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Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

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ABSTRACT

This is the seventh in a series of evaluated sets of rate constants and photochemical cross sections compiled by the NASA Panel for Data Evaluation. The primary application of the data is in the modeling of stratospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena. Copies of this evaluation are available from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

CHEMICAL KINETICS AND PHOTOCHEMICAL DATA FOR USE IN STRATOSPHERIC MODELING

INTRODUCTION

The present compilation of kinetic and photochemical data represents the seventh evaluation prepared by the NASA Panel for Data Evaluation. The Panel was established in 1977 by the NASA Upper Atmosphere Research Program Office for the purpose of providing a critical tabulation of the latest kinetic and photochemical data for use by modelers in computer simulations of stratospheric chemistry. The previous publications appeared as follows:

Evaluation Number	Reference
1	NASA RP 1010, Chapter 1 (Hudson, 1977)
2	JPL Publication 79-27 (DeMore et al., 1979)
3	NASA RP 1049, Chapter 1 (Hudson and Reed, 1979)
4	JPL Publication 81-3 (DeMore et al., 1981)
5	JPL Publication 82-57 (DeMore et al., 1982)
6	JPL Publication 83-62 (DeMore et al., 1983)

The present composition of the Panel and the major responsibilities of each member are listed below:

W. B. DeMore, Chairman (Chapman chemistry)

D. M. Golden (three-body reactions)

R. F. Hampson (halogen chemistry)

C. J. Howard (HO_x chemistry, $O(^1D)$ reactions, metal chemistry)

M. J. Kurylo (SO_x chemistry)

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M. J. Molina (photochemical cross sections)

A. R. Ravishankara (hydrocarbon oxidation)

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As shown above, each Panel member concentrates his effort on a given area or type of data. Nevertheless, the final recommendations of the Panel represent a consensus of the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case. Communications regarding particular reactions should be addressed to the appropriate panel member:

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BASIS OF THE RECOMMENDATIONS

The recommended rate constants and cross sections are based on laboratory measurements. In order to provide recommendations that are as up-to-date as possible, preprints and written private communications are accepted, in the expectation that they will appear as published Journal articles. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel does consider the question of consistency of data with expectations based on kinetics theories, and in cases where a discrepancy appears to exist, this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of a few important rate constants for which no experimental data are available the Panel has provided estimates of rate constant parameters, based on analogy to similar reactions for which data are available.

RECENT CHANGES AND CURRENT NEEDS OF LABORATORY KINETICS

There have been no major changes in stratospheric chemistry since the publication of our previous evaluation, JPL Publication 83-62. There are approximately thirty changes in the rate constant recommendations in the present evaluation, but these are for the most part minor. Twenty-eight new reactions have been added, representing processes which play small but possibly significant roles in the stratosphere. Some important refinements have been made in certain key rate constants, such as those for O + CℓO and OH + HCℓ. These examples are typical of the set of critical reactions which were carefully measured about five or ten years ago, during the early stages of the stratospheric chemistry program. While these measurements have generally stood the test of time, it is appropriate to re-examine them to verify that the kinetic data being used in the models are as accurate as possible. Such refinements will go hand-in-hand with the improved reliability of field measurement methods for the in-situ measurement of trace species, permitting more exacting comparisons of the model with observation. Some reactions which are too slow to be of importance in the stratosphere are included in the evaluation to show that they have been considered.

O_x Reactions

The kinetics of the O, O_2, and O_3 system appear to be well established. There remains some concern about the possible roles of excited states of O_2, especially $O_2(^1\Delta)$, but at present there is no evidence that these states have any important effects on the overall chemistry of the stratosphere.

$O(^1D)$ Reactions

The data base for $O(^1D)$ reaction chemistry is in fairly good condition. There is good to excellent agreement in independent measurements of the absolute rate constants for $O(^1D)$ deactivation by the major atmospheric components, N_2 and O_2, and by the critical radical producing components, H_2O, CH_4, N_2O, and H_2. There are fewer direct studies of the products of the deactivation processes, but in most cases these details appear to be of minor importance. Some processes of interest for product studies include the reactions of $O(^1D)$ with CH_4 and halocarbons. Possible kinetic energy effects from photolytically generated $O(^1D)$ are probably not important in the atmosphere but may contribute complications in laboratory studies.

HO_x Reactions

Our knowledge of the kinetics of HO_x radicals has continued to improve. For example, several new studies have been reported on the $HO_2 + HO_2$ reaction. Although the reaction mechanism is complex and demonstrates both bimolecular and termolecular behavior, independent studies using different experimental techniques are in excellent agreement. Data on the temperature dependence are also consistent. More serious problems remain with the $OH + HO_2$ reaction, where there are indications of a pressure effect but there are few data on this and the temperature dependence. There is a study of the temperature dependence at low pressure, but no studies at high pressures.

NO_x Reactions

The data base for NO_x reactions is relatively well established. Our understanding of the important $OH + HNO_3$ reactions has improved due to confirmation of a small pressure dependence which helps explain some of the earlier divergence between flash and flow studies. The equally important OH + HO_2NO_2 reaction is not as well characterized, particularly with regard to the temperature dependence. Additional studies of the HO_2 + NO_2 + M recombination are also needed, especially on the temperature dependence of the low pressure limit. Recently, direct studies of some key NO_3 reactions have become available, greatly improving the reliability of that data base.

The data for NH_2 reactions are sparse. There are a large number of studies only for the NH_2 + NO reaction, and these show a factor of two discrepancy between flow and flash systems.

Hydrocarbon Oxidation

Our understanding of hydrocarbon oxidation in the atmosphere has improved considerably in the past few years. All hydrocarbons are released at the surface of the earth, and their degradation in the troposphere is initiated by reaction with OH (and with ozone in the case of olefins). Depending on their reactivity with OH, only a fraction of the surface flux of hydrocarbons is transported into the stratosphere where their oxidation serves as a source of water vapor. In addition, the reaction of Cℓ atoms with these hydrocarbons (mainly CH_4) constitutes one of the major sink mechanisms for active chlorine. Even though CH_4 is the predominant hydrocarbon in the stratosphere, we have included in this evaluation certain reactions of a few heavier hydrocarbon species.

In the stratosphere, CH_4 oxidation is initiated by its reaction with either OH or Cℓ (and to a limited extent $O(^1D)$), leading to formation of CH_3 and subsequently CH_3O_2. Several details of the subsequent chemistry are unclear, primarily because three key reactions are not well characterized. These reactions are: (1) CH_3O_2 + HO_2, which exhibits an unusual temperature dependence analogous to that for the $HO_2 + HO_2$ reaction; (2) $CH_3OOH + OH$, which has been recently studied in a competitive system and found to be extremely rapid; and (3) OH + CO, whose temperature dependence as a function of pressure is uncertain. Even though the rate constants for the three reactions mentioned above are not very well known, the effects of these uncertainties on stratospheric O_3 perturbation calculations are negligible.

The rate constant for $CH_3O_2NO_2$ formation from CH_3O_2 and NO_2 is well defined. However, the role of $CH_3O_2NO_2$ in the stratosphere remains unclear, owing to insufficient data on its thermal decomposition and photolysis.

Formaldehyde photo-oxidation to form CO can be considered well understood, especially since the rate of the $HCO + O_2$ reaction is known. The rates of the OH and $O(^3P)$ reactions with CH_2O and the photolysis cross sections of CH_2O are reasonably well known.

Another area of hydrocarbon oxidation which has seen a great deal of improvement is that of product analysis. However, some additional work may be required to measure branching ratios for reactions such as $CH_3O_2 + CH_3O_2$.

The oxidation scheme for higher hydrocarbons has not been fully elucidated. However, the rate of transport of these hydrocarbons into the stratosphere can be easily calculated since the rates of reactions with OH are well known. In most cases it is expected that the radicals formed from the initial OH or Cℓ attack will follow courses analogous to CH_3, and ultimately lead to CO.

Two reactions involving NO_3, with CO and CH_2O, have been added. The tropospherically important reactions of NO_3 with a variety of organic compounds have been studied by Atkinson and coworkers (Atkinson et al., 1984) and are not tabulated here.

Halogen Chemistry

There have been two significant changes in recommendations for ClO_x reactions - the recommendation for OH + HCl has been increased by 20% while that for O + ClO has been decreased by 20%. Otherwise there have been only minor refinements in the data base for halogen reactions. The table now contains ten new entries in this section - these include the reaction of HCl + $ClONO_2$, NO_3 reactions with Cl and ClO, and four reactions of perhalogenated methylperoxy radicals with NO.

