NASA Contractor Report 3007

A Kinetics Investigation of Several Reactions Involving Chlorine Containing Compounds

Douglas D. Davis

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A Kinetics Investigation of Several Reactions Involving Chlorine Containing Compounds

Douglas D. Davis
University of Maryland
College Park, Maryland

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I. INTRODUCTION

Within the last two and one-half years, one of the major environmental questions which has emerged involves the potential long-term impact of anthropogenic emissions of halogenated hydrocarbons on stratospheric ozone levels. This basic hypothesis was first put forward by Rowland and Molina in 1974, and was based on the observations of Lovelock (1971, 1973, 1974) and Wilkniss, et al. (1973), who had measured the levels of Fluorocarbons 11 and 12 at several different locations around the globe. Because the total source inventory for these two compounds appeared close to the calculated total tropospheric burden, Rowland and Molina suggested that these species must be very long-lived in the troposphere. It was suggested, in fact, that the principal mode of degradation for these molecules would be that of photolysis in the stratosphere. The release of chlorine atoms in this region of the atmosphere could then trigger a simple two-step catalytic cycle which, for each complete cycle, would destroy two-odd oxygen species (O and O_3):

(1) $Cl + O_3 \rightarrow ClO + O_2$

(2) $\underline{ClO + O(^3P) \rightarrow Cl + O_2}$

net rx. $O(^3P) + O_3 \rightarrow 2O_2$

Suffice it to say that there are numerous other parallel and competing processes operating in the stratosphere, all of which tend to decrease the efficiency of the catalytic cycle (1) - (2) [see Figure 1].

Since the first publication by Rowland and Molina, several other atmospheric modeling groups have now expanded upon the original stratospheric chlorine-model to further test the validity of the early predictions (Crutzen, 1974, 1976; Wofsy, et al. , 1975; Cicerone, et al., 1974; and Chang and Wuebbles, 1976). At the present time, the two fundamental questions which continue to demand further investigation are: [1] how efficiently do chlorine-containing compounds whose source is in the troposphere reach the stratosphere where Cl atoms can be released? And, [2] once chlorine atoms are released in the stratosphere, how efficiently does the chlorine catalytic cycle (1) and (2) operate? The second of these questions will provide the principal focal point of this report.

Certain commercial materials are identified in this paper in order to specify adequately which materials were investigated in the research effort. In no case does such identification imply recommendation or endorsement of the product by NASA, nor does it imply that the materials are necessarily the only ones or the best ones available for the purpose.

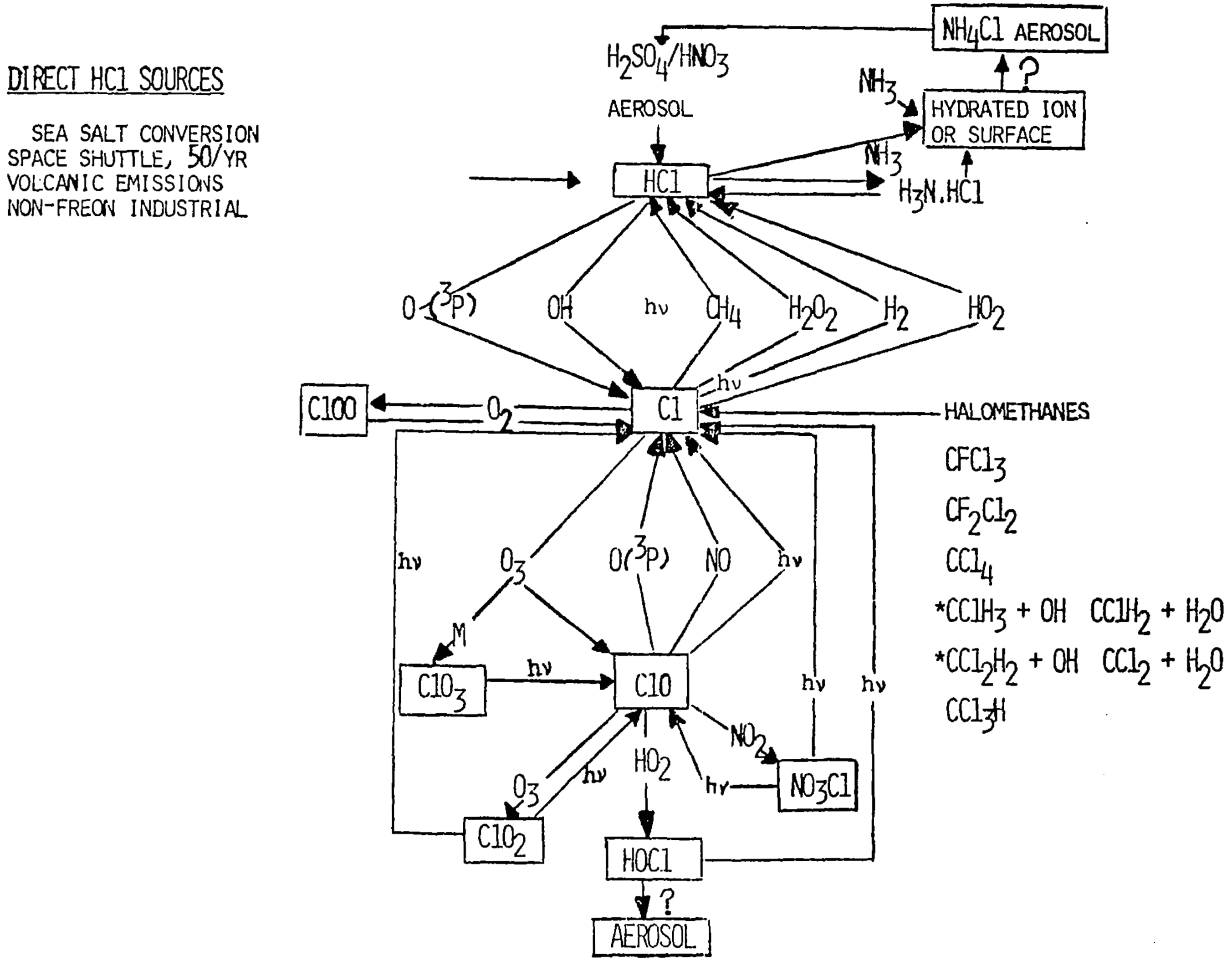

FIG. 1 STRATOSPHERIC CHLORINE CHEMISTRY

II. SUMMARY OF RESULTS

Summarized in Table I are 18 chemical and photochemical processes for which data have been generated during the first 32 months of NASA grant (NG-1031). A detailed discussion on most of the systems listed has been presented in Sections II.B(1) - II.B(5).

TABLE 1

REACTION SYSTEM	STATUS	METHOD	TEMP. RANGE(°K)	RATE CONSTANT$(cm^3 molec^{-1} s^{-1}$
(1) $Cl + CH_4 \rightarrow CH_3 + HCl$	Final	FPRF	219-350	$k = (7.44 \pm .75) \times 10^{-12}$ $\exp-(2437 \pm 110/RT)$
(2) $Cl + H_2 \rightarrow HCl + H$	Final	FPRF	213-350	$k = (1.01 + .06) \times 10^{-10}$ $\exp-(5106 \pm 180/RT)$
(3) $Cl + H_2O_2 \rightarrow HCl + HO_2$	Final	FPRF	300	$k = 5.8 \times 10^{-13}$ ± factor of two
(4) $Cl + O_3 \rightarrow ClO + O_2$	Final	FPRF	220-350	$k = (3.08 \pm .30) \times 10^{-11}$ $\exp - (576 \pm 60/RT)$
(5) $OH + CH_3Cl \rightarrow H_2O + CH_2Cl$	Final	FPRF	240-400	$k = (1.58 \pm .16) \times 10^{-13}$ $\exp - (2098 \pm 120/RT)$
(6) $OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	Final	FPRF	243-375	$k = (4.31 \pm .48) \times 10^{-12}$ $\exp - (2046 \pm 160/RT)$
(7) $OH + CHCl_3 \rightarrow H_2O + CCl_3$	Final	FPRF	245-375	$k = (4.69 \pm .51) \times 10^{-12}$ $\exp - (2268 \pm 214/RT)$
(8) $OH + CH_3Br \rightarrow H_2O + CH_2Br$	Final	FPRF	244-350	$k = (8.25 + .91) \times 10^{-12}$ $\exp - (1800 \pm 100/RT)$
(9) $OH + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$	Final	FPRF	245-375	$k = (3.72 \pm .31) \times 10^{-12}$ $\exp -(3250 \pm 140/RT)$
(10) $OH + C_2Cl_4 \rightarrow$ Product	Prelim.	FPRF	260-375	$k = (1.06 \pm .18) \times 10^{-11}$ $\exp - (2590 \pm 300/RT)$
(11) $OH + C_2HCl_3 \rightarrow$ Product	Prelim.	FPRF	300	$k = (2.35 \pm .25) \times 10^{-12}$
(12) $OH + HCl \rightarrow H_2O + Cl$	Final	FPRF	250-402	$k = (3.3 \pm .3) \times 10^{-12}$ $\exp - (937 \pm 78)/RT$
(13) $O(^3P) + HCl \rightarrow OH + Cl$	Final	FPRF	350-450	$k = (5.2 \pm .91) \times 10^{-11}$ $\exp - (7510 \pm 748/RT)$
(14) $HCl + NH_3 \xrightarrow{M} NH_4Cl$	Final	SFMS	300	$< 10^{-34} cm^6 molec^{-3} s^{-1}$

FPRF - Flash Photolysis Resonance Fluorescence   SFMS - Stop Flow - Mass Spectrometry

TABLE 1 (Continued)

	REACTION SYSTEM	STATUS	METHOD	TEMP. RANGE (K)	RATE CONSTANT(cm3molec^{-1}s^{-1})
(15)	$ClONO_2 + O(^3P) \rightarrow$ Products	Final	FPRF	245	$(2.0 \pm .2) \times 10^{-13}$
(16)	$ClONO_2 + OH \rightarrow$ Products	Final	FPRF	245	$(3.7 \pm .2) \times 10^{-13}$
(17)	$ClONO_2 + Cl(^2P_{3/2}) \rightarrow$ Products	Prelim.	FPRF	245	$\sim 1 \times 10^{-13}$
(18)	$O_3 + h\nu \rightarrow O(^1D) + O_2$	Final	LFP	300	

see discussion later
in text for higher
resolution results
(Sec. II. B-5)

λ(nm)	ϕ
294.0	1.0
300.0	1.0
305.0	.87
308.0	.59
310.0	.34
313.0	.121
314.0	.09
316.0	.02

LFP - Laser Flash Photolysis

III. DETAILED DISCUSSION OF COMPLETED WORK

(1) A Kinetics Study of Several Key Stratospheric Chlorine Atom Reactions.

A temperature dependence kinetics study of the reactions of $Cl(^2P_{3/2})$ with O_3, CH_4, and H_2O_2*

R. Watson, G. Machado, S. Fischer, and D. D. Davis

Atmospheric Sciences Division, Applied Sciences Laboratory, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332

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The technique of flash photolysis–resonance fluorescence has been utilized to study the temperature dependences of two chlorine atom reactions of considerable fundamental importance to stratospheric chemistry. These reactions have been studied using a wide range of experimental conditions to insure the absence of complicating secondary processes. The reactions of interest with their corresponding rate constants are expressed in units of $cm^3 molecule^{-1} s^{-1}$: $Cl+O_3 \xrightarrow{k_1} ClO+O_2$, $\Delta U^{\circ}_{298} = -164$ kJ mol^{-1}, $k_1 = (3.08 \pm 0.30) \times 10^{-11} \exp[-(576 \pm 60/RT)]$, (220–350) K; $Cl+CH_4 \xrightarrow{k_2} CH_3+HCl$, $\Delta U^{\circ}_{298} = +6.4$ kJ mol^{-1}, $k_2 = (7.44 \pm 0.75) \times 10^{-12} \exp[-(2437 \pm 110/RT)]$, (218–401) K. In addition, the following reaction was studied at 300 K: $Cl+H_2O_2 \xrightarrow{k_3} HCl+HO_2$, $\Delta U^{\circ}_{298} = -56.8$ kJ mol^{-1}, $k_3 \simeq 5.8 \times 10^{-13}$ (±factor 2.0), 300 K. A direct implication of the new rate data is the need to revise downward by a factor of 2.4 to 3 the magnitude of the ozone perturbation predicted by earlier model calculations due to the presence of ClO_x species in the stratosphere.

INTRODUCTION

Within the past year, there have been a series of papers appearing in the literature dealing with the possible effects of the presence of chlorine containing species of natural (e.g., CH_3Cl) and anthropogenic (e.g., CF_2Cl_2) origin in the stratosphere.[1–8] It has been proposed that these contaminants, many of which have been observed in the troposphere and lower stratosphere, can photolyze or react with free radicals to produce Cl atoms or ClO radicals and thus promote the destruction of odd oxygen (odd oxygen $\equiv O\,^3P$ and O_3). The results of some model calculations predict that the presence of ClO_x ($ClO_x \equiv ClO$; HCl; Cl; OClO; ClOO) in the stratosphere at concentration levels in excess of 1 ppb (v/v) would cause a significant (> 2%) perturbation upon the integrated ozone column density. Quantitative model calculations require knowledge of the net upward flux of chlorine containing species through the tropopause, and their subsequent fate in the stratosphere, as well as accurate rate constant data for the key reactions.

The key chlorine reactions which participate in stratospheric chemistry are

$$Cl + O_3 \rightarrow ClO + O_2 \ , \qquad (a)$$

$$O + ClO \rightarrow Cl + O_2 \ , \qquad (b)$$

$$NO + ClO \rightarrow NO_2 + Cl \ , \qquad (c)$$

$$Cl + RH \rightarrow R + HCl \ , \qquad (d)$$

$$OH + HCl \rightarrow H_2O + Cl \ , \qquad (e)$$

where $RH \equiv CH_4$, H_2, H_2O_2, and HO_2. Reactions (a) and (b) are primarily responsible for the conversion of odd oxygen into molecular oxygen. It can be shown that the efficiency (ρ) of the ClO_x catalytic cycle is governed by the rate of reaction (b):

$$\rho \propto 2k_b[O][ClO] \ . \qquad (I)$$

Assuming steady state conditions for [O] and [ClO], the following alternate expression can be derived:

$$\rho \propto \frac{2k_a k_b k_e J_a [O_3]^2 [HCl][OH]}{k_d [RH]\{k_b J_a [O_3] + k_c k_f [NO][O_2][M]\}} \ , \qquad (II)$$

where J_a *is the photodissociation constant for* O_3, *and* k_f is the rate constant for the third order recombination reaction of oxygen atoms with molecular oxygen. From Eq. (II) it can be seen that the catalytic efficiency is highly dependent upon several rate constants, many of which have received only limited study.

The present work provides an absolute determination of the chlorine atom rate constants with ozone and methane over a wide range of temperature and pressure to insure that the results can be directly applied to atmospheric model calculations. In addition, a limited study of the chlorine atom plus hydrogen peroxide system was performed at 300 K to ascertain whether this reaction is important in the stratosphere. The experimental technique used in this study was that of flash photolysis–resonance fluorescence.

EXPERIMENTAL

The experimental details and operating principles of the flash photolysis–resonance fluorescence technique have been fully described in the literature.[9] Consequently, only recent modifications and essential details will be discussed.

Two reaction cells were used in this work: (1) a black anodized aluminum cell with an internal volume of ~ 850 cm^3 for methane, and (2) a Pyrex cell with an internal volume of ~ 150 cm^3 for ozone and hydrogen peroxide owing to their susceptibility to heterogeneous decomposition on metal surfaces. The cell temperature was controlled to within ± 0.5 K by flowing methanol (235–325 K) or ethylene glycol (298–400 K) from a thermostated circulating bath through the outer jackets of the reaction vessels. Temperatures below 235 K could be controlled to within ± 2 K using cooled dry N_2. An iron–constantan thermocouple was used in conjunction with a wheatstone bridge resistance box to measure temperature, with a precision of better than 0.5 K.

Atomic chlorine was produced from the flash photolysis of CCl_4 or $CF_2ClCFCl_2$ by a N_2 spark discharge lamp in the presence of a reactive reagent (e.g., CH_4, O_3, H_2O_2) and a large excess of the diluent gas He or Ar. The mechanism for CCl_4 photodecomposition has been shown to be[10]

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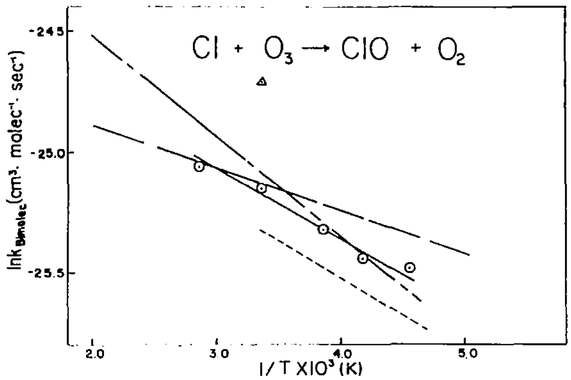

FIG. 1. Arrhenius plot for the $Cl + O_3$ reaction: △, Ref. 18; — – —, Ref. 21; —— ——, Ref. 20; ○, this work.

$$CCl_4 + h\nu\ (\lambda > 165\ \mathrm{nm}) \rightarrow CCl_3 + Cl$$
$$\rightarrow CCl_2 + 2Cl \cdot\ (Cl_2)\ .$$

The spark discharge lamp was equipped with a window made of LiF, MgF_2, sapphire, or Suprasil, depending upon the reagent present in the reaction cell. A Suprasil window was normally chosen to eliminate the production of reactive intermediates from the photodecomposition of the added reagent (i.e., $CH_4 + h\nu \rightarrow CH_2 + H_2$),[11] whose presence could lead to kinetic complications. Chlorine atoms formed in the $^2P_{1/2}$ state would have been rapidly quenched into the $^2P_{3/2}$ ground state by collision with CCl_4.[12] For chlorine atoms thermally equilibrated at 300 K, the population of the $^2P_{1/2}$ state should have been 0.8% (the $^2P_{1/2}$ state lies ~ 800 cm^{-1} above the $^2P_{3/2}$ state).

Using published absorption cross-section data for CCl_4[13] and flash energy of 80 J based on ethylene actinometry, it was calculated that typical chlorine atom concentrations of $\sim 5 \times 10^{10}$ atom cm^{-3} were produced with a CCl_4 concentration of 2×10^{15} molecule cm^{-3}. Initial chlorine atom concentrations were varied from 10^{10}–2×10^{11} atom cm^{-3} by varying the flash energy from 20–250 J ($[CCl_4] = 2 \times 10^{15}$ molecule cm^{-3}), and from 10^{10}–10^{11} atom cm^{-3} by varying $[CCl_4]$ from 3–50 $\times 10^{14}$ molecule cm^{-3} (flash energy = 80 J).

Chlorine atoms were detected using a discharge–flow chlorine resonance lamp, the gas mixture consisting of < 1% of Cl_2 in Ar. As in previous studies,[9] photon-counting electronics were used throughout this study. The linear relationship between chlorine atom concentration and the observed fluorescence intensity was established by varying the [Cl] via a variation in the flash energy over a range of a factor of 20.

Each reaction was studied using pseudo-first-order kinetic conditions, $[\mathrm{Reagent}]_0 \gg [Cl]_0$ ($[\mathrm{Reagent}]_0/[Cl]_0 \geq 600$); and as expected, the chlorine atom concentration decayed exponentially with time. Because the initial chlorine atom concentration was kept low, multiple flashes (5–200) on a single gas mixture were required to produce a single smooth kinetic decay curve. However, the number of flashes per gas mixture was limited such that the decomposition of the added reagent (CH_4, H_2O_2, O_3) was always less than 3%. In some cases, therefore, several fillings of an identical gas mixture were used to develop a single experimental decay curve.

Gas pressures of less than 6 torr were measured using an mks Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (20–800 torr) were made with a two-turn Bourdon gauge (Wallace and Tiernan type FA-145). It was estimated that the precision to which CH_4/He gas mixtures could be made was better than ~ 1%, but only ~ 3%–5% for O_3/He mixtures due to uncertainties in the determination of ozone concentration caused by (a) small but significant amounts of heterogeneous decomposition and (b) experimental error in the measurement of $[O_3]$ by uv absorption at 260 nm. The CCl_4 and CF_2Cl–$CFCl_2$ pressures could not be metered so precisely at low temperatures in the Al cell due to absorption effects on the surfaces of the reaction cell. However, an uncertainty in these quantities did not lead to any inaccuracy in the reported rate data, as these species only acted as the precursor of atomic chlorine whose absolute concentration is not required in data analysis.

The CH_4 used in this study was of two types: (a) Matheson Ultra High Purity (stated purity of 99.97%) Gold Label; this was analyzed mass spectrometrically to contain 70 ppm of C_2H_6 and 20 ppm of C_3H_8, (b) research grade (stated purity of 99.99%) which was shown to contain 20 ppm of C_2H_6 and < 5 ppm of C_3H_8 by mass spectrometric analysis. The CH_4 was thoroughly degassed in liquid N_2 (77 K) prior to use. The helium was Matheson "Gold Label Ultra High Purity" with a stated purity of 99.999%, and was used without further purification. The ozone was generated by flowing molecular oxygen through a commercial ozonizer and collected on silica gel at 196 K. Molecular oxygen was removed from the ozone by vacuum pumping the silica gel for 10–15 min. When required, the ozone was collected in a Pyrex bulb and diluted as required with He. The purity of the ozone was measured by uv spectrophotometry at 255.3 nm and was typically ~ 90% (10% O_2). The ozone cross section at 255.3 nm was taken from published data[14] to be 137 (atm at 273)$^{-1}$ cm^{-1}, base 10. Excellent agreement exists between several investigations of the published absorption cross section data for O_3 at 253.7 nm.[14,15]

RESULTS

A. $Cl + O_3 \xrightarrow{k_1} ClO + O_2$

The results for Reaction (1) are shown in Table I and Figure 1. Reaction (1) was studied under a range of temperature (218–350 K), pressure (5–40 torr) and other experimental parameters. Psuedo-first-order kinetic conditions $[O_3]_0 > [Cl]_0$, $\{[Cl]_0 \simeq 5 \times 10^{10}$ atom cm^{-3}; $[O_3]_0 \simeq (2.5$–$25) \times 10^{13}\}$ were employed so that Eq. (III) could be used to analyze the data.

$$-d[Cl]/dt = k_1[Cl][O_3] + k_{\mathrm{diffusion}}[Cl]\ ,$$
$$\ln([Cl]_0/[Cl]_t) = \{k_1[O_3] + k_{\mathrm{diffusion}}\}t\ . \qquad \mathrm{(III)}$$

TABLE I. Reaction rate data for the process $Cl + O_3 \rightarrow ClO + O_2$.

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	O_3 (mtorr)	Flash energy (J)	k_1' (s^{-1})	$k_{\text{bimolecular}} \times 10^{12}$ $cm^3 molecule^{-1} s^{-1}$)
220	5(He)	65	0.00	88	100	
			1.11		443	
			1.67		580	
			2.12		925	
			2.51		1111	
			3.13		1325	
			3.65		1570	
			4.38		1620	
			4.46		1710	
			4.70		1940	8.57 ± 0.62
239	5(He)	65	1.11	88	730	
			2.12		1075	
			3.28		1550	
			3.92		1702	
			4.33		1870	
			5.45		2425	
			6.39		2873	
			7.65		2900	8.95 ± 1.17
259	5(He)	65	0.80	88	436	
			1.24		595	
			1.67		775	
			2.09		794	
			2.45		1008	
			2.48		1111	
			3.13		1272	
			3.82		1560	
			5.27		2080	
			6.57		2590	10.04 ± 0.5
298	5(He)	65	0.82	88	442	
			1.04		601	
			1.66		740	
			1.71		691	
			2.11		935	
			2.19	20	1040	
			2.19	88	1083	
			2.19	180	928	
		20	2.19	88	1020	
		130	2.19	88	944	
		65	2.58		1048	
			3.13		1366	
			3.23		1344	
			3.44		1425	
			4.38		1818	
			4.97		2200	
			6.26		2450	11.98 ± 0.8
298	40(Ar)	65	0.00	88	40	
			1.57		547	
			2.17		696	
			3.13		1060	
			3.81		1320	
			4.18		1445	
			5.22		1984	
			7.31		2800	11.44 ± 0.50
350	5(He)	65	1.12	88	540	
			1.72		800	
			2.32		1052	
			3.00		1250	
			3.42		1465	
			4.46		1740	13.01 ± 1.0

Numerous preliminary experiments were performed to show that ozone did not decay (< 5%) due to heterogeneous decomposition on the reactor surface. The first order rate constant k_1' was determined for a particular gas mixture after the gas was allowed to reside in the reaction cell for different times (0, 2, 5, 10 min) before the experiment was initiated. After an initial "aging" period it was found that k_1' was independent of residence time. However, it was observed that there was a dependence of k_1' upon residence time if the two resonance lamps were on, indicating long term photolytic decomposition of the ozone (k_1' decreased with residence time). Consequently, the time taken to perform an experiment was limited to < 2 min to eliminate inaccuracies in the measurement of k_1' due to photolytic decomposition of the ozone. Experiments were performed which showed that there was no observable dependence of k_1' upon the flash energy or CCl_4 concentration (Table I). These experiments verified that there was no dependence of the bimolecular rate constant upon initial chlorine atom concentration, and that there was no "flash" decomposition of ozone. Experiments utilizing a variation in the number of flashes per filling of a particular gas mixture showed a decrease in k_1' as the number of flashes increased. This was not due to a regeneration of atomic chlorine, but photolytic decomposition of ozone caused by the increased length of time required to complete the experiment. Consequently the number of flashes per single filling of the reaction cell was limited to ≤ 20 (~ 90 s).

