The bromine used was Fisher ACS reagent grade with a maximum impurity level of 0.06%. Acetaldehyde was obtained from Aldrich and had a stated purity of 99%. Both bromine and acetaldehyde were transferred under nitrogen into vials fitted with high vacuum stopcocks, and were then degassed repeatedly at 77 K before being used to prepare reactant-nitrogen mixtures.

3. Results and discussion

All experiments were carried out under pseudo-first-order conditions with CH\(_3\)CHO and Br\(_2\) in large excess over bromine atoms. Reaction mixtures contained 0 - 0.05 Torr of CH\(_3\)CHO, 1 \(\times\) \(10^{-5}\) - 5 \(\times\) \(10^{-4}\) Torr of Br\(_2\) and 150 Torr of N\(_2\) buffer gas. The nitrogen level was sufficient to facilitate rapid deactivation of bromine atoms in the electronically excited spin-orbit state

\[
\text{Br}_2 + h\nu (355 \text{ nm}) \rightarrow n \text{Br}(^{2}\text{P}_{3/2}) + (2 - n) \text{Br}(^{2}\text{P}_{1/2}) \quad (5)
\]

\[
\text{Br}(^{2}\text{P}_{1/2}) + \text{N}_2 \rightarrow \text{Br}(^{2}\text{P}_{3/2}) + \text{N}_2 \quad (9)
\]

The rate coefficient for reaction (9) is 2.5 \(\times\) \(10^{-15}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) [8]. Both theoretical [9] and experimental [10] information suggests that the parameter \(n\) in eqn. (5) has a value near 2, i.e. little or no Br\((^{2}\text{P}_{1/2})\) is produced when Br\(_2\) is photolyzed in the near UV.

We expect the decay of Br\((^{2}\text{P}_{3/2})\) to be controlled by the following reactions

\[
\text{Br}(^{2}\text{P}_{3/2}) + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{HBr} \quad (6)
\]
\[
\text{CH}_3\text{CO} + \text{Br}_2 \rightarrow \text{CH}_3\text{CBrO} + \text{Br}(^2\text{P}) \tag{7}
\]
\[
\text{Br}(^2\text{P}_{3/2}) \rightarrow \text{removal by diffusion from the detector field of view and reaction with background impurities} \tag{10}
\]
\[
\text{CH}_3\text{CO} \rightarrow \text{removal by processes which do not produce bromine atoms} \tag{11}
\]

The rate equations for the reaction scheme (6), (7), (10) and (11) can be solved analytically

\[
\frac{[\text{Br}]}{[\text{Br}]_0} = \frac{(K + \lambda_1) \exp(\lambda_1 t) - (K + \lambda_2) \exp(\lambda_2 t)}{(\lambda_1 - \lambda_2)} \tag{12}
\]

where

\[
\begin{align*}
\lambda_1 &= 0.5 \cdot (\alpha^2 - 4\beta)^{1/2} - \alpha \tag{13} \\
\lambda_2 &= -0.5 \cdot (\alpha^2 - 4\beta)^{1/2} + \alpha \tag{14} \\
K &= k_{11} + k_1 [\text{Br}_2] \tag{15} \\
\alpha &= K + k_{10} + k_6 [\text{CH}_3\text{CHO}] \tag{16} \\
\beta &= k_{10} K + k_{11} k_6 [\text{CH}_3\text{CHO}] \tag{17}
\end{align*}
\]

The observed temporal profiles can be fitted to the predicted double-exponential functional form (eqn. (12)) to obtain values for \(\lambda_1, \lambda_2\) and \(K\). The rate coefficient \(k_{10}\) was directly measured to be \(35 \pm 7\) s\(^{-1}\) in all experiments (assuming negligible contribution to \(k_{10}\) from impurities in the \(\text{CH}_3\text{CHO}-\text{N}_2\) mixture). Therefore recognizing that

\[
\lambda_1 + \lambda_2 = -\alpha \tag{18}
\]

and

\[
\lambda_1 \lambda_2 = \beta \tag{19}
\]

we obtain the following relationships for the rate coefficients \(k_6, k_7,\) and \(k_{11}\)

\[
\begin{align*}
k_6 &= -\frac{A}{[\text{CH}_3\text{CHO}]} \tag{20} \\
k_7 &= \frac{(K - k_{11})}{[\text{Br}_2]} \tag{21} \\
k_{11} &= \frac{(k_{10} K - \lambda_1 \lambda_2)}{A} \tag{22} \\
A &= K + k_{10} + \lambda_1 + \lambda_2 \tag{23}
\end{align*}
\]

A typical \(\text{Br}(^2\text{P}_{3/2})\) temporal profile observed under conditions of relatively high \([\text{Br}_2]\) is shown in Fig. 2, and the results obtained from the analysis of a number of temporal profiles are summarized in Table 1. Uncertainties in the parameters \(\lambda_1, \lambda_2\) and \(K\) obtained from non-linear least-squares analyses of the observed double-exponential decays are difficult to evaluate quantitatively. However, for data of the quality shown in Fig. 2 (which is typical of all experiments summarized in Table 1), we believe that a reasonable estimate of the \(2\sigma\) uncertainties of all three parameters is \(\pm 15\%\).
Fig. 2. Typical Br($^2P_{3/2}$) temporal profile observed under conditions of relatively high [Br$_2$]. Experimental conditions: 150 Torr N$_2$; 298 K; 1.09 x 10$^{15}$ CH$_3$CHO cm$^{-3}$; 8.94 x 10$^{13}$ Br$_2$ cm$^{-3}$; 1.7 x 10$^{11}$ Br atoms cm$^{-3}$ at $t = 0$; 2048 laser shots averaged. The full line is obtained from a non-linear least-squares fit to eqn. (12). Best fit parameters: $\lambda_1 = -1040$ s$^{-1}$; $\lambda_2 = -5430$ s$^{-1}$; $K = 2040$ s$^{-1}$.

When the two time constants $\lambda_1$ and $\lambda_2$ differ by less than a factor of five, the uncertainties in all three parameters increase in magnitude.

A simple average of the $k_6$ (298 K) values obtained from all 17 experiments summarized in Table 1 is $(4.05 \pm 0.76) \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (error is 2$\sigma$, precision only), which is in good agreement with the literature values of $3.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [1] and $3.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [3]. It should be noted, however, that the most accurate measurements of $k_6$ are expected to be obtained under conditions of very low [Br$_2$] since, under these conditions, the effect of reactions (7) and (11) on the Br($^2P_{3/2}$) temporal profile is minimized. The experiments at very low Br$_2$ concentrations are discussed below.

Inspection of Table 1 shows that $k_{11}$ (298 K) appears to increase with increasing [Br$_2$]. This result, which was unexpected, indicates that CH$_3$CO radicals react with Br$_2$ or an impurity in the Br$_2$ flow via a process which does not produce bromine atoms. A plot of $k_{11}$ (298 K) vs. [Br$_2$] is shown in Fig. 3. Although somewhat scattered, the data are reasonably well represented by a straight line with an intercept of 648 $\pm$ 230 s$^{-1}$ and a slope of $(6.4 \pm 2.5) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (errors are 2$\sigma$, precision only). The rather large background CH$_3$CO decay rate of 648 s$^{-1}$ is probably due, in large part, to the reaction

$$\text{CH}_3\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)OO + M}$$

(3)

The 298 K rate coefficient for reaction (3) is known to be $2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [11]. Hence a background O$_2$ level of 10 mTorr, i.e. 0.007%, in the slow flow system would completely account for CH$_3$CO removal with
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*T = 298 K in all experiments.
Fig. 3. Plot of $k_{11}$ vs. $[Br_2]$ for the results summarized in Table 1. The full line is obtained from an unweighted linear least-squares analysis.

the $Br_2$ flow off. The process which causes $k_{11}$ to increase when $Br_2$ is added cannot be identified with any degree of confidence.

The values of $k_7$ (298 K) obtained from eqn. (21) and summarized in Table 1 do not appear to vary systematically as a function of either the CH$_3$CHO concentration or the $Br_2$ concentration. A simple average of the $k_7$ (298 K) values obtained from all 17 experiments is $(1.06 \pm 0.39) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ where the error is $2\sigma$ and represents precision only. Alternatively, $k_7$ can be evaluated from the slope of a plot of $K - k_{11}$ vs. $[Br_2]$ (Fig. 4). An unweighted linear least-squares analysis of the data plotted in Fig. 4 gives the result $k_7$ (298 K) $\pm 2\sigma = (1.08 \pm 0.22) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The improved precision of the second method for determining $k_7$ results from the fact that data at high $[Br_2]$, where $K - k_{11}$ is relatively large and therefore more accurately determined, are effectively given a higher weight in determining the $K - k_{11}$ vs. $[Br_2]$ slope, whereas all points are weighted equally in the simple average. Hence the “slope” method of analysis is preferred. We estimate the absolute accuracy of our $k_7$ (298 K) determination to be $\pm 35\%$ and, therefore, report the rate coefficient

$$k_7 (298 \text{ K}) = (1.08 \pm 0.38) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

It should be noted that the only important mechanistic assumption required to extract the above value for $k_7(T)$ from the data analysis is that reaction (7) is the only process which regenerates bromine atoms. For the chemical system of interest here, this assumption appears to be justified.

Typical $Br(^2P_3/2)$ temporal profiles observed under conditions of relatively low $[Br_2]$ are shown in Fig. 5. The decays are exponential. However, simulations employing eqn. (12) in conjunction with the rate coefficients determined in the high $[Br_2]$ experiments demonstrate that, over the range of $Br_2$ and CH$_3$CHO concentrations employed, the observed temporal
Fig. 4. Plot of $K - k_{11}$ vs. $[\text{Br}_2]$ for the results summarized in Table 1. The full line is obtained from an unweighted linear least-squares analysis and gives the bimolecular rate coefficient $k_7$.

Fig. 5. Typical Br($^2P_{3/2}$) temporal profiles observed under conditions of relatively low $[\text{Br}_2]$ ($1 \times 10^{12}$ cm$^{-3}$ or less). $P = 150$ Torr $N_2$; $T = 255$ K. [CH$_3$CHO] in units of $10^{14}$ molecules cm$^{-3}$: (a) 0; (b) 2.25; (c) 3.80; (d) 6.63; (e) 13.4. Full lines are obtained from linear least-squares analyses and give the following pseudo-first-order rate coefficients: (a) $40$ s$^{-1}$; (b) $781$ s$^{-1}$; (c) $1310$ s$^{-1}$; (d) $2260$ s$^{-1}$; (e) $4690$ s$^{-1}$.

profiles should be slightly non-exponential due to bromine atom regeneration via reaction (7). To analyze the experimental data, we obtained an uncorrected pseudo-first-order decay rate $k'$ by carrying out a linear least-squares analysis of the first two $1/e$ times of decay (i.e. down to $[\text{Br}]_0/[\text{Br}]_0 = 0.135$); we then corrected $k'$ using the ratio of the simulated decay
rate with the Br$_2$ concentration set equal to zero to the simulated decay rate for the Br$_2$ concentration employed in the experiment. The simulated decay rates were obtained from linear least-squares analyses of the simulated ln [Br] vs. t data for the first two 1/e times of decay. For simulations at temperatures other than 298 K, it was assumed that the nearly gas kinetic $k_1$ value was independent of temperature. Two scenarios were adopted for the temperature dependence of $k_{11}$. One set of simulations was carried out with $k_{11}$ assumed to be independent of temperature. A second set of simulations assumed that the [Br$_2$]-independent component of $k_{11}$, which was speculated to be due primarily to the addition reaction (3), varied according to the expression $k(T) = k(298 \text{ K}) (T/298)^{-4}$; the [Br$_2$]-dependent component of $k_{11}$, which was very small under the conditions of the low [Br$_2$] experiments, was assumed to be independent of temperature.

The results of the "low [Br$_2$]" experiments are summarized in Table 2. The rate coefficients $k_6(T)$ reported in Table 2 were obtained from linear least-squares analyses of plots of $k'$, the pseudo-first-order Br($^2P_{3/2}$) decay rate, vs. CH$_3$CHO concentration. As can be seen from inspection of Table 2, although correction for Br($^2P_{3/2}$) regeneration raised individual $k'$ values by factors ranging from 1.03 to 1.21, corrected $k_6(T)$ values were only about 4% larger than the uncorrected values. The magnitudes of the corrections to $k_6(T)$ did not depend strongly on temperature, and were virtually independent of the temperature dependence adopted for $k_{11}(T)$. It should be noted that the method used to obtain a corrected value for $k_6(T)$ required an initial estimate of $k_6(T)$. However, this estimate could be made quite accurately because the required corrections were so small. For this reason, it was not necessary to employ an iterative procedure to obtain accurate correction factors.

The rate coefficients $k_6(T)$ determined in this study are listed in Table 2 and plotted in Arrhenius form in Fig. 6. An unweighted linear least-squares analysis of the ln $k_6$ vs. $T^{-1}$ data gives the Arrhenius expression (255 K $\leq T \leq$ 400 K)

$k_6(T) = (1.51 \pm 0.20) \times 10^{-11} \exp\{-(364 \pm 41)/T\}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

where the errors are 2$sigma$ and represent precision only. The above Arrhenius parameters seem reasonable. The $A$ factor is typical of that found for a direct atom–molecule hydrogen abstraction reaction and the trend for bromine atom reactions with formaldehyde and acetaldehyde is similar to the trends observed for other radical–aldehyde reactions, i.e. similar $A$ factors but larger activation energies for the formaldehyde reaction than for the acetaldehyde reaction [12].

From the above Arrhenius expression we obtain $k_6(298 \text{ K}) = 4.45 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ — about 25% faster than the two literature values [1, 3]. We estimate the uncertainty in our $k_6(298 \text{ K})$ value to be ±15% (2$sigma$). Niki et al. [1] report a 2$sigma$ uncertainty of ±6% for the ratio $k_6/k_8$, whereas the uncertainty in $k_8$ is estimated to be ±30% [12]. Hence our result agrees well with that of Niki et al. considering the combined uncertainties of the
### TABLE 2
Summary of results obtained at relatively low Br₂ concentrations

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<tr>
<th>T (K)</th>
<th>[Br₂] (10¹¹ molecules cm⁻³)</th>
<th>[CH₃CHO] (10¹¹ molecules cm⁻³)</th>
<th>k' (s⁻¹)</th>
<th>kₖ ± 2σb (10⁻¹² cm³ molecules⁻¹ s⁻¹)</th>
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* [Br]₀ was in the range (1.4-3.5) x 10¹⁰ atoms cm⁻³ in all experiments.

b Errors represent precision only.

cA, uncorrected for bromine atom regeneration via the CH₃CO + Br₂ reaction; B, corrected for bromine atom regeneration via the CH₃CO + Br₂ reaction assuming that k₁₁ is independent of temperature; C, corrected for bromine atom regeneration via the CH₃CO + Br₂ reaction assuming that the [Br₂]-independent component of k₁₁ has a T⁻⁴ temperature dependence (see text for rationale).
Fig. 6. Arrhenius plot for the reaction \( \text{Br} \left( \text{P}_{3} \right) + \text{CH}_{3}\text{CHO} \rightarrow \text{CH}_{3}\text{CO} + \text{HBr} \). The full line is obtained from an unweighted linear least-squares analysis.

two studies. Islam et al. [3] carried out a VLPR study of the kinetics of reaction (6) and obtained the result \( k_{6} \left( 300 \text{ K} \right) \pm 2\sigma = \left( 3.5 \pm 1.0 \right) \times 10^{-12} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \), again in agreement with our result within the combined uncertainties of the studies. Islam et al. observed upward curvature in their plots of \( \frac{[\text{Br}]}{[\text{Br}]} \) vs. \( \text{[CH}_{3}\text{CHO}] \) which they considered to be insignificant due to the relatively large uncertainty associated with the data points at high values of \( \frac{[\text{Br}]}{[\text{Br}]} \). Islam et al. generated bromine atoms by passing a Br–He mixture through a microwave discharge. Incomplete dissociation of Br in the discharge would have resulted in the observed upward curvature of the \( \frac{[\text{Br}]}{[\text{Br}]} \) vs. \( \text{[CH}_{3}\text{CHO}] \) plot, because reaction (7) would have represented a more important bromine atom regeneration step at low \( \text{[CH}_{3}\text{CHO}] \) than at high \( \text{[CH}_{3}\text{CHO}] \). If Br was present in the reactor of Islam et al., it is clear that they would have underestimated \( k_{6} \).

Barnes et al. [13] have recently published the results of a competitive kinetics investigation of bromine atom reactions with a series of alkanes, alkenes and alkynes. These workers used the reactions of bromine atoms with \( \text{CH}_{3}\text{CHO} \) and 2-methylpropane as their reference reactions. The results of Niki et al. [1] and Islam et al. [3] were used to obtain an absolute value for \( k_{6} \), and the recent results of Russell et al. [14] were used to obtain an absolute value for the Br–2-methylpropane rate coefficient. As a consistency check, Barnes et al. studied the Br–propyne reaction using both \( \text{CH}_{3}\text{CHO} \) and 2-methylpropane as competitors. Their Br–propyne rate coefficient was 33% faster when referenced to 2-methylpropane than when referenced to \( \text{CH}_{3}\text{CHO} \); if our value for \( k_{6}(T) \) was used, this would reduce the difference to less than 10%.