SO_x Reactions

This section on homogeneous sulfur chemistry continues to change and expand as we obtain more detailed laboratory data on a number of oxidative processes. In particular, we have considerably more data on SH radical reactions although many gaps in the data base still exist. For example, while we now include data for the reactions of SH with O_3, H_2O_2, NO_2, and NO there is no information on the temperature dependence of these reactions. Further studies of both HSO and SH reactions are needed to develop more completely our picture of H_2S atmospheric oxidation. Since the last evaluation there have been no improvements in our knowledge of the rates and mechanisms of SO oxidation by either radical or molecular species. A complete assessment of the importance of SO reactions with species such as OH, HO_2, ClO, BrO, etc. cannot yet be given. However, the reactions of SO with O_2 and O_3 are expected to dominate throughout the atmosphere.

An area in which our understanding has improved significantly involves the oxidation of SO_2 into sulfuric acid and the concomitant change (if any) in HO_x radical concentrations. Recently Stockwell and Calvert (1983) and Margitan (1984a) have published experimental evidence that the primary fate of the $HOSO_2$

radical produced in the reaction

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$

is to react with O_2 to produce HO_2:

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$

Rate data for this process, derived in the Margitan study and supported by preliminary studies by Bandow and Howard (private communication, 1984), are included in this evaluation. These new experimental results support a homogeneous gas phase SO_2 oxidation mechanism involving no net change in HO_x per H_2SO_4 formed while negating a reaction sequence involving SO_3 formation via the $OH + HOSO_2$ reaction (a mechanism which would have resulted in the loss of two OH radicals per H_2SO_4 formed). However there is a need for still further information on the atmospheric reactivity of $HOSO_2$ and perhaps even on reactions involving its possible complexes with O_2 or H_2O. Along these latter lines, a recent study by Huie and Neta (1984) demonstrates that the formation of the $HOSO_2 \cdot O_2$ adduct predominates in solution. While the acidic natures of both $HOSO_2$ and $HOSO_2 \cdot O_2$ result in their deprotonation in solution and existence as the SO_3^- and SO_5^- anions, these results suggest the possible atmospheric importance of the O_2 adduct in its hydrated form. In this and most discussions, SO_3 has been thought of as equivalent to sulfuric acid. This is supported by recent experiments by Hofmann-Sievert and Castleman (1984) which suggest the rapid isomerization of the adduct $SO_3 \cdot H_2O$ to H_2SO_4 with a barrier to this process of less than 13 kcal/mol. Further information on the reactions of SO_3 with other atmospheric species is needed to assess the competition of these reactions with SO_3 hydrolysis.

Additional progress has been made in developing an understanding of the mechanisms of OCS and CS_2 oxidation. There are now additional studies providing rate constant and primary product information for the reactions of OH with both species. In the case of CS_2 there have been direct observations of reversible adduct formation with OH as well as further confirmation of its O_2-enhanced pressure dependent oxidation by OH. There are no data, however, to suggest similar behavior in the OH + OCS reaction despite the direct observation of SH as a primary product of both reactions and the invocation of similar complex (adduct) mechanisms. New data indicate that the direct bimolecular reactions have markedly different Arrhenius parameters from one another thereby suggesting significant energetic differences in the reaction surfaces describing adduct formation. Further information regarding the elementary steps in the oxidation of both species should further our understanding of complex mechanisms in general.

Metal Chemistry

Several reactions of sodium species have been introduced in this evaluation. Sodium is deposited in the upper atmosphere by meteors along with larger amounts of silicon, magnesium, and iron; comparable amounts of aluminum, nickel, and calcium; and smaller amounts of potassium, chromium, manganese, and other elements. The interest is greatest in the alkali metals because they form the least stable oxides and thus free atoms can be regenerated through photolysis and reactions with O and O_3. The other meteoric elements are expected to form more stable oxides.

It has been proposed that the highly polar metal compounds may polymerize to form clusters and that the stratospheric concentrations of free metal compounds are too small to play a significant role in the chemistry. In any case the total flux of alkali metals through the atmosphere is relatively small, e.g., one to two orders of magnitude less than CFMs. Therefore extremely efficient catalytic cycles would be required in order for Na to have a significant effect on stratospheric chemistry. We emphasize that there are no measurements of metals or metal compounds in the stratosphere which indicate a significant role.

Although little is known about the atmospheric reactions of Na and its compounds, some recent studies have been shown that these materials are surprisingly reactive, e.g.,

$$Na + H_2O_2 \rightarrow NaOH + OH \qquad k \approx 6.9 \times 10^{-11}$$

$$\rightarrow NaO + H_2O$$

and

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad k \approx 2.8 \times 10^{-10}$$

[Silver et al., 1984a]. Unfortunately the available data on this system are very sparse. In order to assess the efficiency of catalytic cycles, data are needed on the reactions of NaO and NaO_2 with atmospheric species and on the photolysis rates of key species such as NaO, NaO_2, NaOH and NaCl. Measurements are also needed on the concentration and chemical form of Na in the atmosphere.

Photochemical Cross Sections

The absorption cross sections of O_2 around 200 mm -- that is, at the onset of the Herzberg continuum -- have been remeasured in the laboratory and are now in better agreement with the values inferred from solar irradiance measurements in the stratosphere. Also, the data base on O_3 cross sections and on their temperature dependency has improved considerably since the previous evaluation (JPL Publication 83-62).

The temperature dependence of the absorption cross sections of HO_2NO_2, H_2O_2 and HNO_3 in the 300 nm region might be significant and should be determined.

ATMOSPHERIC CHEMISTRY

Overview

The ozone content of earth's atmosphere can be considered to exist in three distinct regions, the troposphere, stratosphere, and mesosphere. The unpolluted troposphere contains small amounts of ozone, which come from both downward transport from the stratosphere and from in situ photochemical production. The chemistry of the global troposphere is complex, with both homogeneous and heterogeneous (e.g., rain-out) processes playing important roles. The homogeneous chemistry is governed by coupling between the carbon/nitrogen/hydrogen and oxygen systems and can be considered to be more complex than the chemistry of the stratosphere, due to the presence of higher hydrocarbons, long photochemical relaxation times, higher total pressures, and the high relative humidity which may affect the reactivity of certain key species such as HO_2. Significant progress is being made in understanding the coupling between the different chemical systems, especially the mechanism of methane oxidation, which partially controls the odd hydrogen budget. This is an important development, as reactions of the hydroxyl radical are the primary loss mechanism for compounds containing C-H (CH_4, $CH_3C\ell$, $CHF_2C\ell$, etc.) or C=C ($C_2C\ell_4$, $C_2HC\ell_3$, C_2H_4, etc.), thus limiting the fraction transported into the stratosphere.

The stratosphere is the region of the atmosphere where the bulk of the ozone resides, with the concentration reaching a maximum value of about 5×10^{12} molecule cm^{-3} at an altitude of ~25 km. Ozone in the stratosphere is removed predominantly by catalytic (i.e., non-Chapman) processes, but the assignment of their relative importance and the prediction of their future impact are dependent on a detailed understanding of chemical reactions which form, remove and interconvert the catalytic species. A model calculation of stratospheric composition may include some 150 chemical reactions and photochemical processes, which vary greatly in their importance in controlling the density of ozone. Laboratory measurements of the rates of these reactions have progressed rapidly in recent years, and have given us a basic understanding of the processes involved, particularly in the upper stratosphere. Despite the basically sound understanding of overall stratospheric chemistry which presently exists, much remains to be done to quantify errors, to identify reaction channels positively, and to measure reaction rates both under conditions corresponding to the lower stratosphere (~210 K, ~75 torr) as well as the top of the stratosphere (~270 K, ~1 torr).

The chemistry of the upper stratosphere, i.e. 30-50 km, is thought to be reasonably well defined, although there appear to be some significant differences between the predicted and observed chemical compositions of this region of the atmosphere which may be due to inaccurate rate data or missing chemistry. In this region the chemical composition of the atmosphere is predominantly photochemically controlled and the photolytic lifetimes of temporary reservoir species such as $HOC\ell$, HO_2NO_2, $C\ell ONO_2$, N_2O_5 and H_2O_2 are short and hence they play a minor role. Thus the important processes above 30 km all involve atoms and small molecules. The majority of laboratory studies of these reactions have been carried out under the conditions of pressure and temperature which are encountered in the upper stratosphere, and their overall status appears to be good. No significant changes in rate coefficients for the key reactions such as $C\ell + O_3$, $NO + C\ell O$, $O + NO_2$, $NO + O_3$, etc., have occurred in the last few years. Recent changes of ~20% in the rate constants for $O + C\ell O$ and $OH + HC\ell$ have had offsetting effects for ozone depletion calculations. Historically, a major area of concern in the chemistry of the upper stratosphere has involved the reaction between HO and HO_2 radicals, which has had considerable uncertainty in the rate constant. This HO_x termination reaction plays an important role in determining the absolute concentrations of HO and HO_2, and since HO plays a central role in controlling the catalytic efficiencies of both NO_x and $C\ell O_x$, it is a reaction of considerable importance. Recently the uncertainty in the rate coefficient for the reaction has decreased, now being thought to be about a factor of 1.5 over the entire range of atmospheric conditions. It should be noted that the HO + H_2O_2, HO + HNO_3 and HO + HO_2NO_2 reactions have little effect on controlling the HO_x concentrations above 30 km. For reactions such as O + HO and O + HO_2, which control the HO_x radical partitioning above 40 km, the data base can be considered to be quite good.