Although there was no significant (< 5%) variation of the bimolecular rate constant with total pressure, there was with temperature. A weighted (dependent upon the number of experiments and reliability of the results) least squares fit of the data was performed at each temperature to determine the bimolecular rate constant at that temperature. A weighted least squares fit of the bimolecular rate constants then produced the following Arrhenius expression:

$$k_1 = (3.08 \pm 0.30) \times 10^{-11} \exp[-576 \pm 50 \text{ cal mol}^{-1}/RT)]$$
$$(220\text{–}350 \text{ K}) .$$

A total of 60 experiments were performed where the results were used to compute the Arrhenius expression shown above. The most probable systematic error in this study is that of overestimating the ozone concentration due to a small amount of heterogeneous and/or photolytic decomposition (total < 7%).

Possible complicating secondary reactions which must be considered are

$$ClO + O_3 \rightarrow Cl + 2O_2 , \tag{1a}$$

$$ClO + O \rightarrow Cl + O_2 , \tag{1b}$$

$$Cl + O_2 + M \rightarrow ClOO + M , \tag{1c}$$

$$Cl + O_3 + M \rightarrow ClO_3 + M , \tag{1d}$$

$$Cl + Cl + M \rightarrow Cl_2 + M . \tag{1e}$$

Reactions (1a)–(1e) can be rejected for the following reasons. The rate constant for Reaction (1a) has recently been reported[16] to be $\leq 5 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, which eliminates any possibility that this reaction could regenerate atomic chlorine on the time scale of the experiment. Atomic oxygen could be formed from the photolysis of ozone or molecular oxygen (impurity in the ozone); however, the rate of reaction (b) should be dependent upon the square power of the flash energy. The observed first order rate constants showed no dependence upon flash energy, precluding the need to consider this reaction (in agreement with calculations). The absence of a pressure dependence in the bimolecular rate constant is also in agreement with calculations which indicate that complications due to reactions (c), (d), and (e) should be of negligible importance.

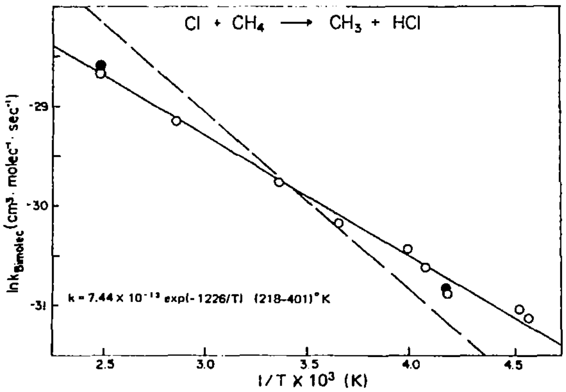

FIG. 2. Arrhenius plot for the $Cl + CH_4$ reaction. — — —, Ref. 22; ○, this work, where CCl_4 was used as the Cl atom precursor; ●, this work, where $CFCl_2CF_2Cl$ was used as the Cl atom precursor.

B. $Cl + CH_4 \xrightarrow{k_2} CH_3 + HCl$

The results of reaction (2) are presented in complete detail in Table II. This reaction was again studied using pseudo-first-order conditions, $[CH_4]_0 \gg [Cl]_0$, so that the individual plots of Cl atom decay with time could be analyzed using Eq. (IV):

$$\begin{aligned} -d[\mathrm{Cl}]/dt &= k_2[\mathrm{Cl}][\mathrm{CH_4}] + k_{\mathrm{diffusion}}[\mathrm{Cl}] , \\ \therefore \ln([\mathrm{Cl}]_0/[\mathrm{Cl}]_t) &= (k_2[\mathrm{CH_4}] + k_{\mathrm{diffusion}})t . \end{aligned} \quad \text{(IV)}$$

Reaction (2) was thoroughly studied over a range of temperature (218–401 K) and pressure (20–100 torr He; 50 torr Ar). The bimolecular rate constant k_2, and the individual pseudo-first-order rate constants k_2' (after correction due to differences in the Cl atom diffusion rates for differing total pressures and diluent gases) were found to be invariant with diluent gas pressure, and the nature of the diluent gas (Table II). These observations verify that the reaction studied was bimolecular, as expected, and that complications due to secondary processes which are third order in nature, were not important under the experimental conditions of low (~ 10^{11} atom cm^{-3}) Cl atom concentration as used in this study. Experiments utilizing variations in CCl_4 concentration (15–150 mtorr) were performed with no significant deviations in the experimental first order rate constants being observed. A series of experiments was performed at 239 and 401 K, where $CF_2ClCFCl_2$ was substituted for CCl_4 as the precursor of atomic chlorine. The concentration of $C_2F_3Cl_3$ was varied by a factor of 20 (10–200 mtorr) and the bimolecular rate constant k_2 was shown to be independent of $C_2F_3Cl_3$ concentration at each temperature, and within the expected experimental uncertainty of our results (< 10%) yielded a similar value for k_2, as the experiments where CCl_4 was used as the atomic precursor. Variations in the flash energy by a factor of ~ 12 (20–250 J) also resulted in no significant variations of the bimolecular rate constant. The observation that large variations in initial Cl atom concentration by factors of ~ 13 (1.1–14 × 10^{10} at 299 K) and ~ 34 (0.43–15 × 10^{10} at 238 K), produced by varying CCl_4 (or $C_2F_3Cl_3$) and the flash energy, resulted in no significant variation in the first order rate constants, is strong evidence that complicating secondary kinetic processes were of no importance in this study. As noted earlier, the flash lamp was equipped with either a sapphire or quartz window to prevent the photolysis of CH_4 below 140 nm, which would result in the production of CH_2 radicals whose presence in concentrations of $\geq 10^{12}$ radical cm^{-3} could cause serious kinetic complications. The experiments which were performed with a large variation in flash energy (20–245 J at 299 K, and 25–245 J at 238.5 K) showed no variation in first order rate constant, which eliminates the possibility of kinetic complications due to labile photolytic fragments reacting rapidly with atomic chlorine.

A third series of experiments was performed in which the number of consecutive flashes per single filling of a particular gas mixture was varied. At 299 and 401 K, the number of flashes per single filling was varied by a factor of 20 (5–100, and 10–200, respectively), and at 239 K by a factor of 10 (20–2000) with no significant variation in the observed first order rate constants. These experiments tend to eliminate kinetic complications due to a buildup in the concentration of a "reactive" stable product.

As stated in the experimental section of this paper, two samples of CH_4 were used in this study. The first was analyzed to contain 70 ppm of C_2H_6 and 20 ppm of C_3H_8, whereas the second contained 20 ppm of C_2H_6 and < 5 ppm of C_3H_8. There was no discernable dependence of the bimolecular rate constant on the particular tank of CH_4 used (see Fig. 2), indicating that these low impurity levels caused no inaccuracy in the reported rate data.

Whereas the bimolecular rate constant showed no variation with diluent pressure, flash energy, or initial chlorine atom concentration, it did vary significantly with temperature. A weighted least squared fit of all the data shown in Table II yields the following Arrhenius expression:

$$k_2 = (7.44 \pm 0.7_5) \times 10^{-12} \exp[-(2436 \pm 100\ \mathrm{cal\ mol^{-1}}/RT)]$$
$$(218\text{–}401\ \mathrm{K}) .$$

In summary, it can be stated that a total of ~ 180 experiments were performed using a wide range of conditions, such that the probability of the Arrhenius expression being significantly incorrect due to complicating secondary kinetic processes seems extremely low. And it should be noted from Fig. 2 that there is no observable curvature in the Arrhenius plot (to be discussed later) over the temperature range studied.

C. $Cl + H_2O_2 \xrightarrow{k_3} HCl + HO_2$

The results of Reaction (3) are shown in Table III. As in the case of Reactions (1) and (2), the study of H_2O_2 was performed using first order conditions where $[H_2O_2]_0/[Cl]_0$ ranged from 9×10^3–8×10^4. The results from the study of Reaction (3) were found to be less reproducible than would normally be acceptable, presum-

TABLE II. Reaction rate data for the process $Cl + CH_4 \rightarrow CH_3 + HCl$.

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k'_2 (s^{-1})	$k_{bimolecular} \times 10^{14}$ ($cm^3 molecule^{-1} s^{-1}$)
218	20(He)	65	0	88	25	S	40	
			50			A	82	
			100			P	135	
			150			P	200	
			200			H	271	
			250			I	355	
			300			R	400	2.98 ± 0.40
						E		
220	40(He)	65	50	88	25	Q	84	
			75			U	117	
			100			A	169	
			125			R	191	
			150			T	240	
			175			Z	272	
			200				322	3.31 ± 0.33
238.5	40(He)	65	25	88	25		94	
			31		15		95	
			31.65		25		105	
			50		25		122	
			75		25		181	
			99		35		212	
		15	100	45	50		187	
		65	100	88	50	Q	198	
			150		125	U	283	
			150		25	A	324	
			150		25	R	268	
			150	25	75	T	267	
			150	210	10	Z	301	
			150	88	150		289	
		15	150		100		253	
		65	200		50		382	
			200		50		407	
		15	200	45	100		328	
		15	200	20	100		326	
		65	200	88	50		338	
		15	200	30	100		348	
		65	200	106	100		400	3.86 ± 0.30
						Q		
239	40(He)	$10(^{TF}_{13})$	25	88	50	U	70.3	
			100			A	193	
			250		75	R	417	3.79 ± 0.09
						T		
						Z		
	40(He)	$50(^{TF}_{13})$	25	88	50		90.5	
			25				105.8	
			100				210	
			100		75		221	
			100				207	
			100	20	150	Q	203	
			100	245	20	U	240	
			160		50	A	313	
			250		75	R	450	
			250			T	467	
			250	25	150	Z	431	
			250	245	25		446	
			250	88	20		397	
			250		200		398	
			268		100		543	4.15 ± 0.50

TABLE II (*Continued*)

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k'_2 (s^{-1})	$k_{bimolecular} \times 10^{14}$ ($cm^3 molecule^{-1} s^{-1}$)
	40(He)	200($^{TF}_{13}$)	25			QUARTZ	138.9	
			100				245	
			250				483	3.81 ± 0.02 3.99 ± 0.18
245	40(He)	65	20	88	25	QUARTZ	89	
			40				137	
			60				172	
			98.5				247	4.94× 0.30
245	40(He)	65	25	88	25	QUARTZ	87	
			50				146	
			75				192	
			100				231	
			125				282	
			150				342	5.00 ± 0.26 4.97 ± 0.30
250	20(He)	65	0	88	30	SAPPHIRE	40	
			20		30		90	
			30		50		117	
			40		50		138	
			40		100		138	
			40	45	100		135	
			40	211	35		144	
			50		50		168	
			60		50		177	
			70		50		216	
			80		50		225	6.01 ± 0.29
	200(He)	65	0	88	40	SAP-PHIRE	18	
			40		75		133	
			80		100		212	6.29 ± 0.29
273	20(He)	65	20	88	50	SAPPHIRE	116	
			30				145	
			50				185	
			60				224	
			70				267	
			80				278	7.92 ± 0.98
298	20(He)	65	0	88	25	SAPPHIRE	36	
			15		50		122	
			30				180	
			45				225	
			45				230	
			60				290	
			75				331	11.90 ± 1.00
	50(Ar)	65	20	88	25	SAP-PHIRE	100	
			40				175	
			60				248	11.4 ± 0.9

TABLE II (*Continued*)

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k_2' (s^{-1})	$k_{\text{bimolecular}} \times 10^{14}$ ($cm^3 molecule^{-1} s^{-1}$)
	20(He)	65	0		25		46	
			0				46	
			15		50		123	
			30			SAPPHIRE	180	
			30		5		196	
			30	45	100		188	
			30	215	20		174	
			45	88	25		240	
			45				232	
			45		100		218	
			60		25		290	
			60				282	
			60		100		300	
			75		25		330	
			90				408	
			90				380	11.50 ± 0.60
	200(He)	65	0	88	30	SAP-	31	
			30		100	PHIRE	151	12.4 ± 2.0
	40(He)	65	0	88	25		45	
			15			QUARTZ	103	
			30				165	
			45				220	
			60				280	
			90				383	
			120				495	11.4 ± 0.2
299	40(He)	65	20	88	25		182	
			20				155	
			70				375	
			70			QUARTZ	369	
			70		100		345	
			70		10		368	
			70		25		342	
			70	20			340	
			70	245	10		363	
			70	45	25		386	
			70	88	25		653	
		150	150	88			707	12.08 ± 0.03
		65	150					
350	100(He)	65	0	88	25	SAPPHIRE	77	
			7		25		125	
			14		50		157	
			21				221	
			28				258	
			35				295	
			42				330	21.83 ± 1.90
401	40(He)	65	25	95	50		460	
			25				462	
			50				676	
			75			QUARTZ	933	
			100				1104	
			100				1004	
			100		200		1082	
			100		10		1042	
		15	100	45	50		1118	
		65	150	95			1577	
			200				1905	
			268		100		2564	35.4 ± 1.2
401	40(He)	50($^{TF}_{13}$)	25	95	50	QUARTZ	526	
		20($^{TF}_{13}$)	100				1203	
		50($^{TF}_{13}$)	100				1199	
		100($^{TF}_{13}$)	100				1205	
		50($^{TF}_{13}$)	268				2778	38.45 ± 0.38

TABLE III. Reaction rate data for the process $Cl + H_2O_2 \rightarrow HCl + HO_2$.

Temp (K)	Diluent (torr)	CCl_4 (mtorr)	H_2O_2 (mtorr)	Flash energy (J)	k_3' (s^{-1})	$k_{bimolecular}$ (cm^3 $molecule^{-1}$ s^{-1})
298	50(Ar)	65	0	100	15.5	
			6.7		46.5	
			11.7		92.4	
			16.7		138	
			16.7		155	
			20.0		260	
			20.0		216	
			21.65		226	
			21.65		333	
			21.65		256	
			21.65		282	
			26.65		370	
			26.65		445	
			33.3		534	
			33.3		295	
			83.25		1000	
			116.6		1667	5.8×10^{-13}

ably due to heterogeneous decomposition of H_2O_2 on the reactor surfaces. Consequently, the uncertainty limits placed upon the final result obtained for the bimolecular rate constant have been made much larger than normal (a factor of 2). A total pressure of 50 torr of argon was used to slow diffusion to the reactor surfaces and thus minimize heterogeneous wall loss. The H_2O_2 concentration was determined by uv spectrophotometry using published absorption cross-section data.[17] These measurements were normally made immediately before mixtures in He were prepared in preconditioned bulbs.

A least squares fit of the data in Table III produce the following bimolecular rate constant:

$$k_3 = 5.8\times10^{-13} \pm (\text{factor } 2)\,cm^3\,molecule^{-1}\,s^{-1}, \quad 298\text{ K}.$$

DISCUSSION AND COMPARISON WITH PREVIOUS RESULTS

A. The $Cl + O_3 \xrightarrow{k_1} ClO + O_2$ reaction

Figure 1 and Table IV summarize the Arrhenius expressions obtained in this and other studies of the kinetic behavior of the chlorine atom–ozone reaction. From Table IV it can be seen that a variety of techniques have been employed to study Reaction (1) within the temperature range of the stratosphere (200–270 K). The original determination of k_1 at 298 K[18] utilized the low pressure discharge flow mass spectrometric technique to monitor the decay of ozone (O_3^+, $m/e = 48$) in the presence of various excess concentrations of atomic chlorine. The study yielded a value of $(1.85 \pm 0.3_6) \times 10^{11}$ cm^3 $molecule^{-1}$ s^{-1}, which is ~50% higher than the mean value $[(1.19 \pm 0.13) \times 10^{-11}$ cm^3 $molecule^{-1}$ $s^{-1}]$ of the four recent studies at 298 K, and just outside the stated uncertainty limits. This apparent discrepancy can only be attributed to the somewhat indirect technique employed to determine the atomic chlorine concentration in the mass spectrometric study. In this and three other recent determinations of the temperature dependence of k_1,[19–21] the decay of atomic chlorine was monitored in the presence of an excess concentration of ozone (pseudo-first order conditions) utilizing the techniques of atomic resonance fluorescence (this work and Refs. 19 and 20) and atomic resonance absorption[21] to detect the chlorine atoms ($^2P_{3/2,1/2}$). All four studies used uv absorption spectroscopy at ~254 nm to determine the ozone concentration. The absorption cross-section data for the Hartley band of ozone has been well documented and should be considered to be accurate to within ~1%.[14,15] Consequently, differences in the rate constant data of the four recent studies and the original mass spectrometric study cannot be attributed to an inaccuracy in the ozone cross-section data. The value of k_1 at 298 K obtained from the four recent studies varies by ~30% $(1.02–1.33\times10^{-11}$ cm^3 $molecule^{-1}$ $s^{-1})$; consequently, the agreement between these studies can only be considered moderately good. At present, it is uncertain whether the mass spectromeric value should be neglected in calculating the best value for k_1 at 298 K. Unit weighting for all five determinations of k_1 results in a mean value of $(1.32 \pm 0.31) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

As stated above, the agreement between the results of this and three other recent studies at 298 K can be considered moderately good. At 220 K, it is somewhat worse, there being a 40% spread in the values of the re-

TABLE IV. Summary of Arrhenius expressions for the process $Cl + O_3 \rightarrow ClO + O_2$.

Reference	Arrhenius expression ($cm^3 molecule^{-1} 3^{-1}$	$k_1(298\text{ K}) \times 10^{11}$ ($cm^3 molecule^{-1} s^{-1}$	Temperature range (K)	Technique[a]
Clyne and Watson[18]	...	$1.8_5 \pm 0.3_6$	298	DF/MS
Kurylo and Braun[19]	$2.72 \pm 0.45) \times 10^{-11}$ $\times \exp[-(592 \pm 78/RT)]$	1.02 ± 0.05	213–298	FP/RF
Kaufman *et al.*[20]	$(2.17 \pm 0.43) \times 10^{-11}$ $\times \exp[-(340 \pm 60/RT)]$	1.22	205–366	DF/RF
Nip and Clyne[21]	$(5.15 \pm 0.5) \times 10^{-11}$ $\times \exp[-(831 \pm 55/RT)]$	1.33 ± 0.26	221–629	DF/RA
This study	$(3.08^{+0.45}_{-0.15}) \times 10^{-11}$ $\times \exp[-(576 \pm 50/RT)]$	1.20 ± 0.10	220–350	FP/RF

[a] DF: discharge flow; FP: flash photolysis; MS; mass spectrometry; RF: resonance fluorescence; RA: resonance absorption.

TABLE V. Summary of Arrhenius expression ratios (k_{H_2}/k_{CH_4}).

Reference	A_{CH_4}/A_{H_2}	$E_{H_2}-E_{CH_4}$	Temperature range (K)
Knox and Nelson[25]	0.30	1650 ± 60	193–593
Pritchard, Pyke, and Trotman-Dickenson[24]	0.32	1650 ± 150	293–488
Mean value	0.31	1650 ± 100	193–593

ported rate constants ($0.7-1.0\times10^{-11}$ cm^3 molecule^{-1}s^{-1}).

The values reported for the activation energy of Reaction (1) range from 340–831 cal mol^{-1}. Obviously, however, the accurate determination of small (< 1 kcal mol^{-1}) activation energies for a reaction is very difficult when measurements are made over a limited temperature range. Consequently, although the values reported for the activation energy E_1 vary by a factor of ~ 2.5 (340–831 cal mol^{-1}) the agreement must be considered to be reasonably good. A least squares fit of the individual bimolecular rate constants reported in this and the other three recent studies yields the following Arrhenius expressions:

(a) $(2.69\pm1.2)\times10^{-11}\exp[-(511\pm211)/RT]$

(205–298) K ,

(b) $(3.34\pm1.0)\times10^{-11}\exp[-(615\pm150)/RT]$

(205–466) K .

All data points were weighted equally. However, the data published by Kurylo and Braun[19] and Kaufman *et al.*[20] have been corrected due to a revision (~ 7.5%) in the value used for the ozone absorption cross section. Expression (a) was evaluated by using all the experimental data collected at 298 K and below, whereas the data points at 350 K (this study); 366 K (Kaufman, *et al.*)[20] and 452 K (Clyne and Nip)[21] were included in the evaluation of expression (b). Both expressions yield essentially the same bimolecular rate constants between 220 and 298 K (e.g., k_1 (240 K): (a) = 9.21×10^{-12}; (b) = 9.20×10^{-12}). Expression (a) is recommended for use in the model calculations of the stratosphere (discussed later).

B. $Cl + CH_4 \xrightarrow{k2} CH_3 + HCl$

Hydrogen abstraction reactions, such as the chlorination of methane, have been the subject of extensive study; however, most of the data was obtained using the competitive photochemical chlorination technique where only relative rate constants could be measured. The reaction between atomic chlorine and molecular hydrogen was used as the primary standard, as its Arrhenius expression was thought to be well established over a wide range of temperature. The only previous direct determination of the temperature dependence of Reaction (2) utilized a low pressure discharge flow system where the decay of methane was monitored mass spectrometrically (CH_4^+, $m/e = 16$) in the presence of a large excess concentration of atomic and molecular chlorine.[22]

Table V presents the results of the competitive chlorination studies[23,24] in the form of (a) ratio of pre-exponential *A factors, and* (b) *difference in activation energies.* The two results differ only by ~ 7% in the magnitude of the pre-exponential factor. Therefore, the mean result of the two competitive studies will be used for comparison purposes with the results of the more recent direct studies. Table VI summarizes the published Arrhenius expressions for the $Cl + H_2$ reference reaction. It can be seen that there is considerable variance between the Arrhenius parameters shown in Table VI (to be discussed) which results in a variety of expressions which can be derived for the $Cl + CH_4$ reaction. The Arrhenius expressions derived for Reaction (2) from the competitive studies are summarized together with those obtained from the direct studies in Table VII. However, a brief discussion on the preferred Arrhenius expression for the $Cl + H_2$ reaction will be necessary before the results of Reaction (2) can be discussed more fully.

As the $Cl + H_2$ rate constant data has recently been reviewed,[13b] it will suffice to present a synopsis of the conclusions. The Arrhenius expressions forwarded by

TABLE VI. Summary of Arrhenius expressions for k ($Cl + H_2$).

Reference		Arrhenius expression k_{H_2} (cm^{3}molecule^{-1}s^{-1})	Temperature range (K)
Fettis and Knox[a]		$(1.38\pm0.1)\times10^{-10}\exp[-(5500\pm140/RT)]$	273–1071
Benson *et al.*[b]		$(8.0\pm2.0)\times10^{-11}\exp[-(5275\pm400/RT)]$	273–1071
Clyne and Walker[c]	(i)	$(3.7\pm0.6)\times10^{-11}\exp[-(4264\pm100/RT)]$	195–610
	(ii)	$(5.6\pm1.2)\times10^{-11}\exp[-(4485\pm137/RT)]$	195–496
Watson *et al.*[d]	(i)	$(5.5\pm1.0)\times10^{-11}\exp[-(4750\pm100/RT)]$	213–350
	(ii)	$(4.7\pm0.4)\times10^{-11}\exp[-(4776\pm59/RT)]$	213–1071

[a] Evaluation based on all previous data (Refs. 26, 29, 42, 43).

[b] Evaluation based on their own data, and reinterpreted data taken from Refs. (26, 29, 42, 43, 40, 44).

[c] i. Evaluation based on determinations of both k_{-H_2} and k_{H_2} (Refs. 27, 31, 40, 44). ii. Evaluation based on k_{-H_2} (Refs. 31, 40, 44).