Acknowledgments

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References

Pulsed laser photolysis kinetics study of the O(2P)+ClO reaction

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A pulsed laser photolysis technique has been employed to study the kinetics of the important stratospheric reaction \( \text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2 \) in \( N_2 \) buffer gas over the temperature and pressure ranges 231-367 K and 25-500 Torr. 351 nm pulsed laser photolysis of \( \text{Cl}_2/\text{O}_2/N_2 \) mixtures produced Cl atoms in excess over \( \text{O}_2 \). After a delay sufficient for the reaction \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \) to go to completion, a small fraction of the ClO was photolyzed at 266 nm to produce \( \text{O}(2P) \). The decay of \( \text{O}(2P) \) in the presence of an excess, known concentration of ClO was then followed by time-resolved resonance fluorescence spectroscopy. We find that \( k_1 \) is independent of pressure, but that \( k_1(T) \) increases with decreasing temperature. Our results suggest that the Arrhenius expression \( k_1(T) = (1.55 \pm 0.33) \times 10^{-11} \exp\left(\frac{263 \pm 60}{T}\right) \) \( \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) is appropriate for modeling stratospheric chemistry. Errors in the Arrhenius expression are 20 and represent precision only. The absolute accuracy of \( k_1 \) at any temperature within the range studied is estimated to be \( \pm 20\% \). Our results agree with other recent measurements of \( k_1 \) at 298 K but give significantly faster rate coefficients at stratospheric temperatures. A few measurements of the rate coefficient for the reaction

\[
\text{ClO} + \text{ClO} \rightarrow \text{products}
\]

were also carried out. These measurements were necessary to assess the time dependence of [ClO].

INTRODUCTION

The reaction of ground state oxygen atoms \( \text{O}(2P) \) with ClO radicals is the rate determining step in the dominant catalytic cycle via which chlorine atoms destroy odd oxygen in the middle stratosphere:

\[
\begin{align*}
\text{O} + \text{ClO} & \rightarrow \text{O}_2 + \text{Cl}, \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{Net: } \text{O} + \text{O}_3 & \rightarrow 2\text{O}_2
\end{align*}
\]

The primary source of stratospheric chlorine atoms is the photolysis of anthropogenic chlorofluorocarbons.

Seven measurements of \( k_1(298 \text{ K}) \) are reported in the literature.\(^1\)\(^-\)\(^7\) There is agreement among the five most recent studies that \( k_1(298 \text{ K}) \) lies in the range 3.5-4.2 \( \times 10^{-11} \) \( \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \). The activation energy for reaction (1) is known to be small,\(^2\)\(^-\)\(^7\) but its value is not as well defined as would be desirable for such an important stratospheric reaction. In fact, it is not clear if \( k_1(T) \) increases or decreases with decreasing temperature. In addition to the abovementioned studies of reaction (1) at atmospheric temperatures, one high temperature (1250 K) shock tube measurement of \( k_1 \) has been reported,\(^8\) as has one theoretical calculation of \( k_1(T) \) over the temperature range 220-1000 K.\(^9\)

Because predictions of chlorine catalyzed ozone loss are very sensitive to the value of \( k_1(T) \) used in model calculations, it is important that this rate coefficient be determined with high precision at stratospheric temperatures. Studies employing a variety of experimental techniques are desirable in order to uncover possible systematic errors. All previous studies of reaction (1) at ambient and subambient temperatures\(^1\)\(^-\)\(^7\) employed discharge flow systems which were limited to total pressures of 10 Torr or less. It is interesting to note that reaction (1) occurs on a potential energy surface with a minimum along the reaction coordinate, i.e., the intermediate complex \( \text{ClOO} \) is a bound species whose ground state correlates with \( \text{O}(2P) + \text{ClO}(X^2\Sigma_g) \).\(^10\) Reactions which occur on potential energy surfaces of this type often exhibit negative activation energies and pressure dependent rates.

We have recently developed a pulsed laser photolysis method for carrying out direct kinetics studies of radical-radical reactions at pressures up to 1 atm, and applied this method to study the temperature and pressure dependences of the \( \text{O} + \text{HO}_2 \) reaction.\(^11\)\(^-\)\(^12\) Using an extension of the technique employed in the \( \text{O} + \text{HO}_2 \) investigations, we have studied the kinetics of reaction (1) in \( N_2 \) buffer gas over the temperature and pressure ranges 231-367 K and 25-200 Torr. Our results, which include observation of a significant negative activation energy, are reported in this paper.

EXPERIMENTAL

A schematic of the apparatus appears in Fig. 1. The two radical species were created via a scheme involving two separate photolysis lasers. Under "slow flow" conditions, a gas mixture containing \( \text{Cl}_2 \) and \( \text{O}_3 \) in a large excess of \( N_2 \) buffer gas was first subjected to photolysis by a XeF excimer laser,

\[
\text{Cl}_2 + h\nu(351 \text{ nm}) \rightarrow 2\text{Cl}.
\]
The combination of the excimer laser fluence and \([\text{Cl}_2]\) was always large enough for the condition \([\text{Cl}_2]_0 > [\text{O}_3]_0\) to hold. During a predetermined delay period, \(t_d\), the reaction

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]  

(2)

was allowed to go to completion. At this time the ozone in the reaction cell had effectively been titrated by Cl atoms and the initial value of \([\text{O}_3]_0\) could be related to \([\text{ClO}]_0\). At the end of this delay a second laser pulse, the fourth harmonic of the fundamental wavelength from a Nd:YAG laser, photolyzed a small fraction of the ClO,

\[
\text{ClO} + h\nu(266\text{ nm}) \rightarrow \text{Cl} + \text{O}.
\]  

(4)

The decay of oxygen atoms in the presence of excess ClO was followed by monitoring the time dependence of fluorescence signal which was continuously excited by a microwave discharge resonance lamp. The lamp was operated with a low pressure of helium (\(< 1\) Torr) containing a small fraction of \(\text{O}_2\). The ozone storage bulb contained a mixture of 1% to 2% \(\text{O}_3\) in nitrogen, while the Cl2 was stored neat. These species were leaked through needle valves into the main gas flow. Ozone in the gas flow was measured in a 35.0 cm absorption cell that was placed within a multipass optical arrangement. Using modified White cell optics, 30 passes of the 254 nm Hg line from a pen-ray lamp were sent through the absorption cell for an effective path length of 10.50 m. The chlorine was measured in a 216 cm absorption cell using a single pass of the 366 nm Hg line, also from a pen-ray lamp. Both atomic lines were isolated using suitable bandpass filters. Typically, the absorption cells were upstream from the reaction cells, although in a few experiments the Cl2 and \(\text{O}_3\) were measured after the flow exited the reaction cell. Because Cl2 absorbance at 254 nm was not totally negligible \([\sigma = 1.6 \times 10^{-21} \text{ cm}^2 \text{ (Ref. 13 })\], the reference light intensity for the \([\text{O}_3]_0\) determination was always measured with Cl2 flowing. The Cl2 absorption cross section at 366 nm and the \(\text{O}_3\) absorption cross section at 254 nm were taken to be \(1.01 \times 10^{-19} \text{ cm}^2\) (Ref. 13) and \(1.147 \times 10^{-17} \text{ cm}^2\) (Ref. 14), respectively.

The Pyrex reaction cell measured 16 cm along its longer axis and had an internal diameter of 4 cm. The two laser beams counterpropagated along the longer axis. Around the middle of the cell were four 1.5 cm diameter side arms, each perpendicular to the long axis of the cell and at 90° to each other. The resonance lamp radiation entered the cell through one of the side arms and the fluorescence signal was collected through a neighboring arm. The central portion of the cell was surrounded by a jacket through which thermostatted liquids were flowed to control the temperature of the
gas mixture inside the reactor. The gas mixture entered the cell through several ports very near the window at one end of the long axis and exited the cell through similar ports near the opposite window. Because the chemistry initiated by the excimer laser beam completely titrated one component ($O_3$) of the gas mixture within much of the cell volume, the cell was designed to have minimum total volume and low dead space, i.e., gas flowed through all volume elements of the cell at approximately equal rates. The typical linear flow rate through the cell was $14 \text{ cm s}^{-1}$ and the repetition rate of the two laser sequence was usually $0.4 \text{ Hz}$. Therefore, the gas mixture within the entire volume of the reaction cell was replenished between excimer laser pulses. The temperature of the gas mixture was measured by replacing one of the end windows with an acrylic flange through which a copper–constantan thermocouple could be inserted. The errors in the reported temperatures are estimated to be no more than $\pm 1.0 \text{ K}$ at the extreme temperatures and less at intermediate temperatures.

Oxygen resonance lamp radiation was focused into the reaction zone by a 2 in. focal length $\text{MgF}_2$ lens. The reaction zone was viewed by a solar blind photomultiplier tube through a similar lens. The volumes between the resonance lamp and the reaction cell, and between the reaction cell and the photomultiplier tube were purged with a mixture of 1% $O_2$ in nitrogen. This excluded room air and also acted as a filter of extraneous emissions from the resonance lamp. A CaF$_2$ window between the cell and the photomultiplier tube eliminated the possibility of hydrogen atom detection. Fluorescence signals were accumulated using photon counting techniques in conjunction with multichannel scaling. Each sweep of the analyzer was triggered simultaneously with the excimer laser. From 50 to 500 flashes were averaged to obtain sufficient signal-to-noise ratio for quantitative kinetic analysis.

The total pressure in the flow system was measured with a capacitance manometer. Due to the necessarily fast flow rate and the small (4.0 mm i.d.) tubing connecting the various components of the flow system, there were measurable pressure gradients between the absorption cells and the reaction cell. Quantitative adjustments were made for these gradients in the calculation of the $Cl_2$ and $O_3$ concentrations in the reaction cell under each set of conditions. The magnitude of the adjustment was largest at the lowest pressure (15% at 25 Torr) and negligible at the highest (1% at 200 Torr). The nitrogen buffer gas comprised at least 94% of the mixture for all experiments and its flow rate was monitored using a calibrated electronic mass flowmeter.

The concentration of $ClO$, the excess species in this technique, was derived from the concentration of ozone as measured "in situ." Therefore, it was not necessary to have an absolute calibration of the photolysis laser fluences. However, it was important to know that following the excimer laser pulse the condition $[Cl] > [O_3]$ held throughout the reaction zone. Therefore, the excimer laser fluence was measured in each experiment. As will be discussed below, it was also important to monitor the 266 nm laser fluence. Both of these quantities were determined using a photodiode-based calibrated radiometer. With the front optic of the excimer laser approximately 2 m from the center of the reaction cell, the beam was rectangular in cross section and measured 2.0 by 4.0 cm. When measured through a 0.5 cm diameter aperture, the fluence peaked at the center of the beam and dropped off by 10% per 0.5 cm distance from the center in both the vertical and horizontal directions. The beam from the Nd:YAG laser was aligned at the center of the volume irradiated by the excimer laser. It was estimated to be $0.4 \pm 0.1 \text{ cm in diameter}$.

The reagent purities and sources were as follows: $N_2$ (99.999%, Spectra Gases, Inc.); $Cl_2$ (99.9%, Matheson Gas Products, Inc.); $O_3$ (99.99%, Spectra Gases, Inc.). Ozone was prepared in a commercial ozonator using UHP oxygen. It was stored at 195 K on silica gel and degassed at 77 K before use. The other gases were used without further purification.

**RESULTS**

In the absence of competing reactions that either deplete or enhance the ground state oxygen atom [$O(1P)\]$ concentration, the temporal behavior of [$O(1P)\]$ following the 266 nm laser pulse can be described by the relationship

$$\ln\left[\frac{[O(1P)\]}{[O(3P)\]}\right] = -(k_1[ClO] + k_6)(t-t_d)$$

where

$$k_6 = k_5[Cl_2] + k_6.$$  (II)

In Eq. (II), $k_5$ and $k_6$ are the rate coefficients for the following processes:

$$O(1P) + Cl_2 \rightarrow \text{products},$$  (5)

$$O(1P) \rightarrow \text{loss by diffusion from the viewing zone and reaction with background impurities}.$$  (6)

A typical experimental $O(1P)\$ temporal profile is shown in Fig. 2. Unexpectedly, a significant buildup and decay of $O(1P)\$ occurred before the 266 nm laser fired, possible sources of this $O(1P)\$ and its implications for our study of reaction (1) are discussed below. It should be noted that the vertical axis in Fig. 2 has units of concentration. To construct Fig. 2, the fluorescence signal before the 266 nm laser fired was scaled to account for the fact that the 351 nm laser photolyzed the entire field of view of the detection system, while the 266 nm laser photolyzed only 15% of the detector viewing zone. The size of the viewing zone was estimated by placing a series of apertures in front of the 351 nm beam and noting the variation of fluorescence signal strength with beam size.

Typical decays of $O(1P)\$ generated by the 266 nm laser pulse are shown in Fig. 3. At each temperature and pressure a minimum of five and an average of eight experiments were performed at various values of $[O_3]_0$. Because the Nd:YAG laser fluence was measured in each experiment, the amount of $ClO$ lost via 266 nm photolysis could be quantified. The expression

$$[ClO]_0 = [O_3]_0 - [O(1P)\]_0$$  (III)

was used to calculate the $ClO$ concentration under the as-
sumption that no loss of ClO occurred during the delay between photolysis laser pulses. The ratio [O(3P)]/[ClO] immediately following the 266 nm laser pulse was determined for each experiment, and was typically in the range 0.01-0.04. Hence, it was appropriate to correct each measured decay rate for slight deviations from pseudo-first-order conditions. These corrections were derived from computer simulations of reactions (1), (5), and (6) under the range of experimental conditions employed. Best fit values for each decay rate (k') were obtained from linear regression analyses of the experimental data over at least 2 1/e times. Each value of k' was then increased by 2% or less using the appropriate non-pseudo-first-order correction. Representative plots of [ClO] vs k' are shown in Fig. 4. These data were subjected to linear least squares analyses to give values for k'. The results are presented in Table I. Note the separate columns for k_0 (uncorrected) and k_c (corrected). The former represents the best fit to the data when k' was not corrected for non-pseudo-first-order behavior and [ClO] was set equal to [O(3P)] less the amount photolyzed to produce [O(3P)]. The latter k_c values include the small non-pseudo-first-order correction to k' and additional corrections to [ClO] discussed below.

The absorption cross section used to calculate the amount of ClO photolyzed by the Nd:YAG laser was estimated experimentally. The signal level immediately after the Nd:YAG laser fired was directly proportional to the concentration of oxygen atoms. If the Nd:YAG laser was not preceded by a pulse from the excimer laser, then the photolyte was O_3. If all the O_3 had been converted to ClO via reaction with Cl atoms created in the 351 nm excimer pulse, then the signal was due to ClO photolysis. In back-to-back experiments with constant [Cl_2], [O_3] and 266 nm fluence, the ratio of O(3P) signal with and without 351 nm photolysis should be identical to the ratio of the ClO and O_3 absorption

FIG. 2. An experimental O atom temporal profile obtained under the following conditions: [Cl] = 1.40 x 10^13 molecules cm^-3; [O_3] = 7.27 x 10^13 molecules cm^-3; [Cl] = 1.82 x 10^14 molecules cm^-3; Total pressure = 25 Torr; temperature = 298 K; MCA dwell time = 25 μs.
cross sections at the Nd:YAG laser wavelength [the O('D) product of O₃ photolysis is rapidly quenched to O('P) by N₂]. This experiment resulted in a value of 0.35 for the signal ratio. If \( \sigma_{283}(O_2) \) is taken to be \( 9.0 \times 10^{-18} \) cm\(^2\) (Ref. 13) then \( \sigma_{283}(CIO) \) is \( \sim 3.1 \times 10^{-18} \) cm\(^2\). This is somewhat lower than the low resolution cross section at this wavelength that is reported in the literature.\(^5\) However, we carried out the identical signal level comparison near 283 nm, a wavelength where the high resolution cross section has been characterized.\(^6\) Using a frequency doubled, Nd:YAG pumped tunable dye laser the rotational structure in the CIO spectrum was reproduced by observing the resonance fluorescence signal as the wavelength was scanned. At 282.95 nm, the peaks of the \( R(19.5) \) and \( P(16.5) \) lines of the \( A'\Pi \) - \( X'\Sigma \) \( ^{1} \) \( \delta \) band, we observed a factor of 1.65 \( \pm \) 0.16 more fluorescence signal when the excimer laser photolyzed Cl₂ than when the excimer laser beam was blocked. Based on the dye laser linewidth employed and the literature values for the ozone and CIO cross sections, we expected a ratio of 1.80 \( \pm \) 0.40. This result confirms our value for \( \sigma_{283}(CIO) \).

As mentioned above, the delay between the two laser pulses \( t_d \) was adjusted to be long enough for reaction (2) to go to completion. The value of the Cl + O₂ rate constant is reasonably well known\(^7\) so an appropriate delay time could be calculated. As a check the delay time was varied until a constant signal and decay rate were observed, indicating that all the O₂ had been converted to CIO. The majority of experiments were carried out with delay periods of either 3.4 or 6.4 ms.