One area in which additional studies may be needed is that of excited state chemistry, i.e., studies to determine whether electronic or vibrational states of certain atmospheric constituents may be more important than hitherto recognized. Possible examples are O_2^*, O_3^*, HO^*, or N_2^*.

The chemistry of the lower stratosphere is quite complex, with significant coupling between the HO_x, NO_x and $C\ell O_x$ families. In this region of the atmosphere (15-30 km), both dynamics and photochemistry play key roles in controlling the trace gas distributions. It is also within this region that the question of the pressure and temperature dependences of the rate coefficients is most critical, due to the low temperatures (210-255 K) and the high total pressures (30-200 torr). The question of possible pressure and temperature dependences of HO and HO_2 reactions is highly pertinent here.

Our view of the chemistry of the lower stratosphere has changed in recent years, due to changes in rate constants which have in turn led to changes in the relative importance of reactions which control the HO_x budget in this region of the atmosphere. Prior to the appearance of improved kinetics data for the $HO + H_2O_2$, $HO + HNO_3$, and $HO + HO_2NO_2$ reactions, the major termination reaction for odd hydrogen species in models of the lower stratosphere was the $HO + HO_2 \rightarrow H_2O + O_2$ reaction. However, the $HO + HNO_3$ and $HO + NO_2NO_2$ reactions are now thought to play a vital role in controlling the HO_x radical concentration in the lower stratosphere. The species HNO_3, HO_2NO_2, $C\ell NO_3$ and $HOC\ell$ illustrate the strong coupling that exists between the HO_x, NO_x and $C\ell O_x$ families. One disturbing problem is that while these species are currently thought to play an important role in stratospheric photochemistry, only HNO_3 has yet been positively observed by any field measurement study.

Heterogeneous Effects

A continuing question in stratospheric modeling is whether or not aerosols perturb the homogeneous chemistry to a significant degree. Effects could arise through the following processes;

1. Surface catalysis of chemical reactions.
2. Production or removal of active species.
3. Effects of aerosol precursors.

The aerosol question now assumes more relevance in view of the 1982 eruption of the El Chichon volcano, which evidently increased the aerosol loading by approximately an order of magnitude. This effect is of course temporary, with a recovery time of the order of a few years.

In NASA Reference Publications 1010 and 1049, processes 1 and 2 above were discussed in general terms. It was shown that, with a few possibly significant exceptions, surface catalysis of chemical reactions is not expected to compete with the rates of homogeneous gas phase reactions. The essential reason was that the frequency of collision of a gas phase molecule with the aerosol surface is typically of the order of 10^{-5} sec^{-1}, whereas most of the key gas phase reactions occur with much greater frequency, for example, conversion of atomic chlorine to $HC\ell$ by the $C\ell + CH_4$ reaction (10^{-2} sec^{-1}). Thus, even in the unlikely case of unit reaction efficiency on the aerosol surface the heterogeneous process cannot be significant. Possible exceptions occur for reactions which are extremely slow in the gas phase, such as hydrolysis of an anhydride, as in the reaction $N_2O_5 + H_2O \rightarrow 2HNO_3$. There remains some uncertainty with regard to the role of these latter processes.

It was also shown in NASA Publications 1010 and 1049 that there is no evidence that aerosols serve as significant sources or sinks of the major active species such as chlorine compounds. However, Hunten et al. (1980) have suggested that dust particles of meteoric origin may scavenge metallic atoms and ions, and in particular may remove Na diffusing from the mesosphere in the form of absorbed NaOH or Na_2SO_4.

Although it appears that aerosols do not greatly perturb the ambient concentrations of active species through direct interaction with the surfaces, the aerosol precursors may significantly perturb the stratospheric cycles through removal of species such as OH radicals. For example, a large injection of SO_2, such as that which occurred in the El Chichon eruption, has the potential of significantly depleting HO_x radical concentrations, as was discussed in the section on SO_x chemistry. It must be reiterated, however, that recent studies of the mechanism of SO_2 oxidation have shown that OH plays a catalytic role, and, therefore, the process does not result in a net loss of OH from the system.

The effects of aerosols on the radiation field and on the temperature may also need to be considered. These effects are probably small, however.

There are two problems with regard to detecting the effects of aerosol injections such as that following the El Chichon eruption. One is that no adequate baseline exists for the unperturbed atmosphere, and therefore a given observation cannot unambiguously be assigned to the enhanced presence of the aerosol loading. A second problem is that, as already discussed, the effects are expected to be subtle and probably of small magnitude. Thus, in spite of the large change that has occurred in the aerosol content of the lower stratosphere, effects on the chemical balance will be difficult to detect.

RATE CONSTANT DATA

In Table 1 (Rate Constants for Second Order Reactions) the reactions are grouped into the classes O_x, $O(^1D)$, HO_x, NO_x, Hydrocarbon Reactions, ClO_x, BrO_x,FO_x, and SO_x. The data in Table 2 (Rate Constants for Three-Body Reactions), while not grouped by class, are presented in the same order as the bimolecular reactions. Further, the presentation of photochemical cross section data follows the same sequence.

Bimolecular Reactions

Some of the reactions in Table 1 are actually more complex than simple two-body reactions. To explain the anomalous pressure and temperature dependences occasionally seen in reactions of this type, it is necessary to consider the bimolecular class of reactions in terms of two subcategories, direct (concerted) and indirect (non-concerted) reactions.

A direct or concerted bimolecular reaction is one in which the reactants A and B proceed to products C and D without the intermediate formation of an AB adduct which has appreciable bonding, i.e., no stable A-B molecule exists, and there is no reaction intermediate other than the transition state of the reaction, $(AB)^{\neq}$.

$$A + B \rightarrow (AB)^{\neq} \rightarrow C + D$$

The reaction of OH with CH_4 forming $H_2O + CH_3$ is an example of a reaction of this class.

Very useful correlations between the expected structure of the transition state $[AB]^{\neq}$ and the A-factor of the reaction rate constant can be made, especially in reactions which are constrained to follow a well-defined approach of the two reactants in order to minimize energy requirements in the making and breaking of bonds. The rate constants for these reactions are well represented by the Arrhenius expression $k = A \exp(-E/RT)$ in the 200-300 K temperature range. These rate constants are not pressure dependent.

The indirect or non-concerted class of bimolecular reactions is characterized by a more complex reaction path involving a potential well between reactants and products, leading to a bound adduct (or reaction complex) formed between the reactants A and B:

$$A + B \rightleftarrows [AB]^{*} \rightarrow C + D$$

The intermediate $[AB]^{*}$ is different from the transition state $[AB]^{\neq}$, in that it is a bound molecule which has a finite lifetime and which can, in principle, be isolated. (Of course, transition states are involved in all of the above reactions, both forward and backward, but are not explicitly shown.) An example of this reaction type is $C\ell O$ + NO, which normally produces $C\ell + NO_2$ as a bimolecular product, but which undoubtedly involves $C\ell ONO$ (chlorine nitrite) as an intermediate. This can be viewed as a chemical activation process forming $(ClONO)^*$ which decomposes unimolecularly to the ultimate products, $Cl + NO_2$. Reactions of the non-concerted type can have a more complex temperature dependence, can exhibit a pressure dependence if the lifetime of $[AB]^*$ is comparable to the rate of collisional deactivation of $[AB]^*$. This arises because the relative rate at which $[AB]^*$ goes to products C + D vs. reactants A + B is a sensitive function of its excitation energy. Thus, in reactions of this type, the distinction between the bimolecular and termolecular classification becomes less meaningful, and it is particularly necessary to study such reactions under the temperature and pressure conditions in which they are to be used in model calculations.

The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius form: $k(T) = A \exp((-\frac{E}{R})(\frac{1}{T}))$ and contains the following information:

1. Reaction stoichiometry and products (if known). The pressure dependences are included, where appropriate.
2. Arrhenius A-factor.
3. Temperature dependence and associated uncertainty ("activation temperature" $E/R \pm \Delta E/R$).
4. Rate constant at 298 K.
5. Uncertainty factor at 298 K.
6. Note giving basis of recommendation and any other pertinent information.

Termolecular Reactions

Rate constants for third order reactions (Table 2) of the type $A + B \rightleftarrows [AB]^* \xrightarrow{M} AB$ are given in the form

$$k_o(T) = k_o^{300}(T/300)^{-n} \ cm^6 \ s^{-1} ,$$

(where the value is suitable for air as the third body), together with the recommended value of n. Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in a similar form:

$$k_\infty(T) = k_\infty^{300}(T/300)^{-m} \text{ cm}^3 \text{ s}^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k(Z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + (k_o(T)[M]/k_\infty(T))}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$$

The fixed value 0.6 which appears in this formula fits the data for all listed reactions adequately, although in principle this quantity may be different for each reaction.