[d] i. Direct determination of k_{H_2} using flash photolysis–resonance fluorescence (Ref. 28). ii. Evaluation based on (*d*i), and data from Refs. 27, 29.

Fettis and Knox[26] and Benson *et al.*[27] have been updated in favor of that suggested by Watson,[25] which was strongly influenced by the recent determination of the temperature dependence of the rate constant using the flash photolysis-resonance fluorescence technique.[28] This recent determination [Expression (a)] represents the most extensive single study yet completed of the $Cl + H_2$ reaction. Extrapolation of these results[28] to higher temperatures are seen to be in excellent agreement with those of Benson *et al.*[27] and Steiner and Rideal.[29] This combined data base has resulted in Expression 4b in Table VI. The expressions forwarded by Clyne and Walker[22] (3a and 3b) were predominantly based on the experimental data for the reverse reaction, $H + HCl \rightarrow Cl + H_2$, and the assumption that this data could be combined with published thermochemical data to yield an Arrhenius expression for the reaction of Cl with H_2. It has recently been reported that there is a significant error in the H + HCl data,[30] the expressions based on this data have been rejected in favor of that using only data from studies of the forward reaction. Therefore, the preferred Arrhenius expression for the $Cl + H_2 \rightarrow HCl + H$ reaction is $4.7 \times 10^{-11} \exp[-4676/RT)]$.

Based on the above value of K_{Cl+H_2} these authors feel that the best value which can be obtained for k_2 from the competitive chlorination studies is Expression d (Table VII): $1.45 \times 10^{-11} \exp[-(3026/RT)]$. From this expression a value of 0.88×10^{-13} can be obtained for k_2 at 298 K, which is in somewhat better agreement with the direct studies but still nearly 40% lower. A more detailed analysis of the possible reasons for the discrepancy between the competitive chlorination technique and that of direct resonance fluorescence measurements has been presented in another manuscript.[28] Suffice it to say, the results of this extensive analysis have indicated that neglecting the reactions $HCl + CH_3 \rightarrow CH_4 + Cl$ and $Cl + CH_3Cl \rightarrow HCl + CH_2Cl$ in the competitive studies involving CH_4 and H_2 would have resulted in the measuring of too small a value for $E_{H_2} - E_{CH_4}$, and hence, too large an activation energy for $Cl + CH_4$. It should be noted, however, that at present the actual magnitude of this effect cannot be estimated for lack of accurate rate data and the absence of certain experimental parameters.

The value (1.5×10^{-13} cm^3 molecule^{-1} s^{-1}) reported by Davis *et al.*[31] is ~20% greater than the average of the other two direct studies (1.24×10^{-13} cm^3 molecule^{-1} s^{-1}). The Davis *et al.*[31] study utilized the flash photolysis-resonance fluorescence technique where it was reported that the relationship between the intensity of fluorescence and chlorine atom concentration could be represented by $I_F \propto [Cl]^{0.9}$. However, if the true relationship had been $I_F \propto [Cl]$ then the value derived for k_2 would have been 1.35×10^{-13} cm^3 molecule^{-1} s^{-1}, in better agreement with the other studies. It should be noted that the relation $I_F \propto [Cl]^{0.9}$ in the work by Davis *et al.*[31] was not based on a direct experimentally measured correlation between I_F and [Cl], but rather on calculations involving chlorine resonance line shapes, growth curves, and estimated Cl concentrations. The preferred value for k_2 at 298 K is now taken to be $(126 \pm 0.07) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (weighted average of this study, Clyne and Walker[22] and the modified value of Davis *et al.*[31]).

There is a large variance in the three values reported for the activation energy of Reaction (2). At present, no explanation can be forwarded for the difference in the results of the two direct studies ($E_a = 2.44$ and 3.56 kcal). However, it should be noted that Clyne and Walker also measured the activation energy for the $Cl + CH_3Cl$ reaction to be ~3.55 kcal; whereas, a value of 2.56 kcal was obtained for this activation energy by these authors. The immediate observation is that the results differ by ~1.0 kcal, as was the case for E_2. A further point which should be noted is that the values obtained for the $Cl + CH_3Cl$ rate constant at 298 K are in good agreement (4.87×10^{-13} vs 4.50×10^{-13}). Thus, in both cases the rate constants measured at 298 K are in excellent agreement; whereas, the activation energies differ by ~1 kcal mole^{-1}. The most likely source of error in the discharge flow study could have been in the determination of the chlorine atom concentration, but this would normally have propagated an error in the pre-exponential A factor, not in the activation energy.

The experimental pre-exponential A factor derived from this study is significantly lower than would be predicted from the activated complex theory, i.e., $A_2 = 5.5 \times 10^{-11}$.[32] However, there are numerous reactions which have low experimental pre-exponential A factors when measured over a restricted low temperature range, e.g.,

$$CO + OH \rightarrow CO_2 + H; \quad A = 2.15 \times 10^{-13} \ (220\text{–}373\ K), \quad (9a)$$

TABLE VII. Summary of Arrhenius expressions for $k(Cl + CH_4)$.

Reference	Arrhenius expression (cm^{3}molecule^{-1}s^{-1})	$k_{298} \times 10^{14}$ (cm^{3}molecule^{-1}s^{-1})	Temperature range (K)
Competitive chlorination[23,24]	(a) $4.28 \times 10^{-11} \exp[-(3850/RT)]$	6.42	193–593
	(b) $2.48 \times 10^{-11} \exp[-(3625/RT)]$	5.44	
	(c) $1.74 \times 10^{-11} \exp[-(2835/RT)]$	14.5	
	(d) $1.45 \times 10^{-11} \exp[-(3026/RT)]$[a]	8.75	
Clyne and Walker[22]	$5.1 \times 10^{-11} \exp[-(3560 \pm 37/RT)]$	13.0	300–686
This work	$(7.44 \pm 0.7) \times 10^{-12} \exp[-(2437 \pm 100/RT)]$	11.8	218–401
Davis, Bass, and Braun[31]	...	15.0	298

[a] Best value, based on the preferred value of k_{H_2}

$CH_4 + OH \rightarrow CH_3 + H_2O$; $A = 2.36\times10^{-12}$ (240–373 K). (9b)

Recent studies of the kinetic behavior of the $OH+CO$[33] and $OH+CH_4$[34] reactions over a wide range of temperature in a single system (300–900 K) have seemingly verified earlier theories of nonlinear Arrhenius behavior. The apparent nonlinear Arrhenius behavior of the other reactions (e.g., $H+CH_4 \rightarrow CH_3+H_2$, $H+C_2H_6 \rightarrow C_2H_5+H_2$, $CH_3+H_2 \rightarrow H+CH_4$) are in good agreement with that predicted from bond energy–bond order calculations of the rate coefficients.[35,36]

Therefore, although no significant curvature was observed in the Arrhenius plot of the rate constant data for Reaction (2), its possibility cannot be excluded.

C. $Cl + H_2O_2 \xrightarrow{k3}$ products

This is the first reported study of Reaction (3). Unfortunately, only the rate of removal of atomic chlorine could be monitored. Thus, the following three primary processes which are exoenergetic must receive serious consideration:

$$Cl + H_2O_2 \xrightarrow{a} HCl + H_2O, \qquad \Delta H_{F298} \approx -13.7 \text{ kcal mol}^{-1}$$
$$\xrightarrow{b} H_2O + ClO, \qquad \Delta H_{F298} \approx -29.8 \text{ kcal mol}^{-1}$$
$$\xrightarrow{c} HOCl + OH, \qquad \Delta H_{F298} \approx -9.2 \text{ kcal mol}^{-1}.$$

Based on steric conditions, process (a) would be favored; however, the results from kinetic studies of the reaction between atomic hydrogen and hydrogen peroxide would argue that at least two primary processes are probably important.[41] Hence, at the moment it appears that there is no scientific basis for excluding the partitioning of the net rate constant for Reaction (3) into separate k values for processes (a), (b), and (c).

ATMOSPHERIC IMPLICATIONS OF NEW RATE DATA

Numerous model calculations have demonstrated that the injection of chlorinated compounds into the stratosphere results in the selective destruction of odd oxygen at midaltitudes (~ 25–45 km),[1–8] where the catalytic efficiency (ρ) can be expressed via Eq. (II).

$$\rho \propto \frac{2k_a k_b k_e Ja[O_3]^2[HCl][OH]}{k_d[RH]\{k_b Ja[O_3] + k_c k_f[NO][O_2][M]\}}. \qquad (II)$$

This study reinvestigated the kinetic behavior of processes (a), ($Cl+O_3 \rightarrow ClO+O_2$), and (d), where $k_d[RH]$ can be written:

$$k_d[RH] = k_2[CH_4] + k_3[H_2O_2] + k_4[H_2] + k_5[HO_2].$$

New results are reported for k_2, k_3, and k_4. The most expedient approach, which can be taken in order to evaluate the effect of the new rate constant data upon the published results of the model calculations, is to assume that the altitude most sensitive to the injection of ClO_x is 35 km, and to discuss the consequences of the new kinetic information at that altitude. The temperature of the standard stratosphere at 35 km is taken to be 237 K.

The early model calculations[4–7] used a temperature invariant rate constant of 1.85×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for k_a. A value of 9.06×10^{-12} cm^3 $molecule^{-1}$ s^{-1} was derived for k_a at 237 K from the Arrhenius expression obtained in the present study. This is in close agreement with the value of 9.09×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, which was obtained from the "evaluated" Arrhenius expression [see discussion on Reaction (1)]. The new value of k_a at 237 K is a factor of 2.0 lower than that used in the early calculations. Consequently, use of Eq. II would predict that the catalytic efficiency (ρ) would be reduced by a factor of 2; however, this simplistic approach predicts the maximum possible change as there will be an increase in the ozone density at lower altitudes produced by the self-healing effect.

The greater the magnitude of $k_d[RH]$, the lower the catalytic efficiency of ClO_x due to the "tying up" of chlorine in the inactive form of HCl. Although concentration profiles for both CH_4 and H_2 have been experimentally determined up to ~ 50 km in the stratosphere,[37] neither HO_2 nor H_2O_2 have been directly monitored. Consequently, the only profiles which exist for $[HO_2]$ and $[H_2O_2]$ are those predicted from the one-dimensional photochemical models. Considerable uncertainty exists in the rate constant data for the reactions which exert control over the atmospheric concentrations of HO_2 and H_2O_2 (and OH), e.g.,

$$OH + HO_2 \xrightarrow{k_i} H_2O + O_2, \qquad k_{(i)} = 2\times10^{-11} - 2\times10^{-10},$$
$$O + HO_2 \xrightarrow{k_{ii}} OH + O_2, \qquad k_{(ii)} = 8\times10^{-11}\exp[-500/T] \pm \text{factor } 4,$$
$$HO_2 + HO_2 \xrightarrow{k_{iii}} H_2O_2 + O_2, \qquad k_{(iii)} = 3\times10^{-11}\exp[-500/T] \pm \text{factor } 2.$$

The magnitude of $[HO]_x$ and its partitioning ($HO_x \equiv H + OH + HO_2 + H_2O_2$) is dependent upon the selection of rate constant data for reactions (i)–(iii). The majority of model calculations have performed using a high value for $k_{(i)}$ (2×10^{-10} cm^3 $molecule^{-1}$ sec^{-1}), the predominant chain termination process for HO_x, resulting in a low $[HO_x]/([H_2O]+[CH_4]+[H_2])$ ratio. Recent rate data[38] for O^1D reactions with N_2, O_2 (quenching), H_2O, CH_4, N_2O, and H_2 (reactive) increases the uncertainty in the accuracy of the published $[HO_x]$ profiles. Model calculations which have used high values for $k_{(i)}$ and $k_{(ii)}$ (2×10^{-10} and 6×10^{-11}, respectively) predict that $[HO_2]$ at 35 km has a value of ~ 1.7×10^7 molecule cm^{-3}[4]; whereas, the model calculations which have used low values for $k_{(i)}$ and $k_{(ii)}$ (2×10^{-11} and 2×10^{-11}, respectively) predict that the concentration of HO_2 at 35 km is ~ 7.8×10^7 molecule cm^{-3}.[39] The H_2O_2 concentration is predicted to range from ~ 2– 10×10^8 molecule cm^{-3} at 35 km. Unfortunately, not only is the HO_2 concentration uncertain due to a lack of reliable rate constant data for the above processes, but k_5 ($Cl+HO_2 \rightarrow HCl+O_2$) has not been experimentally measured. The most

TABLE VIII. Magnitudes of various atomic chlorine sinks at 35 km.

		$k(237\ K)\ cm^3 molecule^{-1} s^{-1}$			$k[Reagent]\ s^{-1}$		
Species	Concentration molecule cm^{-3}	This study	Clyne–Walker	Others	This study	Clyne–Walker	Others
CH_4	1.1×10^{11}	4.2×10^{-14}	2.6×10^{-14}	...	4.6×10^{-3}	2.9×10^{-3}	...
H_2	1.1×10^{11}	2.3×10^{-15}	4.1×10^{-15}	1.1×10^{-15}[c]	2.5×10^{-4}		1.2×10^{-4}[c]
H_2O_2	$(2-10)\times10^{8}$	$\sim2.5\times10^{-13}$[a]	...	2.2×10^{-15}[e]	$(5-25)\times10^{-5}$	...	2.4×10^{-4}[e]
HO_2	$(1.5-8)\times10^{7}$	$\sim2\times10^{-11}$[b]	...	$(1-10)\times10^{-11}$[d]	$(3-16)\times10^{-4}$	...	$(1.5-80)\times10^{-4}$

[a] Calculated using an estimated Arrhenius expression of $1\times10^{-11}\exp[-(875/T)]$, which is compatible with a mean of $\sim5.8\times10^{-13}$ $cm^3 molecule^{-1} s^{-1}$ at 298 K.
[b] Author's estimate.
[c] Benson *et al.*[27]
[d] Estimates.
[e] Westenberg and deHaas.[40]

probable value for k_5 is estimated to be $\sim2\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, but a range of values from 1×10^{-11}–1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} have been used in model calculations. Table VIII presents the range of values that can be expected for atomic chlorine loss rates. For these calculations, the mixing ratio for both H_2 and CH_4 was taken to be 0.67 ppm (v/v).[37] It is unlikely that the mixing ratios are significantly inaccurate although there is a lack of data above 35 km.

From Table VIII it can be seen that either reaction with CH_4 or HO_2 is expected to be the dominant sink for atomic chlorine. Crutzen[5] used the values of Clyne and Walker for $k_2(CH_4)$ and $k_4(H_2)$; 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for $k_5(HO_2)$; 2×10^{-10} and 2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $k_{(i)}$ and $k_{(ii)}$. These k values resulted in an HO_2 concentration of 2.6×10^{7} molecule cm^{-3} at 35 km. Using this concentration for HO_2, the relative rates for Cl atom destruction were 2.9×10^{-3} (CH_4), 4.5×10^{-4} (H_2), and 2.6×10^{-3} (HO_2). The new rate data for k_2 and k_4 would increase $k_2[CH_4]$ to 4.6×10^{-3}, and decrease $k_4[H_2]$ to 2.5×10^{-4}. Thus $k_d[RH]$ would increase from 5.95 to 7.25×10^{-3} (~22%). Wofsy and McElroy[4] used the values of Clyne and Walker for $k_2(CH_4)$, and Westenberg and deHaas[40] for $k_4(H_2)$; 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $k_5(HO_2)$, 2×10^{-10} and 6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $k_{(i)}$ and $k_{(ii)}$. This resulted in an HO_2 concentration of $\sim1.7\times10^{7}$ molecule cm^{-3} at 35 km. With this HO_2 concentration, the relative rates for Cl atom destruction were $2.9\times10^{-3}(CH_4)$, $2.4\times10^{-4}(H_2)$, and $1.7\times10^{-4}(HO_2)$. The new rate data for k_2 and k_4 would increase $k_2[CH_4]$ to 4.6×10^{-3}, but leave $k_4[H_2]$ the same. Therefore, $k_d[RH]$ is increased from 3.3 to 5.0×10^{-3} (~52%). From these simple calculations, it is evident that the new rate constant data causes a small but significant decreases in the catalytic efficiency ρ. A conclusion of this paper is that the $Cl+H_2O_2$ reaction is not a significant sink ($<0.05k_d[RH]$) for atomic chlorine for any combination of HO_x rate constants; whereas, experimental data is required for the $Cl+HO_2$ reaction to determine its importance. If the rate constants for $k_{(i)}$, $k_{(ii)}$, and $k_{(iii)}$ are 2×10^{-11}, 2×10^{-11}, and 3×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively, then the $[HO_2]$ profile will be the maximum possible. Under these conditions, if $k_5\geq6\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} then the magnitude of $k_5[HO_2]\geq k_2[CH_4]$. However, the greatest effect of perturbing the above combination of $k_{(i)}$, $k_{(ii)}$, and $k_{(iii)}$ would be to increase [OH] leading to an enhancement of ρ due to the increased regeneration of atomic chlorine via the $OH+HCl$ reaction.

In summary, the maximum impact of the new rate data reported here would be to decrease the earlier predictions of ozone depletion by a factor of 2.4 to 3.

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*Present address: Jet Propulsion Laboratory, Bldg 183-601, 4800 Oak Road Drive, Pasadena, CA 91103.

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(2) A Kinetics Study of the OH-Initiated Degradation of Several Carbon-Chlorine Compounds.

(a) "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br"

A temperature dependent kinetics study of the reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br*

D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson

Atmospheric Sciences Division, Applied Sciences Laboratory, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332

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Reported in this study are temperature dependent rate data for the reaction of OH with the partially halogenated methane species CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. The nominal temperature range covered was 245–375 K. The appropriate Arrhenius expressions are $k_A = (1.84 \pm 0.18) \times 10^{-12} \exp[-(2181 \pm 70/RT)]$, $k_B = (4.27 \pm 0.63) \times 10^{-12} \exp[-(2174 \pm 161/RT)]$, $k_C = (4.69 \pm 0.71) \times 10^{-12} \exp[(2254 \pm 214/RT)]$, $k_D = (7.93 \pm 0.79) \times 10^{-11} \exp[-(1766 \pm 116/RT)]$. Units are $cm^3 molecule^{-1} \cdot s^{-1}$. No simple correlations between E_{act} and C–H bond strengths were found. The impact of these halogenated species on stratospheric ozone is also discussed.

INTRODUCTION

The reactivity of OH toward partially halogenated hydrocarbons has become of increasing interest in the last few years both because of the increased level of activity in the field of fire research (with the use of halogenated species as flame retardants) and in the area of stratospheric ozone chemistry. Presented here are the final results of a flash photolysis–resonance fluorescence study which was first reported on at two scientific meetings earlier this year.[1,2] The molecules of interest in this study are CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. The details of this study as well as a discussion of the atmospheric significance of the results are presented in the following text.

EXPERIMENTAL

The flash photolysis–resonance fluorescence system used in this study was identical to that described in detail in an earlier publication.[3] For this reason, no further description will be presented here. Treatment of the experimental data from this study was also handled as before.[3] In all cases, the halogenated reactant was in large excess ($>10^3$) over the concentration of OH (typically 10^{11} molecule/cm^3); hence, pseudo-first-order kinetics prevailed.

Low pressure measurements in this study (1–3000 mTorr) were made using an MKS Baratron. High pressure measurements, on the other hand, were carried out using a two turn Bourdon gauge (Wallace and Tiernan type FA145). The precision to which gas mixtures could be prepared using the above pressure gauges was estimated to be ~3% or better. The one gaseous species which could not be handled with the same precision as quoted above was H_2O. Owing to its high tendency to absorb on the walls of the reaction vessel, the H_2O pressure was typically known to only ±20% on a given gas filling. This uncertainty affected the absolute OH concentration to the extent of ±20%; however, since all experiments were carried out under pseudo-first-order kinetics, this small variation in [OH] was of no consequence.

The purity of each of the halocarbons used in this investigation was as follows: CH_3Cl (Matheson > 99.5%); CH_2Cl_2 (Fisher > 99.92%); $CHCl_3$ (Dow Corning, > 99.94%); CH_3Br (Matheson, > 99.%). The helium diluent gas was Matheson "Gold Label Ultra-High Purity" and was used without further purification.

RESULTS AND DISCUSSION

The results from this investigation have been summarized in the form of Tables I–IV. It can be seen from these tables that numerous experimental variations were carried out for each molecule studied. Of major interest are those variations performed at 298 K to test for the possible importance of secondary reactions, especially those of the radical–radical type. Those experimental parameters which were varied extensively were flash energy, total pressure, and water concentration. These experimental permutations were designed to test for reaction processes of the type

$$OH + OH + M \rightarrow H_2O_2 + M, \tag{1}$$

$$OH + OH \rightarrow H_2O + O, \tag{2}$$

$$OH + H + M \rightarrow H_2O + M, \tag{3}$$

$$OH + Cl + M \rightarrow HOCl + M, \tag{4}$$

$$OH + Br + M \rightarrow HOBr + M, \tag{5}$$

$$OH + CH_mCl_n \rightarrow \text{products}, \quad m + n \leq 3, \tag{6}$$

$$OH + CH_uBr_v \rightarrow \text{products}, \quad u + v \leq 3. \tag{7}$$

In each case, it is apparent that the rate of disappearance of OH would depend on the square power of the total radical concentration and hence on the square power of the flash intensity. These reactions, if important, should have resulted in a significant dependence of the measured pseudo-first-rate constants, K_1, on the flash intensity as well as the H_2O pressure. As can be seen from Tables I–IV, only at the very highest flash intensities (e.g., 450–500 J range) was there any significant deviation in the values of K_1. The change in the OH concentration when compared with more or less standard operating conditions, 88 J, would have been somewhat greater than a factor of 5. The increase in K_1 observed for all four molecules with this change in the OH concentration ranged from 8% to 25%. Thus, although the observed increase was small, it most certainly was indicative of secondary radical–radical processes becoming of slight importance at the highest flash intensities employed. It should be noted that further reductions in the OH concentration by nearly a fac-

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TABLE I. Reaction rate data for the process $OH + CH_3Cl \rightarrow H_2O + CH_2Cl$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_3Cl (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{bi} \times 10^{14}$ (cm^3 $molecule^{-1} \cdot s^{-1}$)
350	100(He)	200	0	Suprasil	88	41	
	100	200	20	Suprasil	88	80	
	100	200	30	Suprasil	88	114	
	100	200	50	Suprasil	88	160	
	100	200	75	Suprasil	88	210	
	100	200	100	Suprasil	88	267	
	100	200	100	Suprasil	88	257	
	100	200	125	Suprasil	88	332	
	100	200	150	Suprasil	88	385	8.28 ± 0.28
298	20(He)	200	0	LiF	88	57	
	20	200	25	LiF	88	108	
	20	200	30	Suprasil	88	130	
	20	200	50	Suprasil	88	170	
	20	200	50	LiF	88	160	
	20	200	65	LiF	88	187	
	20	200	65	LiF	211	250	
	20	200	65	LiF	31	168	
	20	200	75	Suprasil	88	190	
	20	200	75	Suprasil	88	200	
	20	200	75	Suprasil	88	200	
	20	200	75	Suprasil	245	225	
	20	400	75	Suprasil	88	204	
	20	200	80	LiF	88	190	
	20	200	100	LiF	88	208	
	20	200	110	Suprasil	88	235	
	20	200	125	LiF	88	266	
	20	200	140	LiF	88	303	
	20	200	150	LiF	88	311	
	20	200	150	LiF	88	338	
	20	200	150	LiF	45	325	
	20	200	200	LiF	88	357	
	20	200	200	Suprasil	88	382	
	20	200	250	LiF	88	422	4.29 ± 0.21
	200(He)	200	50	Suprasil	88	95	
	200	200	75	Suprasil	88	126	
	200	200	150	Suprasil	88	225	
	200	200	225	Suprasil	88	312	3.98 ± 0.04
273	20(He)	200	0	Suprasil	88	70	
	20	200	30	Suprasil	88	102	
	20	200	50	Suprasil	88	130	
	20	200	75	Suprasil	88	157	
	20	200	100	Suprasil	88	185	
	20	200	120	Suprasil	88	205	
	20	200	150	Suprasil	88	240	
	20	200	200	Suprasil	88	302	3.26 ± 0.06
250	20(He)	200	0	Suprasil	88	40	
	20	200	50	Suprasil	88	80	
	20	200	65	Suprasil	88	96	
	20	200	80	Suprasil	88	118	
	20	200	95	Suprasil	88	121	
	20	200	105	Suprasil	88	135	
	20	200	120	Suprasil	88	144	
	20	200	150	Suprasil	88	190	
	20	200	175	Suprasil	88	200	2.38 ± 0.14

tor of 4 from that generated at 88 J and 200 mTorr of H_2O (typical conditions) resulted in no experimentally significant change in the measured value of K_1. It is also noteworthy that under typical operating conditions, a variation of the total pressure by a factor of 5 (5 times higher) resulted in no significant change in the value of K_1 for any of the molecules studied. We must conclude, therefore, that under our typical operating conditions no complications were encountered as a result of radical–radical reactions. In the calculation of the bimolecular rate constants for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br, none of the high flash intensity data were included. From Tables I–IV it can be seen that at 298 K the rate constants for reaction of OH with CH_3Cl,