The temporal behavior of CIO could be monitored by following both the O('P) signal level produced by 266 nm photolysis and the measured value of \( k' \). For some conditions (lower temperature, higher pressures) it was observed that CIO was decreasing on the time scale of the delay between the two lasers. The disappearance of CIO is probably due to self-reaction, a process that has not been completely characterized.\(^8\) In order to make a correction for the amount of CIO lost during the delay between laser pulses and also during the O atom decay, a series of experiments were carried out in which the delay time was varied at fixed \([O_2]\), \([Cl_2]\), and laser fluences.

For the process

\[
CIO + CIO \rightarrow \text{products}
\]

the time dependence of [CIO] is described by the relationship

\[
2k_{r} = [\text{CIO}]^{-1} - [\text{CIO}]^{-1}
\]

(IV)

If we define \( k_{r} \) to be the second-order rate coefficient for CIO removal under our experimental conditions, then plotting [CIO]\(^{-1}\) vs \( t \) should yield a straight line of slope \( 2k_{r} \) and intercept equivalent to [CIO]\(^{-1}\). The absolute concen-

---

**TABLE I: Summary of \( \kappa \), determinations.**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (Torr)</th>
<th>( \kappa \times 10^{11} ) (uncorrected)(^a) ( (\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) )</th>
<th>( \kappa \times 10^{11} ) (corrected) ( (\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>231</td>
<td>25</td>
<td>( 4.64 \pm 0.16 )</td>
<td>( 4.99 \pm 0.17 )</td>
</tr>
<tr>
<td>238</td>
<td>25</td>
<td>( 4.25 \pm 0.43 )</td>
<td>( 4.47 \pm 0.43 )</td>
</tr>
<tr>
<td>252</td>
<td>200</td>
<td>( 3.10 \pm 0.22 )</td>
<td>( 3.97 \pm 0.30 )</td>
</tr>
<tr>
<td>255</td>
<td>25</td>
<td>( 4.15 \pm 0.20 )</td>
<td>( 4.42 \pm 0.20 )</td>
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<tr>
<td>255</td>
<td>200</td>
<td>( 3.25 \pm 0.20 )</td>
<td>( 3.95 \pm 0.32 )</td>
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<tr>
<td>257</td>
<td>25</td>
<td>( 3.86 \pm 0.15 )</td>
<td>( 4.10 \pm 0.11 )</td>
</tr>
<tr>
<td>257</td>
<td>25</td>
<td>( 4.30 \pm 0.15 )</td>
<td>( 4.47 \pm 0.19 )</td>
</tr>
<tr>
<td>275</td>
<td>25</td>
<td>( 3.94 \pm 0.17 )</td>
<td>( 4.10 \pm 0.16 )</td>
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<tr>
<td>298</td>
<td>25</td>
<td>( 3.55 \pm 0.21 )</td>
<td>( 3.84 \pm 0.14 )</td>
</tr>
<tr>
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<td>25</td>
<td>( 3.47 \pm 0.25 )</td>
<td>( 3.59 \pm 0.25 )</td>
</tr>
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<td>( 3.51 \pm 0.14 )</td>
<td>( 3.62 \pm 0.13 )</td>
</tr>
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<td>( 3.87 \pm 0.36 )</td>
<td>( 3.93 \pm 0.36 )</td>
</tr>
<tr>
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<td>25</td>
<td>( 3.89 \pm 0.15 )</td>
<td>( 4.07 \pm 0.17 )</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>( 3.91 \pm 0.23 )</td>
<td>( 4.07 \pm 0.24 )</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>( 3.62 \pm 0.15 )</td>
<td>( 3.98 \pm 0.18 )</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>( 3.70 \pm 0.12 )</td>
<td>( 3.91 \pm 0.14 )</td>
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<td>( 3.76 \pm 0.16 )</td>
<td>( 3.98 \pm 0.14 )</td>
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<td>( 3.73 \pm 0.68 )</td>
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<td>( 3.39 \pm 0.27 )</td>
<td>( 3.73 \pm 0.24 )</td>
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<td>( 3.39 \pm 0.28 )</td>
<td>( 3.71 \pm 0.32 )</td>
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<td>200</td>
<td>( 3.55 \pm 0.12 )</td>
<td>( 3.76 \pm 0.13 )</td>
</tr>
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<td>500</td>
<td>( 3.18 \pm 0.16 )</td>
<td>( 4.03 \pm 0.20 )</td>
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<td>333</td>
<td>25</td>
<td>( 3.16 \pm 0.60 )</td>
<td>( 3.26 \pm 0.12 )</td>
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<td>359</td>
<td>25</td>
<td>( 2.99 \pm 0.14 )</td>
<td>( 3.09 \pm 0.15 )</td>
</tr>
<tr>
<td>360</td>
<td>25</td>
<td>( 2.89 \pm 0.13 )</td>
<td>( 2.96 \pm 0.12 )</td>
</tr>
<tr>
<td>367</td>
<td>25</td>
<td>( 3.35 \pm 0.13 )</td>
<td>( 3.44 \pm 0.13 )</td>
</tr>
</tbody>
</table>

\(^a\)Errors are \( 2\sigma \) and represent precision only.

\(^b\)Uncorrected values have not been adjusted for non-pseudo-first-order conditions and (ClO) loss by reaction (5). See the text for details.

\(^c\)Carried out with 283 nm photolysis of CIO, under "reversed" and "normal" flow conditions.
Nicovich, Wine, and Ravishankara: Kinetics of the \( \text{O}^\text{3} + \text{ClO} \) reaction. 5675

![Graph showing the plot of [ClO] \(^{-1}\) vs delay time. The open circles are based on ClO concentrations calculated from the O atom decay at each delay and the closed circles are based upon the fluorescence signal immediately following the 266 nm laser pulse. The triangular point on the abscissa represents [O\(_3\)]

Experimental conditions: \( T = 252 \text{ K} \); \( P = 200 \text{ Torr} \).

The concentration of ClO needed to determine \( k_+ \) was deduced in two manners. In the first method, Eq. (I) was rearranged to calculate [ClO]. Here \( k_1 \) was taken from fixed delay experiments at the same experimental temperature and pressure. \( k_+ \) was determined from Eq. (IV). Then the values for [ClO] in the fixed delay experiments were adjusted to account for the loss of ClO during the delay. This procedure was iterated until constant values of \( k_1 \) and \( k_+ \) were obtained. The second method involved relating the signal level immediately following the 266 nm laser pulse to the value of [ClO]. The signal calibration could be arrived at by two procedures. When enough data was available under the same experimental conditions, a [ClO] vs signal calibration curve was constructed. Otherwise, signal vs delay time was plotted and extrapolated to time zero and that signal level normalized to [O\(_3\)]. This normalization factor was then used to put the signal level at each delay time on an absolute concentration scale. Because of the reciprocal relation in Eq. (IV), the value of \( k_+ \) is quite sensitive to the scaling factor used in setting the value of [ClO]. Also the signal level is quite dependent on the operating conditions of the resonance lamp. Therefore, the values of \( k_+ \) determined from the first method are more precise. However, when using \( k_+ \) as a measure of [ClO], we assume that O atoms are removed only by reaction with ClO and Cl\(_2\); this assumption appears to be justified. A typical plot of [ClO] \(^{-1}\) vs \( t \) appears in Fig. 5. The end results of a number of such experiments appear in Table II. These results are presented only as a measure of the phenomenological loss rate of ClO in our system, not as a definitive measurement of \( k_+ \).

Hayman et al.\(^{17}\) report 298 K values for \( k_+ \), which are substantially faster than the values for \( k_+ \) (298 K, \( P \)) we have determined. However, our 255 K results appear to agree reasonably well with Hayman et al.'s low temperature values for \( k_+ \). According to Hayman et al.\(^{17}\), reaction (7) has an important branch to form a weakly bound dimer which can either decompose or react rapidly with chlorine atoms. The relevant reaction scheme is given below:

\[
\begin{align*}
\text{ClO} + \text{ClO} + \text{M} & \rightarrow (\text{ClO})_2 + \text{M}, \quad (7a, - 7a) \\
\text{ClO} + \text{ClO} - \text{OCIO} + \text{Cl}, \quad (7b) \\
\text{ClO} + \text{ClO} - \text{other products}, \quad (7c) \\
\text{Cl} + (\text{ClO})_2 & \rightarrow \text{Cl}_2 + \text{ClOO}, \quad (8) \\
\text{ClOO} + \text{M} & \rightarrow \text{Cl} + \text{O}_2 + \text{M}, \quad (9) \\
\text{Cl} + \text{ClOO} & \rightarrow \text{Cl}_2 + \text{O}_2 \quad \text{(major)}, \quad (10a) \\
\text{Cl} + \text{OCIO} & \rightarrow 2\text{ClO} \quad \text{(minor)}, \quad (10b) \\
\text{Cl} + \text{OCIO} & \rightarrow 2\text{ClO} \quad (11)
\end{align*}
\]

Hayman et al.\(^{17}\) obtained their kinetic data from a molecular modulation study. They observed much smaller apparent values for \( k_+ \) during the lights-off cycle (no chlorine atoms present) than during the lights-on cycle (large concentration of chlorine atoms present). Hence, a plausible explanation for the difference between our \( k_+ \) (298 K) determinations and the \( k_+ \) (298 K) values reported by Hayman et al.\(^{17}\)

**TABLE II. Summary of \( k_+ \) determinations.**

<table>
<thead>
<tr>
<th>( T (K) )</th>
<th>( P (\text{Torr}) )</th>
<th>( 10^{-14}[\text{Cl}]_0^* )</th>
<th>( 10^{-13}[\text{O}_3]^* )</th>
<th>No. of experiments</th>
<th>Range of ( t_\epsilon (\text{ms}) )</th>
<th>( 10^{15}k_+ ) ( ^{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>252</td>
<td>200</td>
<td>4.0-4.8</td>
<td>10.4</td>
<td>6</td>
<td>1.5-45</td>
<td>2.27 ± 0.18</td>
</tr>
<tr>
<td>255</td>
<td>25</td>
<td>4.0-5.1</td>
<td>9.8</td>
<td>6</td>
<td>3.0-45</td>
<td>0.47 ± 0.19</td>
</tr>
<tr>
<td>255</td>
<td>200</td>
<td>3.4-4.7</td>
<td>12.2</td>
<td>8</td>
<td>3.0-50</td>
<td>2.47 ± 0.18</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>1.7-2.5</td>
<td>7.3</td>
<td>7</td>
<td>1.5-60</td>
<td>0.17 ± 0.12</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>4.3-7.8</td>
<td>13.0</td>
<td>6</td>
<td>5.0-60</td>
<td>0.40 ± 0.09</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>2.2-5.2</td>
<td>8.3</td>
<td>8</td>
<td>1.5-60</td>
<td>0.36 ± 0.09</td>
</tr>
<tr>
<td>298</td>
<td>200</td>
<td>1.9-4.6</td>
<td>9.7</td>
<td>12</td>
<td>1.5-60</td>
<td>1.12 ± 0.11</td>
</tr>
<tr>
<td>298</td>
<td>200</td>
<td>2.6-3.9</td>
<td>11.5</td>
<td>12</td>
<td>1.5-60</td>
<td>0.92 ± 0.18</td>
</tr>
<tr>
<td>298</td>
<td>500</td>
<td>3.2-3.4</td>
<td>11.3</td>
<td>6</td>
<td>2.0-45</td>
<td>1.63 ± 0.17</td>
</tr>
<tr>
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<td>500</td>
<td>3.7-4.0</td>
<td>5.9</td>
<td>5</td>
<td>1.5-35</td>
<td>2.94 ± 0.63</td>
</tr>
<tr>
<td>359</td>
<td>200</td>
<td>2.0-2.5</td>
<td>9.3</td>
<td>5</td>
<td>3.0-45</td>
<td>0.38 ± 0.15</td>
</tr>
</tbody>
</table>

*Units are molecules per cm\(^3\).*

*Errors are 2\( \sigma \), precision only.

is that \( k_{-7a} \) (298 K) was substantially faster than \( k_{+} \) [Cl] under our experimental conditions; this is, of course, a favorable situation for measurement of \( k_{+} \) but would result in systematic underestimation of \( k_{+} \). No clear variation of \( k_{+} \) with [Cl] is evident in our data, although our experiments spanned a rather narrow range of chlorine atom concentrations (Table II).

In order to make appropriate corrections for the loss of ClO during the delay between laser pulses, a reaction system consisting of reactions (2) and (7) was modeled under a variety of initial conditions using literature values for \( k_{2}(T) \) and setting \( k_{+} = k_{-7a} \). From these calculations a set of correction factors (\( F \)) could be derived:

\[
F_{r} = \left( \frac{[\text{ClO}]_{r}}{[\text{O}_{3}]_{0}} \right) .
\]

Values of \( F_{r} \) at \( t_{r} = 3.4 \) ms are given in Table III as a function of temperature, pressure, \([\text{O}_{3}]_{0}\) and \([\text{Cl}]_{0}/[\text{O}_{3}]_{0}\). Note that the maximum correction is made for the highest value of \([\text{ClO}]_{0}\) for a given experiment; also, the longer the delay used in an experiment the larger the correction applied. For a few experimental conditions where \( k_{+} \) was great enough (i.e., high pressure, low temperature) a correction was made to the observed \( k' \) for loss of ClO during the delay itself; this correction never exceeded 1.4%.

As a further check on the consistency of our experiments, the rate coefficient for reaction (1) was determined at 298 K in 50 Torr Nz using 283 nm photolysis of ClO rather than 266 nm photolysis. The additional photolysis wavelength was provided by the frequency doubled, Nd:YAG pumped tunable dye laser. Also, to ensure that neither \( \text{O}_{3} \) nor \( \text{Cl}_{2} \) were being lost in the flow system, a measurement of \( k_{1}(298 \text{ K}) \) was carried out with the two absorption cells plumbed downstream from the reaction cell rather than in the "normal" upstream position. Neither of these variations in experimental parameters affected the observed kinetics.

As mentioned above, a significant O atom signal was generated subsequent to the excimer laser pulse (Fig. 2). Leu\(^a\) and Vanderzanden and Birks\(^b\) have observed O atoms from the reaction of chlorine atoms with ozone. The following chemistry was proposed to explain their observations:

\[
\begin{align*}
\text{Cl} + \text{O}_{3} & \rightarrow \text{ClO} + \text{O}_{2}(b \: \Sigma_{u}^{+}), & (2') \\
\text{O}_{2}(b \: \Sigma_{u}^{+}) & \rightarrow \text{O} + 2\text{O}_{2}. & (12)
\end{align*}
\]

Subsequently, Choo and Leu\(^c\) monitored \( \text{O}_{2}(b \: \Sigma_{u}^{+}) \) directly by observing its near infrared emission and put an upper limit of \(-0.05\%\) on the \( \text{O}_{2}(b \: \Sigma_{u}^{+}) \) yield from reaction (2). Such a yield is much too small to account for the observed levels of \( \text{O}(\frac{3}{2} \: \varpi) \) produced in the \( \text{Cl} + \text{O}_{3} \) studies.\(^d\)\(^e\) Choo and Leu have suggested that the O atoms may be generated by reactions of vibrationally excited ClO formed in reaction (2), i.e.,

\[
\text{Cl} + \text{O}_{3} \rightarrow \text{ClO}^*(v' < 18) + \text{O}_{2},
\]

followed by

\[
\text{ClO}^*(v' > 12) + \text{O}_{3} \rightarrow \text{O}_{3} + \text{O} + \text{ClO}
\]

or

\[
\text{ClO}^*(v' > 3) + \text{Cl} \rightarrow \text{Cl}_{2} + \text{O}.
\]

In our system Cl atoms are in excess over \( \text{O}_{3} \), and, therefore, in excess over the ClO created in reaction (2). Also, the occurrence of reaction (14) results in loss of two ClO molecules which otherwise would have been present at \( t_{r} \) while the occurrence of reaction (13) results in loss of only one ClO molecule. Hence, reaction (14) would potentially have the larger effect on the ClO concentration in our experiments. To examine the potential role of reaction (14) in consuming ClO, we simulated the system chemistry using a Gear routine to solve the rate equations numerically. The following scheme was modeled:

\[
\begin{align*}
\text{Cl} + \text{O}_{3} & \rightarrow \text{ClO}^* + \text{O}_{2}, & (2') \\
\text{Cl} + \text{ClO}^* & \rightarrow \text{Cl} + \text{O}, & (14) \\
\text{ClO}^* + \text{M} & \rightarrow \text{ClO} + \text{M} (M = \text{N}_{2}), & (15) \\
\text{O} + \text{ClO} & \rightarrow \text{O} + \text{Cl}, & (1) \\
\text{ClO} & \rightarrow \text{products}, & (7') \\
\text{O} + \text{Cl}_{2} & \rightarrow \text{Cl} + \text{ClO}. & (5a)
\end{align*}
\]

Although reactions (2') and (14) may have other channels, this scheme was devised to have the greatest impact on the [ClO] at the end of the reaction period; therefore, only the branches that deplete ClO were used. It should be noted that a large dependence of the extraneous \( \text{O}(\frac{3}{2} \: \varpi) \) signal on the total pressure in the system was observed. This observation would be consistent with quenching of either ClO* or \( \text{O}_{2}(b \: \Sigma_{u}^{+}) \) by \( \text{N}_{2} \); \( k_{1} \) and \( k_{2} \) are known, and the other rate coefficients were adjusted to reproduce the magnitude and
temporal behavior of the O atom signal observed. Typical results are shown in Fig. 6. It was found that the above reaction scheme lead to no more than a 2% perturbation in the concentration of CIO. Of course there is no direct proof that the assumed reaction scheme is correct. However, it is the worst case of the suggested possibilities and any corrections would be quite small. Since the mechanism for O atom formation following the excimer laser pulse is not well understood, the effect of this chemistry on the CIO concentration was not taken into account in the determination of "corrected" values for $k_1$ (Table 1).