Thus, a compilation of rate constants of this type requires the stipulation of the four parameters, $k_o(300)$, n, $k_\infty(300)$, and m. These can be found in Table 2. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources.

Low-Pressure Limiting Rate Constant [$k_o^x(T)$]

Troe (1977) has described a simple method for obtaining low-pressure limiting rate constants. In essence this method depends on the definition:

$$k_0^x(T) = \beta_x k_{0,sc}^x(T)$$

Here sc signifies "strong" collisions, x denotes the bath gas, and β_x is an efficiency parameter ($0 < \beta < 1$), which provides a measure of energy transfer.

The coefficient β_x is related to the average energy transferred in a collision with gas x, $\langle \Delta E \rangle_x$, via:

$$\frac{\beta_x}{1-\beta_x^{1/2}} = \frac{\langle \Delta E \rangle_x}{F_E \, kT}$$

Notice that $\langle \Delta E \rangle$ is quite sensitive to β. F_E is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

For many of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to evaluate and unify this data by calculating $k_{0,sc}^x(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value [Troe (1977)]. A recent compilation (Patrick and Golden, 1983) gives details for many of the reactions considered here.

From the β_x values (most of which are for N_2, i.e., β_{N_2}), we compute $\langle \Delta E \rangle_x$ according to the above equation. Values of $\langle \Delta E \rangle_{N_2}$ of approximately 0.3-1 kcal $mole^{-1}$ are generally expected. If multiple data exist, we average the values of $\langle \Delta E \rangle_{N_2}$ and recommend a rate constant corresponding to the β_{N_2} computed in the equation above.

Where no data exist, we have estimated the low-pressure rate constant by taking $\beta_{N_2} = 0.3$ at $T = 300$ K, a value based on those cases where data exist.

Temperature Dependence of Low-Pressure Limiting Rate Constants: n

The value of n recommended here comes from a calculation of $\langle\Delta E\rangle_{N_2}$ from the data at 300 K, and a computation of β_{N_2} (200 K) assuming that $\langle\Delta E\rangle_{N_2}$ is independent of temperature in this range. This β_{N_2} (200 K) value is combined with the computed value of k_o^{sc}(200 K) to give the expected value of the actual rate constant at 200 K. This latter in combination with the value of 300 K yields the value of n.

This procedure can be directly compared with measured values of k_o(200 K) when those exist. Unfortunately, very few values at 200 K are available. There are often temperature-dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data is to be extrapolated out of the measured temperature range, a choice must be made as to the functional form of the temperature dependence. There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression $k_o(T) = A\exp(-E/RT)$ or the form $k_o(T) = A' T^{-n}$ is employed. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method explained earlier as the basis of our recommendations.

High-Pressure Limiting Rate Constants [$k_\infty(T)$]

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being guesses based upon some model, and the second extrapolation of fall-off data up to higher pressures. Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit, and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of $k_\infty(T)$ not very precise, a "reasonable guess" of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is always in effect over the entire range of stratospheric conditions.

Temperature Dependence of High-Pressure Limiting Rate Constants: m

There is very little data upon which to base a recommendation for values of m. Values in Table 2 are estimated, based on models for the transition state of bond association reactions and whatever data are available.

Isomer Formation

A particular problem associated with association reactions arises when there are easily accessible isomeric forms of the molecule AB. In this situation, if the laboratory measurement of the rate constant is accomplished by following the disappearance of reactants, the value ascertained may be the sum of two or more processes that should be measured and tabulated independently. A specific example of such a case is found in Table 2 for the reactions of $C\ell$-atoms with NO_2. These reactants may come together to form either $C\ell NO_2$ or $C\ell ONO$.

Whether or not isomer formation, such as discussed above, is important depends on the relative stability of the possible products. At the moment the only example that we are sure about is the example already included. In the past however, there was some thought that all the data on the reaction between $C\ell O$-radicals and NO_2 could be understood in terms of the formation of both chlorine nitrate ($C\ell ONO_2$) and other isomers ($C\ell OONO$, $OC\ell ONO$). Experiments have shown that this is not the case and that chlorine nitrate is the sole product. This question is discussed at some length in note 14 of Table 2.

There are many other possibilities for isomer formation in the reactions listed in Table 2. In some of the notes we have specifically pointed this out, but even for reactions where no mention is made of isomers, because we felt that they could not contribute under atmospheric conditions, extrapolation to higher pressures and lower temperatures should be done with the possibilities kept in mind.

Uncertainty Estimates

For second-order rate constants in Table 1, an estimate of the uncertainty at any given temperature may be obtained from the following expression:

$$f_T = f_{298} \exp(\frac{\Delta E}{R}\left[\frac{1}{T} - \frac{1}{298}\right])$$

An upper or lower bound (corresponding approximately to one standard deviation) of the rate constant at any temperature T can be obtained by multiplying or dividing the value of the rate constant at that temperature by the factor f_T. The quantities f_{298} and $\Delta E/R$ are, respectively, the uncertainty in the rate constant at 298 K and in the Arrhenius temperature coefficient, as listed in Table 1.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_0 and k_∞ are given for these rate constants at room temperature. The additional uncertainty arising from the temperature extrapolation is expressed as an uncertainty in the temperature coefficients n and m.

The assigned uncertainties represent the subjective judgment of the Panel. They are not determined by a rigorous, statistical analysis of the data base, which generally is too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the experimenters, the difficulties of the experiments, and the potential for systematic errors. There is obviously no way to quantify these "unknown" errors. The spread in results among different techniques for a given reaction may provide some basis for an uncertainty, but the possibility of the same, or compensating, systematic errors in all the studies must be recognized. Furthermore, the probability distribution may not follow the normal, Gaussian fashion. For measurements subject to large systematic errors, the true rate constant may be much further from the recommended value than would be expected based on a Gaussian distribution with the stated uncertainty. As an example, the rate constants for the reactions HO_2 + NO and Cℓ + $C\ell ONO_2$ have changed by factors of 30-50, occurrences which could not have been allowed for with any reasonable values of σ in a Gaussian distribution.

Units

The rate constants are given in units of concentration expressed as molecules per cubic centimeter and time in seconds. Thus, for first-, second-, and third-order reactions the units of k are s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1}, respectively. Cross sections are expressed as cm^2 $molecule^{-1}$, base e.

Table 1. Rate Constants for Second Order Reactions

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
		O_x Reactions			
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
$O + O_3 \rightarrow O_2 + O_2$	$8.0\text{x}10^{-12}$	2060±250	$8.0\text{x}10^{-15}$	1.15	A1
		$O(^1D)$ Reactions			
$O(^1D) + N_2O \rightarrow N_2 + O_2$	$4.9\text{x}10^{-11}$	0±100	$4.9\text{x}10^{-11}$	1.3	A2, A3
$\rightarrow NO + NO$	$6.7\text{x}10^{-11}$	0±100	$6.7\text{x}10^{-11}$	1.3	A2, A3
$O(^1D) + H_2O \rightarrow OH + OH$	$2.2\text{x}10^{-10}$	0±100	$2.2\text{x}10^{-10}$	1.2	A2, A4
$O(^1D) + CH_4 \rightarrow OH + CH_3$	$1.4\text{x}10^{-10}$	0±100	$1.4\text{x}10^{-10}$	1.2	A2, A5
$\rightarrow H_2 + CH_2O$	$1.4\text{x}10^{-11}$	0±100	$1.4\text{x}10^{-11}$	1.2	A2, A5
$O(^1D) + H_2 \rightarrow OH + H$	$1.0\text{x}10^{-10}$	0±100	$1.0\text{x}10^{-10}$	1.2	A2
$O(^1D) + N_2 \rightarrow O + N_2$	$1.8\text{x}10^{-11}$	-(107±100)	$2.6\text{x}10^{-11}$	1.2	A2
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)	–			
$O(^1D) + O_2 \rightarrow O + O_2$	$3.2\text{x}10^{-11}$	-(67±100)	$4.0\text{x}10^{-11}$	1.2	A2
$O(^1D) + O_3 \rightarrow O_2 + O_2$	$1.2\text{x}10^{-10}$	0±100	$1.2\text{x}10^{-10}$	1.3	A2, A6
$\rightarrow O_2 + O + O$	$1.2\text{x}10^{-10}$	0±100	$1.2\text{x}10^{-10}$	1.3	A2, A6
*$O(^1D) + HC\ell \rightarrow$ products	$1.5\text{x}10^{-10}$	0±100	$1.5\text{x}10^{-10}$	1.2	A2, A7
$O(^1D) + CC\ell_4 \rightarrow$ products	$3.3\text{x}10^{-10}$	0±100	$3.3\text{x}10^{-10}$	1.2	A2, A8
$O(^1D) + CFC\ell_3 \rightarrow$ products	$2.3\text{x}10^{-10}$	0±100	$2.3\text{x}10^{-10}$	1.2	A2, A8
$O(^1D) + CF_2C\ell_2 \rightarrow$ products	$1.4\text{x}10^{-10}$	0±100	$1.4\text{x}10^{-10}$	1.3	A2, A8