TABLE II. Reaction rate data for the process $OH+CH_2Cl_2 \rightarrow H_2O+CHCl_2$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_2Cl_2 (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{bi}\times10^{14}$ (cm^3 molecule$^{-1}\cdot s^{-1}$)
375	100(He)	200	5	Sapphire	88	74	
	100	200	10	Sapphire	88	94	
	100	200	20	Sapphire	88	156	
	100	200	25	Sapphire	88	182	
	100	200	30	Sapphire	88	208	
	100	200	35	Sapphire	88	247	
	100	200	40	Sapphire	88	266	
	100	200	45	Sapphire	88	303	22.3 ± 0.5
298	40(He)	200	20	Sapphire	88	103	
	40	200	30	Sapphire	88	148	
	40	200	50	Sapphire	88	220	
	40	200	60	Sapphire	88	242	
	40	200	60	Sapphire	88	240	
	40	50	60	Sapphire	88	215	
	40	400	60	Sapphire	88	238	
	40	200	60	Sapphire	45	240	
	40	200	60	Sapphire	500	287	
	40	200	75	Sapphire	88	318	
	40	200	80	Sapphire	88	333	
	40	200	90	Sapphire	88	373	
	40	200	100	Sapphire	88	403	11.6 ± 0.5
	200(He)	200	50	Sapphire	88	190	
	200	200	65	Sapphire	88	222	
	200	200	80	Sapphire	88	281	
	200	200	95	Sapphire	88	344	10.4 ± 1.2
245	20(He)	100	20	Sapphire	88	43	
	20	100	40	Sapphire	88	79	
	20	100	60	Sapphire	88	120	
	20	100	80	Sapphire	88	144	
	20	100	97	Sapphire	88	200	
	20	100	120	Sapphire	88	225	4.75 ± 0.57

CH_2Cl_2, $CHCl_3$, and CH_3Br are as follows:

$$OH+CH_3Cl \rightarrow CH_2Cl+H_2O, \qquad (A)$$

$$k_A=(4.29\pm0.21)\times10^{-14},$$

$$OH+CH_2Cl_2 \rightarrow CHCl_2+H_2O, \qquad (B)$$

$$k_B=(1.16\pm0.05)\times10^{-13},$$

$$OH+CHCl_3 \rightarrow CCl_3+H_2O, \qquad (C)$$

$$k_C=(1.14\pm0.07)\times10^{-13},$$

$$OH+CH_3Br \rightarrow CH_2Br+H_2O, \qquad (D)$$

$$k_D=(4.14\pm0.43)\times10^{-14}.$$

Units are cm^3 molecule$^{-1}\cdot s^{-1}$. The temperature dependence of Reactions (A)–(D) was examined over the nominal temperature range of 245–375 K. Arrhenius expressions for each of the reactions investigated were determined from a weighted least squares treatment of the k_{bi} values given in Tables I–IV. The relative weighting factor for each temperature was determined by the relative number of experimental runs performed with each compound. The resulting Arrhenius expressions are given below (see also Fig. 1):

$$k_A=(1.84\pm0.18)\times10^{-12}\exp-(2181\pm70/RT),$$

$$k_B=(4.27\pm0.63)\times10^{-12}\exp-(2174\pm161/RT),$$

$$k_C=(4.69\pm0.71)\times10^{-12}\exp-(2254\pm214/RT), \qquad (8)$$

$$k_D=(7.93\pm0.79)\times10^{-13}\exp-(1766\pm116/RT)$$

Units for the above k values are cm^3 molecule$^{-1}\cdot s^{-1}$. The activation energy has been expressed in terms of cal mol$^{-1}\cdot$ deg^{-1}. The uncertainties quoted for k_A–k_D apply to only the temperature range over which each system was studied and represent the 90% confidence limits of the data. The indicated uncertainty limits shown in Tables I–IV for the bimolecular rate constants represent one standard deviation (1σ) as determined from a weighted least squares treatment of the data. The error limits quoted for the pre-exponential A factors in Arrhenius expressions (A)–(D) reflect 2σ error limits, whereas those for the activation energy represent 1σ. Both were determined from a weighted least squares treatment of the temperature data.

Of considerable interest with regards to the temperature dependence data is the observed trend in activation energies for the sequence CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. Summarized in Table V are the activation energies measured in this study along with the appropriate bond dissociation energies for the C–H bond in each halogenated molecule studied. Also included in Table V are the activation energies for the reaction of Cl $^2P_{3/2}$

TABLE III. Reaction rate data for the process $OH + CHCl_3 \rightarrow H_2O + CCl_3$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	$CHCl_3$ (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{bi} \times 10^{14}$ (cm^3 $molecule^{-1} \cdot s^{-1}$)
375	100(He)	200	10	Suprasil	88	90	
	100	200	20	Suprasil	88	148	
	100	200	25	Suprasil	88	183	
	100	200	30	Suprasil	88	195	
	100	200	35	Suprasil	88	230	
	100	200	40	Suprasil	88	260	
	100	200	45	Suprasil	88	290	21.8 ± 1.4
298	40(He)	200	20	Suprasil	88	93	
	40	200	30	Suprasil	88	139	
	40	200	40	Suprasil	88	182	
	40	200	50	Suprasil	88	206	
	40	50	50	Suprasil	88	200	
	40	200	50	Suprasil	45	213	
	40	200	50	Suprasil	500	263	
	40	200	57	Suprasil	88	242	
	40	200	65	Suprasil	88	260	
	40	200	75	Suprasil	88	308	
	40	200	80	Suprasil	88	322	
	40	200	90	Suprasil	88	377	
	40	200	100	Suprasil	88	380	11.4 ± 0.7
	200(He)	200	25	Suprasil	88	87	
	200	200	35	Suprasil	88	132	
	200	200	50	Suprasil	88	171	
	200	200	75	Suprasil	88	260	
	200	200	100	Suprasil	88	362	11.0 ± 0.5
245	40(He)	50	20	Suprasil	88	40	
	40	50	40	Suprasil	88	73	
	40	50	50	Suprasil	88	96	
	40	50	60	Suprasil	88	99	
	40	50	75	Suprasil	88	122	
	40	50	80	Suprasil	88	124	
245	40(He)	50	100	Suprasil	88	165	
	40	50	100	Suprasil	88	168	
	40	50	120	Suprasil	88	218	
	40	50	150	Suprasil	88	254	
	40	50	200	Suprasil	88	328	
	40	50	200	Suprasil	88	360	4.39 ± 0.28

with several of the same molecules examined in this study.

From Table V, it is apparent that there is no simple correlation between C–H bond strength and the measured OH activation energies from this study. There is, of course, a major decrease in the activation energy in going from CH_4 to CH_3Cl or CH_3Br, which would seem to correlate with a significant decrease in the respective C–H bond energies. However, it is interesting to see no such trend develop in the case of chlorine atom attack on these same two molecules. For this reaction system, even though there appears to be a systematic error in one or both of the studies by Clyne *et al.*[7] and Watson and Davis,[8] there is good agreement between both of these direct measurements that chlorine atom attack on CH_4 and CH_3Cl results in the same activation energy. In comparing OH activation energies for the compounds CH_3Cl, CH_2Cl_2, and CCl_3H, we see that within the experimental uncertainty of the measurements it can be concluded that the activation energies are either unchanged or that they might show a slight positive increase in going from CH_3Cl and CCl_3H. This insignificant change in activation energy is to be compared with an ~4 kcal change in the C–H bond energy between CH_3Cl and CH_2Cl_2 and $CHCl_3$. For chlorine atom attack on CH_3Cl, CH_2Cl_2, and $CHCl_3$, no obvious conclusions can be drawn, in that the data of Fettis and Knox[6] show a quite different trend in activation energies than do the data of Clyne *et al.*[7] At the present time, therefore, these authors can only speculate that there are probably several factors which might explain individually or collectively the observed activation energy bond correlations for both the OH and Cl reaction systems. These include (1) erroneous assignments of C–H bond strengths for some of the halogenated methanes, (2) incorrect measurements of the respective activation energies, and (3) the strong electronic repulsion effects of neighboring chlorine atoms to the incoming OH and/or Cl radical attack.

A comparison of the results from this study with published as well as unpublished rate data from other laboratories is shown in Table VI. From this table of

TABLE IV. Reaction rate data for the process $OH + CH_3Br \rightarrow H_2O + CH_2Br$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_3Br (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{b1} \times 10^{14}$ (cm^3 $molecule^{-1} \cdot s^{-1}$)
350	100(He)	200	25	Suprasil	88	90	
	100	200	50	Suprasil	88	119	
	100	200	75	Suprasil	88	186	
	100	200	100	Suprasil	88	216	
	100	200	100	Suprasil	45	220	
	100	200	125	Suprasil	88	259	
	100	200	150	Suprasil	88	300	
	100	200	200	Suprasil	88	380	6.08 ± 0.4
298	20(He)	200	25	Suprasil	88	100	
	20	200	50	Suprasil	88	128	
	20	200	75	Suprasil	88	166	
	20	200	100	LiF	88	192	
	20	200	100	Suprasil	86	190	
	20	200	100	Suprasil	45	198	
	20	200	100	Suprasil	500	263	
	20	50	100	Suprasil	88	180	
	20	400	100	Suprasil	88	192	
	20	200	125	Suprasil	88	253	
	20	200	150	Suprasil	88	277	
	20	200	200	LiF	88	322	4.14 ± 0.43
	200(He)	200	0	Suprasil	88	13	
	200	200	50	Suprasil	88	84	
	200	200	100	Suprasil	88	148	
	200	200	150	Suprasil	88	202	3.89 ± 0.03
273	20(He)	200	30	LiF	88	95	
	20	200	50	Suprasil	88	108	
	20	200	75	LiF	88	134	
	20	200	100	LiF	88	171	
	20	200	125	LiF	88	205	
	20	200	150	LiF	88	229	
	20	200	150	LiF	45	227	
	20	200	150	LiF	320	260	
	20	200	175	LiF	88	250	
	20	200	200	LiF	88	270	
	20	200	250	LiF	88	294	3.16 ± 0.15
244	20(He)	100	50	LiF	88	93	
	20	100	75	LiF	88	100	
	20	100	100	LiF	88	131	
	20	100	125	LiF	88	143	
	20	100	150	LiF	88	160	
	20	100	150	LiF	45	150	
	20	100	150	LiF	320	202	
	20	100	175	LiF	88	193	
	20	100	206	LiF	88	221	
	20	100	250	LiF	88	243	2.01 ± 0.12

compiled results, it is readily seen that at 298 K virtually all results are in excellent agreement within the quoted experimental uncertainties. In the study by Howard and Evenson,[5] a discharge flow system with laser magnetic resonance of OH was used to examine the reaction of the OH radical with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. Perry, Atkinson, and Pitts,[9] as in this investigation, employed the flash photolysis–reso-

TABLE V. Correlation of E_{act} with C–H bond strengths.[4,5]

	$OH + CH_yX_z \rightarrow H_2O + CH_{y-1}X_z$			$Cl(^2P_{3/2}) + CH_yX_z \rightarrow HCl + CH_{y-1}X_z$		
		C–H(kcal/mol)	E_{act} (cal/mol)	Fettis and Knox[6]	Clyne *et al.*[7]	Watson and Davis[8]
CH_4	CH_3–H	103	3400 Ref. 3		3580	2437
CH_3Cl	$CClH_2$–H	99	2181 This work	3300	3574	2557
CH_2Cl_2	CCl_2H–H	95	2174 This work	2980	2980	
$CHCl_3$	CCl_3–H	95	2254 This work	3340	2760	
CH_3Br	$CBrH_2$–H	97	1766 This work			

TABLE VI. Comparison of rate data for reaction of OH with halogenated methane species.[a]

	298			Temperature dependence	
	Howard and Evenson[5]	Perry, Atkinson, and Pitts[9]	This work	Perry, Atkinson, and Pitts[9]	This work
CH_3Cl	$(3.6 \pm 0.8) \times 10^{-14}$	$(4.4 \pm 0.3) \times 10^{-14}$	$(4.29 \pm 0.21) \times 10^{-14}$	$4.1 \times 10^{-12} \exp - (2700 \pm 300/RT)$ (298–423) K	$(1.84 \pm 0.18) \times 10^{-12} \exp - (2181 \pm 70/RT)$
CH_2Cl_2	$(15.5 \pm 3.4) \times 10^{-14}$	$(14.5 \pm 2.0) \times 10^{-14}$	$(11.6 \pm 0.5) \times 10^{-14}$		$(4.27 \pm 0.6) \times 10^{-12} \exp - (2174 \pm 16RT)$
$CHCl_3$	$(10.1 \pm 1.5) \times 10^{-14}$		$(11.4 \pm 0.7) \times 10^{-14}$		$(4.69 \pm 0.71) \times 10^{-12} \exp - (2254 \pm 214/RT)$
CH_3Br	$(3.5 \pm 0.8) \times 10^{-14}$		$(4.14 \pm 0.43) \times 10^{-14}$		$(7.93 \pm 0.79) \times 10^{-12} \exp - (1766 \pm 105/RT)$

[a] All units are in cm^3 $molecule^{-1} \cdot s^{-1}$.

nance fluorescence technique in their study. In the one system, CH_3Cl, where another temperature dependence study has also been completed, by Perry, Atkinson and Pitts,[9] apparently only fair agreement exists. In this case, the experimental uncertainties do not allow for overlapping activation energies, the differences between the E_{act} values being 20%–25%. However, the results obtained in these studies are in excellent agreement both at 298 and 350 K. The value of k_1 measured by Perry *et al.* at 423 K is only ~18% greater than would be predicted from Arrhenius expression (A) obtained in this study. A least squares fit of all the data points (this study and Perry *et al.*) resulted in the following Arrhenius expression:

$$k_1 = (2.47 \pm 0.37) \times 10^{-12} \exp - (2353 \pm 94/RT) \quad (250\text{–}423)\text{K}.$$

All data points are within 10% of that predicted by this expression.

The atmospheric significance of the OH reaction rate study reported in this work lies in the prediction of reliable tropospheric lifetimes for the halogenated methanes. The concern about these halogenated methanes involves their possible impact on stratospheric ozone due to either chlorine[10] or bromine[11] catalytic ozone destruction processes, i.e.,

$$Cl + O_3 \rightarrow ClO + O_2 \tag{9}$$

$$\frac{ClO + O \rightarrow Cl + O_2}{O + O_3 \rightarrow O_2 + O_2} \tag{10}$$

or

$$Br + O_3 \rightarrow BrO + O_2 \tag{11}$$

$$\frac{BrO + O \rightarrow Br + O_2}{O + O_3 \rightarrow O_2 + O_2}\,. \tag{12}$$

The extent to which the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br could provide halogen atoms to promote the catalytic cycles 9, 10 and 11, 12 is predicated on their rate of destruction in the troposphere via attack from atmospheric OH. This destruction rate,

$$-d[CH_yX_z]/dt = k[OH][CH_yX_z]$$

or, more appropriately, the average tropospheric life-

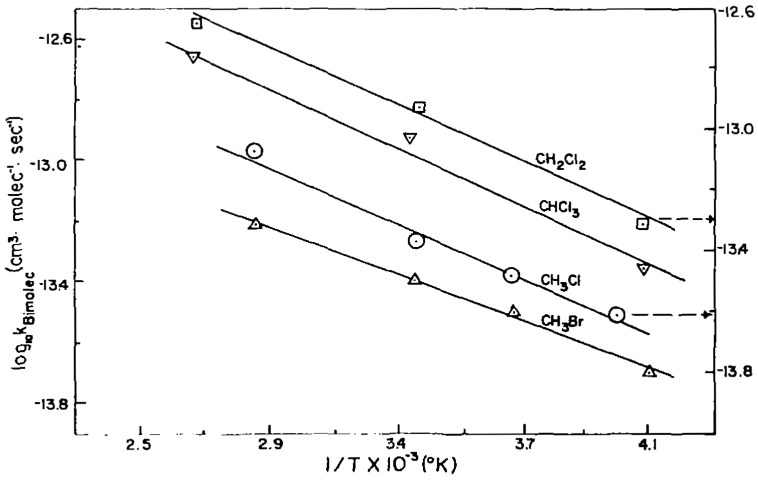

FIG. 1. Arrhenius plot of temperature data on the reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br.

TABLE VII. Tropospheric lifetimes for the molecules CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br.

Compound	K_{265}	Lifetime (years)
CH_3Cl	3.0×10^{-14}	1.19
CH_2Cl_2	8.7×10^{-14}	0.39
$CHCl_3$	6.4×10^{-14}	0.56
CH_3Br	2.7×10^{-14}	1.32

time of a partially halogenated species, is controlled (1) by the value of the bimolecular rate constant for OH attack, and (2) on the global seasonally averaged OH steady state concentration. In Table VII we have calculated the tropospheric lifetimes of all four compounds investigated in this study. These calculations have been based on a weighted average temperature for the troposphere of 265 K and a seasonally, diurnally averaged OH concentration of 9×10^5 OH's/cm^3. The latter value has been estimated using results from Crutzen's 2-D atmospheric model[12] and data from recent direct measurements of atmospheric OH at 32 and 21 °N latitude at 7 and 11.5 km by Davis, McGee, and Heaps.[13]

Thus, on the basis of the lifetimes calculated in Table VII, it can be seen that all compounds have very short tropospheric lifetimes and their potential impact on stratospheric ozone should be minimal.

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†Present Address: Jet Propulsion Laboratories, Bldg 183-601, 4800 Oak Road Drive, Pasadena, CA 91103.

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[(2) A Kinetics Study of the OH-Initiated Degradation of Several Carbon-Chlorine Compounds.]

(b) "A Temperature-Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3, CH_3CF_2Cl, and $CF_2ClCFCl_2$"

A TEMPERATURE-DEPENDENT KINETICS STUDY OF THE REACTION OF OH WITH CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3, CH_3CF_2Cl and $CF_2ClCFCl_2$*

R. T. Watson**, G. Machado, B. Conaway, S. Wagner and D. D. Davis

Georgia Institute of Technology
Applied Sciences Laboratory
Engineering Experiment Station
339 Baker Building
Atlanta, Georgia 30332

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**Present Address:

Physics Department
Jet Propulsion Laboratory
Pasadena, California

Abstract

The flash photolysis resonance fluorescence technique has been utilized to determine the Arrhenius parameters for several reactions between the hydroxyl radical and halogenated hydrocarbons. The reactions studied, and their corresponding Arrhenius expressions in units of cm^3 $molecule^{-1}s^{-1}$, are shown:

(1) $OH + CH_2ClF \rightarrow CHClF + H_2O$

$k_1 = (2.84 \pm 0.3) \times 10^{-12} \exp(-(1259 \pm 50)/T)$ (245-375)K

(2) $OH + CHCl_2F \rightarrow CCl_2F + H_2O$

$k_2 = (1.87 \pm 0.2) \times 10^{-12} \exp(-(1245 \pm 26)/T)$ (245-375)K

(3) $OH + CHClF_2 \rightarrow CClF_2 + H_2O$

$k_3 = (9.25 \pm 1.0) \times 10^{-13} \exp(-(1575 \pm 71)/T)$ (250-350)K

(4) $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$

$k_4 = (3.72 \pm 0.4) \times 10^{-12} \exp(-(1627 \pm 50)/T)$ (260-375)K

(5) $OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$

$k_5 = (1.15 \pm 0.15) \times 10^{-12} \exp(-(1748 \pm 30)/T)$ (273-375)K

(6) $OH + CF_2ClCFCl_2 \rightarrow$ PRODUCTS

$k_6 < 3 \times 10^{-16}$ 298K

Tropospheric lifetimes have been calculated for the above species by combining the rate constant data with global seasonally and diurnally averaged hydroxyl radical concentrations.

INTRODUCTION:

It has been proposed that the injection of chlorinated compounds into the stratosphere will lead to a catalytic reduction in the integrated column density of ozone due to the interaction of odd oxygen (odd oxygen $\equiv O(^3P) + O_3$) with ClO_x species ($ClO_x = Cl + ClO + ClOO$)(1). Numerous chlorinated compounds have already been shown to be present in the atmosphere and their concentrations determined by gas chromatographic detection(2). These compounds can be classified into two separate groups; (a) fully halogenated, e.g. $CFCl_3$; CF_2Cl_2 and CCl_4, and (b) hydrogen containing, e.g. CH_3Cl; CHF_2Cl, etc. To date, no tropospheric sink mechanism has been identified for the fully halogenated compounds (i.e. the chemical lifetimes of these compounds in the troposphere far exceed the total atmospheric lifetime that would be calculated based on stratospheric photodissociation alone. Consequently, for this type of compound, the principal atmospheric sink is believed to be vertical diffusion into the stratosphere, followed by photodissociation. However, some caution must be exercised here as there is still considerable scatter in the published results on the tropospheric concentrations of fluorocarbons. Within the range of this scatter, there could yet exist a significant unrecognized sink mechanism.(3) For those compounds reaching the lower and mid-stratosphere, photodissociation, and to a lesser extent reaction with electronically excited atomic oxygen (O^1D), can result in the production of odd chlorine (Cl, ClO) which can directly participate in the destruction of odd oxygen:

$$\begin{array}{lll} & Cl + O_3 \rightarrow & ClO + O_2 \\ & \underline{O + ClO \rightarrow} & \underline{Cl + O_2} \\ \text{net:} & O + O_3 \rightarrow & O_2 + O_2 \end{array}$$

In contrast to the fully halogenated species, those compounds containing hydrogen atoms are expected to react with hydroxyl radicals, resulting in chemical lifetimes in the troposphere significantly shorter than would be expected from photolysis alone.(4) The relatively short lifetimes of these halocarbons (∿1-20 years) would inhibit the build-up of large concentrations of these species in the troposphere, thus limiting the flux of chlorine into the stratosphere.

This paper presents the results of a kinetic study of the behavior of hydroxyl radicals with several C_1 and C_2 halogenated compounds. The reactions were studied over a wide range of temperature and total pressure utilizing the technique of flash photolysis-resonance fluorescence. Recent measurements of tropospheric hydroxyl radical concentrations(5) have also permitted the calculation of tropospheric lifetimes for the various fluorocarbons studied. A comparison of our kinetic results with other recent data (6-9), and a discussion of the atmospheric implications of our results is presented.

Experimental:

The experimental details and operating principles of the flash photolysis-resonance fluorescence technique have been fully described in the literature, and only a brief summary will therefore be presented in this text.(10)

The reaction vessel used in this work was a jacketed black anodized aluminum cell with an internal volume of ∿850cm^3. The cell temperature was controlled to within ± 0.5K by flowing methanol (240-325K) or ethylene glycol (298-400K) from a thermostated circulating bath through the outer jacket of the reaction vessel. An iron-constantan thermocouple was used to measure temperature with a precision of better than 0.5K.

As in earlier studies involving the kinetic behavior of the hydroxyl radical, photolysis of H_2O by a N_2 spark discharge lamp was used as the source of OH:(10)

$$H_2O + h\nu \rightarrow H + OH \quad (X^2\Pi)$$

The spark discharge lamp was normally equipped with a quartz window in order to eliminate the transmittance of light at wavelengths shorter than 165 nm, thus minimizing the production of reactive intermediates from the photodecomposition of the added reagent. Based on the known absorption spectrum of H_2O, and previously conducted actinometry using ethylene as the actinic gas, it was determined that typical OH concentrations of $\sim 3 \times 10^{11}$ radical cm^{-3} were produced with an H_2O concentration of 6×10^{15} molecule cm^{-3}, and a flash energy of 88J.

Excitation of OH was accomplished via the use of a discharge-flow hydroxyl resonance lamp which primarily produced the emission characteristic of the $(A^2\Sigma^+:v'=0) \rightarrow (X^2\Pi:v''=0)$ transition of OH. A small fraction of the OH, produced by the photolysis of H_2O, was continuously excited by the resonance radiation emitted from the lamp. Fluorescence from excited OH was measured using a photomultiplier tube located at right angles to the lamp. As in previous studies, photon-counting electronics were used throughout this study. The intensity of the fluorescence was observed to be linearly proportional to the hydroxyl radical concentration in the reaction cell.