The combination of Cl$_2$ photolysis, Cl + O$_3$ reaction, and CIO photolysis could result in some heating of the gas in the reaction zone. Calculations which assume worst case conditions, i.e., $P = 25$ Torr N$_2$, [Cl]$_0 = 6 \times 10^{14}$ molecules per cm$^3$, [O$_3$]$_0 = 1 \times 10^{14}$ molecules per cm$^3$, [O], the loss rate of CIO determined in the same system, a correction was made to [CIO] for the CIO that undergoes self-reaction (or other loss processes) during the delay time between laser firings. The largest corrections were made at higher pressures, lower temperatures, and in long delay experiments. Because the simulation of the production and loss of CIO was sensitive to the errors in our measurements of $k_+$, this correction has a rather large uncertainty.

(d) A few decays were corrected for CIO loss during the decay itself; however, this correction was insignificant under most experimental conditions.

e) It was concluded that of the known possibilities for the source of O atoms prior to CIO photolysis, none could have had more than a 2% effect on [CIO]$_0$; no corrections were made for this chemistry.

Even though there were several corrections made in order to reach a final value for $k_1$ at each temperature and pressure, the magnitudes of the corrections were small in most cases (see Table 1), the corrections could be quantitatively applied, and in general, the results are self-consistent. An Arrhenius plot of our data appears in Fig. 7. An unweighted least squares analysis of all data yields the expression

$$k_1(T) = (1.68 \pm 0.31) \times 10^{-11} \exp\left\{ \frac{(241 \pm 53)}{T} \right\} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1},$$

(6)
where the errors represent $2\sigma$, precision only, and $\sigma_\Delta \equiv \Delta \theta^{1/2}$. For the 25 Torr data only, the expression

$$k_1(T) = \left(1.55 \pm 0.33\right) \times 10^{-11} \exp\left(\frac{263 \pm 60}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (VII)$$

is obtained from an unweighted least squares analysis. The difference between the Arrhenius expression obtained from the 25 Torr data and that obtained from the complete data set is primarily due to the slightly lower rate coefficients obtained at high pressure (200 Torr) and low temperature (252-255 K). These rate coefficients required rather large corrections for contributions from reactions (1) and, therefore, are more likely to be in error than rate coefficients obtained at higher temperatures and/or lower pressures. For this reason, we believe the Arrhenius expression obtained from the 25 Torr data only should be preferred. The absolute accuracy of $k_1$ at any temperature within the range studied is estimated to be $\pm 20\%$.

**DISCUSSION**

In all prior investigations, reaction (1) was studied by flow tube techniques at pressures less than 10 Torr. The results of all studies are summarized in Table IV. In the earliest study Bemand et al. measured $k_1(298 \text{ K})$ using resonance fluorescence to monitor $O(3P)$ in excess ClO. The ClO was produced by the reaction

$$\text{Cl} + \text{OCIO} \rightarrow 2\text{ClO} \quad (11)$$

assuming a stoichiometric factor of 2. These workers reported $k_1(298 \text{ K}) = (5.3 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. They also measured the rate coefficient by following the decay of ClO mass spectrometrically in excess oxygen atoms and obtained the result $(5.7 \pm 2.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In a subsequent study in the same laboratory Clyne and Nip measured the temperature dependence of $k_1$. Again, $O(3P)$ was monitored by resonance fluorescence in excess ClO, the latter species being generated via reaction (2). The room temperature rate coefficient was in good agreement with their previous study. They report a significant activation energy and quote the Arrhenius expression

$$k_1(T) = (1.07 \pm 0.30) \times 10^{-10} \exp\left(-\frac{(224 \pm 76)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$  

Zahniser and Kaufman measured the temperature dependence of the ratio $k_1/k_2$. Using a value of $k_2$ measured directly in the same system these workers report $k_1(T) = (3.38 \pm 0.50) \times 10^{-11} \exp\left(-\frac{(75 \pm 40)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The next reported investigation of $k_1(T)$ was performed by Leu using resonance fluorescence detection of $O(3P)$ in excess ClO. ClO radicals were produced using three different source reactions in order to validate stoichiometric assumptions necessary to arrive at ClO concentration levels. Reactions (2), (11), and

$$\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{ClO} + \text{Cl}_2 \quad (16)$$

were the three sources used at room temperature. Reaction (2) was used at all other temperatures. Leu's value for $k_1(298 \text{ K})$ is lower than the previously reported values and he measured a small positive activation energy with $k_1(T) = (5.0 \pm 1.0) \times 10^{-11} \exp\left(-\frac{(96 \pm 20)}{T}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The use of reaction (2) as the only ClO source in all experiments at $T \neq 298 \text{ K}$ could result in a systematic error in Leu's reported temperature dependence. At the low pressures employed in Leu's study, the ClO* + Cl reaction may have competed favorably with ClO* deactivation, thus leading to overestimation of [ClO]. Since the ratio of $k_{14}/k_{15}$ may be temperature dependent, such an effect could have been more important at one end of the investigated temperature range than at the other end. It should be emphasized that while the abovementioned systematic error in Leu's [ClO] determination is possible, there currently exists insufficient information concerning ClO* chemistry to prove or disprove this conjecture.

**TABLE IV. Comparison of measurements of $k_1$**

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Reference</th>
<th>Experimental method*</th>
<th>Temperature range (K)</th>
<th>Pressure range (Torr)</th>
<th>$k_1(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bemand, Clyne,</td>
<td>1</td>
<td>DF-RF(0)</td>
<td>298</td>
<td>1.0</td>
<td>$3.3 \pm 0.8$</td>
</tr>
<tr>
<td>and Watson</td>
<td>1</td>
<td>DF-MS(0)</td>
<td>298</td>
<td>0.75</td>
<td>$5.7 \pm 2.3$</td>
</tr>
<tr>
<td>Clyne and Nip</td>
<td>2</td>
<td>DF-RF(0)</td>
<td>220-426</td>
<td>0.90</td>
<td>$3.68$</td>
</tr>
<tr>
<td>Zahniser and Kaufman</td>
<td>3</td>
<td>DF-RF(ClO)*</td>
<td>220-298</td>
<td>2.0-4.0</td>
<td>$4.83$</td>
</tr>
<tr>
<td>Schwaar, Toohey,</td>
<td>4</td>
<td>DF-RF(0)</td>
<td>236-422</td>
<td>1.0-3.5</td>
<td>$3.17$</td>
</tr>
<tr>
<td>Brune, and Anderson</td>
<td>5</td>
<td>DF-LMR(ClO)</td>
<td>252-347</td>
<td>0.8-2.0</td>
<td>$3.50$</td>
</tr>
<tr>
<td>Ongstad and Birks</td>
<td>6</td>
<td>DF-CL(0)*</td>
<td>220-387</td>
<td>2.3</td>
<td>$4.14$</td>
</tr>
<tr>
<td>Margitan</td>
<td>7</td>
<td>DF-LFP-RF(0)</td>
<td>241-298</td>
<td>10</td>
<td>$4.20$</td>
</tr>
<tr>
<td>Nicovich, Wine, and Ravishankara</td>
<td>8</td>
<td>LFP-RF(0)</td>
<td>231-367</td>
<td>25-500</td>
<td>$5.29$</td>
</tr>
</tbody>
</table>

*DF—discharge flow; RF—resonance fluorescence; MS—mass spectrometry; LMR—laser magnetic resonance; CL—chemiluminescence; LFP—laser flash photolysis.

*The monitored species is given in parentheses.

*Calculated from reported Arrhenius expressions.

*Measurements relative to $k(\text{Cl} + \text{O}_2)$.

*NO added to produce chemiluminescence via $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + h\nu + \text{NO}_2$. 

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Schwab et al. employed an experimental apparatus in which both reactants [ClO by laser magnetic resonance and O(^3P) by resonance fluorescence] could be monitored. Interestingly, this is the only O + ClO study where ClO was directly measured in the reaction zone. Again, a somewhat lower value was measured \( k_1(298 \text{ K}) = (3.5 \pm 0.5) \times 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \) and these workers observed essentially no temperature dependence for \( k_1 \).

Ongstad and Birs measured \( k_1(T) \) in a discharge flow system using the same three sources of ClO as Leu. O(^3P) was followed via the chemiluminescence from NO\(^2\) generated by reacting the oxygen atoms with NO added to the detection region of their flow tube. These workers measured \( k_1(T) \) directly and also relative to the reaction

\[
O + NO_2 \rightarrow NO + O_2.
\]

In a successive measurement scheme \( k_1(T) \) was also measured. The relative measurements yielded somewhat higher values, presumably due to nonpure source gases (Cl\(_2\)O, ClO\(_2\), O\(_3\)) or other channels for the source reactions. Ongstad and Birsks measured a value for \( k_1(298 \text{ K}) \) that agrees with the other more recent studies and a small "negative activation energy." They reported the expression

\[
k_1(T) = (2.61 \pm 0.60) \times 10^{-11} \exp\left\{ (97 \pm 64)/T \right\} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}.
\]

The only other study of \( k_1 \) at or near room temperature reported in the literature was by Margitan.\(^7\) CIO radicals were generated in a flow tube via reaction (16). Downstream from this source O(^3P) was created by laser photolysis of the ClO and followed by resonance fluorescence. The ClO concentration was measured directly in the flow by absorption. However, large corrections (up to 20%) had to be made for ClO loss between the ClO detection region and the O(^3P) detection region. Margitan used literature values for \( k_\Phi \) to make these corrections. Given the recent advances in our understanding of reaction (7),\(^7\) a large uncertainty must be associated with the magnitude of Margitan's correction for ClO loss via the self-reaction. His results are also very dependent on the value chosen for the ClO absorption cross section. Margitan reports that \( E/R \) lies within the range \( \pm 200 \text{ K} \) and \( k_1(298 \text{ K}) = (4.2 \pm 0.8) \times 10^{-11} \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \).

As seen by the comparison in Table IV, there is very little difference between the value of \( k_1(298 \text{ K}) \) from our experiments and from any of the other recent studies. However, at the lower temperatures typical of the middle stratosphere our results indicate significantly faster values for \( k_1(T) \) than any of the other recent investigations (see Table IV). Hence, model calculations which employ our expression for \( k_1(T) \) would predict somewhat larger ozone depletion due to chlorofluorocarbon injection than calculations which take \( k_1(T) \) from previously available data.

**SUMMARY**

We have measured \( k_1 \) as a function of temperature and pressure. Our results indicate a lack of any pressure dependence at 298 K over the range 25 to 500 Torr. Although our 298 K rate coefficient agrees well with previous studies, our observation of an activation energy that is more negative than any previously reported leads to a significant difference between our result and other recent measurements at temperatures relevant to stratospheric chemistry.

**ACKNOWLEDGMENTS**

We thank M. McQuaid for carrying out some of the computer simulations. This work was supported by the fluorocarbon program panel of the Chemical Manufacturer's Association (Contract No. FC-84-499) and by the National Aeronautics and Space Administration (Grant No. NAGW-1001).

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Kinetics of the Reactions of F(2P) and Cl(2P) with HNO₃

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The kinetics of the reactions of HNO₃ with fluorine (k₁) and chlorine (k₂) atoms have been studied by using a time-resolved long-path laser absorption technique to monitor the appearance of product NO₂ radicals following 351-nm pulsed laser photolysis of X₂/HNO₃/He mixtures (X = F, Cl). Absolute rate coefficients for the F(2P) + HNO₃ reaction have been determined over the temperature range 260-373 K. Between 260 and 320 K, the data are adequately represented by the Arrhenius expression k₁(T) = (6.0 ± 2.6) × 10⁻¹² exp[(400 ± 120)/T] cm³ molecule⁻¹ s⁻¹. Between 335 and 373 K the rate coefficient is found to be (2.0 ± 0.3) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ independent of temperature. The observed temperature dependence suggests that reaction proceeds via competing direct abstraction and complex pathways. No NO₂ production was observed in the experiments with X = Cl, thus establishing that k₂(298K) < 2 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹. The Cl(2P) + HNO₃ reaction was also investigated by using a pulsed laser photolysis-resonance fluorescence technique to monitor the decay of Cl(2P). Upper limit values for k₂ obtained from these experiments, in units of 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹, are 13 at 298 K and 10 at 400 K.

Introduction

The nitrate radical (NO₃) is a key reactive intermediate in the atmosphere. Motivated primarily by the need to quantitatively understand its role in atmospheric chemistry, numerous studies of NO₃ kinetics, photochemistry, and spectroscopy have been reported in the literature. A number of these studies employed the reaction

F(2P) + HNO₃ → HF + NO₂

(1)

as the nitrate radical source.¹⁻¹² Despite its widespread use as an NO₃ source in both fast flow¹⁻⁰ and flash photolysis¹⁻¹² studies, the first room temperature measurement of k₁ has only recently been reported,⁹ and the temperature dependence of k₁ has not been investigated. In this paper we report a determination of the absolute rate coefficient for reaction 1 as a function of temperature over the range 260–373 K. We also report new results on the related reaction

Cl(2P) + HNO₃ → HCl + NO₂

(2)

There have been several previous studies of reaction 2, but reported values for k₂(298K) span a range of more than 3 orders of magnitude.¹⁻¹³

References


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An absorption path length of 1820 cm. The dye laser line width of the strong NO$_3$ absorption band at 662 nm, was multipassed through the reactor. A CW ring dye laser beam, tuned to the peak of the cylindrical white cell optics; typically 90-129 passes were employed, giving extensions, was 33 cm, and the total length of the cell, including the reactor windows, a four-port gas input/output system was employed (Figure 1). $X_2$ and 85-90% of the He buffer gas entered the reactor through an outer port and a dilute HNO$_3$/He mixture was determined directly in the slow now system by UV photometry at either 202.6 nm (Zn$^+$ line) or 213.9 nm (Zn line). Absorption across sections used to convert measured absorbances to HNO$_3$ concentrations were $4.16 \times 10^{-10}$ cm$^{-2}$ at 202.6 nm and $4.70 \times 10^{-10}$ cm$^{-2}$ at 213.9 nm; these cross sections were measured during the course of the investigation and are in good agreement with literature values.$^{26,27}$ The reaction mixture flowed through the 150-cm absorption cell after exiting the reactor.

Because nitric acid vapor can damage the antireflection coating on the reactor windows, a Pechiglas plate fitted with a cajan fitting through which a jacketed copper-constantan thermocouple could be inserted. Hence, the temperature could be measured under the precise pressure and flow conditions of the experiment. Preliminary tests at both low and high temperatures showed that the measured temperature was constant within ±0.5 °C throughout the volume of intersection of the probe beam with the photolysis beam.

The gases used in this study had the following stated minimum purities: He, 99.999%; Cl$_2$, 99.9%; F$_2$, 98.0%. Helium and a 5% F$_2$ in He mixture were used without purification. Cl$_2$ was degassed repeatedly at 77 K; dilute Cl$_2$/He mixtures were then prepared manometrically in 12-L bulbs for use in experiments. Anhydrous HNO$_3$ was admitted to the reactor by diverting a small fraction of the main buffer gas flow through a needle valve, then through a bubbler containing a mixture of 1 part reagent grade HNO$_3$ (70% in H$_2$O) and 2 parts reagent grade H$_2$SO$_4$, and then to the reactor. A temperature-controlled bath maintained the bubbler temperature at 250 K during storage and at ~280 K during the course of the experiment.