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$O(^1D) + CF_4 \rightarrow CF_4 + O$	1.8×10^{-13}	0±100	1.8×10^{-13}	2.0	A2, A8
$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0±100	3.6×10^{-10}	2.0	A2, A9
$O(^1D) + CFClO \rightarrow$ products	1.9×10^{-10}	0±100	1.9×10^{-10}	2.0	A2, A9
$O(^1D) + CF_2O \rightarrow$ products	7.4×10^{-11}	0±100	7.4×10^{-11}	2.0	A2, A9
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0±100	2.5×10^{-10}	1.3	A2, A10
$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	-(117±100)	1.1×10^{-10}	1.2	A2
#$O(^1D) + HF \rightarrow OH + F$	1.4×10^{-10}	0±100	1.4×10^{-10}	2.0	A11
		HO_x Reactions			
$H + O_2 \xrightarrow{M} HO_2$	(See Table 2)				
$H + O_3 \rightarrow OH + O_2$	1.4×10^{-10}	470±200	2.9×10^{-11}	1.25	B1
$H + HO_2 \rightarrow$ products	7.4×10^{-11}	0±400	7.4×10^{-11}	1.6	B2
$O + OH \rightarrow O_2 + H$	2.2×10^{-11}	-(117±100)	3.3×10^{-11}	1.2	B3
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-(200±200)	5.9×10^{-11}	1.2	B4
$O + H_2O_2 \rightarrow OH + HO_2$	1.4×10^{-12}	2000±1000	1.7×10^{-15}	2.0	B5
*$OH + HO_2 \rightarrow H_2O + O_2$	1.7×10^{-11}	-(416±200)	7.0×10^{-11}	1.3	B6
$\xrightarrow{M} H_2O + O_2$	$3.0\times10^{-31}[M]$	-(500±500)	$1.6\times10^{-30}[M]$	2.0	B6
$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940±300	6.8×10^{-14}	1.3	B7
$OH + OH \rightarrow H_2O + O$	4.2×10^{-12}	242±242	1.9×10^{-12}	1.4	B8
$\xrightarrow{M} H_2O_2$	(See Table 2)				
*$OH + H_2O_2 \rightarrow H_2O + HO_2$	3.1×10^{-12}	187^{+100}_{-300}	1.7×10^{-12}	1.3	B9
$OH + H_2 \rightarrow H_2O + H$	6.1×10^{-12}	2030±400	6.7×10^{-15}	1.2	B10

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.3×10^{-13}	$-(590\pm200)$	1.7×10^{-12}	1.3	B11
$\xrightarrow{M} H_2O_2 + O_2$	$1.7\times10^{-33}[M]$	$-(1000\pm400)$	$4.9\times10^{-32}[M]$	1.3	B11
$HO_2 + O_3 \rightarrow OH + 2O_2$	1.4×10^{-14}	580^{+500}_{-100}	2.0×10^{-15}	1.5	B12
		NO_x Reactions			
$N + O_2 \rightarrow NO + O$	4.4×10^{-12}	3220 ± 340	8.9×10^{-17}	1.25	C1
$N + O_3 \rightarrow NO + O_2$	-	-	$<1.0\times10^{-15}$	-	C2
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0 ± 100	3.4×10^{-11}	1.3	C3
$N + NO_2 \rightarrow N_2O + O$	-	-	3.0×10^{-12}	3	C4
$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	0^{+0}_{-150}	9.3×10^{-12}	1.1	C5
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0 ± 150	1.0×10^{-11}	1.5	C6
$O + N_2O_5 \rightarrow$ products	-	-	$<3.0\times10^{-16}$	-	C7
$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0\times10^{-17}$	-	C8
$O + HO_2NO_2 \rightarrow$ products	7.0×10^{-11}	3370 ± 750	8.6×10^{-16}	3.0	C9
$O_3 + NO \rightarrow NO_2 + O_2$	1.8×10^{-12}	1370 ± 200	1.8×10^{-14}	1.2	C10
$NO + HO_2 \rightarrow NO_2 + OH$	3.7×10^{-12}	$-(240\pm80)$	8.3×10^{-12}	1.2	C11
*$NO + NO_3 \rightarrow 2NO_2$	1.3×10^{-11}	$-(250\pm250)$	3.0×10^{-11}	1.3	C12
$OH + NO \xrightarrow{M} HONO$	(See Table 2)				

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				
*$OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note C13 and ≠ below)			1.3	C13
$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380^{+270}_{-500})$	4.6×10^{-12}	1.5	C14
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
$O_3 + NO_2 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450±140	3.2×10^{-17}	1.15	C15
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0 \times 10^{-19}$	-	C16
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
#$N_2O_5 + H_2O \rightarrow 2HNO_3$	-	-	$<2 \times 10^{-21}$	-	C17
*$OH + NH_3 \rightarrow H_2O + NH_2$	3.5×10^{-12}	925±200	1.6×10^{-13}	1.4	C18
$NH_2 + HO_2 \rightarrow$ products	-	-	3.4×10^{-11}	2	C19
*$NH_2 + NO \rightarrow$ products	3.8×10^{-12}	-(450±150)	1.7×10^{-11}	2	C20
*$NH_2 + NO_2 \rightarrow$ products	2.1×10^{-12}	-(650±250)	1.9×10^{-11}	3	C21
$NH_2 + O_2 \rightarrow$ products	-	-	$<3 \times 10^{-18}$	-	C22
*$NH_2 + O_3 \rightarrow$ products	4.8×10^{-12}	930±500	2.1×10^{-13}	3	C23
		Hydrocarbon Reactions			
*$OH + CO \rightarrow CO_2 + H$	See Note		$1.5 \times 10^{-13}(1+0.6P_{atm})$	1.3	D1
$OH + CH_4 \rightarrow CH_3 + H_2O$	2.4×10^{-12}	1710±200	7.7×10^{-15}	1.2	D2
*$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	1.1×10^{-11}	1090±250	2.8×10^{-13}	1.25	D3
$OH + C_3H_8 \rightarrow H_2O + C_3H_7$	1.6×10^{-11}	800±250	1.1×10^{-12}	1.5	D4

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

≠$OH + HNO_3$ pressure and temperature dependence fit by

$$k(M,T) = k_o + \frac{k_3[M]}{1 + \frac{k_3[M]}{k_2}} \quad \text{with} \quad \begin{aligned} k_o &= 7.2 \times 10^{-15} \exp(785/T) \\ k_2 &= 4.1 \times 10^{-16} \exp(1440/T) \\ k_3 &= 1.9 \times 10^{-33} \exp(725/T) \end{aligned}$$

Table 1. (Continued)