Each reaction was studied using psuedo first order kinetic conditions, $[\text{Reagent}]_0 >> [\text{OH}]_0$ $([\text{Reagent}]_0/[\text{OH}]_0 \approx 1.5 \times 10^3 - 1.5 \times 10^5)$, and as expected the hydroxyl radical concentration decayed exponentially with time. Because the initial hydroxyl radical concentration was kept low to prevent secondary reactions, multiple flashes on a single gas mixture were required to produce a smooth kinetic curve. However, the number of flashes per gas filling was limited (i.e. less than 50) so as to minimize the possible accumulation of reactive photolysis or reaction products which might participate in secondary removal of hydroxyl radicals. For this reason, several fillings of an identical gas mixture were normally used to develop a single experimental decay curve. The hydroxyl radical decay was observed to be linear for at least two half-lives.

Gas pressures of 10-5000 mtorr were measured using a MKS Baratron which was frequently checked for accuracy. High pressure measurements (10-800 torr;1 torr=133 Pa)were made with a two-turn

Bourdon Gauge (Wallace and Tiemman type FA-145). The precision to which gas mixtures could be made up, with the exception of H_2O, was estimated to be ∿3% or better. The H_2O pressure could not be metered so precisely due to absorption on the reaction vessel surfaces.

The purity of each of the halocarbons used in this study was as follows: CH_2FCl (Dupont, >99.92%); $CHCl_2F$ (Dupont, >99.8%); $CHClF_2$ (Dupont, >99.8%); CH_3CCl_3 (Dow Corning, >99.95%); CH_3CF_2Cl (Dupont, >99.8%); $CF_2ClCFCl_2$ (Dupont, >99.9%). The Helium diluent gas was Matheson "Gold Label Ultra-High Purity" and was used without further purification. Even though the CH_3CCl_3 provided by Dow was uninhibited (did not contain an antioxidant), it contained trace amounts (< .1%) of a chlorinated olefin which was removed by fractional distillation before use. The nature of the trace impurities present in each of the gases was quantitatively known, and calculations verified that they were of no importance in the present study. Each of the halocarbons were subjected to a freeze and thaw purification process prior to use.

Results and Discussion

(a) OH + C_1 and C_2 Halogenated Alkanes

Since the kinetic behavior of hydroxyl radicals with CH_2ClF(1); $CHCl_2F$(2); $CHClF_2$(3); CH_3CCl_3(4); CH_3CF_2Cl(5) and $CF_2ClCFCl_2$(6) was studied using psuedo-first order conditions, the hydroxyl radical decay rates could be analyzed using equation (I):

$$OH + RH \xrightarrow{k_{bi}} R + H_2O;\ [RH]_o >> [OH]_o$$

$$\ln([OH]_o/[OH]_t) = K\ [RH]_o t \qquad (I)$$

where $K = k_{bi}/[RH]_o$

A wide variation in experimental conditions was performed in order to verify that kinetic complications due to secondary processes were not affecting the observed OH decay rates. These variations were normally performed at 298K and included: H_2O pressures of 50-400 mtorr; flash energies of 45-245 J; total pressures of 40-200 torr; and the number of flashes per single filling of the reaction cell of 25-200 (not shown in the tables). The number of flashes per filling was varied to demonstrate that the formation of significant concentrations of reactive photolytic or reaction products was unimportant. In these experiments, the measured psuedo first order rate constants, K, were always observed to be invariant within the expected experimental uncertainty (∿5%) of the measurements. Removal of hydroxyl radicals by processes such as (a)-(c) were also shown to be unimportant under typical operating conditions by examining the dependence of K upon flash energy, H_2O concentration and total pressure.

(a) $OH + OH \rightarrow H_2O + O$

(b) $OH + OH + M \rightarrow H_2O_2 + M$

(c) $OH + H + M \rightarrow H_2O + M$

In these experiments, only when the flash energy was increased to 245 J were significantly higher K values (20%) measured over those obtained at lower flash energies, thus indicating some importance of radical-radical processes. Under these conditions, a nine fold increase in the radical concentration would have resulted. It should be noted, however, that no change was observed in the first order rate constant when the flash energy was reduced from 88 to 45 J. In the calculation of K values for reactions 1-6, only data taken with flash energies of 88 J or less was used. The bimolecular rate constants for CH_2FCl; $CHCl_2F$; CHF_2Cl; CH_3CCl_3; CH_3CF_2Cl and $CF_2ClCFCl_2$ were determined from a weighted least squares treatment of the data shown in Tables I-VI. At 298K, these k values are:

(1) $OH + CH_2ClF \rightarrow CHClF + H_2O$

$k_1 = (4.21 \pm 0.41) \times 10^{-14}$

(2) $OH + CHCl_2F \rightarrow CCl_2F + H_2O$

$k_2 = (2.88 \pm 0.24) \times 10^{-14}$

(3) $OH + CHClF_2 \rightarrow CClF_2 + H_2O$

$k_3 = (4.8 \pm 0.46) \times 10^{-15}$

(4) $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$

$k_4 = (1.59 \pm 0.16) \times 10^{-14}$

(5) $OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$

$k_5 = (3.22 \pm 0.48) \times 10^{-15}$

(6) $OH + CF_2ClCFCl_2 \rightarrow$ Products

$k_6 < 3 \times 10^{-16}$

Units are cm^{3}molecule^{-1}s^{-1}. For those reactions where several different total pressures were employed, a weighted averaged k value has been reported. The uncertainty limits shown for the above 298 K data, as well as those given in Tables I-VI for other temperatures are the two sigma values calculated from a weighted least squares treatment of the data.

The temperature dependence of each reaction was studied over a nominal temperature range of ∿(100-130)°C. The limiting factors which determined the lowest temperature used in these measurements were: (a) the vapor pressure of H_2O at low temperatures; and (b) the magnitude of the rate constant. (The concentration of fluorocarbon was limited to 1500 mtorr due to electronic quenching of the $A^2\Sigma^+$ state of OH.). Fig. (1) shows the Arrhenius plots for reactions (1)-(5). The resulting Arrhenius expressions are summarized below:

$$
\begin{aligned}
k_1 &= (2.84 \pm 0.3) \times 10^{-12} \exp - (1259 \pm 50/T) \\
k_2 &= (1.87 \pm 0.2) \times 10^{-12} \exp - (1245 \pm 26/T) \\
k_3 &= (9.25 \pm 1.0) \times 10^{-13} \exp - (1575 \pm 71/T) \\
k_4 &= (3.72 \pm 0.4) \times 10^{-12} \exp - (1627 \pm 50/T) \\
k_5 &= (1.15 \pm 0.15) \times 10^{-12} \exp - (1748 \pm 30/T)
\end{aligned}
$$

Units for the above k values are cm^{3}molecule^{-1}s^{-1}. The activation energy has been expressed in terms of small calories. The uncertainties quoted for k_1-k_5 apply only to the temperature range over which each system was studied represent the 90% confidence limits.

Comparison and Discussion of Recent Work:

A comparison of the results from this study with the published rate data from other laboratories (see refs. 6, 7, 8, and 9) is shown in Table VII. It is readily seen that at 298K virtually all results are in excellent agreement within the quoted experimental uncertainties. An exception to this is the compound $CHClF_2$ where the result quoted by Howard and Evenson is lower than that of the other two studies by ∿25-30%. At present, no explanation can be forwarded for this apparent discrepancy. Howard and Evenson(6,7) used a low pressure discharge flow system with Laser Magnetic Resonance detection of the hydroxyl radical to determine the rate constants for reactions (1)-(5) at 298K. Pitts, Atkinson, et.al.(8,9), as in this investigation, utilized the technique of flash photolysis-resonance fluorescence to examine the kinetic behavior of reactions (2) and (3) between 298 and ∿430K. The results of the two high pressure flash photolysis studies are in excellent agreement for both reactions (2) and (3). This is especially encouraging in that the temperature ranges used in the two studies only partially overlapped, and yet the experimental data of one study was always within the stated experimental uncertainties of that predicted from the Arrhenius expression reported from the other study. A least squares treatment of all the data points obtained in the two temperature dependence studies of k_2 and k_3 resulted in the following evaluated Arrhenius expressions:

$$k_2 = (1.59 \pm 0.2) \times 10^{-12} \exp-(1204 \pm 50/T) \quad (245-423)K$$
$$k_3 = (1.21 \pm 0.17) \times 10^{-12} \exp-(1648 \pm 75/T) \quad (250-434)K$$

Atmospheric Implications of Rate Data

The chemical degradation of halogenated alkanes via hydroxyl radical attack was discussed in the introduction with particular reference to the tropospheric lifetimes of these compounds. The most significant consequence of a short tropospheric lifetime for partially hydrogenated halocarbons is that of restricting the stratospheric burden of chlorine from these compounds. Table VIII, for example, shows the results of a calculation(11) which gives the fraction of a given halocarbon which would diffuse into the stratosphere and photolyze as a function of its tropospheric lifetime at steady state.

Table VIII

Lifetime (yrs)	$CFCl_3$	CF_2Cl_2
∞	1.0	1.0
50	.66	.4
40	.53	.32
20	.27	.16
10	.13	.08

It can readily be seen that a lifetime of 10 years or less drastically reduces the flux of these compounds into the stratosphere at steady state (see comments on reference 11). The destruction rate for a halocarbon containing hydrogen is given by:

$$-d[RX]/dt = k[OH]\,[RX]$$

and $$\tau_e(\text{tropospheric lifetime}) = [k[OH]_{AV}]^{-1}$$

Thus, the two parameters required to calculate tropospheric lifetimes are; (a) the value of the bimolecular rate constant for a given OH reaction and (b) the global seasonally and diurnally averaged OH steady state concentration. In Table IX, we have calculated the tropospheric lifetimes of all six compounds investigated in this study. These calculations have been based on a weighted average temperature for the troposphere of 265K and a global seasonally and diurnally averaged OH concentration of 9×10^5 cm^{-3}. The latter value has been estimated using results from Crutzen's 2-D atmospheric model(12) and data from recent direct measurements of atmospheric OH at 32 and 21°N latitude at 7 and 11.5 km reported by Davis, McGee and Heaps(5).

From Table IX, it can be seen that the tropospheric lifetimes of CH_2ClF (Fluorocarbon 31); $CHCl_2F$ (Fluorocarbon 21) and CH_3CCl_3 are sufficiently short that their potential impact on stratospheric ozone should be minimal. However, the predicted lifetimes for $CHClF_2$ (Fluorocarbon 22) and CH_3CF_2Cl (Fluorocarbon 142) are sufficiently long that the sink for 10-20% of the anthropogenic production rate could be expected to be photodissociation in the stratosphere at steady state. Additional factors of importance, however, are that both these compounds contain only one chlorine atom per molecule in contrast to Fluorocarbons 11 and 12 which contain three and two chlorine atoms, respectively. This fact combined with the predicted shorter tropospheric lifetime of Fluorocarbons 22 and 142 would indicate that the potential impact of an equal source strength of these compounds compared to Fluorocarbon 11 or 12 would be four to ten times less. As expected, no observable reaction was detected between

OH and $CF_2ClCFCl_2$ (TF 13), suggesting a chemical lifetime in the troposphere comparable to that for Fluorocarbons 11 and 12.

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TABLE I

$OH + CH_2ClF \rightarrow CHClF + H_2O$

TEMPERATURE (°K)	REACTANT (mtorr)	DILUENT (torr)	FLASH ENERGY' (JOULES)	PHOTOLYLE (mtorr)	k' (s^{-1})	$k_{bimolecular}$ ($cm^3 molecule^{-1} s^{-1}$)
245	0	40	88	100	24	
	50	"	"	"	61	
	97	"	"	"	91	
	100	"	"	"	85	
	125	"	"	"	119	
	150	"	"	"	120	
	200	"	"	"	155	
	250	"	"	"	192	$(1.65 \pm 0.36) \times 10^{-14}$
298	0	40	88	200	41	
	25	"	"	"	70	
	50	"	"	"	111	
	59	"	"	"	116	
	75	"	"	"	146	
	100	"	"	"	184	
	100	"	45	"	180	
	100	"	245	"	190	
	100	"	88	50	166	
	100	"	"	300	183	
	125	"	"	200	221	
	150	"	"	"	243	
	175	"	"	"	285	
	200	"	"	"	326	$(4.42 \pm 0.24) \times 10^{-14}$
	0	200	88	200	12.5	
	50	"	"	"	79	
	100	"	"	"	138	
	125	"	"	"	170	
	150	"	"	"	194	$(3.79 \pm 0.30) \times 10^{-14}$
375	25	100	88	200	95	
	40	"	"	"	135	
	50	"	"	"	154	
	75	"	"	"	219	
	100	"	"	"	280	
	125	"	"	"	350	$(9.80 \pm 0.34) \times 10^{-14}$

TABLE II

$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$

Temperature (°K)	Reactant (mtorr)	Diluent (torr)	Flash Energy (J)	Photolyle (mtorr)	k^1 (s^{-1})	$k_{bimolecular}$ ($cm^3 molecule^{-1} s^{-1}$)
245	50	40	88	100	51	
	100	"	"	"	81	
	150	"	"	"	103	
	200	"	"	"	119	
	250	"	"	"	143	
	300	"	"	"	158	
	350	"	"	"	186	
	400	"	"	"	229	$(1.12 \pm 0.12) x10^{-14}$
273	75	40	88	200	102	
	100	"	"	"	120	
	150	"	"	"	161	
	200	"	"	"	196	
	250	"	"	"	240	
	300	"	"	"	270	
	350	"	"	"	303	
	400	"	"	"	351	$(2.09 \pm 0.18) x10^{-14}$
298	0	40	88	200	38	
	50	"	"	"	75	
	75	"	"	"	108	
	100	"	"	"	123	
	125	"	"	"	161	
	150	"	"	"	180	
	"	"	45	"	175	
	"	"	245	"	217	
	"	"	88	50	174	
	"	"	"	400	204	
	175	"	"	200	206	
	200	"	"	"	210	
	200	"	45	"	222	
	250	"	88	"	263	
	275	"	"	"	302	
	300	"	"	"	340	$(2.99 \pm 0.24) x10^{-14}$
298	0	200	88	200	12	
	50	"	"	"	60	
	100	"	"	"	98	
	125	"	"	"	115	
	150	"	"	"	140	
	175	"	"	"	173	
	200	"	"	"	185	
	200	"	"	"	180	
	225	"	"	"	238	
	250	"	"	"	229	
	250	"	"	"	206	
	300	"	"	"	263	$(2.66 \pm 0.58) x10^{-14}$

TABLE II(continued)

Temperature (°K)	Reactant (mtorr)	Diluent (torr)	Flash Energy(J)	Photolyle (mtorr)	k^1 (s^{-1})	$k_{bimolecular}$ ($cm^3 molecule^{-1} s^{-1}$)
375	0	100	88	200	70	
	15	"	"	"	104	
	25	"	"	"	116	
	40	"	"	"	135	
	50	"	"	"	157	
	65	"	"	"	175	
	75	"	"	"	206	
	90	"	"	"	217	
	100	"	"	"	232	
	110	"	"	"	263	
	125	"	"	"	298	$(6.68\pm0.82)\times10^{-14}$

TABLE III

$$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$$

TEMPERATURE (°K)	REACTANT (mtorr)	DILUENT (torr)	FLASH ENERGY (J)	PHOTOLYLE (mtorr)	k' (s^{-1})	k bimolecular $(cm^3 molecule^{-1} s^{-1})$
250	300	40	88	200	47	
	500	"	"	"	60	
	700	"	"	"	70	
	900	"	"	"	87	
	1100	"	"	"	93	
	1300	"	"	"	116	$(1.70 \pm 0.40) \times 10^{-15}$
273	300	40	88	200	63	
	400	"	"	"	73	
	500	"	"	"	84	
	600	"	"	"	89	
	700	"	"	"	102	
	800	"	"	"	115	
	900	"	"	"	121	$(2.77 \pm 0.38) \times 10^{-15}$
298	0	40	88	200	25	
	100	"	"	"	53	
	300	"	"	"	87	
	400	"	"	"	99	
	500	"	"	"	117	
	"	"	45	"	111	
	"	"	245	"	123	
	"	"	88	500	120	
	600	"	"	200	131	
	700	"	"	"	141	
	800	"	"	"	166	
	900	"	"	"	178	
	960	"	"	"	190	$(4.84 \pm 0.46) \times 10^{-15}$
	0	200	88	200	15	
	400	"	"	"	66	
	600	"	"	"	90	
	700	"	"	"	114	
	800	"	"	"	128	
	900	"	"	"	151	$(4.69 \pm 1.06) \times 10^{-15}$
350	0	100	88	200	34	
	200	"	"	"	82	
	300	"	"	"	110	
	400	"	"	"	136	
	500	"	"	"	168	
	600	"	"	"	193	$(1.01 \pm 0.08) \times 10^{-14}$

TABLE IV

$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$

TEMPERATURE (°K)	REACTANT (mtorr)	DILUENT (torr)	FLASH ENERGY (J)	PHOTOLYLE (mtorr)	k' (s^{-1})	k bimolecular ($cm^3molecule^{-1}s^{-1}$)
260	0	40	88	200	25	
	100	"	"	"	54	
	200	"	"	"	65	
	250	"	"	"	68	
	300	"	"	"	110	
	400	"	"	"	115	
	500	"	"	"	155	
	700	"	"	"	204	
	750	"	"	"	210	
	1000	"	"	"	285	$(7.12 \pm 0.94) x10^{-15}$
298	0	40	88	200	38	
	100	"	"	"	87	
	150	"	"	"	117	
	200	"	"	"	140	
	250	"	"	"	150	
	300	"	"	"	205	
	400	"	"	50	280	
	"	"	"	200	255	
	"	"	"	400	273	
	405	"	"	200	249	
	500	"	"	"	285	
	800	"	"	"	450	$(1.59 \pm 0.16) x10^{-14}$
	200	40	245	200	171	
	400	"	"	"	270	
	600	"	"	"	373	$(1.56 \pm 0.04) x10^{-14}$
	200	40	31	200	120	
	400	"	"	"	~215	$\sim 1.5 x10^{-14}$
375	25	40	88	200	125	
	50	"	"	"	150	
	100	"	"	"	225	
	150	"	"	"	296	
	200	"	"	"	347	
	250	"	"	"	400	$(4.85 \pm 0.58) x10^{-14}$

TABLE V

$OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$

TEMPERATURE (°K)	REACTANT (mtorr)	DILUENT (torr)	FLASH ENERGY (J)	PHOTOLYLE (mtorr)	k' (s^{-1})	k bimolecular ($cm^3 molecule^{-1} s^{-1}$)
273	250	40	88	200	32	
	500	"	"	"	77	
	750	"	"	"	101	
	1000	"	"	"	117	
	1250	"	"	"	126	
	1500	"	"	"	139	$(1.92 \pm 0.48) \times 10^{-15}$
298	200	40	88	200	51	
	400	"	"	"	77	
	600	"	"	"	99	
	800	"	"	"	117	
	1000	"	"	"	147	
	1200	"	"	"	156	
	"	"	45	"	167	
	"	"	245	"	200	
	"	"	88	400	161	
	1400	"	"	200	177	
	1500	"	"	"	181	
	1600	"	"	"	199	$(3.12 \pm 0.48) \times 10^{-15}$
	0	200	88	200	12.5	
	600	"	"	"	90	
	800	"	"	"	117	
	1000	"	"	"	116	
	1400	"	"	"	172	$(3.42 \pm 0.68) \times 10^{-15}$
375	75	100	88	200	65	
	150	"	"	"	86	
	200	"	"		111	
	300	"	"		123	
	400	"	"		147	
	500	"	"		178	
	600	"	"		216	
	800	"	"		273	$(1.09 \pm 0.14) \times 10^{-14}$

Table VI

$OH + CF_2ClCFCl_2 \rightarrow$ PRODUCTS

TEMPERATURE (°K)	REAGENT (mtorr)	DILUENT (torr)	FLASH ENERGY (Joules)	PHOTOLYLE (mtorr)	k' (s^{-1})	k bimolecular ($cm^3 molecule^{-1} s^{-1}$)
298	250	40	88	200	27	$< 3 \times 10^{-16}$
	500				36	
	750				31	
	1250				39	

TABLE VII. COMPARISON OF RATE DATA

COMPOUND	$k(298K) \times 10^{15}$ $cm^3 molecule^{-1} s^{-1}$			ARRHENIUS EXPRESSIONS	
	This Work	Howard & Evenson	Pitts, Atkinson, et.al.	This Work	Pitts, Atkinson et.al. (8,9))
CH_2ClF	42.1±4	37±6	-	$2.84x10^{-12}exp-(1259/T)$	
$CHCl_2F$	28.8±3	26±4	27±3	$1.87x10^{-12}exp-(1245/T)$	$1.75x10^{-12}exp-(1253/T)$
$CHClF_2$	4.8±0.3	3.4±0.7	4.75±0.48	$9.25x10^{-13}exp-(1575/T)$	$1.21x10^{-12}exp-(1636/T)$
CH_3CCl_3	15.9±2	15±3	-	$3.72x10^{-12}exp-(1627/T)$	-
CH_3CF_2Cl	3.22±0.3	2.8±0.4	-	$1.15x10^{-12}exp-(1748/T)$	-
$CF_2ClCFCl_2$	<0.3	-	-	-	-

TABLE IX. CALCULATED TROPOSPHERIC LIFETIMES

COMPOUND	$k_{bimolecular}$ (265K)	LIFETIME (YEARS)
CH_2ClF	2.45×10^{-14}	1.44
$CHCl_2F$	1.70×10^{-14}	2.07
$CHClF_2$	2.43×10^{-15}	14.50
CH_3CCl_3	8.02×10^{-15}	4.39
CH_3CF_2Cl	1.57×10^{-15}	22.44
$CF_2ClCFCl_2$	$<3 \times 10^{-16}$	>117

Lifetime: $\ln ({}^{A_o}/A) = k[OH]_{Ave.}\, t$

where $\ln ({}^{A_o}/A) = 1.$

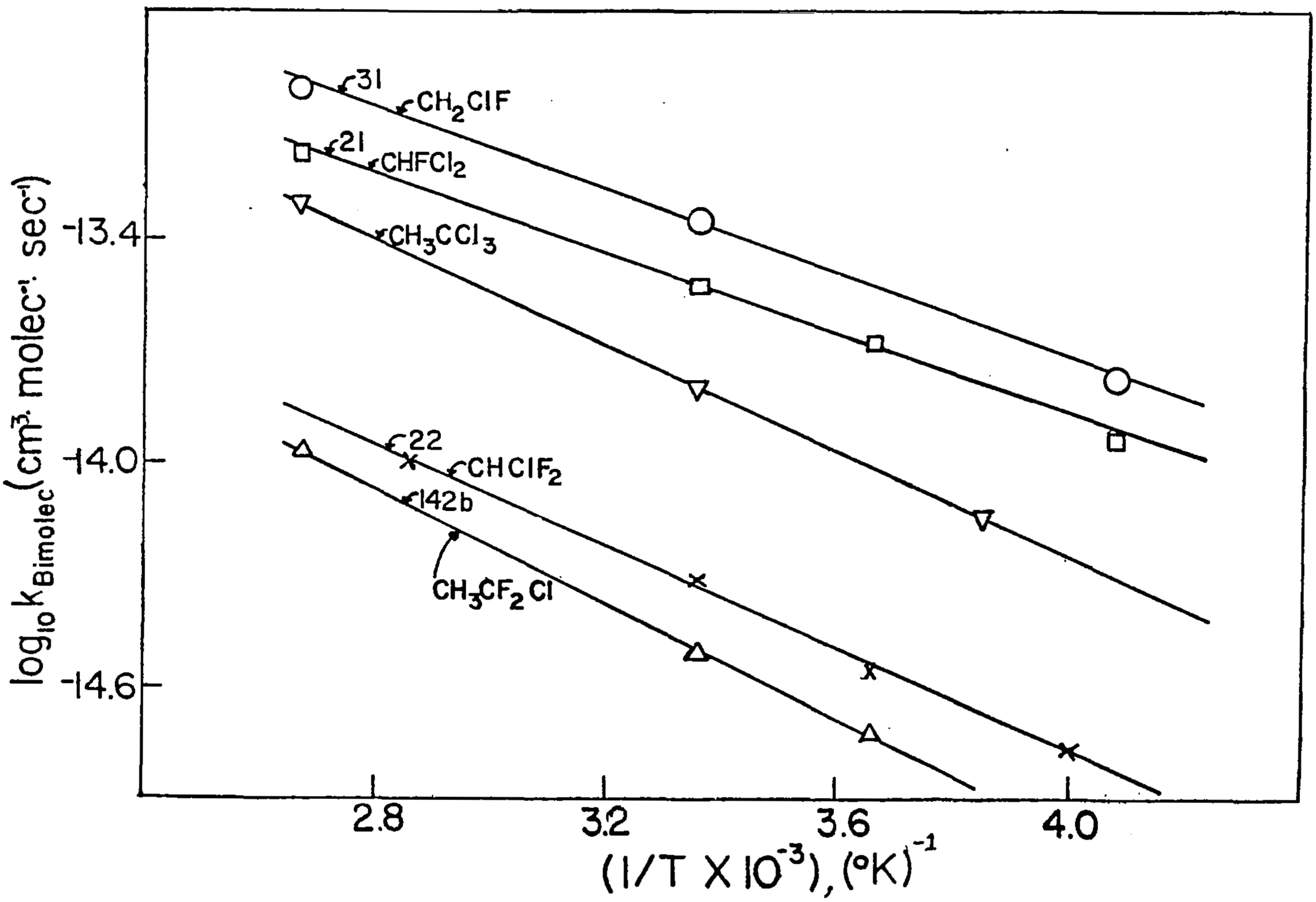

FIGURE 1

Arrhenius plots of bimolecular rate constants for reactions (1)-(5) as follows:

(1) $OH + CH_2ClF \rightarrow CHClF + H_2O$
(2) $OH + CHCl_2F \rightarrow CCl_2F + H_2O$
(3) $OH + CHClF_2 \rightarrow CClF_2 + H_2O$
(4) $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$
(5) $OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$

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(3) A Kinetics Study of the Chemical Decomposition of Stratospheric HCl.