Measurement of the temperature in the reaction zone was achieved by replacing one of the AR coated probe beam entrance windows with a Flexiglas plate fitted with a cajan fitting through which a jacketed copper-constantan thermocouple could be inserted. Hence, the temperature could be measured under the precise pressure and flow conditions of the experiment. Preliminary tests at both low and high temperatures showed that the measured temperature was constant within ±0.5 °C throughout the volume of intersection of the probe beam with the photolysis beam.
experiments. The use of anhydrous HNO₃ eliminates the potential side reactions

\[ \text{F}(2P) + H_2O \rightarrow HF + OH \]  

(3)

\[ OH + HNO_3 \rightarrow H_2O + NO_3 \]  

(4)

**Results and Discussion**

The **F + HNO₃ Reaction**. Reaction mixtures employed to study reaction 1 contained 0.3–1.7 Torr of F₂, 0.009–0.037 Torr of HNO₃, and 150 Torr of helium. The relevant reaction scheme is

\[ F_2 + HNO_3 \rightarrow 2F + H_2O \] (5)

\[ F_2 + HNO_3 \rightarrow HF(e\geq3) + NO_3^* + \text{other products} \] (7)

\[ NO_3^* + He \rightarrow NO_3 + He \] (6)

\[ \text{NO}_3 \rightarrow \text{NO}_3^* \text{loss by diffusion or flow from the detector field of view and by reaction} \] (7)

\[ \text{F}(2P) \rightarrow \text{with background impurities} \] (8)

In the above reaction scheme NO₃* represents vibrationally excited NO₃; our detection method is not sensitive to NO₃. In a recent study we showed that NO₃* produced from 248-nm photolysis of NO₃ is deactivated by helium with an effective rate coefficient of \(2.7 \times 10^{-12} \text{ cm}^2 \text{ molecule}^{-1} \text{s}^{-1}\). Hence, under our experimental conditions, reaction 6 proceeds with a pseudo-first-order rate coefficient \(k_2 = k_2(\text{He}) \) of \(1.3 \times 10^{-9} \text{ s}^{-1}\). Measured pseudo-first-order NO₃ appearance rate coefficients \(k_1\) ranged from 4 to 100 times slower than \(k_2\). We conclude that cascade from undetected excited vibrational levels into the ground vibrational level did not interfere with our determination of \(k_1\). Another potential interference is the fast secondary reaction

\[ \text{F}(2P) + \text{NO}_3 \rightarrow \text{FO} + \text{NO}_2 \] (9)

To avoid this potential complication, all experiments were carried out under conditions where \([\text{HNO}_3]/[\text{F}_2]\) was greater than 150. Variation of the F₂ concentration by a factor of 4 at constant laser fluence did not affect the observed kinetics nor did variation of the laser fluence by a factor of 3 at constant \([\text{F}_2]\).

Under our experimental conditions, the NO₃ appearance rate was always more than 2500 times faster than the background NO₃ decay rate (\(k_1 \approx 5 \text{ s}^{-1}\)). Hence, the appearance of NO₃ could be analyzed as a single exponential rise:

\[ \frac{[\text{NO}_3]}{[\text{NO}_3]_{\text{max}}} = 1 - \exp(-k_1t) \]  

(11)

where

\[ k_1 = k_1([\text{HNO}_3] + k_4) \]  

(II)

and \([\text{NO}_3]_{\text{max}}\) is the NO₃ concentration after all fluorine atoms had reacted away, but before any significant decay of NO₃ had occurred. Assuming NO₃ absorption obeys Beer's law, the above equations predict that a plot of \(\ln([\text{NO}_3]/[\text{NO}_3]_{\text{max}}) - \ln([\text{NO}_3]/[\text{NO}_3])\) versus \(t\) should be linear with slope \(= -k_1\), and that a plot of \(k_1\) versus [HNO₃] should be linear with slope \(= k_1\). The predicted linear dependencies were observed in all cases. These observations, along with the above-mentioned invariance of the observed kinetics to variations in \([\text{F}_2]\) and laser photon fluence, strongly suggest that the NO₃ temporal profile was governed entirely by reactions 1 and 5–7. Reaction of F(2P) with NO₃ impurity in the nitric acid sample could not have been important unless impurity levels reached several percent. UV photometry at 366 nm confirmed that NO₃ levels in the nitric acid samples were always less than 0.5%.

Our experimental data for reaction 1 are summarized in Table I. Errors quoted for individual \(k_1\) determinations are 2σ and refer only to the precision of the \(k_1\) versus [HNO₃] data. The absolute accuracy of the results is limited by precision, uncertainties in the determination of the nitric acid concentration, and other unidentified systematic errors which we believe to be negligible. We estimate that the absolute accuracy of a typical \(k_1\) determination is ±15%.

Our experimental results are plotted in Arrhenius form in Figure 4. The ln \(k_1\) versus 1/\(T\) plot is nonlinear. Over the temperature

---

**TABLE 1: Kinetic Data for the F + HNO₃ Reaction**

<table>
<thead>
<tr>
<th>T, K</th>
<th>no. of exp*</th>
<th>(F_2 \times 10^{14})</th>
<th>([\text{NO}<em>3]</em>{\text{max}} \times 10^{15})</th>
<th>([\text{HNO}_3] \times 10^{15})</th>
<th>(k_1 \times 10^{14} \text{ cm}^2 \text{ molecule}^{-1} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>5</td>
<td>1.5–6.3</td>
<td>1.5–7.2</td>
<td>0.75–5.03</td>
<td>1.93–14.3</td>
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<tr>
<td>273</td>
<td>6</td>
<td>3.2–3.8</td>
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<td>0.98–13.1</td>
<td>2.43–32.0</td>
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<tr>
<td>275</td>
<td>5</td>
<td>2.9</td>
<td>4.0–5.0</td>
<td>0.83–6.79</td>
<td>2.20–17.0</td>
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<tr>
<td>296</td>
<td>4</td>
<td>2.8</td>
<td>2.7–3.0</td>
<td>1.12–6.0</td>
<td>2.64–15.3</td>
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<tr>
<td>298</td>
<td>6</td>
<td>1.0–3.4</td>
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<tr>
<td>320</td>
<td>4</td>
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<td>1.21–10.4</td>
<td>2.97–22.3</td>
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<tr>
<td>335</td>
<td>8</td>
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<td>350</td>
<td>7</td>
<td>2.5–2.7</td>
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<td>373</td>
<td>4</td>
<td>2.8–4.0</td>
<td>1.7–2.5</td>
<td>0.65–5.45</td>
<td>1.34–11.1</td>
</tr>
</tbody>
</table>

*Experiment = determination of one pseudo-first-order NO₃ appearance rate. Calculated based on an assumed absorption cross section of \(1.8 \times 10^{-13} \text{ cm}^2\), independent of temperature. Errors are 2σ and refer to precision only.

---

A plausible explanation for the observed temperature dependence is that the overall reaction proceeds via two distinct pathways:

\[
\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \quad (4)
\]

Figure 3. Typical plots of \(k_s\) versus [HNO\(_3\)] observed in the F(P) + HNO\(_3\) study. Solid lines are obtained from linear least-squares analyses and give the bimolecular rate coefficients listed in Table 1.

Figure 4. Arrhenius plot for the reaction F(P) + HNO\(_3\) → products range 260–320 K, the data are well represented by the expression (units are cm\(^3\) molecule\(^{-1}\) s\(^{-1}\))

\[
k_s(T) = (6.0 \pm 2.6) \times 10^{-12} \exp[(400 \pm 120)/T]. \quad 260 \text{ K} \leq T \leq 320 \text{ K} \quad (III)
\]

Uncertainties in the above expression are 2σ and represent only the precision of the ln \(k_s\) versus \(1/T\) fit. Over the temperature range 335–373 K, our data support the temperature-independent rate coefficient (in units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\))

\[
k_s(T) = (2.0 \pm 0.3) \times 10^{-11}. \quad 335 \text{ K} \leq T \leq 373 \text{ K} \quad (IV)
\]

The quoted error in expression IV represents our estimate of the 2σ absolute uncertainty in \(k_s(T)\).

The only published value of \(k_s\) with which to compare our results is the very recent 298 K measurement of Melloul et al.\(^9\)

These authors employed the discharge flow–EPR technique with uncertainties in the magnitude of the NO\(_3\) cross section, the temperature dependence of both the NO\(_3\),\(^{15}\) and F\(_2\) cross sections prevent quantitative determination of the NO\(_3\) yield.

Comparison of [F\(_2\)] (calculated from measurements of [F\(_2\)] and laser fluence, and the known F\(_2\) absorption cross section at the photolysis wavelength\(^{29}\)) with [NO\(_3\)]\(^{15}\) (calculated from the estimated path length and an assumed absorption cross section of 1.8 × 10\(^{-17}\) cm\(^2\) at 662 nm) indicates that reaction 1a is the major channel over the entire temperature range of our study. However, uncertainties in the magnitude of the NO\(_3\) cross section, and the temperature dependences of both the NO\(_3\),\(^{15}\) and F\(_2\) cross sections prevent quantitative determination of the NO\(_3\) yield.

The occurrence of reaction 1b as a minor channel represents a potential kinetic complication in our study because reaction 4 would result in conversion of OH to NO\(_3\). However, since \(k_s\) at 298K is about 200 times slower than \(k_s\) at 298K,\(^{31}\) the occurrence of reactions 1b and 4 would lead to readily observable nonexponential NO\(_3\) appearance profiles, such nonexponential temporal profiles were not observed. As a further check for the possible occurrence of reaction 1b, a few experiments were carried out where sufficient CO was added to the reaction mixture to scavenger more than 90% of any OH produced. In back-to-back experiments with and without added CO, no change in [NO\(_3\)]\(^{15}\) was observed. On the basis of the above observations, we are able to conclude that, at 298 K, \(k_{1b}/k_s < 0.02\).

The Cl + HNO\(_3\) Reaction. Reaction 2 was studied by two different experimental methods. The first was identical with the


(34) Deleted in proof.
Kinetics of Reactions of F(2P) and Cl(2P) with HNO₃

The approach used to study reaction 1 but with Cl₂ replacing F₂ as the photolyte (PLP-LPLA technique). In the other experimental approach, the decay of Cl(2P) was monitored by time-resolved resonance fluorescence following 355-nm pulsed laser photolysis of Cl₂/HNO₃/He mixtures (PLP-RF technique).

The PLP-LPLA study of reaction 2 employed reaction mixtures containing 0.6–2.5 Torr of HNO₃, 0.2–1.5 Torr of Cl₂, and 80 Torr of helium. No evidence for NO₂ production was observed. Typical data are shown in Figure 3. Also shown in Figure 3 are the results of a series of numerical simulations of the NO₂ absorption temporal profile. The following mechanism was assumed for the simulations:

\[
\begin{align*}
\text{Cl}_2 + h\nu (351 \text{ nm}) & \rightarrow 2\text{Cl}(2P) & (10) \\
\text{Cl}(2P) + \text{HNO}_3 & \rightarrow \text{HCl} + \text{NO}_2 & (2) \\
\text{Cl}(2P) + \text{NO}_3 & \rightarrow \text{ClO} + \text{NO}_2 & (11) \\
\text{Cl}(2P) + \text{NO}_2 + \text{He} & \rightarrow \text{ClNO}_2 + \text{He} & (12) \\
\text{NO}_2 + \text{NO}_2 + \text{He} & \rightarrow \text{N}_2\text{O}_5 + \text{He} & (13) \\
\end{align*}
\]

\( \text{NO}_2 \) loss by diffusion or flow from the detector field of view and by reaction

\( \text{Cl}(2P) \) with background impurities

Values for \( k_{11}, k_{12}, \) and \( k_{13} \) were taken from the literature. 35–38 In units of cm³ molecule⁻¹ s⁻¹, the rate coefficients used in the simulations were \( k_{11} = 5.5 \times 10^{11}, k_{12} = 2.0 \times 10^{12}, \) and \( k_{13} = 6.2 \times 10^{11}. \) The Cl(2P) concentration was calculated from the measured laser photon fluence and Cl₂ concentration by assuming a quantum yield of 2 for Cl(2P) production; for the data shown in Figure 5, \( [\text{Cl}(2P)]_0 = 7.1 \times 10^{12} \) molecules/cm³. The background Cl(2P) loss rate was set at 100 s⁻¹, an upper limit value based on PLP-RF measurements of Cl(2P) decay rates and the geometry of the PLP-LPLA reactor—a geometry that minimizes the rate of diffusion and/or flow out of the detector field of view. The NO₂ decay rate was determined by photolyzing the reaction mixture at 248 nm, a wavelength where HNO₃ rather than Cl₂ is the dominant absorber:

\[
\begin{align*}
\text{HNO}_3 + h\nu (248 \text{ nm}) & \rightarrow \text{OH} + \text{NO}_2 & (15) \\
\text{OH} + \text{HNO}_3 & \rightarrow \text{NO}_2 + \text{H}_2\text{O} & (4) \\
\text{NO}_2 & \rightarrow \text{loss} & (7')
\end{align*}
\]

For the reaction mixture used to obtain the data shown in Figure 5, we obtained the result \( k_7 = 8.0 \pm 0.7 \) s⁻¹. The value for \( k_7 \) was used in conjunction with the literature value for \( k_{11} \) to establish an upper limit NO₂ concentration (for the reaction mixture used to obtain the data shown in Figure 5, \([\text{NO}_2] \leq 1.8 \times 10^{15} \) molecules/cm³). Since the upper limit NO₂ concentrations were used in the simulations, \( k_7 \) was set equal to zero. The results of the simulations are very insensitive to \( k_{13} \) and \( k_7 \) as long as \( k_7 \leq 25 \) s⁻¹.

The results shown in Figure 5 support the conclusion that \( k_5(298 \text{K}) < 2 \times 10^{14} \) cm³ molecule⁻¹ s⁻¹. Experiments over a range of values of [HNO₃], [Cl₂], and laser fluence all showed no evidence for NO₂ production from reaction 2, and simulations led to upper limit values for \( k_5 \) similar to that obtained from Figure 5. We feel that the reported upper limit is conservative because (1) values for \( k_{14} \) and [NO₂] used in the simulations are upper limits and (2) even the simulation with \( k_5 \) equal to \( 1 \times 10^{14} \) cm³ molecule⁻¹ s⁻¹ predicts more absorbance than was actually observed (Figure 5).

The PLP-RF experiments employed reaction mixtures containing 0.1–1 mTorr of Cl₂, 0–0.41 Torr of HNO₃, and 25 Torr of helium. The relatively low total pressure served to minimize the interference from reaction 12. Initial chlorine atom concentrations were always less than \( 1 \times 10^{11} \) per cm³, so radical-radical side reactions were relatively unimportant. Some typical Cl(2P) temporal profiles observed in 298 K experiments are shown in Figure 6. A plot of the pseudo-first-order Cl(2P) decay rate as a function of the HNO₃ concentration is shown in Figure 7. A linear least-squares analysis of the data in Figure 7 gives the bimolecular rate coefficient \( 8.3 \pm 4.5 \times 10^{-16} \) cm³ molecule⁻¹ s⁻¹, where the uncertainty is \( 2 \sigma \) and represents precision only.

the long extrapolation, suggested 2 × 10^{-17} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} as an upper limit for k_2(298K). Recently, Poulet and co-workers employed a discharge flow system with EPR detection of Cl(\text{P}) to study reaction 2 at 293 K and obtained an upper limit value of 5 × 10^{-16} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} for k_2(293K).^{17}

Clark et al.\textsuperscript{13} and Kurylo et al.\textsuperscript{14} employed flash photolysis methods to study the kinetics of reaction 2. These authors monitored the decay of Cl(\text{P}) by resonance absorption\textsuperscript{13} or resonance fluorescence\textsuperscript{14} in the presence of excess \text{HNO}_3. The flash photolysis experiments were carried out at total pressures 1–2 orders of magnitude larger than the discharge flow experiments. Both Clark et al. and Kurylo et al. obtained very large values for k_2(298K)–3.6 × 10^{-14} and 1.7 × 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}, respectively. Neither of these investigators employed \text{HNO}_3 concentrations above 3 × 10^{-15} \text{molecules/cm}^3 due to attenuation of the chlorine resonance line by \text{HNO}_3. While we also observed reduction in resonance radiation intensity with added \text{HNO}_3, we were able to obtain good quality data even at \text{HNO}_3 concentrations above 1 × 10^{-14} \text{molecules/cm}^3 (Figure 6). Potential experimental problems that are specific to flash photolysis experiments include reaction of Cl(\text{P}) with impurities in the \text{HNO}_3 sample (particularly \text{NO}_2) and reaction of Cl(\text{P}) with flash generated radicals. Although both Clark et al. and Kurylo et al. recognized these potential problems and took measures to minimize them, it appears possible that \text{NO}_2 generated via nitric acid photolysis followed by reaction 4, was responsible for a significant fraction of Cl(\text{P}) removal in both earlier flash photolysis studies.\textsuperscript{13,14}

The most recent study of the kinetics of reaction 2 has been reported by Cantrell et al.\textsuperscript{15} These authors measured the rate of reaction 2 relative to that for the reaction,

\[
\text{Cl(\text{P})} + \text{CH}_2 \rightarrow \text{CH}_3 + \text{HCl} \tag{16}
\]

They obtained the result k_2/k_1 \leq 0.033. Since k_1 \approx 1 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}, their result implies that k_2 \leq 3.3 \times 10^{-15} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. Cantrell et al. also investigated the kinetics of the reverse reaction

\[
\text{NO}_2 + \text{HCl} \rightarrow \text{Cl(\text{P})} + \text{HNO}_3 \tag{-2}
\]

They observed that HCl reactions with \text{NO}_2 and/or \text{N}_2\text{O}_5 led to production of CINO\textsubscript{3}, but they attributed CINO\textsubscript{3} production primarily to heterogeneous pathways. They were able to place an upper limit of 7 \times 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} on the homogeneous gas-phase value for k_2(298K). On the basis of thermodynamic considerations, this result suggests\textsuperscript{16} that k_2(298K) is slower than 1.6 \times 10^{-14} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}. Our observation of minimal \text{NO}_3 production following 351-nm pulsed laser photolysis of Cl\textsubscript{2}/\text{HCl}/\text{HNO}_3 mixtures is in agreement with the low upper limits for k_2(298K) reported by Cantrell et al.\textsuperscript{15} and Poulet and co-workers\textsuperscript{16} but in conflict with the faster rate coefficients reported by Leu and DeMore,\textsuperscript{13} Kurylo et al.,\textsuperscript{15} and Clark et al.\textsuperscript{14}

\textbf{Acknowledgment.} We thank C. J. Shackelford and E. P. Dayton for assisting with some of the experiments. This work was supported by the National Science Foundation through Grant ATM-86-00892 and by the National Aeronautics and Space Administration through Grant NAGW-1001.