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
$OH + C_2H_4 \rightarrow$ products	(See Table 2)				
$OH + C_2H_2 \rightarrow$ products	(See Table 2)				
$OH + H_2CO \rightarrow H_2O + HCO$	1.0×10^{-11}	0 ± 200	1.0×10^{-11}	1.25	D5
$OH + CH_3OOH \rightarrow$ products	1.0×10^{-11}	0 ± 200	1.0×10^{-11}	2.0	D6
$OH + HCN \rightarrow$ products	1.2×10^{-13}	400 ± 150	3.1×10^{-14}	3.0	D7
*$OH + CH_3CN \rightarrow$ products	4.5×10^{-13}	900 ± 400	2.2×10^{-14}	2.0	D8
$HO_2 + CH_2O \rightarrow$ adduct	-	-	4.5×10^{-14}	10.0	D9
$O + C_2H_2 \rightarrow$ products	2.9×10^{-11}	1600 ± 300	1.4×10^{-13}	1.3	D10
$O + H_2CO \rightarrow$ products	3.0×10^{-11}	1550 ± 250	1.6×10^{-13}	1.25	D11
$O + CH_3 \rightarrow$ products	1.1×10^{-10}	0 ± 250	1.1×10^{-10}	1.3	D12
$CH_3 + O_2 \rightarrow$ products	-	-	$<3 \times 10^{-16}$	-	D13
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(See Table 2)				
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	-	-	2×10^{-12}	10	D14
*$CH_3O + O_2 \rightarrow CH_2O + HO_2$	8.4×10^{-14}	1200 ± 300	1.5×10^{-15}	2	D15
$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	$-(140 \pm 140)$	5.5×10^{-12}	1.3	D16
$CH_3 + O_3 \rightarrow$ products	5.4×10^{-12}	220 ± 150	2.6×10^{-12}	2	D17
$CH_3O_2 + O_3 \rightarrow$ products	-	-	$<1 \times 10^{-17}$	-	D18
$CH_3O_2 + CH_3O_2 \rightarrow$ products	1.6×10^{-13}	$-(220 \pm 220)$	3.4×10^{-13}	1.25	D19
*$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	$-(180 \pm 180)$	7.6×10^{-12}	1.2	D20
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	7.7×10^{-14}	$-(1300^{+500}_{-1300})$	6.0×10^{-12}	3.0	D21
#$NO_3 + CO \rightarrow$ products	-	-	$<1\times10^{-15}$	-	D22
#$NO_3 + CH_2O \rightarrow$ products	-	-	6×10^{-16}	1.5	D23
		$C\ell O_x$ Reactions			
$C\ell + O_3 \rightarrow C\ell O + O_2$	2.8×10^{-11}	257±100	1.2×10^{-11}	1.15	E1
$C\ell + H_2 \rightarrow HC\ell + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	E2
$C\ell + CH_4 \rightarrow HC\ell + CH_3$	9.6×10^{-12}	1350±150	1.0×10^{-13}	1.1	E3
$C\ell + C_2H_6 \rightarrow HC\ell + C_2H_5$	7.7×10^{-11}	90±90	5.7×10^{-11}	1.1	E4
$C\ell + C_3H_8 \rightarrow HC\ell + C_3H_7$	1.4×10^{-10}	-(40±250)	1.6×10^{-10}	1.5	E5
$C\ell + C_2H_2 \rightarrow$ products	-	-	1×10^{-12}	10	E6
$C\ell + CH_3OH \rightarrow CH_2OH + C\ell$	6.3×10^{-11}	0±250	6.3×10^{-11}	2.0	E7
$C\ell + CH_3C\ell \rightarrow CH_2C\ell + HC\ell$	3.4×10^{-11}	1260±200	4.9×10^{-13}	1.2	E8
$C\ell + CH_3CC\ell_3 \rightarrow CH_2CC\ell_3 + HC\ell$	-	-	$<4\times10^{-14}$	-	E9
$C\ell + H_2CO \rightarrow HC\ell + HCO$	8.2×10^{-11}	34±100	7.3×10^{-11}	1.15	E10
$C\ell + H_2O_2 \rightarrow HC\ell + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	E11
$C\ell + HOC\ell \rightarrow$ products	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	E12
$C\ell + HNO_3 \rightarrow$ products	-	-	$<1.7\times10^{-14}$	-	E13
$C\ell + HO_2 \rightarrow HC\ell + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	E14
$\rightarrow OH + C\ell O$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	E14
$C\ell + C\ell_2O \rightarrow C\ell_2 + C\ell O$	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	E15

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
$C\ell + OC\ell O \rightarrow C\ell O + C\ell O$	5.9×10^{-11}	0 ± 250	5.9×10^{-11}	1.25	E16
$C\ell + C\ell ONO_2 \rightarrow$ products	6.8×10^{-12}	$-(160\pm200)$	1.2×10^{-11}	1.3	E17
$C\ell + NO \xrightarrow{M} NOC\ell$	(See Table 2)				
$C\ell + NO_2 \xrightarrow{M} C\ell ONO\ (C\ell NO_2)$	(See Table 2)				
$C\ell + C\ell NO \rightarrow NO + C\ell_2$	2.3×10^{-11}	0^{+500}_{-250}	2.3×10^{-11}	3.0	E18
$C\ell + O_2 \xrightarrow{M} C\ell OO$	(See Table 2)				
$C\ell + C\ell OO \rightarrow C\ell_2 + O_2$	1.4×10^{-10}	0 ± 250	1.4×10^{-10}	3.0	E19
$\rightarrow C\ell O + C\ell O$	8.0×10^{-12}	0 ± 250	8.0×10^{-12}	3.0	E19
*$C\ell O + O \rightarrow C\ell + O_2$	4.7×10^{-11}	50 ± 100	4.0×10^{-11}	1.3	E20
$C\ell O + NO \rightarrow NO_2 + C\ell$	6.2×10^{-12}	$-(294\pm100)$	1.7×10^{-11}	1.15	E21
$C\ell O + NO_2 \xrightarrow{M} C\ell ONO_2$	(See Table 2)				
$C\ell O + HO_2 \rightarrow HOC\ell + O_2$	4.6×10^{-13}	$-(710^{+250}_{-700})$	5.0×10^{-12}	1.4	E22
$C\ell O + H_2CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>2060	$<1.0\times10^{-15}$	-	E23
*$C\ell O + OH \rightarrow$ products	1.0×10^{-11}	$-(120\pm150)$	1.5×10^{-11}	1.6	E24
$C\ell O + CH_4 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	E25
$C\ell O + H_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>4800	$<1.0\times10^{-19}$	-	E25
$C\ell O + CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	E25
$C\ell O + N_2O \rightarrow$ products	$\sim1.0\times10^{-12}$	>4260	$<6.0\times10^{-19}$	-	E25
$C\ell O + C\ell O \rightarrow$ products	-	-	-	-	E26

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$C\ell O + O_3 \rightarrow C\ell OO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	E27
$\rightarrow OC\ell O + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	E27
*$OH + HC\ell \rightarrow H_2O + C\ell$	2.6×10^{-12}	350±100	8.0×10^{-13}	1.2	E28
$OH + HOC\ell \rightarrow H_2O + C\ell O$	3.0×10^{-12}	150^{+850}_{-150}	1.8×10^{-12}	10	E29
$OH + CH_3C\ell \rightarrow CH_2C\ell + H_2O$	1.8×10^{-12}	1112±200	4.3×10^{-14}	1.2	E30
$OH + CH_2C\ell_2 \rightarrow CHC\ell_2 + H_2O$	4.5×10^{-12}	1032±200	1.4×10^{-13}	1.2	E30
$OH + CHC\ell_3 \rightarrow CC\ell_3 + H_2O$	3.3×10^{-12}	1034±200	1.0×10^{-13}	1.2	E30
$OH + CHFC\ell_2 \rightarrow CFC\ell_2 + H_2O$	8.9×10^{-13}	1013±200	3.0×10^{-14}	1.3	E30
$OH + CHF_2C\ell \rightarrow CF_2C\ell + H_2O$	7.8×10^{-13}	1530±200	4.6×10^{-15}	1.2	E30
$OH + CH_2C\ell F \rightarrow CHC\ell F + H_2O$	2.0×10^{-12}	1134±150	4.4×10^{-14}	1.2	E30
$OH + CH_3CC\ell_3 \rightarrow CH_2CC\ell_3 + H_2O$	5.4×10^{-12}	1820±200	1.2×10^{-14}	1.3	E31
$OH + C_2C\ell_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	E32
$OH + C_2HC\ell_3 \rightarrow$ products	5.0×10^{-13}	-(445±200)	2.2×10^{-12}	1.25	E33
$OH + CFC\ell_3 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3650	$<5.0\times10^{-18}$	-	E34
$OH + CF_2C\ell_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3560	$<6.5\times10^{-18}$	-	E34
$OH + C\ell ONO_2 \rightarrow$ products	1.2×10^{-12}	333±200	3.9×10^{-13}	1.5	E35
$O + HC\ell \rightarrow OH + C\ell$	1.0×10^{-11}	3340±350	1.4×10^{-16}	2.0	E36
$O + HOC\ell \rightarrow OH + C\ell O$	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10	E37
$O + C\ell ONO_2 \rightarrow$ products	3.0×10^{-12}	808±200	2.0×10^{-13}	1.5	E38
$O + C\ell_2O \rightarrow C\ell O + C\ell O$	2.9×10^{-11}	630±200	3.5×10^{-12}	1.4	E39

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$O + OC\ell O \rightarrow C\ell O + O_2$	2.5×10^{-11}	1160±300	5.0×10^{-13}	1.5	E40
$NO + OC\ell O \rightarrow NO_2 + C\ell O$	2.5×10^{-12}	600±300	3.4×10^{-13}	1.5	E41
#$C\ell + CH_3CN \rightarrow$ products	-	-	$<2.0\times10^{-15}$	-	E42
#$C\ell + NO_3 \rightarrow C\ell O + NO_2$	-	-	7.6×10^{-11}	2.0	E43
#$C\ell O + NO_3 \rightarrow$ products	-	-	4.0×10^{-13}	2.0	E43
#$OH + C\ell_2 \rightarrow HOC\ell + C\ell$	-	-	6.5×10^{-14}	1.2	E44
#$HC\ell + C\ell ONO_2 \rightarrow$ products	-	-	$<1.0\times10^{-18}$	-	E45
#$HC\ell + HO_2NO_2 \rightarrow$ products	-	-	$<1\times10^{-20}$	-	E46
		BrO_x Reactions			
$Br + O_3 \rightarrow BrO + O_2$	1.4×10^{-11}	755±200	1.1×10^{-12}	1.2	F1
$Br + H_2O_2 \rightarrow HBr + HO_2$	1.0×10^{-11}	>2500	$<2.0\times10^{-15}$	-	F2
$Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	F3
*$Br + HO_2 \rightarrow HBr + O_2$	-	-	8.0×10^{-13}	3.0	F4
$BrO + O \rightarrow Br + O_2$	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	F5
$BrO + C\ell O \rightarrow Br + OC\ell O$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	F6
$\rightarrow Br + C\ell + O_2$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	F6
$BrO + NO \rightarrow NO_2 + Br$	8.7×10^{-12}	-(265±130)	2.1×10^{-11}	1.15	F7
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(See Table 2)				
$BrO + BrO \rightarrow 2\,Br + O_2$	1.4×10^{-12}	-(150±150)	2.3×10^{-12}	1.25	F8
$\rightarrow Br_2 + O_2$	6.0×10^{-14}	-(600±600)	4.4×10^{-13}	1.25	F8