A TEMPERATURE DEPENDENT KINETICS STUDY OF THE REACTIONS OF HCl WITH OH AND $O(^3P)$*

A. R. Ravishankara, G. Smith, R. T. Watson** and D. D. Davis†

Atmospheric Sciences Division
Applied Sciences Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

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** Present Address:

Jet Propulsion Laboratories
Building 183-601
4800 Oak Road Drive
Pasadena, California 91103

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ABSTRACT

The flash photolysis-resonance fluorescence technique was employed to determine the temperature dependencies of the rate constants for the reaction of $O(^3P)$ and OH radicals with HCl. These reactions were studied under pseudo-first order conditions and in the absence of interfering secondary reactions. The Arrhenius expression for each bimolecular rate constant is given below in units of cm^3 $molecule^{-1}s^{-1}$.

$k_1 = (3.3 \pm 0.3) \times 10^{-12} \exp [-937 \pm 78) \text{ cal mol}^{-1}/RT]$ 250-402K

(1) $OH + HCl \rightarrow H_2O \quad Cl$ and

$k_2 = (5.2 \pm 1.0) \times 10^{-11} \exp[-(7510 \pm 750) \text{cal mol}^{-1}/RT]$ 350-454K

(2) $O(^3P) + HCl \rightarrow \dot{O}H + Cl.$

The stratospheric implications of this new rate data are discussed.

INTRODUCTION

According to present atmospheric models, hydrogen chloride is predicted to be one of the principal chlorine containing species in the stratosphere.(1) Recent measurements of the HCl concentration in the lower stratosphere now support this prediction. (2) In the stratosphere the formation of HCl proceeds through the reaction of chlorine atoms with RH species (i.e. CH_4, H_2, H_2O_2, and/or HO_2), thus removing reactive chlorine from the catalytic cycle:

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ \underline{ClO + O \rightarrow Cl + O_2} \\ O + O_3 \rightarrow 2O_2 \end{array}$$

The chlorine atom in HCl, however, can be reintroduced into catalytic ozone destruction cycle via reaction of OH or $O(^3P)$ with HCl and/or by photolysis of HCl, e.g.

$$OH + HCl \xrightarrow{k_1} H_2O + Cl \qquad (1)$$

$$O(^3P) + HCl \xrightarrow{k_2} OH + Cl \qquad (2)$$

$$HCl \xrightarrow{h\nu} H + Cl \qquad (3)$$

Since HCl is the dominant "temporary sink" for Cl atoms in the stratosphere, reliable rate constants for reactions (1) and (2) are essential for stratospheric modelling calculations.

Five measurements of the rate constant k_1 have been reported. Wilson, et al.,(4) measured k_1 at high temperatures, while Takacs and Glass(5) and Hack, et al., (6) obtained room temperature values. In addition, there have been two measurements of k_1 over an extended temperature range, one by Smith and Zellner(7) and the other by Zahniser, et al.(8) All measurements are in very good agreement at 300 K; however, at stratospheric temperatures of 225 K; the k value reported by Zahniser, et al. is approximately 20% higher than that of Smith and Zellner.

Several investigations of reaction (2) have been reported over an extended temperature range where the activation energy could be evaluated. Balakhnin, et al., were the first to study the kinetic behavior of reaction (2). These authors reported an activation energy of 4.52 K cal/mole. Brown and Smith (10) later obtained an E value of 5.95 K cal/mole, a number which agrees well with some recent work reported by Singleton and Cvetanovic. Hack, et al.,(7) and Wong and Belles(12), however, have reported values for reaction (2) of 6.44 and 7.2 K cal/mole^{-1}, respectively. Thus, at the present time the activation energy for process (2) must be considered poorly defined.

Reported here are the results of a new study on both reactions (1) and (2), the purpose of which was to further test the reliability of the earlier rate data using a completely different experimental technique -- flash photolysis-resonance fluorescence.

EXPERIMENTAL:

Detailed descriptions of the flash photolysis-resonance fluorescence technique employed in this investigation have been described previously.(13,14,15) In this manuscript, therefore, we have pointed out only those experimental features necessary for an understanding of the present study. In this investigation, an all-pyrex cell with an internal volume of $\sim$150 cm^3 was used to study both reactions (1) and (2). The reaction mixture was maintained at a known constant temperature by circulating either methanol (250-300 K) or silicone oil (300-450 K) from a thermostated circulating bath through an outer jacket of the reaction cell. The temperature of the reaction cell was measured with an Iron-Constantan thermocouple. The transient species OH and O(^{3}P) were formed by the photolysis of a suitable photolyte using a nitrogen spark discharge.

The technique for detection of OH radicals by resonance fluorescence has been documented elsewhere.(13) The OH radicals in this study were produced either by directly photolyzing H_2O or by photolyzing a mixture of 50m Torr of O_3 and 100m Torr of H_2. In the latter case, OH was formed through the sequence of reactions:

$$O_3 \xrightarrow[\lambda < 310\text{nm}]{\nu} O(^1D) + O_2$$

$$O(^1D) + H_2 \longrightarrow OH + H$$

$$H + O_3 \longrightarrow OH + O_2 \quad .$$

Photolysis of H_2O was used as the source of OH at temperatures above 270 K. Below 270 K, the photolysis of O_3 and H_2 was employed as a means of avoiding the problem of HCl absorbing on the water-coated reaction vessel walls. To demonstrate that the rate constant for Reaction (1) was independent of the OH source, k_1 was measured at 298 K using both photolytes. The results listed in Table I clearly show this independence.

$O(^3P)$ was produced by the vacuum UV photolysis of 150m Torr of O_2. Since 100 Torr of Ar was used as the diluent gas in these experiments, all $O(^1D)$ formed during the photolysis was quenched to $O(^3P)$ within a few microseconds after its formation. The concentration of $O(^3P)$ was monitored using an atomic oxygen resonance lamp as described in previous work from this laboratory.(14,15) One minor change in our present investigation was the inclusion of an EMR solarblind VUV photomultiplier tube (Model 542G) to detect atomic oxygen resonance radiation at ∿1300Å. In all cases, a calcium fluoride window was placed over the photomultiplier tube to filter out any background Lyman-α radiation. Reaction (2) was not studied at temperatures below 350 K due to the very small value of k_2 which dictated the use of very high concentrations of HCl. These high concentrations of HCl resulted in a significant increase in the background noise level, making high-precision measurements difficult. An additional complication was the attenuation of the atomic oxygen resonance line at 1303Å ($\varepsilon \simeq 81$ atm^{-1} cm^{-1})[16].

Both reactions (1) and (2) were studied under pseudo-first order conditions, with the concentration of HCl in excess. Typically, the concentrations of OH and $O(^3P)$ were in the range of 1×10^{11} to $5 \times 10^{11}/cm^3$. The ratio of reactants was as follows: $[HCl]/[O(^3P)] > 10^{14}$ and $[HCl]/[OH] > 600$.

A MKS Baratron and a two turn Bourdon gauge (Wallace and a Tiernan Type FA145) were used to measure low pressures (1-300m Torr) and high pressures (800 Torr), respectively. The precision with which reaction gas mixtures could be made up was ∿4%.

The argon and oxygen used in this study were Air Products UHP grade gases with a stated purity of 99.999%. Matheson 'Electronic grade' HCl was purified to remove Cl_2 by bulb-to-bulb distillation at 195 K and was degassed before use. O_3 was prepared by passing O_2 through an Ozonator and stored at 195 K. Before use, ozone was purified by continuously pumping while at 195 K; its purity was checked by UV spectroscopy. Matheson UHP hydrogen was used without further purification. The H_2O used in this investigation was glass distilled and degassed at liquid N_2 temperatures prior to use.

RESULTS AND DISCUSSION:

The results from the OH-HCl study are shown in Table I. Reaction (1) was studied at five temperatures and over a wide range of experimental parameters. As pointed out earlier, pseudo-first order conditions (i.e., [HCl] >> [OH]) were maintained throughout the investigation. In those experiments where water was used as the source of OH radicals, the first order rate constant k_1 was also measured as a function of the residence time for the HCl gas mixture in the reaction cell (e.g., 0, 10 and 15 min.). As can be seen from Table I, k_1 at 298 K was found to be only slightly dependent on the residence time of the gas mixture up to times of 15 minutes. These measurements indicate that HCl was not being depleted by its dissolution into water absorbed on the reaction cell wall within the normal operating time of 5 minutes. In another series of tests at 270 K, k_1 was shown to decrease by ∿10% in 10 minutes. Hence, at this temperature, all experiments were carried out within 3 minutes after the introduction of the reactant gas mixture to ensure only a very minor loss of reactant on the cell walls.

At each temperature, the bimolecular rate constant, k_1, was computed from the measured pseudo-first order rate constant using a linear least square analysis. The quoted errors for each k_{bi} are 2σ. A plot of $\ln k_1$ against $1/T$ is shown in Figure 1. A least squares fit of this data produced the following Arrhenius expression:

$$k_1 = (3.3 \pm 0.3) \times 10^{12} \exp[-(837 \pm 78)\mathrm{cal\ mol}^{-1}/RT]\mathrm{cm}^3\mathrm{molecule}^{-1}\mathrm{s}^{-1}.$$

Again the quoted errors are 2σ for the temperature range covered. This expression has been defined from a total of 39 experiments.

In previous kinetic investigations in our laboratory of the OH radical, under conditions similar to the present measurements, it was demonstrated that radical-radical reactions of the type H + OH and OH + OH were of negligible importance. Moreover, both calculations, as well as experimental variations of the OH concentration in this study tend to confirm the negligible contribution of the above processes, as well as others (e.g. OH + Cl) to the measured rate constants [see Table I].

The results obtained from the $O(^3P)$ + HCl study are shown in Table II. We could not measure k_2 below 350 K since below this temperature (i.e. 298 K) there was no measureable increase in the observed decay rate of $O(^3P)$, even when 1 Torr of HCl was present in the reaction cell. Since the FPRF technique in this case was capable of measuring a change of 10 s^{-1} in k_2', it can be concluded that the value of k_2 is less than 3×10^{-16} cc molecule^{-1}s^{-1} at 298 K. This result suggests that the HCl pressure would have to be greater than 10 Torr to obtain an accurate value for k_2 at 298 K. At these high HCl concentrations, however, numerous complications develop, as were described earlier in the experimental section.

At 350 K, experiments were carried out to determine the possible importance of secondary reactions resulting from the high concentrations of HCl employed. In this case, the flash energy was varied by a factor of $\sim$6. As seen from Table II, this variation in the radical concentration did not affect our measured value of k_2'. These results would tend to indicate that our measured values of k_2' were free of major errors originating from radical-radical processes.

The bimolecular rate constant, k_2, at each temperature was computed by subjecting the pseudo-first order data to a linear least square analysis. From these temperature dependent bimolecular rate constants, the following Arrhenius expression was derived:

$$k_2 = (5.2 \pm 1.03) \times 10^{-11} \exp[-(7510 \pm 750)\,\mathrm{cal\ mol^{-1}}/RT]\,\mathrm{cm^3\,molecule^{-1}s^{-1}}.$$

The quoted errors are 2σ for both k_{bi} and k_2. It is to be noted that the larger error in the A factor for reaction (2) versus reaction (1) is the result of the more limited temperature range covered, the higher degree of uncertainty in each of the individual measurements, and the more limited number of experiments performed.

COMPARISON WITH PREVIOUS STUDIES:

Table III lists the three Arrhenius expressions which have now been reported for reaction (1). The calculated 298 K rate constants are seen to be in remarkably good agreement with each other. These values suggest that at room temperature, k_1 can be given as $(6.6 \pm 0.6) \times 10^{-13}$ cc molecule^{-1}s^{-1}. The temperature dependence of k_1 obtained in the present study is seen to be in reasonably good agreement with previous measurements. The most significant disagreement is with the work of Zahniser, et al.(8) As can be seen from Figure 1, the error bars on k_1, measured in this work, overlap the Arrhenius lines of both Zahniser, et al.,(8) and Smith and Zellner(7) at temperatures higher than 270 K. Below 270 K, our k_1 values are in good agreement with those of Smith and Zellner, but are ∿20% lower than those measured by Zahniser, et al.(8) at temperatures of 225 K. At the present time, we can give no explanation for this observed difference in k_1 at low temperatures.

Concerning reaction (2), the results from four previous studies, as well as the present investigation, are listed in Table IV. The most recent results obtained by Singleton and Cvetanovic(11) have not been included in Table IV since these authors have yet to provide printed rate data at different temperatures. However, a value for $E_{act.}$ was verbally reported by these investigators (11) as ∿6 K cal mol^{-1}. From Table IV, it would appear that the activation energy of 4.5 K cal mol^{-1}, obtained by Balakhnin et al.(9), is quite low and probably incorrect. There is a discrepancy of

$\sim$1.5 K cal mol^{-1} between Brown and Smith's (10) value of E_2 and that reported in this work. The results from the other three investigations lie between these two values. And, at this juncture, there appears to be no basis for rejecting or accepting any one of these five values for E_2 (i.e., 6 K cal mol^{-1} (10), $\sim$6 K cal mol^{-1} (11), 6.44 K cal mol^{-1} (6), 7.15 K cal mol^{-1} (12), and 7.5 K cal mol^{-1}). It should be noted, in fact, that the seemingly large discrepancy of $\sim$25% in E_2 is not that unreasonable in view of the small value for the bimolecular rate constant. In virtually all studies reported, involving four different techniques, it appears that the sensitivity of each apparatus was at its ultimate limit.

ATMOSPHERIC IMPLICATIONS

The three processes which re-introduce Cl atoms into the stratospheric O_3 destruction cycle are chemical reactions (1) and (2) and the photochemical process (3), i.e.:

$$OH + HCl \rightarrow H_2O + Cl \qquad (1)$$

$$O(^3P) + HCl \rightarrow OH + Cl \qquad (2)$$

$$HCl \xrightarrow{h\nu} H + Cl \qquad (3)\ .$$

At photochemical equilibrium with respect to Cl atoms, it can be shown that

$$[Cl]/_{[HCl]} = (k_1\ [OH] + k_2\ [O(^3P)] + J_{HCl})/k_4[RH], \qquad I$$

where J_{HCl} is the photodissociation rate constant for HCl and process (4) is given as:

$$Cl + RH \rightarrow HCl + R\ . \qquad (4)$$

Presented in Table V are the values of $k_1[OH]$, $k_2[O(^3P)]$, and J_{HCl} as a function of altitude. From this table, it can be seen that reaction (1) totally dominates the conversion of HCl back to active chlorine atoms below 50 km. In point of fact, at the most favorable altitude of 50 K, reaction (2) makes only an approximate 3% contribution to the total conversion process. Thus, below 50 km, equation I can be simplified to:

$$[Cl]/_{[HCl]} = \frac{k_1}{k_4}\frac{[OH]}{[RH]} \qquad II$$

The maximum impact on stratospheric models from the k_1 value reported in this work would be in the stratospheric region of 13 to 30 K. In this region, our value of k_1 would predict an approximate 20% lower value for the steady-state Cl atom concentration than that suggested from the measurements of Zahniser, et al.(8) It should again be noted, however, that no basis presently exists for excluding the Zahniser, et al.(8) value; hence, it would seem reasonable to take a simple average of the k_1 values for modelling purposes.

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TABLE I

REACTION DATA FOR OH + HCl → H_2O + Cl

Temperature	Diluent	Photolyte	P_{HCl} in mTorr	Flash Energy in Joules	k_1' (sec^{-1})	$k_{bimol.}$ x 10^{13} in cc $molecule^{-1} sec^{-1}$
250 K	40 Torr He	50mTorr O_3 + 100mTorr H_2	0.0	88	90	
			2.5		125	
			5.0		166	
			10.0		263	
			15.0		361	
			20.0		438	4.8 ± .2
270 K	50 Torr He	150m Torr H_2O	0.0	88	47	
			2.5		53	
			5.0		89	
			7.5		169	
			10.0		207	
			12.5		256	
			15.0		293	
			17.5		414	
			20.0		444	5.9 ± .6
298 K	20 Torr He	150mTorr H_2O	0.0	88	55 a	
			5.0		150 a	
			10.0		270 a	
			15.0		393	
			20.0		472	6.7 ± .4
	40 Torr He	50mTorr O_3 + 100mTorr H_2	0.0	88	120	
			5.0		215	
			10.0		320	6.4 ± 0.6
	20 Torr He	150mTorr H_2O	5.0	250	160	
			10.0	88	260 c	
			10.0	88	250 b,d	

TABLE I (continued)

Temperature	Diluent	Photolyte	P_{HCl} in mTorr	Flash Energy in Joules	k_1' (sec^{-1})	$k_{bimol.} \times 10^{13}$ in cc $molecule^{-1} sec^{-1}$
356 K	50mTorr He	150 mTorr H_2O	0.0	88	40	
			2.5		62	
			5.0		142	
			7.5		173	
			10.0		260	
			15.0		397	
			20.0		487	8.8 ± .6
402 K	50mTorr He	150 mTorr H_2O	0.0	88	130	
			2.5		179	
			5.0		238	
			10.0		335	
			12.5		413	
			15.0		500	9.9 ± 1.0

The quoted errors for the values of $k_{bimol.}$ are two standard deviations.

[a] Average of two runs

[b] Not used in the calculation of bimolecular rate constant

[c] Experiments carried out 10 minutes after the reactants were introduced into the cell

[d] Similar to c, however, with a 15 minute delay

TABLE II

REACTION RATE DATA FOR $O(^3P) + HCl \longrightarrow OH + Cl$

TEMPERATURE in K	P_{HCl} in Torr	Flash Energy in J	$k'_2(sec^{-1})$	$k_{bimol.} \times 10^{15}$ $(cm^3 molecule^{-1} s^{-1})$
350	0.0	88	16	
	0.5		31	
	1.0		48	
	1.5		58	
	2.0		71	(0.99 ± 0.09)
392	1.0	210	85	
	1.0	37	83	
401	0.0	88	22	
	0.25		52	
	0.25		63	
	0.50		87	
	0.75		118	
	1.00		136	
	1.00		145	
	1.25		165	(4.8 ± 0.4)
454	0.0	88	28	
	0.25		73	
	0.50		131	
	0.75		213	(11.6 ± .4)

The quoted errors for the values of $k_{bimol.}$ are two standard deviations.

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TABLE III

SUMMARY OF RATE DATA FOR $OH + HCl \quad H_2O + Cl$

Reference	Arrhenius Expression ($cm^3 molecule^{-1} sec^{-1}$)	$k_1(298) \times 10^{13}$ ($cm^3 molecule^{-1} s^{-1}$)	Temperature (in K) Range	Technique[a]
Takacs and Glass (1973)		6.4 ± 1.5 (295 K)		F/ESR
Davis, et al. (1974)		6.5 ± 0.4		FF/RF
Hack, et al. (1976)		6.7 ± 1.7 (293 K)		DF/ESR
Smith and Zellner (1974)	$(4.1^{+2.0}_{-1.4}) \times 10^{-12} \exp[-\frac{(1050 \pm 50)}{RT}]$	6.9 ± 1.0	220-480	FF/RA
Zahniser et al. (1974)	$(2.0 \pm 0.1) \times 10^{-12} \exp[-\frac{(620 \pm 20)}{RT}]$	6.7 ± 0.4	224-440	DF/RF
This Work	$(3.3 \pm 0.3) \times 10^{-12} \exp[-\frac{(937 \pm 78)}{RT}]$	$6.6 \pm .4$	250-402	FF/RF

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[a] The symbols are: F/ESR, Flow tube with an ESR detection system.
FF/RF, Flash Photolysis with Resonance Fluorescence detection system
FF/RA, Flash Photolysis with Resonance Absorption detection system
DF/RF, Dischrge Flow with Resonance Fluorescence detection system
DF/ESR, Discharge Flow with Electron Spin Resonance detection system

TABLE IV

SUMMARY OF RATE DATA FOR $O(^3P) + HCl \rightarrow OH + Cl(^2P_{3/2})$

Reference	Arrhenius Expression ($cm^3 molecule^{-1} s^{-1}$)	Temperature Range (in K)	Technique[a]
Balakhnin, et al.	$(1.75 \pm 0.6) \times 10^{-12} \exp(-\frac{2260}{RT})$	295-371	DF/ESR
Smith and Brown	$(2.5 \begin{smallmatrix}+1.2\\-0.8\end{smallmatrix}) \times 10^{-12} \exp[-\frac{(2970 \pm 150)}{T}]$	293-440	F/AG
Wong And Belles	$(1.9 \pm 0.3) \times 10^{-11} \exp[-\frac{(3584 \pm 70)}{T}]$	356-628	SF/MS
This Work	$(5.2 \pm 0.9) \times 10^{-11} \exp[-\frac{(3755 \pm 200)}{T}]$	350-454	FF/RF
Hack, et al.	$(8.5 \pm 1.7) \times 10^{-12} \exp\left[-\frac{(3220 \pm 150)}{T}\right]$	293-718	DF/ESR

[a] The symbols are: DF/ESR, Discharge flow with ESR - detection system.

F/AG, flow tube with after glow as detection system.

SF/MS, stirred flow realtor with mass spec as detection system.

FF/RS, Flash Photolysis purity resonance fluorescence as detection system.