\textbf{Registry No.} Fp, 7782-41-4; Cl\textsubscript{2}, 7782-50-5; HNO\textsubscript{3}, 7697-37-2; F, 14762-94-8; Cl, 22537-15-1; NO\textsubscript{2}, 12033-49-7.
Temperature-Dependent Absorption Cross Sections for Hydrogen Peroxide Vapor

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Relative absorption cross sections for hydrogen peroxide vapor were measured over the temperature ranges 285-381 K for 230 nm ≤ λ ≤ 295 nm and 300-381 K for 193 nm ≤ λ ≤ 350 nm. The well-established 298 K cross sections at 202.6 and 228.8 nm were used as an absolute calibration. A significant temperature dependence was observed at the important tropospheric photolysis wavelengths, λ > 300 nm. Measured cross sections were extrapolated to lower temperatures, using a simple model which attributes the observed temperature dependence to enhanced absorption by molecules possessing one quantum of O-O stretch vibrational excitation. Upper tropospheric photodissociation rates calculated using the extrapolated cross sections are about 25% lower than those calculated using currently recommended 298 K cross sections.

INTRODUCTION

Hydrogen peroxide (H₂O₂) is an important trace constituent of the atmosphere. H₂O₂ is formed primarily via the HO₂ self reactions,

(R1a) \[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_3 + \text{O}_2 \]

(R1b) \[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_3 + \text{O}_2 \]

and is removed from the atmosphere by three processes which occur at similar rates:

(R2) \[ \text{H}_2\text{O}_3 + h\nu \rightarrow 2 \text{OH} \]

(R3) \[ \text{OH} + \text{H}_2\text{O}_3 \rightarrow \text{HO}_2 + \text{H}_2\text{O} \]

(R4) \[ \text{H}_2\text{O}_3 \rightarrow \text{rainout} \]

Reaction (R2) regenerates the HO₂ radicals which were lost in (R1); hence when removed by photolysis, H₂O₂ has acted as an HO₂ reservoir. On the other hand, (R1), followed by (R3) and (R4), represents a sink for gas phase HO₂. Both the overall H₂O₃ lifetime and the branching ratios for loss via (R2), (R3), and (R4) must be known quantitatively in order to accurately model atmospheric HO₂ chemistry.

Most calculations of the atmospheric H₂O₂ photolysis rate, jH₂O₂, employ absorption cross sections recommended by the NASA panel for chemical kinetics and photochemical data evaluation [DeMore et al., 1985]. The recommended cross sections are the average of those reported by Lin et al. [1978] and by Molina and Molina [1981]. Both studies were carried out at 298 K, with cross sections reported in 5-nm increments over the range 190-350 nm; they agree very well, except at wavelengths longer than 325 nm, where Molina and Molina estimate 298 K cross sections at 202.6 and 1.86 x 10⁻¹⁹ cm² at 228.8 nm.

With the above considerations in mind, we have measured absorption cross sections for H₂O₂ over the wavelength range 193-350 nm as a function of temperature. Our results are reported in this paper. Extrapolation of our results to upper tropospheric temperatures leads to significantly lower values for jH₂O₂ at 5 and 10 km than would be calculated from currently recommended cross sections.

EXPERIMENTAL TECHNIQUE

Cross-section measurements were carried out using the well-established 298 K cross sections at 202.6 and 228.8 nm for absolute calibration [Lin et al., 1978; Molina and Molina, 1981]. A schematic of the experimental apparatus is shown in Figure 1. The measurements were performed in a slow flow system consisting of three absorption cells in tandem. The temperature in the middle cell was varied by circulating thermostated liquid through an outer jacket. A broadband UV light source (deuterium lamp) was used and the wavelength was resolved with a 0.22-m monochromator. The temperature-controlled cell was 244 cm in length. All experiments employed a spectral band pass of 0.6 nm full width at half maximum. The first and last absorption cells were maintained at room temperature. 298 ± 1 K. A cadmium pen-ray lamp was used as the light source for the first cell, and a narrow bandpass filter was employed to isolate the 228.8-nm Cd resonance line. A zinc hollow cathode lamp was used as a light source for the last absorption cell, and a 0.25-m monochromator was employed to isolate the 202.6-nm Zn line. The first and last absorption cells were 216 and 111 cm in length, respectively. The assumed 298 K cross sections were 4.32 x 10⁻¹⁹ cm² at 202.6 nm and 1.86 x 10⁻¹⁹ cm² at 228.8 nm.

H₂O₂ was added to the gas flow by diverting some of the Nz buffer gas through a Pyrex bubbler containing 90% (by weight) H₂O₂ solution. The total pressure was maintained at 100 torr in all experiments. Measurement of the H₂O₂ concentration in the gas flow at both the inlet and outlet from the temperature-controlled cell not only allowed determination of the absolute H₂O₂ concentration, but also allowed potential
systematic errors from H$_2$O$_2$ loss by decomposition or condensation to be assessed quantitatively. The difference in H$_2$O$_2$ concentrations measured at the inlet and outlet of the temperature-controlled cell did not exceed 5% in any of the experiments used to obtain H$_2$O$_2$ cross sections. The H$_2$O$_2$ concentration in the temperature-controlled cell was always taken to be the temperature-corrected average of the concentrations measured at the inlet and outlet. At temperatures above 381 K, H$_2$O$_2$ decomposition became a problem, while the relatively low vapor pressure of H$_2$O$_2$ prevented meaningful data from being obtained at temperatures below 285 K.

In preliminary experiments, instead of using a single-pass temperature-controlled absorption cell, a multipass White cell setup was employed. Using a xenon arc lamp light source, a pathlength of 25 m could readily be obtained (70 passes through a 36-cm cell). However, at longer wavelengths, i.e., $\lambda > 300$ nm, a systematic error was uncovered in the multipass absorption measurements. The cross section measured at a given wavelength was found to depend upon the antireflection coating wavelength (of maximum transmission) of the White cell windows. Under certain conditions an improvement in the index match was obtained with H$_2$O$_2$ flowing; this resulted in measurement of an apparent negative absorbance! At long wavelengths, where gas phase absorption was very weak, the magnitude of the artifact became intolerable.

Use of a single-pass temperature-controlled absorption cell seemed to overcome this problem. While the pathlength was a factor of 10 shorter than in the White cell arrangement, system stability was somewhat improved. Hence meaningful measurements could be made for $\lambda \leq 350$ nm. To ensure that "window effects" were totally absent, at each temperature and wavelength the absorbance was also measured in a second shorter cell (20.0-cm pathlength) using the same windows as in the longer cell. Cross sections were then determined using the difference in absorbances and the difference in pathlengths between the long and short cells. Care was taken to collimate the light from the deuterium lamp in such a manner that no reflections from the walls of the absorption cells reached the detector.

**RESULTS**

Measured H$_2$O$_2$ absorption cross sections as a function of temperature and wavelength are tabulated in Table 1. Our 300 K cross sections are in good agreement with current recommendations [Demure et al., 1985] throughout the 193- to 350-nm wavelength range. However, a distinct temperature dependence is observed, which is most pronounced in the atmospherically important 310- to 350-nm wavelength region.

**EXTRAPOLATION OF MEASURED CROSS SECTIONS TO LOWER TEMPERATURES**

Experimental measurements of H$_2$O$_2$ absorption cross sections at temperatures typical of the upper troposphere and lower stratosphere are unavailable and will be extremely difficult to obtain at any time in the future. In the absence of experimental data, we have employed a simple model to extrapolate our results to lower temperatures. The basic assumption in the model is that the observed temperature dependence in the H$_2$O$_2$ absorption cross section results from the fact that ground electronic state H$_2$O$_2$ with one quantum of O–O stretch excitation absorbs more strongly at longer wavelengths than does unexcited H$_2$O$_2$. Semiempirical and ab initio calculations of ground- and excited-state H$_2$O$_2$ potential energy surfaces [Evelth, 1976; Rank and Barriel, 1977; Evelth and Kassab, 1978; Chevaldonnet et al., 1986; Gericke et al., 1986] strongly support this assumption, i.e., the lowest energy spin allowed transition is from the relatively anharmonic $X^1A'$ ground state to the steeply repulsive $A^1A'$ excited state. The O–O stretching frequency is 877 cm$^{-1}$ [Giguère, 1950]. Hence
for $T \leq 400$ K, the fraction of H$_2$O$_2$ molecules with one quantum of O–O stretch excitation is $\leq 0.04$ and the fraction with more than one quantum of O–O stretch excitation is negligible.

According to our simple model, the absorption cross section at a particular wavelength and temperature is given by the expression

$$
\sigma(\lambda, T) = X_0(T)\sigma_0(\lambda) + X_1(T)\sigma_1(\lambda)
$$

(1)

where the subscripts refer to the number of quanta of O–O stretch excitation. The mole fractions $X_0$ and $X_1$ are readily computed from the following equations:

$$
Q = 1 + \exp(-\Delta E/RT)
$$

(2)

$$
X_0 = 1/Q
$$

(3)

$$
X_1 = 1 - X_0 = (Q - 1)/Q
$$

(4)

where $\Delta E$ is the energy of one quantum of O–O stretch, i.e., 877 cm$^{-1}$. It should be noted that (2) is a simplified form for the vibrational partition function which ignores the low-frequency torsional mode. Inclusion of torsional frequencies [Hunt et al., 1965; Helminger et al., 1981; Ticich et al., 1986] has a negligible effect on computed values for $X_0$ and $X_1$.

The data analysis involved least squares fitting the temperature-dependent cross sections at each wavelength to obtain best fit values for $\sigma_0(\lambda)$ and $\sigma_1(\lambda)$. The results are plotted in Figure 2. “Recommended” values for $\sigma_0(\lambda)$ and $\sigma_1(\lambda)$ are obtained from the smoothed results (solid lines in Figure 2); they are tabulated in Table 2. The smooth curve drawn through the $\sigma_1(\lambda)$ data assumes that $\sigma_1(\lambda)$ is wavelength independent for $\lambda < 260$ nm (obviously a rather gross approximation). However, since nearly all absorption at $\lambda < 260$ nm is from vibrationally unexcited H$_2$O$_2$, this approximation has little effect on the calculated cross sections ($\sigma$).

“Recommended” values for $\sigma$ as a function of wavelength and temperature can be calculated from the recommended $\sigma_0(\lambda)$ and $\sigma_1(\lambda)$ using (1)-(4). Some representative results are shown in Figure 3, plotted in the form $\sigma$ versus $1/Q$, which,

---

**TABLE 1.** Measured Hydrogen Peroxide Absorption Cross Sections as a Function of Wavelength and Temperature

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>285 K</th>
<th>300 K</th>
<th>327 K</th>
<th>355 K</th>
<th>381 K</th>
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<td>582</td>
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<td>0.50</td>
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**TABLE 2.** Values for $\sigma_0$ and $\sigma_1$ Used to Calculate “Recommended” H$_2$O$_2$ Absorption Cross Sections as a Function of Wavelength and Temperature

<table>
<thead>
<tr>
<th>$\lambda$, nm</th>
<th>$\sigma_0$, 10$^{-21}$ cm$^2$</th>
<th>$\sigma_1$, 10$^{-21}$ cm$^2$</th>
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<tr>
<td>193</td>
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<td>230</td>
<td>181</td>
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<td>235</td>
<td>150</td>
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<td>240</td>
<td>122</td>
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<tr>
<td>245</td>
<td>99.0</td>
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</tr>
<tr>
<td>250</td>
<td>80.0</td>
<td>244</td>
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<tr>
<td>255</td>
<td>64.0</td>
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<tr>
<td>260</td>
<td>50.8</td>
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<td>265</td>
<td>40.0</td>
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<td>280</td>
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<td>285</td>
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<td>300</td>
<td>5.80</td>
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<td>1.60</td>
<td>34.3</td>
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<td>340</td>
<td>0.428</td>
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<tr>
<td>345</td>
<td>0.310</td>
<td>10.5</td>
</tr>
<tr>
<td>350</td>
<td>0.220</td>
<td>8.0</td>
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TABLE 3. H$_2$O, Photolysis Rates Versus Altitude at a Solar Zenith Angle of 60°

<table>
<thead>
<tr>
<th>Z, km</th>
<th>T, K</th>
<th>10$^{-12}$Q</th>
<th>$\sigma$, cm$^2$</th>
<th>Qd, cm$^{-2}$s$^{-1}$s$^{-1}$</th>
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<tbody>
<tr>
<td>0</td>
<td>288</td>
<td>300-310</td>
<td>3.3</td>
<td>486</td>
</tr>
<tr>
<td>310-320</td>
<td>31.0</td>
<td>267</td>
<td>82.8</td>
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<tr>
<td>320-330</td>
<td>73.4</td>
<td>145</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>330-340</td>
<td>109.1</td>
<td>80.6</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td>340-350</td>
<td>126.5</td>
<td>44.9</td>
<td>56.8</td>
<td></td>
</tr>
<tr>
<td>350-360</td>
<td>139.4</td>
<td>26.0</td>
<td>36.3</td>
<td></td>
</tr>
<tr>
<td>360-370</td>
<td>161.0</td>
<td>15.1</td>
<td>24.3</td>
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</tr>
<tr>
<td>370-380</td>
<td>174.5</td>
<td>8.8</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>380-390</td>
<td>178.5</td>
<td>5.3</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>390-400</td>
<td>228.4</td>
<td>3.3</td>
<td>4.4 x 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>257</td>
<td>300-310</td>
<td>0.5</td>
<td>462</td>
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<tr>
<td>310-320</td>
<td>50.7</td>
<td>250</td>
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<td></td>
</tr>
<tr>
<td>320-330</td>
<td>112.4</td>
<td>133</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>330-340</td>
<td>160.4</td>
<td>72.2</td>
<td>116.</td>
<td></td>
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<tr>
<td>340-350</td>
<td>178.7</td>
<td>39.0</td>
<td>69.7</td>
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</tr>
<tr>
<td>350-360</td>
<td>189.9</td>
<td>22.0</td>
<td>41.7</td>
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<tr>
<td>360-370</td>
<td>212.9</td>
<td>12.4</td>
<td>26.3</td>
<td></td>
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<tr>
<td>370-380</td>
<td>225.2</td>
<td>7.0</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>380-390</td>
<td>225.1</td>
<td>4.0</td>
<td>9.1</td>
<td></td>
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<tr>
<td>390-400</td>
<td>281.3</td>
<td>2.4</td>
<td>6.7</td>
<td></td>
</tr>
</tbody>
</table>

Q is equal to the total photonic flux in the given wavelength range. $\sigma$ is equivalent to the average cross section in the given wavelength range. $\sigma(\lambda)$ and $\sigma_i(\lambda)$ values at each wavelength (i.e., the data points in Figure 2) and the solid lines are calculated using “recommended” values for $\sigma(\lambda)$ and $\sigma_i(\lambda)$ (i.e., solid lines in Figure 2).

In Table 4 we compare H$_2$O, photodissociation rates obtained in this work with those calculated using currently recommended absorption cross sections [DeMore et al., 1985] and with estimated rates of H$_2$O, removal by reaction with OH and by rainout. The first-order rate of reaction with OH was calculated using the currently recommended rate coefficient for (R3) [DeMore et al., 1985] and a diurnally averaged OH concentration obtained by interpolating the OH altitude profiles calculated by Logan et al. [1981] at 15° and 45°N to a latitude of 41°N; Chameides and Tan [1981] have argued that

TABLE 4. Comparison of Diurnally Averaged H$_2$O, Removal Rates Under Atmospheric Conditions Typical of 41°N Latitude

<table>
<thead>
<tr>
<th>Z, km</th>
<th>NASA*</th>
<th>This Work</th>
<th>$k_{OH}$</th>
<th>$k_{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10$^{-7}$s$^{-1}$</td>
<td>10$^{-7}$s$^{-1}$</td>
</tr>
<tr>
<td>0</td>
<td>23</td>
<td>22</td>
<td>9.0</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>29</td>
<td>14.0</td>
<td>2.20</td>
</tr>
<tr>
<td>10</td>
<td>42</td>
<td>33</td>
<td>9.5</td>
<td>0.50-1.5</td>
</tr>
</tbody>
</table>

*Based on recommendations of DeMore et al. [1985].

**High values are predicted when cycling between wet and dry periods is rapid; low values are predicted when storm cycle is long [Giorgi and Chameides, 1985].
41°N is the latitude at which the average daytime solar zenith angle is 60°, as assumed in the j-value calculations. A range of values is given in Table 4 for the H$_2$O$_2$ rainout rate. It has been argued that for a highly soluble species such as H$_2$O$_2$, the time-averaged rainout rate depends not only on the average rainfall, but also on the period of the storm cycle [Thompson and Cicerone, 1982; Giorgi and Chameides, 1985]. The upper limit values for $k_4$ were calculated assuming infinitely rapid cycling between wet and dry periods, while the lower limits are representative of a boundary layer storm cycle of about 1 month [Giorgi and Chameides, 1985].