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$BrO + O_3 \rightarrow Br + 2\ O_2$	~$1x10^{-12}$	>1600	<$5.0x10^{-15}$	-	F9
$BrO + HO_2 \rightarrow$ products	-	-	$5.0x10^{-12}$	3.0	F10
$BrO + OH \rightarrow$ products	-	-	$1.0x10^{-11}$	5.0	F11
*$OH + HBr \rightarrow H_2O + Br$	$1.1x10^{-11}$	0±250	$1.1x10^{-11}$	1.3	F12
$OH + CH_3Br \rightarrow CH_2Br + H_2O$	$6.1x10^{-13}$	825±200	$3.8x10^{-14}$	1.25	F13
$O + HBr \rightarrow OH + Br$	$6.6x10^{-12}$	1540±200	$3.7x10^{-14}$	1.3	F14
#$OH + Br_2 \rightarrow HOBr + Br$	-	-	$4.8x10^{-11}$	1.3	F15
		FO_x Reactions			
$F + O_3 \rightarrow FO + O_2$	$2.8x10^{-11}$	226±200	$1.3x10^{-11}$	2.0	G1
$F + H_2 \rightarrow HF + H$	$1.6x10^{-10}$	525±250	$2.7x10^{-11}$	1.3	G2
$F + CH_4 \rightarrow HF + CH_3$	$3.0x10^{-10}$	400±300	$8.0x10^{-11}$	1.5	G3
*$F + H_2O \rightarrow HF + OH$	$4.2x10^{-11}$	400±200	$1.1x10^{-11}$	3.0	G4
$F + O_2 \xrightarrow{M} FO_2$	(See Table 2)				
$F + NO \xrightarrow{M} FNO$	(See Table 2)				
$F + NO_2 \xrightarrow{M} FNO_2(FONO)$	(See Table 2)				
$NO + FO \rightarrow NO_2 + F$	$2.6x10^{-11}$	0±250	$2.6x10^{-11}$	2.0	G5
$FO + FO \rightarrow 2\ F + O_2$	$1.5x10^{-11}$	0±250	$1.5x10^{-11}$	3.0	G6
$FO + O_3 \rightarrow F + 2\ O_2$	-	-	-	-	G7
$\rightarrow FO_2 + O_2$	-	-	-	-	G7
$FO + NO_2 \xrightarrow{M} FONO_2$	(See Table 2)				

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$O + FO \rightarrow F + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	3.0	G8
$O + FO_2 \rightarrow FO + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	5.0	G9
#$CF_3O_2 + NO \rightarrow CF_3O + NO_2$	3.9×10^{-12}	-(400±200)	1.5×10^{-11}	1.3	G10
#$CF_2C\ell O_2 + NO \rightarrow CF_2C\ell O + NO_2$	3.1×10^{-12}	-(500±200)	1.6×10^{-11}	1.3	G10
#$CFC\ell_2O_2 + NO \rightarrow CFC\ell_2O + NO_2$	3.5×10^{-12}	-(430±200)	1.5×10^{-11}	1.3	G10
#$CC\ell_3O_2 + NO \rightarrow CC\ell_3O + NO_2$	5.7×10^{-12}	-(330±200)	1.7×10^{-11}	1.3	G10
		SO_x Reactions			
$OH + H_2S \rightarrow SH + H_2O$	5.9×10^{-12}	65±65	4.7×10^{-12}	1.2	H1
*$OH + OCS \rightarrow$ products	3.9×10^{-13}	1780±500	1.0×10^{-15}	10	H2
$OH + CS_2 \rightarrow$ products	(See Note)	-	-	-	H3
$OH + SO_2 \xrightarrow{M} HOSO_2$	(See Table 2)				
$O + H_2S \rightarrow OH + SH$	1.0×10^{-11}	1810±550	2.2×10^{-14}	1.7	H4
$O + OCS \rightarrow CO + SO$	2.1×10^{-11}	2200±150	1.3×10^{-14}	1.2	H5
$O + CS_2 \rightarrow CS + SO$	3.2×10^{-11}	650±150	3.6×10^{-12}	1.2	H6
$O + SH \rightarrow H + SO$	-	-	1.6×10^{-10}	5.0	H7
$S + O_2 \rightarrow SO + O$	2.3×10^{-12}	0±200	2.3×10^{-12}	1.2	H8
$S + O_3 \rightarrow SO + O_2$	-	-	1.2×10^{-11}	2.0	H9
$S + OH \rightarrow SO + H$	-	-	6.6×10^{-11}	3.0	H10
$SO + O_2 \rightarrow SO_2 + O$	2.4×10^{-13}	2370±500	8.4×10^{-17}	2	H11
$SO + O_3 \rightarrow SO_2 + O_2$	3.6×10^{-12}	1100±200	9.0×10^{-14}	1.2	H12

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$SO + OH \rightarrow SO_2 + H$	-	-	8.6×10^{-11}	2.0	H13
$SO + NO_2 \rightarrow SO_2 + NO$	-	-	1.4×10^{-11}	1.3	H14
$SO + C\ell O \rightarrow SO_2 + C\ell$	-	-	2.3×10^{-11}	3.0	H15
$SO + OC\ell O \rightarrow SO_2 + C\ell O$	-	-	1.9×10^{-12}	3.0	H15
$SO + BrO \rightarrow SO_2 + Br$	-	-	$>4.0\times10^{-11}$	-	H15
$SO_2 + HO_2 \rightarrow$ products	-	-	$<1.0\times10^{-18}$	-	H16
$CH_3O_2 + SO_2 \rightarrow$ products	-	-	$<5.0\times10^{-17}$	-	H17
*$SH + O_2 \rightarrow OH + SO$	-	-	$<1.0\times10^{-17}$	-	H18
$C\ell + H_2S \rightarrow HC\ell + SH$	-	-	7.3×10^{-11}	1.4	H19
$C\ell + OCS \rightarrow SC\ell + CO$	-	-	$<1.1\times10^{-16}$	-	H20
$C\ell O + OCS \rightarrow$ products	-	-	$<2.4\times10^{-16}$	-	H20
$C\ell O + SO_2 \rightarrow C\ell + SO_3$	-	-	$<4.0\times10^{-18}$	-	H20
#$SH + H_2O_2 \rightarrow$ products	-	-	$<5\times10^{-15}$	-	H21
#$SH + O_3 \rightarrow HSO + O_2$	-	-	3.2×10^{-12}	3.0	H22
#$HSO + O_3 \rightarrow$ products	-	-	1×10^{-13}	5.0	H22
#$SH + NO_2 \rightarrow HSO + NO$	-	-	3.2×10^{-11}	1.5	H23
#$SH + NO \xrightarrow{M} HSNO$	(See Table 2)				
#$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	-	-	4.0×10^{-13}	3.0	H24
#$SO_2 + NO_2 \rightarrow$ products	-	-	$<2\times10^{-26}$	-	H25
#$SO_3 + NO_2 \rightarrow$ products	-	-	1.0×10^{-19}	10	H25

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
#$SO_2 + O_3 \rightarrow SO_3 + O_2$	3.0×10^{-12}	>7000	$<2\times10^{-22}$	-	H26
#$CS + O_2 \rightarrow OCS + O$	-	-	2.9×10^{-19}	2.0	H27
#$CS + O_3 \rightarrow OCS + O_2$	-	-	3.0×10^{-16}	3.0	H28
#$CS + NO_2 \rightarrow OCS + NO$	-	-	7.6×10^{-17}	3.0	H28
		Metal Reactions			
#$Na + O_3 \rightarrow NaO + O_2$	5×10^{-10}	0±400	5×10^{-10}	1.5	J1
$\rightarrow NaO_2 + O$	$<3\times10^{-11}$	0±400	$<3\times10^{-11}$	-	J1
#$Na + O_2 \xrightarrow{M} NaO_2$	(See Table 2)				
#$NaO + HCl \rightarrow$ products	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J2
#$NaOH + HCl \rightarrow NaCl + H_2O$	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J3

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

NOTES TO TABLE 1

A1. $O + O_3$. The recommended rate expression is from Wine et al. (1983) and is a linear least squares fit of all data (unweighted) from Davis et al. (1973b), McCrumb and Kaufman (1972), West et al. (1978), Arnold and Comes (1979), and Wine et al. (1983).