TABLE V

RATE OF HCl DEGRADATION IN THE STRATOSPHERE

Altitude, A in KM	Temperature, T, in K at Altitude A	k_1 at Temperature T x 10^{13} [c]	OH Concentration in Radicals per cm^3 at Altitude A x 10^{-7}	$k_1 \times [OH] \times 10^9$	k_2 at Temperature T x 10^{17} [d]	$O(^3P)$ Atom Concentration in Atoms per cm^3 [a]	$k_2 \times [O(^3P)] \times 10^9$	$\frac{k_1 [OH]}{k_2 [O]}$	J_{HCl} [b]
20	220	4.2	0.11	463	0.20	0.02	0.004	1.2×10^5	$< 10^{-10}$
25	220	4.2	0.18	737	0.20	0.14	0.03	2.6×10^4	$\sim 6 \times 10^{-10}$
30	230	4.6	0.30	1370	0.42	0.62	0.26	5.3×10^3	$\sim 8 \times 10^{-9}$
35	240	5.0	0.63	3120	0.83	2.4	2.0	1.6×10^3	$\sim 2.5 \times 10^{-8}$
40	250	5.3	1.4	7450	1.6	8	12	6.0×10^2	$\sim 4 \times 10^{-8}$
45	265	5.9	1.6	9380	3.7	22	80	1.2×10^2	$\sim 5.5 \times 10^{-8}$
50	270	6.0	1.1	6640	4.7	36	171	3.9×10^1	$\sim 6.5 \times 10^{-8}$

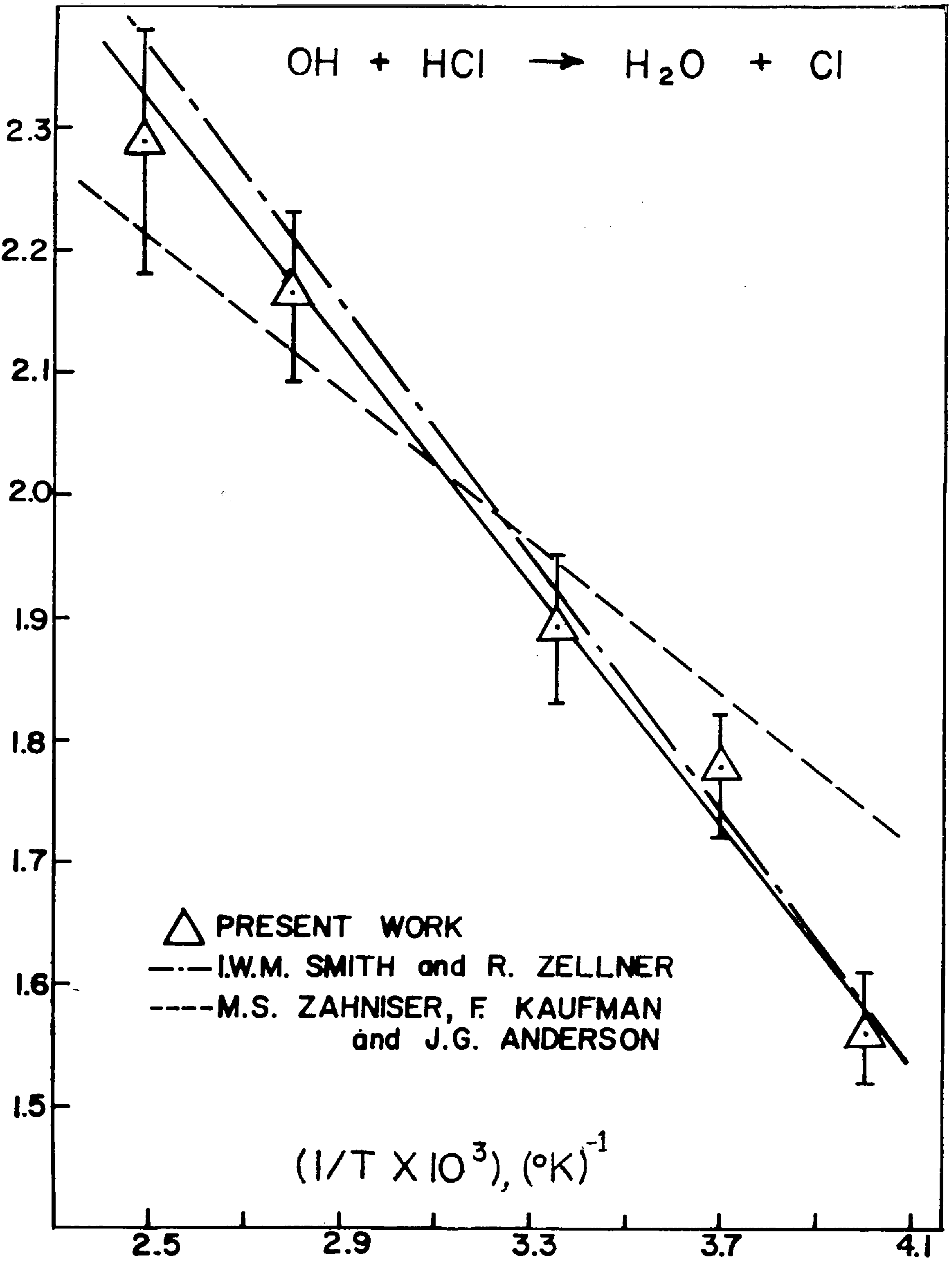
a: Reference (20)

b: Reference (18)

c: k_1 from this work

d: k_2 from this work

Figure. (1): Arrhenius Plots for the Reaction OH + HCl → H_2O + Cl.



$OH + HCl \rightarrow H_2O + Cl$
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
ln k (cm³ · molec⁻¹ · sec⁻¹)
△ PRESENT WORK
—·— I.W.M. SMITH and R. ZELLNER
---- M.S. ZAHNISER, F. KAUFMAN and J.G. ANDERSON
(1/T X 10³), (°K)⁻¹
2.5
2.9
3.3
3.7
4.1

(4) A Kinetics Study of the Chemical Decomposition of Stratospheric $ClONO_2$.

A STUDY OF THE CHEMICAL DEGRADATION OF $ClONO_2$ IN THE STRATOSPHERE*

A. R. Ravishankara and D. D. Davis**

Atmospheric Sciences Branch
Applied Sciences Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

and

G. Smith and G. Tesi†

Department of Chemistry
University of Maryland
College Park, Maryland 20742

and

J. Spencer

Chemistry Department
University of California, Irvine
Irvine, California

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†On sabbatical leave from NSF.

ABSTRACT

The flash photolysis-resonance fluorescence technique has been utilized to measure the rate constants for the reactions of chlorine nitrate ($ClONO_2$) with two stratospheric radicals, $O(^3P)$, and OH. Both rate constants were measured at a pressure of 20 Torr and a temperature of 245 K. The reactions with their corresponding rate constant in units of cc molecule^{-1}s^{-1} are: $O(^3P) + ClONO_2 \longrightarrow$ Products, $k_1 = (2.0 \pm 0.2) \times 10^{-13}$; $OH + ClONO_2 \longrightarrow$ Products, $k_2 = (3.7 \pm 0.2) \times 10^{-13}$.

The above results, coupled with the photolysis rate of $ClONO_2$, indicate that chemical degradation pathways contribute less than 10% to the removal of $ClONO_2$ in the stratosphere.

INTRODUCTION

Recent modelling calculations by Crutzen (1976), Crutzen and McAfee (1976), Chang and Wuebbles (1976), and Molina (1976), have indicated that stratospheric chlorine nitrate ($ClONO_2$) might be of importance as a temporary sink for both chlorine and nitrogen oxides. If so, the impact of injected NO_x and/or chlorine on stratospheric ozone profiles could be significantly reduced. The effectiveness of this potential sink in altering model calculated stratospheric ozone profiles depends primarily on two factors: (1) the rate of formation, and (2) the rate of destruction of $ClONO_2$. The work to be reported here deals with the rate of destruction of $ClONO_2$ under stratospheric conditions. There are two possible modes of destruction of $ClONO_2$; viz, photolysis by sunlight and removal by chemical reactions. In the latter case, which will be the primary focus of this paper, likely reaction paths would involve the two free radical species $O(^3P)$ and OH, i.e.:

$$O(^3P) + ClONO_2 \longrightarrow \text{Products} \qquad (1)$$

$$OH + ClONO_2 \longrightarrow \text{Products} \qquad (2)$$

Presented in the following text will be recently measured gas kinetic data on Reactions (1) and (2). Rates of destruction via the above processes will then be compared with that resulting from direct photochemical decomposition.

EXPERIMENTAL

The flash photolysis-resonance fluorescence system used in this study has been described in detail in earlier publications (Davis et al., 1974, 1972). Hence, only a limited description of the system is presented here. In this investigation, a pyrex cell with an internal volume of ∿150 cm^3 was used to examine both Reactions (1) and (2). The reaction mixture was maintained at 245 K by circulating methanol from a thermostated circulation bath through the outer jacket of the reaction cell. The temperature of the cell was monitored using an Iron-Constantan thermocouple.

$O(^3P)$ was produced by the vacuum UV photolysis of 150 m Torr of O_2. Since 20 Torr of Ar was used as the diluent gas in these experiments, all $O(^1D)$ formed during the flash would have been quenched to $O(^3P)$ within a few microseconds after its formation. OH was produced by the photolysis of a mixture of 25 m Torr of O_3, 100 m Torr of H_2, and 20 Torr of Ar through the sequence of reactions,

$$O_3 \xrightarrow[\lambda\ <3100]{h\ \nu} O(^1D) + O_2$$

$$O(^1D) + H_2 \rightarrow OH + H$$

$$H + O_3 \rightarrow OH + O_2.$$

The change in concentration of $O(^3P)$, or OH was followed by the resonance fluorescence technique using either an EMR vacuum UV photomultiplier tube (1300Å), or an RCA 8850 tube (3095Å).

In carrying out experiments on both reactions, the gas handling system and the reaction cell were "conditioned" by filling them with chlorine nitrate at a low pressure (<30 mTorr) to remove any active spots on the glass surfaces. This procedure was carried out immediately prior to the direct introduction of a measured amount of chlorine nitrate into the reaction cell. In all experiments, the concentration of chlorine nitrate was in large excess ($>10^3$) over the concentration of $O(^3P)$, or OH; hence, pseudo-first order kinetics prevailed.

Chlorine nitrate was purified by bulb to bulb distillation and its purity was checked by recording both its IR (Miller, et al., 1967) and UV spectrum. On the basis of these analyses, together with calculations of the $O(^3P)$ loss due to the reaction, $O(^3P) + NO_2 \rightarrow NO + O_2$ (Davis et al., 1973), the NO_2 impurity level was placed at less than .5%. It should be noted, however, that at 298 K there was evidence indicating that $ClONO_2$ decomposed in the glass reaction cell when allowed to stand for several minutes. This decomposition was evident from repeated measurements of the rate constant k_1', and finding steadily increasing k_1' values with an increase in the residence time. However, at 245 K, there was no evidence for the decomposition of $ClONO_2$. For this reason, both reactions were studied at the reduced temperature of 245 K.

Ozone was prepared by passing O_2 through an ozonator. Before use, O_3 was purified by continuously pumping while at 195 K; its purity was checked by UV absorption spectroscopy. UHP grade Matheson H_2 and O_2, and UHP gold label Ar were used without further purification.

RESULTS AND DISCUSSION

The rate constants for both Reactions (1) and (2) were measured at 245 K simulating stratospheric temperatures. The pseudo-first order rate constants, k_1' and k_2', for the disappearance of $O(^3P)$ and OH are shown as a function of the $ClONO_2$ pressure in Figure 1. A linear least square analysis of the data was carried out to obtain the bimolecular rate constants, k_{bi}. At 245 K, the k_{bi} values are

$$k_1 = (2.0 \pm .2) \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}$$

and

$$k_2 = (3.7 + .2) \times 10^{-13} \text{ cc molecule}^{-1} \text{ sec}^{-1}.$$

For Reaction (1) and (2), the quoted errors are two standard deviations.

In the investigation of Reactions (1) and (2), the concentration of $ClONO_2$ ($>10^{14}$ molecule cm^{-3}) was typically a thousand times greater than that of either $O(^3P)$ ($<10^{11}$ atom cm^{-3}) or OH ($<10^{12}$ radical cm^{-3}). Under these conditions, it can be calculated that secondary reactions should have been negligible. Supporting evidence for this point of view was provided by carrying out several experiments with varying flash energy, typically a factor of four, and finding that the pseudo-first order rate constants k_1 and k_2 were independent of the flash intensity. Since any secondary reaction would necessarily have involved either the photofragments from $ClONO_2$ or products from Reactions (1) and (2), the decay rate of $O(^3P)$ or OH would have been proportional to the square of the flash energy. As noted above, no such observation was recorded.

Table I lists the relative chemical degradation rates (R_1 and R_2) as a function of altitude resulting from Reactions (1) and (2). The destruction of $ClONO_2$ through its reaction with $Cl(^2P_{3/2})$ has not been included in the quoted total chemical degradation rate because: (1) the rate constant for the reaction of $Cl(^2P_{3/2})$ with $ClONO_2$ is only $\sim 1 \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$, according to preliminary results obtained in our laboratory, and (2) the concentration of $Cl(^2P_{3/2})$ at mid-stratospheric altitudes is very much lower than that of either OH or $O(^3P)$. Along with the chemical degradation rates, we have listed the photochemical destruction rate (J), as well as the total degradation rate of $ClONO_2$ ($R_1 + R_2 + J$). As can be seen from the Table, chemical processes (1) and (2) contribute less than 10% to the total rate of $ClONO_2$ destruction at altitudes less than 30 Km. Since the concentration of $ClONO_2$ is calculated to be near its maximum around 25 Km and drops off very significantly at higher altitudes, it must be concluded that the photochemical decomposition of $ClONO_2$ in the stratosphere is by far the most important degradation path for this molecule.

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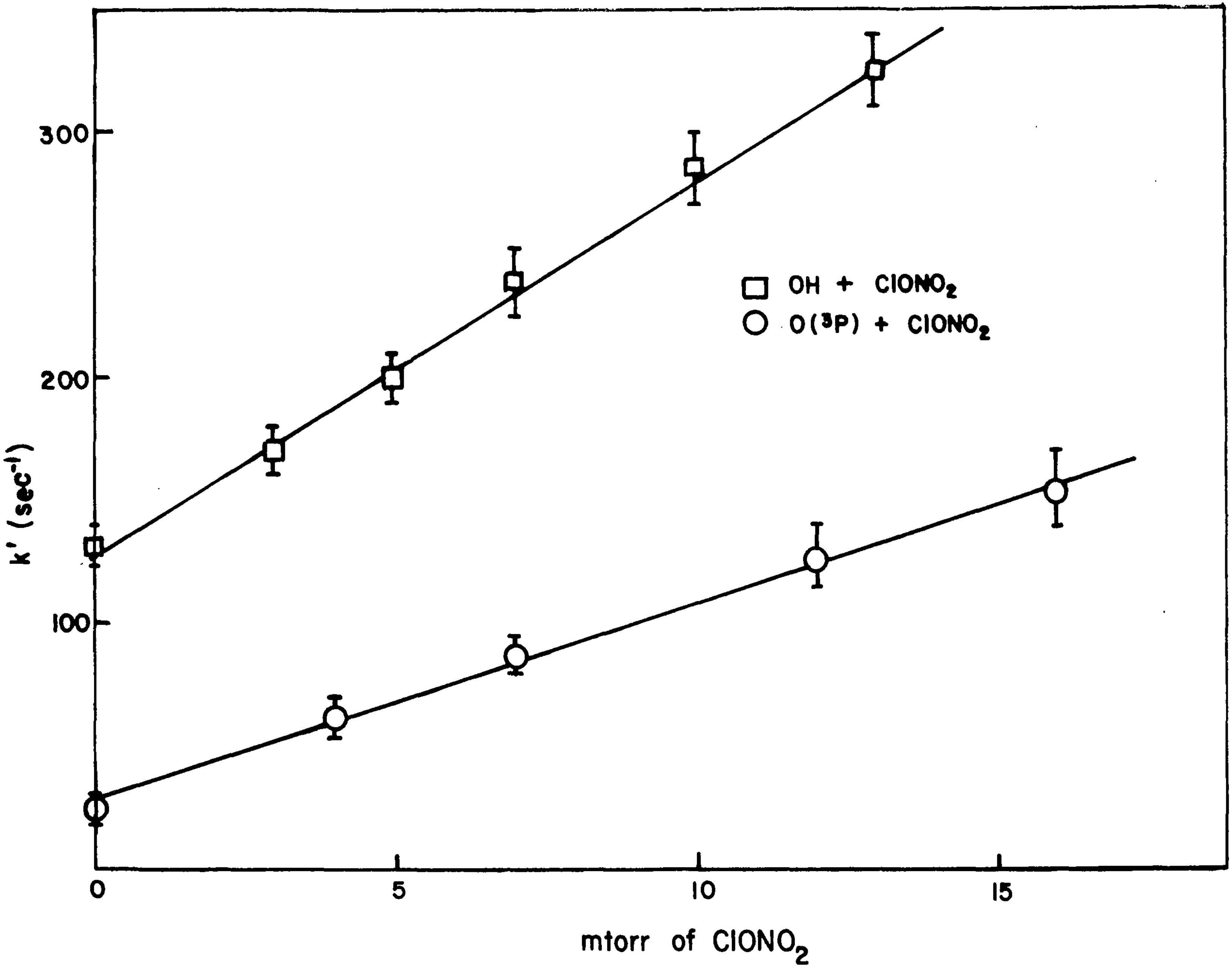
FIGURE 1

A plot of the pseudo-first order rate constant for the decay of OH [□] or O(^{3}P) [O] as a function of ClONO$_2$ pressure at 245 K. The error bars in these plots show the total uncertainty observed in three to four independent measurements of the first order rate constant at a given ClONO$_2$ pressure.


300
200
100
k' (sec^{-1})
0
5
10
15
mtorr of ClONO$_2$
□ OH + ClONO$_2$
○ O(^{3}P) + ClONO$_2$

(5) A Photochemical Study of the Decomposition of O_3 Over the Wavelength Range 2935 - 3165Å: Φ Values for Production of $O(^1D)$.

A QUANTUM YIELD DETERMINATION OF O(^{1}D) PRODUCTION FROM OZONE VIA LASER FLASH PHOTOLYSIS*

D. L. Philen, R. T. Watson**, and D. D. Davis†

Atmospheric Sciences Division
Applied Sciences Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

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**Present Address:
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

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ABSTRACT

The quantum yield for $0(^1D)$ production from ozone photolysis has been measured at 298 K from 293.0 to 316.5 nm. The $O(^1D)$ was monitored by its reaction with N_2O to form excited NO_2^*. The photolysis source was a frequency doubled flashlamp pumped dye laser which provided tunable UV in the desired spectral region with a 0.1 nm line width. The results show ϕ to be constant below 300 nm, taken to be unity, with a sharp decrease centered at 308 nm and a value of less than 0.1 above 313.5 nm.

INTRODUCTION

It is generally accepted that the $OH(^2\Pi)$ free radical is one of the most important oxidizing agents in the troposphere and stratosphere since it controls the chemistry of numerous trace gases. The principal source of the hydroxyl radical is the reaction of electronically excited atomic oxygen, (O^1D), with atmospheric water vapor, $O(^1D) + H_2O \rightarrow OH + OH$ (a much smaller contribution is made via the reaction of $O(^1D)$ with methane and molecular hydrogen). The source of $O(^1D)$ is that of photolysis of ozone in the Hartley continuum, and possibly in the Huggins band, i.e.

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \rightarrow O(^1D) + O_2\ (^1\Delta_g) \qquad (1)$$

$$O_3 + h\nu\ (\lambda < 410\ \text{nm}) \rightarrow O(^1D) + O_2\ (^3\Sigma_g^-). \qquad (2)$$

On thermochemical grounds, processes (1) and (2) are allowed to occur at wavelengths shorter than 310 nm and 410 nm, respectively. However, it has now been established (1) that process (1) is the dominant photolytic process below 300 nm and all evidence suggests that it occurs with unit quantum efficiency. Processes 3a or 3b

$$O_3 + h\nu \ (\lambda < 611 \text{ nm}) \rightarrow O(^3P) + O_2 \ (^1\Delta_g) \qquad (3a)$$

$$O_3 + h\nu \ (\lambda < 463 \text{ nm}) \rightarrow O(^3P) + O_2 \ (^1\Sigma_g^+) \qquad (3b)$$

have been shown (2,3) to be the only processes occuring at 340 nm, thus indicating that process (2) is of no importance. In the 300-320 nm range, conflicting results have been reported for the $O(^1D)$ quantum yield. This wavelength region has now been designated as the fall-off region for $O(^1D)$ production.(2-9) Even though the absorption cross-section for ozone is rapidly decreasing above 300 nm, the exact nature of the fall-off in O^1D production between 300 and 320 nm is of particular importance in the troposphere and lower stratosphere due to the lack of radiation at wavelengths shorter than 300 nm. (Absorption cross-section data for ozone have been determined for both the visible and UV spectral regions, (7,10-15) and have been recently reviewed (16) and tabulated (7).)

Ozone photolysis studies have been performed in both the liquid (17,18) and gaseous (2-9) phases by several groups utilizing a variety of techniques. However, the scope of this investigation has been limited to photolytic processes occuring only in the gaseous phase. Jones and Wayne (3), at 313 nm,measured the variation in O_3 disappearance, $\Phi(O_3)$, as a function of the O_3 concentration in pure O_3 and O_3/H_2 mixtures. These authors concluded that the quantum yield for O^1D production had a value of 0.1 relative to a value of unity at wavelengths shorter than 300 nm. Castellano and Schumacher (2), however, have reported a ϕ value of 1.0 at 313 nm, their results coming from an experiment very similar to that of Jones and Wayne. Simonaitis et al.(4), Kuis et al.(9), and Kajemoto and Cvetanovic(5) photolyzed ozone at 313 nm in the presence of N_2O and from the amount of N_2 formed deduced ϕ to be 0.35 (modified(9) downward from their original report of 0.5), 0.29 and 0.44, respectively. The latter two groups(5,9) also studied the variation of ϕ $O(^1D)$ with temperature. Moortgat and Warneck(7) and Martin et al.,(8) also photolyzed ozone at 313 nm in the presence of N_2O and deduced ϕ to be 0.29 and 0.32, respectively. In these studies, ϕ was established by monitoring the infrared chemiluminescence associated with the formation of electronically excited NO_2^*. Lin and DeMore (6) measured the yield of isobutanol from the photolysis of O_3 with isobutane at 233 K and reported a value of ≤ 0.08 for ϕ (O^1D), again at 313 nm.

To be reported here is a new investigation on the photochemical production of $O(^1D)$ in the spectral region of 293.0 to 316.5 nm. Of considerable importance in this study was the wavelength resolution of the light source employed. In this investigation, a tunable dye laser was employed having a spectral width of ∿.15 nm.

EXPERIMENTAL

The chemical scheme which describes the photochemical degradation of pure ozone can be written:

$$O_3(^1A) + h\nu \longrightarrow O(^1D) + O_2(^1\Delta_g) \qquad (1)$$

$$O_3(^1A) + h\nu \longrightarrow O(^3P) + O_2(^1\Delta_g,\ ^1\Sigma_g^+) \qquad (3)$$

$$O(^1D) + O_3 \xrightarrow{(a)} O_2 + O_2(^1\Delta_g,\ ^1\Sigma_g^+)$$

$$\xrightarrow{(b)} O_2 + 2\ O(^3P) \qquad (4)$$

$$O_2(^1\Delta_g,\ ^1\Sigma_g) + O_3 \longrightarrow 2\ O_2 + O(^3P) \qquad (5)$$

$$O(^3P) + O_3 \longrightarrow 2\ O_2 \qquad (6)$$

In the presence of N_2O, the following additional reactions can occur:

$$\begin{aligned} O(^1D) + N_2O &\xrightarrow{(a)} N_2 + O_2 \\ &\xrightarrow{(b)} 2\ NO \end{aligned} \tag{7}$$

$$\begin{aligned} NO + O_3 &\xrightarrow{(a)} NO_2 + O_2 \\ &\xrightarrow{(b)} NO_2^{*} + O_2 \end{aligned} \tag{8}$$

$$\begin{aligned} NO_2^{*} + M &\xrightarrow{(a)} NO_2 + M \\ NO_2^{*} &\xrightarrow{(b)} NO_2 + h\nu\ (\lambda > 600\ nm)^{(19)} \end{aligned} \tag{9}$$

$$O(^3P) + NO + M \longrightarrow NO_2^{**} + M \tag{10}$$

$$\begin{aligned} NO_2^{**} + M &\xrightarrow{(a)} NO_2 + M \\ NO_2^{**} &\xrightarrow{(b)} NO_2 + h\nu\ (\lambda > 400\ nm)^{(20)} \end{aligned} \tag{11}$$

$$O(^3P) + NO_2 \longrightarrow NO + O_2 \tag{12}$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{13}$$

It will be shown later that processes (10) - (12) are of no importance under the experimental conditions employed in the present study. Therefore, the amount of $O(^1D)$ produced in process (1) can be quantitatively monitored via the infrared chemiluminescence (9b) which is associated with the production of the excited electronic state of NO_2^{*} in reaction 8b. The intensity of emission, $I(\lambda)$, can be expressed as:

$$I(\lambda) = \beta\phi(\lambda)\ N_{abs}(\lambda)\gamma \qquad \text{I}$$

Where, $\phi(\lambda)$ is the quantum yield for $O(^1D)$ production, β is the geometrical collection efficiency of the chemiluminescence detector, $N_{abs}(\lambda)$ is proportional to the number of quanta of the photolysis radiation absorbed by ozone in the region of the reaction cell as viewed by the chemiluminescence detector, and γ is given by:

$$= \frac{2(k_{8b}/k_8)\ k_{7b}(N_2O)\ k_{9b}}{(k_7(N_2O) + k_4(O_3))\ (k_{9a}(N_2O + O_3) + k_{9b})} \qquad \text{II}$$

As can be seen from equation II, the magnitude of γ depends upon the values of several rate constants as well as the concentrations of N_2O and O_3. Consequently, if the initial concentrations of N_2O and O_3 are kept constant, and the consumption of ozone during photolysis is limited to <1%, then the value of λ is constant. However, it can be shown that the intensity of fluorescence (I_F) is relatively insensitive to the chemical composition of the photolysis mixture as it is directly proportional to (O_3 + N_2O) through processes (1) and (7) and inversely proportional to (O_3) and (N_2O) through process (9a), the electronic quenching of NO_2^*. Calculations based on recent rate constant data(21) for reactions (4) and (7) predict that under our experimental conditions ∿ 82% of the $O(^1D)$ produced in process (1) reacts with N_2O to produce an equal concentration of NO. N_{abs} (λ) can be calculated using the Beer-Lambert expression of $\ell n(I_o/I_t) = \sigma(\lambda)\ (O_3)\ell$, and knowledge of the incident photolysis flux ($N_o(\lambda)$). $\sigma(\lambda)$ is the absorption cross-section of ozone.