Values for $j_{H_2O_2}$ calculated using currently recommended cross sections are higher than those calculated using our temperature-dependent cross sections by a factor of 1.2 at 5 km and a factor of 1.3 at 10 km. Photodissociation appears to be the single most important H=O removal mechanism at these altitudes, though both reaction with OH and rainout are important, particularly at 5 km. Incorporation of our results into models of free tropospheric chemistry should result in a small but significant decrease in calculated HO$_2$ levels.

**Acknowledgments.** Support for this work was provided by the Fluorocarbon Program Panel of the Chemical Manufacturers Association (contract FC-85-557), The National Aeronautics and Space Administration (grant ATM-86-00892), and the National Science Foundation (contract FC-85-5576). The National Aeronautics and Space Administration (grant NAGW 1001), and the National Science Foundation (grant ATM-86-00892).

$^{*}$ Values for $j_{H_2O_2}$ calculated using currently recommended cross sections are higher than those calculated using our temperature-dependent cross sections by a factor of 1.2 at 5 km and a factor of 1.3 at 10 km. Photodissociation appears to be the single most important H=O removal mechanism at these altitudes, though both reaction with OH and rainout are important, particularly at 5 km. Incorporation of our results into models of free tropospheric chemistry should result in a small but significant decrease in calculated HO$_2$ levels.

**References**


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Temperature Dependence of the O + HO₂ Rate Coefficient

J. M. Nicovich and P. H. Wine*

Molecular Sciences Branch, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332 (Received: February 2, 1987; In Final Form: May 19, 1987)

A pulsed laser photolysis technique has been employed to investigate the kinetics of the radical–radical reaction O(3P) + HO₂ → OH + O₂ over the temperature range 266–391 K in 80 Torr of N₂ diluent gas. O(3P) was produced by 248.5-nm KrF laser photolysis of O₃ followed by rapid quenching of O('D) to O(3P), while HO₂ was produced by simultaneous photolysis of H₂O₂ to create OH radicals which, in turn, reacted with H₂O to yield HO₂. The O(3P) temporal profile was monitored using time-resolved resonance fluorescence spectroscopy. The HO₂ concentration was calculated based on experimentally measured parameters. The following Arrhenius expression describes our experimental results:

\[ k_1 = (2.91 \pm 0.70) \times 10^{-10} \exp[(228 \pm 75)/T] \]

where the errors are 2σ and represent precision only. The absolute uncertainty in \( k_1 \) at any temperature within the range 266–391 K is estimated to be ±22%. Our results are in excellent agreement with a discharge flow study of the temperature dependence of \( k_1 \) in 1 Torr of He diluent reported by Keyser, and significantly reduce the uncertainty in the rate of this important stratospheric reaction at subambient temperatures.

Introduction

The reaction of ground-state oxygen atoms with hydroperoxyl radicals

\[ \text{O}(\text{3P}) + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 \]  (1)

is a major odd oxygen destruction pathway in the upper stratosphere and mesosphere. Along with the reactions

\[ \text{O}(\text{3P}) + \text{OH} \rightarrow \text{H} + \text{O}_2 \]  (2)
\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  (3)
\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}_1 \]  (4)

reaction 1 plays a major role in controlling the partitioning among H, OH, and HO₂ radicals in the upper atmosphere. Hence, accurate kinetic data for reaction 1 are needed in order to model upper atmospheric chemistry.

Several kinetics studies of reaction 1 are reported in the literature. Four recent direct measurements of \( k_1 \) at 298 K are

Temperature Dependence of the $\text{O} + \text{H}_2\text{O}_2$ Rate Coefficient


**Figure 1.** Schematic of the apparatus: AC, absorption cell; BPF, band-pass filter; CDL, cadmium lamp; CE, counting electronics; CI, coolant inlet; DG, delay generator; F, flow meter; M, monochromator; MCA, multichannel analyzer; µWPS, microwave power supply; PG, pulse generator; PA, picosemameter; P, pressure gauge; PL, photolysis laser; PM, photomultiplier; R, radiometer; RC, reaction cell; SAO, segmented aperture optical integrator; SBPM, solar blind photomultiplier; ZnL, zinc lamp. For the sake of clarity, the solar blind photomultiplier and resonance lamp are shown at 180°. In reality, the SBPM, resonance lamp, and laser beam were at right angles to each other.

In excellent agreement,8 with reported rate coefficients all within the range $(5.2-6.2) \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. However, there has been only one investigation of the temperature dependence of $k_1$, Keyser2 studied reaction 1 over the temperature range 229-372 K in a discharge flow system at 1-Torr total pressure and observed that $k_1$ (7) increased with decreasing temperature; his reported “negative activation energy” was $-0.4 \text{ kcal mol}^{-1}$. Although Keyser’s study of reaction 1 was a high-quality experiment which appears to be free of significant systematic errors, the uncertainty in his reported activation energy will remain undesirably high8 until independent confirmation is reported.

Several years ago, we developed a pulsed laser photolysis technique for studying the kinetics of radical–radical reactions at pressures up to 1 atm. We first applied this technique to investigate reaction 1 at 298 K over the pressure range 10-500 Torr.8 In this paper, we report the results of a pulsed laser photolysis–resonance fluorescence study of the temperature dependence of $k_1$. Our results, obtained by using a much different experimental approach than that employed by Keyser,8 confirm his reported temperature dependence and also demonstrate that $k_1$ is independent of pressure at subambient temperatures.

**Experimental Section**

With a few modifications, the experiments were carried out in the same manner as our previous room-temperature study.8 A review of the experimental approach, along with details pertinent to this investigation, is given below. A schematic of the apparatus is shown in Figure 1.

All experiments were carried out under slow-flow conditions using a jacketed Pyrex reactor with an internal volume of 320 cm$^3$. The cell was maintained at a constant temperature by circulating ethylene glycol from a thermostatted bath through the outer jacket. A copper–constantan thermocouple with a stainless steel jacket was inserted into the reaction zone through a vacuum seal, thus allowing measurement of the gas temperature under the precise pressure and flow conditions of the experiment.

Reactants were produced with $\text{H}_2\text{O}_2$ in excess by 248.5-nm pulsed laser photolysis of $\text{H}_2\text{O}_2$/$\text{N}_2$ mixtures:

$$\text{H}_2\text{O}_2 + h(248.5 \text{ nm}) \rightarrow 2\text{OH}$$ (5)

A Lambda Physik Model 200E KrF excimer laser was used as the photolysis light source. Kinetic data were obtained by time-resolved resonance fluorescence detection of $\text{OH}(\text{P})$. The laser pulse width was 20 ns while, under our experimental conditions, reactions 7 and 8 proceeded at rates of $(3-10) \times 10^7$ and $7 \times 10^7 \text{ s}^{-1}$, respectively. $\text{OH}(\text{P})$ decay rates were typically in the range 30–500 s$^{-1}$.

As in our previous study, the concentration of the excess reactant, $\text{H}_2\text{O}_2$, was not directly measured but was calculated based on experimentally measured and other known parameters. To obtain [HO$_2$], one must determine [OH], the initial concentration of photolytically produced OH, and the yield of HO$_2$ from reaction 7 and competing side reactions. The chemistry of conversion of OH to HO$_2$ is discussed in detail in a later section. Since the concentrations of HO$_2$ and OH were such that the system was optically thin at 248.5 nm, [OH]$_0$ could be calculated from the following relationship

$$\text{[OH]}_0 = \Phi_{\text{OH}} \sigma(H_2O_2,248.5 \text{ nm}, T)[H_2O_2] \text{F}$$ (1)

where $\Phi_{\text{OH}}$ is the quantum yield for OH production from 248.5-nm photolysis of $\text{H}_2\text{O}_2$, $\sigma(H_2O_2,248.5 \text{ nm}, T)$ is the absorption cross section for $\text{H}_2\text{O}_2$ at 248.5 nm and temperature $T$, and $\text{F}$ is the laser photon fluence. The determination of each factor in eq 1 is discussed in detail below. $\Phi_{\text{OH}}$: It is known8 that $\Phi_{\text{OH}} = 2$.

$$\sigma(H_2O_2,248.5 \text{ nm}, T)$$: The absorption cross section for $\text{H}_2\text{O}_2$ at 248.5 nm is known to be $8.8 \times 10^{-20} \text{ cm}^2$ at 298 K.8 We have recently measured temperature-dependent absorption cross sections for hydrogen peroxide over the wavelength range 193-350 nm.12 At 248.5 nm, the following expression describes the observed temperature dependence (units are cm$^2$ molecule$^{-1}$):

$$\sigma(H_2O_2,248.5 \text{ nm}, T) = 1.023 \times 10^{-18} \text{exp}(-45 \pm 20)/T$$ (2)

$[\text{H}_2\text{O}_2]$: Hydrogen peroxide can be lost in the slow-flow system either by decomposition (particularly at higher temperatures) or by condensation (at lower temperatures). To ensure that the H$_2$O$_2$ concentration in the reactor was known, we monitored H$_2$O$_2$ by UV photometry before the gas mixture entered the reactor and after the gas mixture exited the reactor. The absorption cells were 216.2 and 90.0 cm in length. The monitoring wavelengths were 228.8 nm in the longer cell (Cd line) and 202.6 nm in the shorter cell (Zn$^+$ line). Both cells were kept at ambient temperature, and the absorption at these wavelengths was never more than a few percent. At 391 K, the highest temperature at which experiments were performed, 15–20% of the H$_2$O$_2$ was lost upon traversal of the reactor. The H$_2$O$_2$ concentration in the reaction zone was always taken to be the temperature-corrected average of the concentrations measured in the two absorption cells. Under our experimental conditions, absorption by ozone was negligible compared to absorption by H$_2$O$_2$ at 202.6 nm. At 228.8 nm, ozone made a small but significant contribution to the total absorbance. Care was taken to ensure that [O$_2$] was constant during the $I_0$ and $I_2$ measurements required for the [H$_2$O$_2$] determination.

(9) Volman, D. H. Adv. Photochem. 1963, 1, 43
(12) Nicovich, J. M.; Wine, P. H., to be submitted for publication.
F. The photolysis laser beam was made spatially uniform through use of a segmented aperture optical integrator. Virtually the whole cross-sectional area of the cell was irradiated, and the depth of focus of the integrated beam was such that radical concentrations were nearly uniform down the entire length of the cell. The laser beam fluence was measured as the beam exited the reactor by using an EG&G photodiode based radiometer capable of measuring individual pulses. Pulse-to-pulse stability, a requirement for signal averaging in this type of experiment, was found to be very good. Only an occasional pulse energy deviated from the average by more than ±5%. In order to avoid having to correct the measured fluence for reflection off the back window, an antireflection coated window with >99.9% transmission at 248.5 nm was employed. The radiometer was calibrated by using a novel ozone actinometry method which has been described in detail previously.

As mentioned above, all experiments were carried out under slow-flow conditions. The linear flow velocity through the reactor was typically 12 cm s⁻¹, and the laser repetition rate was typically 0.4 Hz. The reactor was 23 cm in length, so the reactor volume was completely replenished with a fresh gas mixture between laser pulses. All experiments employed nitrogen as the buffer gas at a total pressure of 80 Torr. Data were obtained over the temperature range 266–391 K. The temperature range was limited at the low end by the vapor pressure of H₂O₂ and at the high end by the thermal instability of H₂O₂.

The gases used in this study had the following stated minimum purities: N₂, 99.999%; O₂, 99.99%. Hydrogen peroxide was 90 wt % in water. It was concentrated further by bubbling N₂ through the sample for several days before experiments were undertaken and continuously during the course of the experiments. To prevent significant decomposition of H₂O₂, all components traversed by H₂O₂ between the bubbler and the exit from the last absorption cell were Pyrex or Teflon with the exception of a few stainless steel fittings. The needle valve and flowmeter in the H₂O₂ line were positioned so that N₂ flowed through these components before entering the bubbler. Ozone was prepared by passing O₂ through a commercial ozonator and was stored on silica gel at 197 K. Before use it was degased at 77 K to remove O₃. Dilute O₃/N₂ mixtures were prepared in 12-L Pyrex bulbs for use in experiments.

A typical experiment was initiated by flowing (3–10) × 10¹² O₃ molecules cm⁻³ in 80 Torr of N₂ through the reactor and absorption cells. J₀ and Jₚ the intensities of 228.8- and 202.6-nm light transmitted through the absorption cells, were measured. Next, H₂O₂ was introduced into the gas flow, the N₂ flow was reduced so the total flow rate and total pressure were the same after addition of H₂O₂ as before addition of H₂O₂, and J₀ and Jₚ, the reduced intensities of 228.8- and 202.6-nm light transmitted through the reactor, were measured. Using the measured values of L₀, J₀, Jₚ and Jₚ we calculated the concentration of H₂O₂ in the gas stream entering and exiting the reactor; it ranged from (2-6) × 10¹⁵ molecules cm⁻³. J₀ and Jₚ were continuously monitored during the course of an experiment. The multichannel analyzer was pretriggered before the photolysis laser fired to obtain the background count rate. The concentration of O(P) was monitored as a function of time after the photolysis pulse. A total of 50–200 laser shots were averaged to obtain one pseudo-first-order kinetic decay. The fluorescence of each laser pulse was measured by using the radiometer and a calibrated aperture. The laser fluorescence was varied at constant [O₃] and [H₂O₂] to obtain pseudo-first-order decays as a function of [H₂O₂]. Five to ten fluorescence values were employed to determine each bimolecular rate constant, kᵣ, from the slope of a kᵣ vs. [H₂O₂] plot (kᵣ = the O(P) pseudo-first-order decay rate). After the fluorescence variations were completed, the H₂O₂ flow was turned off, the total pressure and total flow rate were readjusted, and J₀ and Jₚ were remeasured. All H₂O₂ concentrations employed in the kᵣ determinations were in the range (0.15–8.5) × 10¹³ molecules cm⁻³. It should be noted that, in a series of runs involving variation of the laser fluence at constant [O₃] and [H₂O₂], the ratio [OH]/[O(P)]₀ is not altered; to change this ratio, the composition of the reaction mixture must be varied.

Results and Discussion

In the absence of competing side reactions which affect the HO₂ concentration, the kinetic system is inherently pseudo-first-order; i.e., all HO₂ lost via reaction 1 is rapidly regenerated via reaction 7. However, as will be discussed in detail below, the importance of certain side reactions is suppressed when [HO₂] >> [O(P)]. Most of our experiments were carried out under experimental conditions where [HO₂] = 10[O(P)]₀, although this ratio was varied as a check on the kinetic model used to extract kᵣ. At low temperature, where relatively low HO₂ concentrations had to be employed, the HO₂ to O(P) ratio was typically somewhat lower than that employed at higher temperatures.

Photolytically produced O(P) can be lost via the following (pseudo) first-order processes:

\[ O(P) + HO₂ \rightarrow OH + O₂ \]  

\[ O(P) + HO₂ \rightarrow OH + HO₂ \]  

\[ O(P) + O₃ \rightarrow O₃O₂ \]  

O(P) → loss by diffusion from the detector field of view and reaction with background impurities

Under our experimental conditions, reaction 1 dominated O(P) removal except at very low HO₂ levels. Reaction 10 was of negligible importance while reaction 9 was minor but not negligible, k₉ was determined to be ~5 s⁻¹. Orders of magnitude slower than k₉[HO₂] under most experimental conditions.