The experimental arrangement employed in this study utilized a frequency doubled, flashlamp pumped, tunable dye laser as the photolytic source of radiation in the region of 293 nm to 316 nm (see Figure 1). This dye laser system was operated with Rhodamine 6G, Rhodamine B, or a mixture of both dyes to provide continuous tunable output from 586 nm to 633 nm in the fundamental. Doubled UV radiation was obtained by use of three different temperature tuned crystals (ADA, 293-306 nm; ADP, 305-315 nm; RDP, 313-316.5 nm). Temperature tuning was used in favor of angle turning so as to minimize beam "walk off" (i.e., it is essential that the photolysis beam traverse the reaction cell in exactly the same position at all wavelengths) and thus maintain the geometric cell factor, β, constant. The line width of the doubled output was $\sim$.15 nm. The combination of three doubling crystals and different dyes provided continuous tuning over the entire photolysis region. The output wavelength of the dye laser was calibrated to within ±0.1 nm for the fundamental frequency relative to the He/Ne laser line at 632.8 nm. The latter was achieved with the use of a 3/4 meter spectrograph. The UV photon flux incident on the reaction cell was monitored using an RCA-935 calibrated photodiode which was traceable to an NBS standard. In an effort to eliminate any saturation problems on the 935 photodiode, the intensity of the laser pulse was reduced by two quartz beam-splitters (see Figure 1).

The NO_2* fluorescence was monitored, through a cut-off filter (λtransmitted >610 nm), by a cooled EMI-9658 R photomultiplier (extended S20 response) positioned at right angles to the incident UV radiation. In order to prevent dye laser fundamental radiation from scattering into the reaction cell, two UG-5 filters were placed on the output end of the frequency doubling crystal. Both the fluorescence and the incident radiation signals were stored on a Textronix dual trace storage oscilloscope, and the ratio of their intensities taken. A short series of experiments was also performed where the oscilloscope was replaced by a Northern 610 multichannel analyzer (discussed later).

In all experiments, the reaction cell was evacuated to a vacuum of 1×10^{-6} torr or lower before each experiment, using a liquid N_2 trapped oil diffusion pump system. Mixtures of 0.9 torr of O_3 and 9.1 torr of N_2O were used for all data points to give a total mixture of 1:10 O_3 to N_2O. Each mixture was frequently changed to minimize any possibility of ozone destruction by homogeneous gas phase reactions, or by heterogeneous decomposition on the cell walls.

The nitrous oxide was Matheson Research Grade having a stated purity of 98%. Ozone was prepared using a commercial ozonizer, and then stored on silica gel at 193 K. Before each experiment, the ozone was purified by vacuum pumping on the silica gel while at 193 K. Frequent tests of the O_3 purity showed levels of at least 95% (95% O_3; 5% O_2).

RESULTS

At each wavelength, several sets of experiments were performed where the ratio of the infrared fluorescence, I_F, and incident UV laser radiation, N_o, signals were measured. The ratio was measured for at least ten individual laser pulses within each set of experiments, and then averaged. The resulting ratios, corrected for the ozone absorption cross-section and the photodiode response curve, gave the desired relative quantum efficiency for $O(^1D)$ production as a function of wavelength. The quantum yield, ϕ, has been tabulated (Table 1) and plotted (Figure 2) as a function of wavelength from 293.0 nm to 316.5 nm. The expressed uncertainties represent the 90% confidence limits on the data. At wavelengths shorter than 300 nm, the quantum yields were normalized to unity. Above 302.5 nm the quantum yield was observed to deviate from unity with the maximum rate of decrease appearing at 308 nm. At the wavelengths 313.5 and 316.5 nm, it can be seen that ϕ decreased to 0.1 and 0.02, respectively. Determinations of ϕ at still longer wavelengths were precluded due to experimental difficulties. Further improvements in the experimental technique could yield more data in this region, if needed. It should be noted that while the absolute value of the uncertainty in Figure 2 appears to decrease as one goes to longer wavelengths the relative error associated with each point (that is, the uncertainty divided by the mean value of the quantum yield) remains approximately constant over the spectral region of interest.

A series of experiments was also performed to show that there were no unrecognized sources of detectable radiation which could have resulted in an erroneous interpretation of the data. These included (a) eliminating the 610 nm cut-off filter, or replacing it with a 540 nm cut-off filter; (b) a variation in the incident UV photolysis flux by a factor of $\sim$ 10; and (c) a variation in chemical composition. The most likely source of unwanted fluorescence would have been associated with the formation of electronically excited NO_2^{**} via reaction 10 followed by process 11 b. In this case, the fluorescence associated with the formation of NO_2^{**} is shifted to shorter wavelengths (relative to that associated with NO_2^{*}) due to the increased exothermicity of reaction 10 compared to reaction 8. However, the observation that the intensity of detected fluorescence was (a) invariant to the type of cut-off filter employed, and (b) varied linearly with the incident flux, strongly indicates that reaction 10 was of no significance. If process 10 had been important, the resulting fluorescence intensity would have been (a) dependent upon the choice of cut-off filter, and (b) varied with the square of the photolytic flux. These experiments, therefore, confirmed our calculations which showed that process 10 should not have been important. Preliminary experiments conducted at wavelengths shorter than 305 nm, with a chemical composition of 0.25 torr each of N_2O and O_3, resulted in similar results for ϕ, again indicating that reaction 10 was unimportant. As expected, there was no observable fluorescence signal when pure O_3 or pure N_2O was photolyzed within the spectral region of interest. Fluorescence due to the $O(^3P) \leftarrow O(^1D)$ electronic transition at 630 nm was not important due to the long radiative lifetime(25) associated with this spin-forbidden process.

Several experiments were performed where a multichannel analyzer was used in the single photon counting mode to accumulate the NO_2* fluorescence emitted from 10-20 laser pulses. Typical concentrations of O_3 and N_2O were 0.25-0.5 torr. The resulting fluorescence intensity-time profiles were recorded and observed to be logarithmic with typical 1/e decay times (I_F maximum occurs at $t \simeq 10^{-5}$ sec) of $\sim 3 \times 10^{-4}$ sec. An analysis of the reaction scheme reveals that the only process involved in the formation of NO_2* which has a lifetime exceeding a few microseconds is reaction 8. Therefore, the time profile of I_F is equivalent to monitoring the rate of removal of NO ($(I_F)_t \propto (NO)_t$). The predicted reaction lifetime for NO was expected to be typically 5×10^{-3} ($\tau = 0.7/(O_3)\ k_8$), assuming the accepted value(22) for k_8 of

$1.8 \times 10^{-14} cm^3$ molecule^{-1} s^{-1}at 298 K. Therefore, it can be seen that the predicted lifetime is approximately an order of magnitude longer than that observed experimentally. This observation is most easily rationalized by invoking the production of vibrationally excited NO in process 7b which reacts with O_3 at a rate 10-20 times greater than that of $NO(v = 0) + O_3(0,0,0)$. This hypothesis is strongly supported by the quantitative observations of Chamberlain et al.(26) where $NO(v'' = 1,2,3)$ were observed as products of reaction 7b.

DISCUSSION

The wavelength limit for process (1) can be determined from the basic thermodynamic properties of $O_3(^1A)$, $O(^1D)$ and $O_2(a^1\Delta_g)$;

$$O_3(^1A) + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D) \qquad (1)$$

The electronic excitation energies of $O(^1D)$ and $O_2(^1\Delta_g)$ are 45.4 k cal mol^{-1} and 22.5 k cal mol^{-1}, respectively, and the bond dissociation energy of O_3at 0^oK is 24.3 ± 0.4 k cal mol^{-1}. Therefore, the calculated energy limit for process (1) is 92.2 ± 0.4 K cal mol$^-$ which corresponds to a wavelength limit of 310.3 ± 1.3 nm.

Table II summarizes the reported values for $\phi(O^1D)$ at 313 nm. It can be seen that there is significant disagreement with values ranging from 0.1 to 1.0 at 298 K. It should be noted, however, that a significant difference between this and previous studies which have measured $\phi(O^1D)$ as a function of wavelength is the utilization in this investigation of a narrow line (0.15 nm) dye laser as the photolytic source. Hence, this investigation should have exhibited a higher degree of definition in the fall-off region than has heretofore been possible where CW arc lamps have been coupled to scanning monochromators for wavelength selectivity.(6-8) Experiments performed with the latter type of photolysis source might have been subject to overestimating the values of $\phi(O^1D)$ in the fall-off region due to the transmission of a small quantity of short wavelength light where both $\phi(O^1D)$ and $J(O_3)$ are greater. However, in several of the earlier studies involving the determination of $\phi(O^1D)$ at 313 nm, a medium pressure mercury lamp was employed having two spectral lines of near equal intensity at 313.16 and 312.57 nm. These lines were isolated from others using special chemical filters which <u>should</u> have insured the spectral purity of the photolysis radiation. Consequently, if these lamps did provide spectrally pure radiation at ∿313 nm, then no explanation can at present be forwarded for the large discrepancies reported for $\phi(O^1D)$ between these earlier studies and the present work.

The value determined in this study for $\phi(O^1D)$ at 313 nm is in good agreement with that reported by Jones and Wayne(3) and Lin and DeMore(6) (after a correction for the temperature dependence -- to be discussed), but a factor of 2-3 lower than Kuis et al.(9), Kajimoto and Cvetanovic(5), Martin et al.(8) and Moortgat and Warneck(7). Although Jones and Wayne(3) reported high values for the quantum yield for the loss of O_3 (probably due to HO_x impurities), this should not have invalidated their results for Φ, $O(^1D)$. Indeed, their results were unchanged when using the H_2/O_3 system.

It can be seen from Figure (2) that the value of $\phi(O^1D)$ decreases from unity at wavelengths significantly shorter than the thermodynamically allowed limit. This observation has been previously(6-8) reported and is not at all unexpected. Process (1) probably involves a vertical transition from the $^1A_1$ ground state to the $^1B_2$ bound state(23), which correlates to $O(^1D) + O_2(^1\Delta_g)$, while processes 3a or 3b involve the same vertical transition followed by curve crossing to a repulsive potential surface. The exit channel of the process may have a low energy barrier which would be expected to decrease the value of $\phi(O^1D)$ below unity prior to the thermodynamic energy cut-off. Therefore, if there is an energy barrier to dissociation, any value of $O(^1D)$ greater than zero at the thermodynamic limit must be explained by certain available rotational states supplying energy to overcome this barrier. This availability of rotational energy for overcoming the energy barrier for dissociation also explains the long wavelength (λ >310 nm) tail. An alternate and more likely explanation for the fall-off in $\phi(O^1D)$ above the thermodynamic limit is that there exists a curve crossing to a repulsive potential surface in the vicinity of the thermodynamic limit for $O(^1D) + O_2(^1\Delta_g)$ production, thus decreasing the value of $\phi O(^1D)$ below unity. Kuis et al.(9) and Kajimoto and Cvetanovic(5) measured $\phi(O^1D)$ as a function of temperature at 313 nm, and reported $\phi(O^1D)$ to vary from 0.29 at 293 K to 0.11 at 221 K, and 0.53 at 313 K to 0.21 at 198 K, respectively. Both groups calculated the population distribution of rotational states with temperature. Kajimoto and Cvetanovic(5) assumed that all the rotational energy was available for overcoming any barrier to dissociation and it appears that when the absolute values for $\phi(O^1D)$ were calculated as a function of temperature at 313 nm, it was assumed that $\phi(O^1D)$ has a value of unity at the thermodynamic energy limit.

Kuis et al.(9) performed several classical and quantum mechanical calculations, preferring that calculation where it was assumed that only two degrees of rotational freedom could contribute to overcoming the energy barrier (due to conservation of angular momentum consideration). Kuis et al. used their experimentally determined temperature dependency for $\phi(O^1D$, 313 nm) to determine that the best value for E_ε (the energy barrier for O_3 dissociation at 313 nm) was 0.86 k cal mol^{-1}. This would correspond to a value of 24.32 k cal/mole for the dissociation enthalpy of O_3 at $0^\circ K$, provided that there were no barrier height for dissociative crossover from the excited $^1B_2$ electronic state of O_3. A conclusion that one can draw from this calculation, therefore, is that $\phi(O^1D)$ should be unity at the thermodynamic energy limit.

Both of the above calculations(5,9) assume that the rate of change of $\phi(O^1D)$ in the fall-off region is totally governed by the rotational population distribution of ozone molecules in the ground electronic state. However, the results obtained in both the present and earlier studies(6-8) do not support this assumption since the observed fall-off is significantly slower than that calculated from the rotational distribution. (A more complete discussion of the functional dependence of $\phi(O^1D)$ with wavelength has been presented by Moortgat and Warneck(7).)

It thus appears that these calculations may provide reasonably accurate values for the relative population distribution of rotational states lying above the theoretical energy cut-off as a function of temperature. If so, this would enable one to predict the rate of change of $\phi(O^1D)$ with temperature at any wavelength beyond that set by the thermodynamic limit, but would not permit the assignment of absolute values of $\phi(O^1D)$ without further knowledge of the potential energy surfaces of O_3.

As noted earlier in the text, the absolute values of $\phi(O^1D)$ predicted from the two sets of calculations are significantly different due to the different number of degrees of rotational freedom which were assumed to be required to overcome the energy barrier (i.e. $\phi(O^1D)$ at 298 K = 0.26, Kuis et al. and 0.42 Kajimoto and Cvetanovic). By comparison, Moortgat and Warneck calculated that 44% of the ozone molecules had sufficient rotational energy (278 cm^{-1}) to photodissociate to produce $O(^1D)$ atoms at 313 nm. These calculations once again took the thermodynamic limit for the production of $O(^1D)$ from ozone photolysis to be 310 nm.

The calculated ratios reported for $\phi(O^1D)_{298\ K}/\phi(O^1D)_{233K}$ were 1.42 (Kuis et al.) and 1.65 (Kajimoto and Cvetanovic), resulting in a mean ratio of 1.54. Therefore, modifying the data of Lin and DeMore (ϕO^1D) = 0.08 at 233 K) leads to a value of 0.123 at 298 K in excellent agreement with that reported in the present study. As stated earlier, no explanation can be forwarded for the disagreement with other studies.

A final comment on the results reported here concerns the possibility that the normalization of our Φ values to unity at wavelengths less than 3000 Å may not in the final analysis be the correct normalization factor. For example, in a recent study by Stone and Lawrence (unpublished), results were obtained which showed $\Phi(O^1D)$ to vary monotonically from .87 to .93 in the wavelength region 274-300 nm. If these results are later confirmed by other studies our Φ values would want to be systematically shifted downward by a small factor.

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Table 1.

Experimentally Determined Quantum Yields for $O(^1D)$

Wavelength (nm)	$O(^1D)$
293.5	0.968 ± 0.07
294.0	1.050 ± 0.09
296.5	0.970 ± 0.11
297.0	1.006 ± 0.07
298.0	1.093 ± 0.07
298.5	1.077 ± 0.07
299.0	0.950 ± 0.91
300.0	1.004 ± 0.065
301.5	0.943 ± 0.068
302.0	0.986 ± 0.067
302.5	1.009 ± 0.073
303.0	1.069 ± 0.053
304.0	0.917 ± 0.11
305.0	0.871 ± 0.086
305.5	0.760 ± 0.057
306.0	0.883 ± 0.11
306.2	0.916 ± 0.078
306.5	0.906 ± 0.096
307.0	0.684 ± 0.114
308.0	0.592 ± 0.07
309.0	0.484 ± 0.086
309.5	0.364 ± 0.028
310.0	0.344 ± 0.068
311.0	0.224 ± 0.032
311.5	0.185 ± 0.022
312.5	0.154 ± 0.024
313.0	0.121 ± 0.029
313.5	0.080 ± 0.017
314.0	0.090 ± 0.026
315.0	0.035 ± 0.02
316.5	0.022 ± 0.015

Table 2.

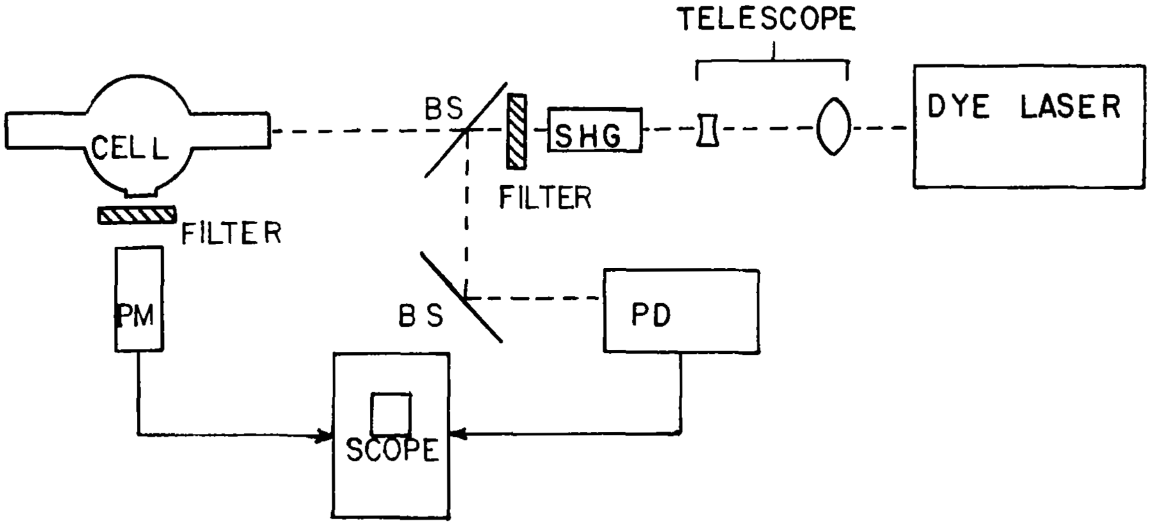
Summary of $O(^1D)$ Quantum Yields

Investigator	$\phi O(^1D)$	Temp(°K)	Technique	Photolytic Source
Castellano, Schumacher[2]	0.75	248	Gas phase O_3; decrease in O_3 pressure	CW Lamp
	1.0	298		
Kajimoto, Cvetanovic[5]	0.53	313	Gas phase O_3, N_2O; Increase in N_2	CW Lamp Chemical Filter
	0.21	198		
Simonaitis, Braslavsky, Heicklen, Nicolet[4]	0.35	298	Gas phase O_3, N_2O; Increase in N_2	CW Lamp Chemical Filter
Martin, Girman, Johnston[8]	0.32	298	O_3, N_2O; N_2O chemiluminescence	CW Lamp
Moortgat, Warneck[7]	0.29	298	O_3, N_2O; NO_2 chemiluminescence	CW Lamp
Kuis, Simonaitis, Heicklein[9]	0.29	293	Gas phase O_3, O_2, N_2O; Increase in N_2	CW Lamp Chemical Filter
	0.22	258		
	0.11	221		
Jones-Wayne[3]	0.1	298	Decrease in O_3	CW Lamp
Lin-DeMore[6]	0.08	235	O_3, IsoButane	CW Lamp
This work	0.12	298	O_3, N_2O; NO_2 chemiluminescence	Pulsed Dye Laser

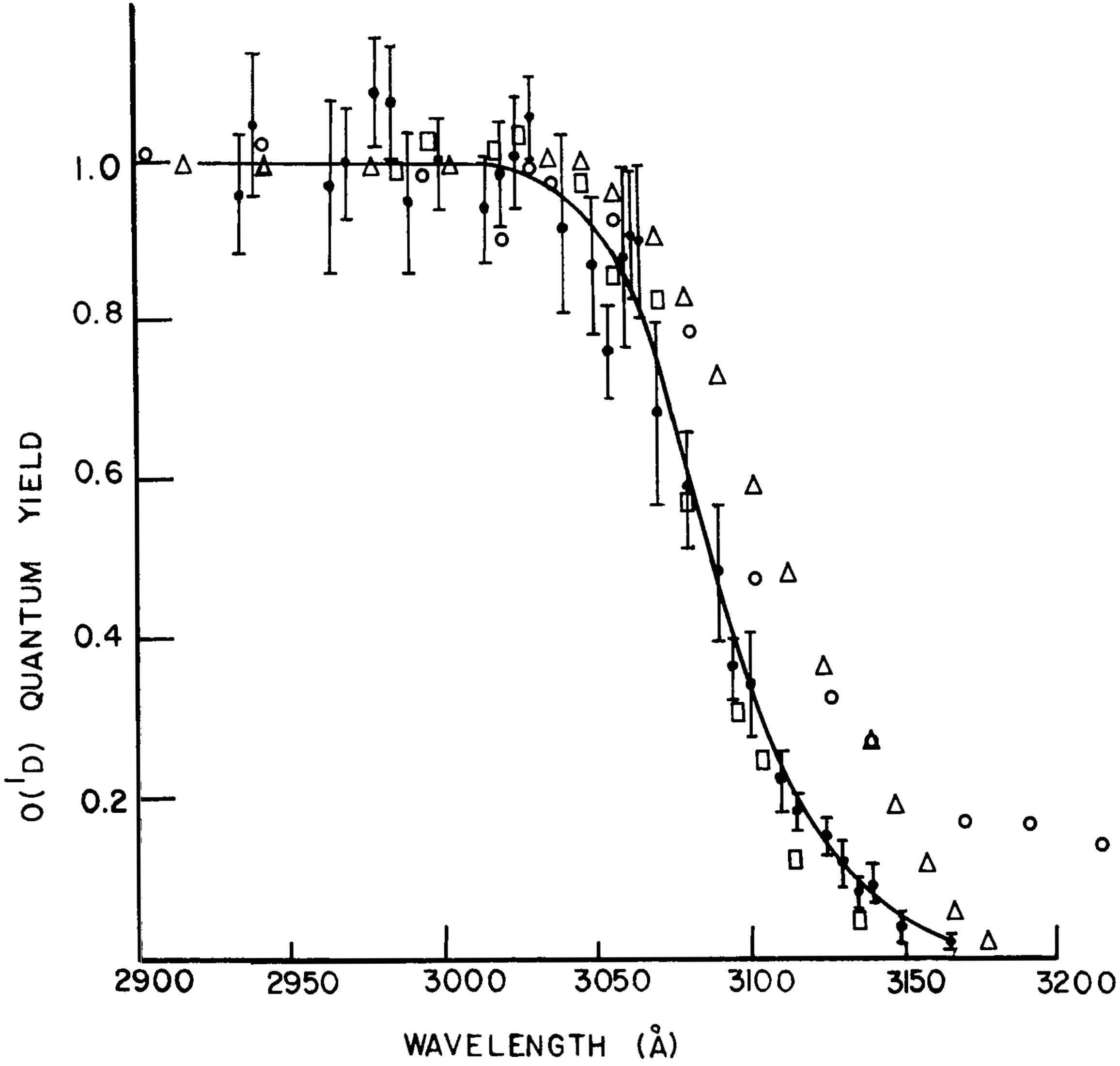
Figure Captions

Figure 1. Experimental arrangement of ozone photolysis experiment using a frequency doubled dye laser.

Figure 2. Experimental quantum yield of O(^{1}D); □, Lin-DeMore; Δ, Moortgat et al.; O, Martin et al; ●, this work.



BS	BEAM SPLITTER
PD	PHOTODIODE
PM	PHOTOMULTIPLIER
SHG	SECOND HARMONIC GENERATION


1.0
0.8
0.6
0.4
0.2
O(^{1}D) QUANTUM YIELD
2900
2950
3000
3050
3100
3150
3200
WAVELENGTH (Å)

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16. Abstract

The technique of flash photolysis-resonance fluorescence has been utilized to study nine reactions of stratospheric importance. Also, the tropospheric degradation reactions of seven halogenated hydrocarbons have been studied to assess their possible influx into the stratosphere. There are reactions of either Cl, OH, or $O(^3P)$ species with hydrogenated species, O_3 or chlorinated compounds. Apart from the kinetic measurements, the quantum yield for the production of $O(^1D)$ from O_3 in the crucial wavelength region of 293 to 316.5 nm has been studied by utilizing a narrow wavelength laser as the photolysis source. The product formation was monitored by measuring the fluorescence of NO_2^* formed through $O(^1D)$ reaction with N_2O followed by NO reaction with O_3 to give NO_2^*.

17. Key Words (Suggested by Author(s))
Kinetics, Gas Phase, Stratosphere, Chlorine Atoms, Quantum Yield, Halogenated Hydrocarbons

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