In the absence of competing side reactions which affect the concentrations of O(P) or HO₂, removal of O(P) should obey first-order kinetics

\[ \ln \frac{[O(P)]₀}{[O(P)]} = (k₁[HO₂] + k₉)t = k₁' \text{exp}(t) \]  

where

\[ k₁' = k₁[HO₂] + k₉[O₃] \]
Temperature Dependence of the $O + HO_2$ Rate Coefficient

**Figure 3.** Typical plots of $k'_\text{exp}$ vs. [OH]$_0$ (open circles) and $k'_\text{c}$ vs. [HO$_2$]$_\text{max}$ (closed circles). Experimental conditions: $T = 281$ K, $P = 80$ Torr, [H$_2$O] = 3.9 x 10$^{12}$ molecules cm$^{-2}$, [O$_3$] = 6 x 10$^{12}$ molecules cm$^{-2}$. The dashed line is obtained from a linear least-squares analysis of the $k'_\text{exp}$ vs. [OH]$_0$ data and gives the "uncorrected" rate coefficient ($5.24 \pm 0.38$) x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The solid line is obtained from a linear least-squares analysis of the $k'_\text{c}$ vs. [HO$_2$]$_\text{max}$ data and gives the "corrected" rate coefficient ($6.15 \pm 0.54$) x 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

**TABLE I: Reaction Set for Computer Simulations**

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient$^{a}$</th>
</tr>
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<tbody>
<tr>
<td>O + HO$_2$ $\rightarrow$ O + H$_2$O</td>
<td>$k_1 = 3 \times 10^{-11}$ exp$(200/7)$</td>
</tr>
<tr>
<td>O + HO$_2$ $\rightarrow$ H + O$_2$</td>
<td>$k_2 = 2.2 \times 10^{-11}$ exp$(117/7)$</td>
</tr>
<tr>
<td>H + O$_2$ $\rightarrow$ OH + O</td>
<td>$k_3 = 1.4 \times 10^{-10}$ exp$(-470/7)$</td>
</tr>
<tr>
<td>OH + HO$_2$ $\rightarrow$ HO + H$_2$O</td>
<td>$k_4 = 3.1 \times 10^{-12}$ exp$(-187/7)$</td>
</tr>
<tr>
<td>O + HO$_2$ $\rightarrow$ OH + HO$_2$</td>
<td>$k_5 = 1.4 \times 10^{-12}$ exp$(-2000/7)$</td>
</tr>
<tr>
<td>O + O$_2$ $\rightarrow$ O$_2$</td>
<td>$k_6 = 8 \times 10^{-10}$ exp$(-2600/7)$</td>
</tr>
<tr>
<td>O $\rightarrow$ loss</td>
<td>$k_7 = 5 \times 10^{-11}$</td>
</tr>
<tr>
<td>OH + HO$_2$ $\rightarrow$ O$_2$ + H$_2$O</td>
<td>$k_8 = 1.7 \times 10^{-11}$ exp$(416/7) + 3 \times 10^{-11}$[M] exp$(500/7)$</td>
</tr>
<tr>
<td>HO + HO$_2$ $\rightarrow$ H$_2$O + O$_2$</td>
<td>$k_9 = 2.3 \times 10^{-12}$ exp$(900/7) + 1.7 \times 10^{-13}$[M] exp$(1000/7)$</td>
</tr>
<tr>
<td>HO$_2$ $\rightarrow$ loss</td>
<td>$k_{10} = 5 \times 10^{-11}$</td>
</tr>
<tr>
<td>HO$_2$ + OH $\rightarrow$ OH + 2O</td>
<td>$k_11 = 1.4 \times 10^{-14}$ exp$(-580/7)$</td>
</tr>
<tr>
<td>H + HO$_2$ $\rightarrow$ 2OH</td>
<td>$k_12 = 6.4 \times 10^{-13}$ exp$(0/7)$</td>
</tr>
</tbody>
</table>

*All rate coefficients are taken from ref 9 except $k_7$, which was measured and $k_{11}$, which was set equal to $k_7$. All rate coefficients except $k_7$ and $k_{11}$ are in units of cm$^3$ molecule$^{-1}$ s$^{-1}$.

Figure 2 shows typical plots of ln [O(3P)] vs. $t$. Equation III does indeed appear to be obeyed. If side reactions were unimportant, the bimolecular rate coefficient would be obtained from the slope of a $k'_\text{exp}$ vs. [OH]$_0$ plot, such as shown in Figure 3.

**Secondary Chemistry.** In the paper describing our 298 K study (Secondary Chemistry), a series of computer simulations were carried out where the temporal profiles of key species were produced via processes such as reaction 13 has occurred, to [OH]$_0$. Representative correction curves are plotted in Figure 4. For the 101 experiments used in the $k'_\text{c}$ determinations, the average value for [HO$_2$]$_\text{max}/[O(3P)]_0$ was 0.947 while the minimum value under any set of experimental conditions was 0.845.

As pointed out above, loss of O(3P) via reactions 1 and 9–11 occurs on a time scale which is long compared to the time scale for HO$_2$ formation. Hence, if the concentration of HO$_2$ were constant over the time period of O(3P) removal, $k_7$ could be obtained from the slope of a $k'_\text{exp}$ vs. [HO$_2$]$_\text{max}$ plot. Unfortunately, small but significant time variation of [HO$_2$]$_\text{max}$ can result from the occurrence of reactions 9, 13, and 14. Reactions 9 and 14 are most important at low laser fluences, i.e., low [HO$_2$]. Reaction 9 is strongly temperature dependent and increases in importance at high temperature. Reaction 9 is also a more important source of HO$_2$ when [OH]$_0$/[O(3P)]$_0$ is relatively low. Reaction 13 becomes an important HO$_2$ removal mechanism at relatively high HO$_2$ concentrations. To avoid large corrections for HO$_2$ loss via reaction 13, all experiments were carried out with [HO$_2$]$_\text{max} < 9 \times 10^{12}$ molecules cm$^{-2}$ and all data analyses were restricted to two 1/e times of O(3P) decay, i.e., no data where [O(3P)]/[O(3P)]$_0 < 0.13$ were used in the data analysis. Computer simulations were carried out under a variety of experimental conditions which were expected to play very minor roles in the O(3P) and HO$_2$ kinetics were included in the mechanism. The complete sets of reactions and rate coefficients used in the simulations are given in Table I.

Reaction 12 competes with reaction 7 during the period immediately after the laser pulse when OH is being converted to HO$_2$. Each time reaction 12 occurs, two HO$_2$ radicals are lost which would otherwise have been present to react with O(3P). Reaction 12 is most important at high laser fluence, i.e., high fluences.
TABLE II: Summary of Our O + HO₂ Kinetic Data

<table>
<thead>
<tr>
<th>T, K</th>
<th>no. of</th>
<th>[H₂O₂], 10⁻²⁰ cm⁻³</th>
<th>[OΗ]₀/[Ο]₀</th>
<th>range of</th>
<th>k', 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, 96 = 2°C</th>
<th>range of</th>
<th>k, 10⁻¹¹ cm³ molecule⁻¹ s⁻¹,</th>
<th>uncorrected</th>
<th>corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>266</td>
<td>6</td>
<td>2.98</td>
<td>5.0</td>
<td>100–268</td>
<td>5.22 ± 0.51</td>
<td>298</td>
<td>5.22 ± 0.39</td>
<td>7.00 ± 0.70</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>6</td>
<td>2.37</td>
<td>6.8</td>
<td>28–209</td>
<td>5.92 ± 0.39</td>
<td>298</td>
<td>5.92 ± 0.39</td>
<td>7.14 ± 0.52</td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>6</td>
<td>3.90</td>
<td>11</td>
<td>57–608</td>
<td>5.58 ± 0.54</td>
<td>298</td>
<td>5.58 ± 0.54</td>
<td>6.60 ± 0.75</td>
<td></td>
</tr>
<tr>
<td>354</td>
<td>6</td>
<td>2.05</td>
<td>6.8</td>
<td>54–188</td>
<td>5.24 ± 0.58</td>
<td>298</td>
<td>5.24 ± 0.58</td>
<td>6.15 ± 0.54</td>
<td></td>
</tr>
<tr>
<td>399</td>
<td>7</td>
<td>3.81</td>
<td>6.9</td>
<td>32–293</td>
<td>5.51 ± 0.73</td>
<td>298</td>
<td>5.51 ± 0.73</td>
<td>6.34 ± 0.73</td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>6</td>
<td>5.46</td>
<td>13</td>
<td>66–358</td>
<td>4.81 ± 0.52</td>
<td>298</td>
<td>4.81 ± 0.52</td>
<td>5.69 ± 0.56</td>
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</tr>
<tr>
<td>328</td>
<td>8</td>
<td>3.07</td>
<td>8.0</td>
<td>66–326</td>
<td>5.44 ± 0.24</td>
<td>298</td>
<td>5.44 ± 0.24</td>
<td>6.28 ± 0.09</td>
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</tr>
<tr>
<td>354</td>
<td>8</td>
<td>3.90</td>
<td>16</td>
<td>55–418</td>
<td>5.14 ± 0.45</td>
<td>298</td>
<td>5.14 ± 0.45</td>
<td>5.86 ± 0.34</td>
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<tr>
<td>359</td>
<td>5</td>
<td>4.63</td>
<td>15</td>
<td>92–168</td>
<td>4.52 ± 0.69</td>
<td>298</td>
<td>4.52 ± 0.69</td>
<td>5.11 ± 0.70</td>
<td></td>
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<tr>
<td>374</td>
<td>8</td>
<td>4.62</td>
<td>15</td>
<td>75–361</td>
<td>4.40 ± 0.40</td>
<td>298</td>
<td>4.40 ± 0.40</td>
<td>4.87 ± 0.43</td>
<td></td>
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<tr>
<td>380</td>
<td>9</td>
<td>4.71</td>
<td>19</td>
<td>72–466</td>
<td>5.11 ± 0.39</td>
<td>298</td>
<td>5.11 ± 0.39</td>
<td>5.63 ± 0.40</td>
<td></td>
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<tr>
<td>391</td>
<td>8</td>
<td>3.94</td>
<td>11</td>
<td>111–438</td>
<td>4.87 ± 0.32</td>
<td>298</td>
<td>4.87 ± 0.32</td>
<td>5.28 ± 0.38</td>
<td></td>
</tr>
</tbody>
</table>

*Experiment = determination of one pseudo-first-order rate coefficient. *Errors represent precision only. *Obtained from the slopes of k' vs. [OH]₀ plots. *Obtained from the slopes of k' vs. [HO₂]max plots.

<table>
<thead>
<tr>
<th>T, K</th>
<th>range of</th>
<th>exp! method</th>
<th>exp! conditions</th>
<th>A</th>
<th>E/R. K</th>
<th>k, (298 K)*</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.0</td>
<td>He</td>
<td>DFLMR</td>
<td>rative to k₁</td>
<td>2.7 ± 0.1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>0.8–2.3</td>
<td>He</td>
<td>DF-LMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>3.7 ± 1.1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>2.8–3.4</td>
<td>He</td>
<td>DF-LMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>4.2 ± 1.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>3.7–5.5</td>
<td>He</td>
<td>DFLMR/ESR</td>
<td>relative to k₂</td>
<td>3.0 ± 0.9</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>1200</td>
<td>Ar/H₂O₂</td>
<td>PR-UVA</td>
<td>k₁ extracted by modeling complex chemistry</td>
<td>7 ± 2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>1200</td>
<td>He</td>
<td>DFLMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>5.4 ± 0.9</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>1200</td>
<td>He</td>
<td>DFLMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>6.1 ± 0.4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.0–4.0</td>
<td>He</td>
<td>DFLMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>5.2 ± 0.8</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>266–391</td>
<td>80</td>
<td>N₂</td>
<td>DFLMR/ESR</td>
<td>[O(3P)] &gt;&gt; [HO₂]</td>
<td>2.9 ± 0.7</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

*DF, discharge flow; LMR, laser magnetic resonance; ESR, electron spin resonance; PR, pulsed radiolysis; UVA, ultraviolet absorption; R.F, resonance fluorescence; LIF, laser-induced fluorescence; PLP, pulsed laser photolysis; R.A., resonance absorption. *Units are 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. *k₁, recalculated with presently recommended (ref 9) values for the reference reactions. *Corrected downward from reported value by 1.3% to account for small change in recommended HO₂ absorption cross section.

Conditions. The first two I/6 times of the slightly noneponential computer generated O(3P) temporal profiles were least squares fit to an exponential decay to obtain k', the simulated decay rate. The simulated decay rates were then compared to the "real" decay rates, k', to obtain a set of correction curves, some of which are shown in Figure 5. The first two I/6 times of each experimental O(3P) temporal profile were least squares fit to eq III to obtain k', uncorrected. A corrected value of k' was then computed from the expression

\[ k' = k'_{uncorrected} \times \left( \frac{1}{k'/k'} \right) \]  

One source of uncertainty in the computer simulations concerns the fact that k₁ was not measured; it was estimated that k₁ = k₁ = 5 s⁻¹. Lack of knowledge of the exact value of k₁ increases the uncertainty in the k'/k' factors at low concentrations of HO₂. The low [HO₂] data are relatively unimportant in defining k₁, so the uncertainty in k₁ makes only a minor contribution to the overall uncertainty in k'. For the 101 experiments used in the k₁(T) determinations, the average value of k'/k' was 1.06 and the maximum value under any set of experimental conditions was 1.18.

As discussed above, k₁ values corrected for secondary chemistry were obtained from the slopes of plots of k' vs. [HO₂]max. Typical data are shown in Figure 3. For all 15 rate coefficients measured, the corrected k₁ values were larger than the values which would have been obtained from plots of k' vs. [OH]₀ (see Figure 3, for example). The magnitude of the secondary chemistry corrections was largest at the lowest temperatures. For the 15 rate coefficients reported, the average difference between the corrected and uncorrected bimolecular rate coefficients was 16% while the largest difference was 26%.

Summary of Results. The experimental results are summarized in Table II. Errors quoted for individual "corrected" k₁ determinations are ±2e and refer only to the precision of the k' vs. [HO₂]max data. The absolute accuracy of our k₁ determinations is limited not only by precision but also by uncertainties in measurement of the laser photon fluences (F), the HO₂ concentration, the correction factor used to obtain [HO₂]max from [OH]₀, the correction factor used to obtain k' from k' (i.e., k'/k'), and unidentified systematic errors. We estimate the pertinent 2σ uncertainties to be as follows: F, 10%; [HO₂], 5%; [HO₂]max/[OH]₀, 5%; k₁/k' = 10% at 298 K and above; unidentified systematic errors, 5%. Precision did not appear to be temperature dependent and averaged 9%. Hence, the absolute accuracy of an individual k₁ determination is estimated to be ± 1-2% at 298 K and above.

An Arrhenius plot of our results is shown in Figure 6. An unweighted linear least-squares analysis of the In k₁(T) vs. 1/T data gives the following expression (units are cm² molecule⁻¹ s⁻¹)

\[ k₁(T) = (2.91 ± 0.70) \times 10⁻¹¹ \exp[(228 ± 75)/T] \]

The uncertainties quoted in the above expression are 2σ and represent precision only.

Comparison with Previous Work. Our results are compared with those reported by other investigators in Table III. The 298 K value reported in this paper is identical with our previously reported value and at the upper end of the group of recent direct determinations which span the range (5.2–6.2) x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Other than our studies, the other recent direct measurements all employed low-pressure discharge flow systems.
all measured not only O(3P) but also HO2 (either directly or indirectly by conversion to OH), and all carefully considered the role of competing side reactions. Hence, there is no obvious reason to prefer one value over another. The early work of Burrows et al. and Hack et al. give \( k_1(298 \text{ K}) \) values which are considerably lower than those reported in ref 4-7. Possible reasons for the apparently erroneous results reported in ref 1 and 2 are discussed elsewhere. Lii et al. obtained a value for \( k_1 \) by comparing computer simulations with \( \text{H}_2 \text{O}_2 \) and \( \text{CH}_2 \text{O} \) concentration profiles observed following pulsed radiolysis of \( \text{O}_2-\text{H}_2-\text{Ar} \) mixtures. Their reported rate coefficient agrees well with our results. However, as pointed out by Keyser, the experimental data of Lii et al. are very insensitive to the value of \( k_1 \); hence, their error limits should be \( \sim 500\% \) rather than the reported 30%.

Very little temperature-dependent data are available for reaction 1. Values for \( k_1 \) of \( 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 1600 K10 and \( 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 1050 K16 have been inferred from flame studies. The only previous temperature dependence study in the atmospheric temperature regime is that of Keyser. As seen from the comparisons in Table III and Figure 6, our results are in excellent agreement with those of Keyser. Since our experiments were very different in methodology from Keyser's and are subject to different sources of systematic errors, the uncertainty of \( k_1(T) \) for atmospheric modeling purposes is now greatly reduced. Keyser's study employed helium buffer gas at a pressure of 1.0 Torr while our study employed nitrogen buffer gas at a pressure of 80 Torr. Thus, agreement between the two studies strongly suggests that \( k_1 \) is independent of pressure over the relevant upper atmospheric temperature and pressure ranges.

Reaction 1 could proceed via a hydrogen abstraction mechanism (1a) or via formation of an energized HOOCO "pseudo-intermediate" (1b):

\[
\begin{align*}
O + \text{H}_2\text{O}_2 &\rightarrow \text{OH} + \text{OH}_2 \\
O + \text{O}_2\text{H} &\rightarrow \text{O} + \text{O}_2 + \text{OH}
\end{align*}
\]

Implications for Atmospheric Chemistry. Model calculations of OH and HO2 concentration profiles in the upper stratosphere are very sensitive to the choice of \( k_1(T) \). Kaye and Jackman, considering both sensitivity of their model to various parameters and uncertainties in these parameters, have concluded that the uncertainty of \( k_1 \) contributes more to the uncertainty in [OH] and [HO2] at 35° N, 40-km altitude than any parameter in their model except \( k_{12} \). The currently recommended value4 for \( k_1(T) \) is

\[
k_1(T) = 3 \times 10^{-11} \exp[(200 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

The results reported in this paper will have little effect on the recommended \( A \) factor and activation energy but will substantially reduce the uncertainty in the above expression; this will, in turn, significantly reduce the overall uncertainty in model calculations of upper stratospheric OH and HO2 concentrations and facilitate meaningful comparisons of stratospheric measurements with photochemical models.

Jackman et al.23 have recently compared O3 concentrations at 5° N and 43-km altitude measured by LIMS (limb infrared monitor of the stratosphere) with those calculated from a photochemical model using LIMS measurements of \( \text{H}_2\text{O}, \text{HNO}_3, \) and \( \text{NO}_2 \) and temperature and SAMS (stratospheric and mesospheric sounder) measurements of \( \text{CH}_4 \) as input. The model predicted lower O3 levels than those actually observed. A sensitivity analysis showed that the overall uncertainty in the model calculation was a factor of 1.7, about the same magnitude as the discrepancy between model and measurement. Of the many parameters used in the model, the uncertainty of \( k_1 \) was found to make the sixth largest contribution to the overall uncertainty of the calculation. Our results will therefore result in a small but significant reduction in the model uncertainty.

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