A2. $O(^1D)$ Reactions. These recommendations are based on averages of the absolute rate constant measurements reported by Streit et al. (1976), Davidson et al. (1977) and Davidson et al. (1978) for N_2O, H_2O, CH_4, H_2, N_2, O_2, O_3, $HC\ell$, $CC\ell_4$, $CFC\ell_3$, $CF_2C\ell_2$, NH_3, and CO_2; by Amimoto et al. (1978), Amimoto et al. (1979), and Force and Wiesenfeld (1981a,b) for N_2O, H_2O, CH_4, N_2, H_2, O_2, O_3, CO_2, $CC\ell_4$, $CFC\ell_3$, $CF_2C\ell_2$, and CF_4; by Wine and Ravishankara (1981, 1982, 1983) for N_2O, H_2O, N_2, H_2, O_3, CO_2, and CF_2O; by Brock and Watson (private communication, 1980) for N_2, O_2 and CO_2; by Lee and Slanger (1978 and 1979) for H_2O and O_2; and by Gericke and Comes (1981) for H_2. The weight of the evidence from these studies indicates that the results of Heidner and Husain (1973), Heidner et al. (1973) and Fletcher and Husain (1976a, 1976b) contain a systematic error. For the critical atmospheric reactants, such as N_2O, H_2O, and CH_4, the recommended absolute rate constants are in good agreement with the previous relative meaurements when compared with N_2 as the reference reactant. A similar comparison with O_2 as the reference reactant gives somewhat poorer agreement. Wine and Ravishankara (1982) have determined the yield of $O(^3P)$ from $O(^1D) + H_2$ is $<4.9\%$.

A3. $O(^1D) + N_2O$. The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or $NO + NO$ is an average of the values reported by Davidson et al. (1979); Volltrauer et al. (1979); Marx et al. (1979) and Lam et al. (1981), with a spread in $k(NO + NO)/k(TOTAL) = 0.52 - 0.62$. The recommended branching ratio agrees well with earlier measurements of the N_2 quantum yield from N_2O photolysis (Calvert and Pitts 1966b). The $O(^1D)$ translational energy and temperature dependence effects are not clearly resolved. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + N_2O$ is $<4.0\%$.

The uncertainty for this reaction includes factors for both the overall rate coefficient and the branching ratio.

A4. $O(^1D) + H_2O$. Measurements by Zellner et al. (1980) indicate 1(+0.5 or -1)% of the $O(^1D) + H_2O$ reaction products are $H_2 + O_2$. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + H_2O$ is <(4.9 ± 3.2)%.

A5. $O(^1D) + CH_4$. The branching ratio for the reaction of $O(^1D)$ with CH_4 to give $OH + CH_3$ or $CH_2O + H_2$ is from Lin and DeMore (1973). A molecular beam study by Casavecchia et al. (1980) indicates that an additional path forming CH_3O (or CH_2OH) + H may be important. This possibility requires further investigation. Wine and Ravishankara (1982) have determined that the yield of $O(^3P)$ from $O(^1D) + CH_4$ is <4.3%.

A6. $O(^1D) + O_3$. The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al. (1972). This is supported by measurements of Amimoto et al. (1978) who reported that on average one ground state O is produced per $O(^1D)$ reaction with O_3. It seems unlikely that this could result from 100% quenching of the $O(^1D)$ by O_3.

A7. $O(^1D) + HCl$. The recommendation is the average of measurements by Davidson et al., (1977) and Wine et al. (private communication, 1984). Product studes by the latter indicate: $O(^3P) + HCl$ (10 ± 3)%; $H + ClO$ (23 ± 5)%; and $OH + Cl$ > 59%.

A8. $O(^1D)$ + halocarbons. The halocarbon rate constants are for the total disappearance of $O(^1D)$ and probably include physical quenching. Products of the reactive channels may include $CX_3O + X$, $CX_2O + X_2$, and $CX_3 + XO$, where X = H, F, or Cl in various combinations. Chlorine and hydrogen are more easily displaced than fluorine from halocarbons as indicated by approximately 100% quenching for CF_4. A useful formula for estimating $O(^1D)$ removal rates by methane and ethane type halocarbons was given by Davidson et al. (1978): $k(C_nH_aF_bCl_c) = 0.32a + 0.030b + 0.74c$ (in units 10^{-10} cm^3 $molecule^{-1}$ s^{-1}). This expression does not work for molecules with extensive fluorine substitution. Some values have been reported for the fractions of the total rate of disappearance of $O(^1D)$ proceeding through quenching and reactive channels. For $CC\ell_4$: quenching = (14±6)% and reaction = (86±6)%, (Force and Wiesenfeld, 1981a); for $CFC\ell_3$: quenching = (25±10)%, $C\ell O$ formation = (60±15)% (Donovan, private communication, 1980); for $CF_2C\ell_2$: quenching = (14±7)% and reaction = (86±14)% (Force and Wiesenfeld, 1981a), quenching = (20±10)%, $C\ell O$ formation = (55±15)% (Donovan, private communication, 1980); for CF_4: quenching = 100% (Force and Wiesenfeld, 1981a).

A9. $O(^1D) + CC\ell_2O$, $CFC\ell O$ and CF_2O. For the reactions of $O(^1D)$ with $CC\ell_2O$ and $CFC\ell O$ the recommended rate constants are derived from data of Fletcher and Husain (1978). For consistency, the recommended values for these rate constants were derived using a scaling factor (0.5) which corrects for the difference between rate constants from the Husain Laboratory and the recommendations for other $O(^1D)$ rate constants in this table. The recommendation for CF_2O is from the data of Wine and Ravishankara (1983). Their result is preferred over the value of Fletcher and Husain (1978) because it appears to follow the pattern of decreased reactivity with increased fluorine substitution observed for other halocarbons. These reactions have been studied only at 298 K. Based on consideration of similar $O(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to k(298 K).

A10. $O(^1D) + NH_3$. Sanders *et al*. (1980a) have detected the products $NH(a^1\Delta)$ in addition to OH formed in the reaction $O(^1D) + NH_3$. They report the yield of $NH(a^1\Delta)$ is in the range 3-15% of the amount of OH detected.

A11. $O(^1D) + HF$. Rate coefficient and product yield measured by Wine *et al*. (1984, private communication). The $O(^3P)$ yield is less than 4%.

B1. $H + O_3$. The recommendation is an average of the recent results of Lee *et al*. (1978b) and Keyser (1979), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhouse (1977) is in very good agreement on the T dependence in the range 300-560 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhouse values, we prefer the two studies that are in excellent agreement, especially since they were carried out over the T range of interest. Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendations. Reports of a channel forming HO_2 + O (Finlayson-Pitts and Kleindienst, 1979: ~25%, and Force and Wiesenfeld, 1981b: ~40%) have been contradicted by other studies (Howard and Finlayson-Pitts, 1980: < 3%; Washida et al., 1980a: < 6%; and Finlayson-Pitts et al., 1981: < 2%). Secondary chemistry is believed to be responsible for the observed O atoms in this system. Washida et al. (1980c) measured a low limit (< 0.1%) for the production of singlet molecular oxygen in the reaction H + O_3.

B2. H + HO_2. There are four recent studies of this reaction: Hack et al. (1978b), Hack et al. (1979c), Thrush and Wilkinson (1981b), and Sridharan et al. (1982). Related early work and combustion studies are referenced in the latter paper. All four studies used discharge flow systems. It is difficult to obtain a direct measurement of the rate constant for this reaction because both reactants are radicals and the products OH and O are very reactive toward the HO_2 reactant. The recommendation is based on the data of Sridharan et al. because their measurement was the most direct and required the fewest corrections. The other measurements, $(5.0 \pm 1.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} by Thrush and Wilkinson (1981b) and $(4.65 \pm 1) \times 10^{-11}$ by Hack et al. (1979c) are in reasonable agreement with the recommended value. Hack et al. (1978b) and Sridharan et al. (1982) reported 3 product channels: (a) 2OH, (b) H_2O + O, and (c) H_2 + O_2. The former gave $k_a/k = 0.69$, $k_b/k \leq 0.02$, and $k_c/k = 0.29$ and the latter gave $k_a/k = 0.87 \pm 0.04$, $k_b/k = 0.04 \pm 0.02$, and $k_c/k = 0.09 \pm .045$. Hislop and Wayne (1977) reported on the possibility of $O_2(b^1\Sigma)$ being formed in channel (c) in $(2.8 \pm 1.3) \times 10^{-4}$ of the total reactions. There are no studies of the temperature dependence of the rate constant or the product ratios in the range of atmospheric interest. It is likely that the dominant channel at room temperature, (a), which occurs on a radical-radical recombination surface will increase with decreasing temperature and that the others which involve insertion or abstraction will decrease with decreasing temperature. Further high quality studies are needed.

B3. $O + OH$. The rate constant for $O + OH$ is a fit to three temperature dependence studies: Westenberg et al. (1970a), Lewis and Watson (1980), and Howard and Smith (1981). This recommendation is consistent with earlier work near room temperature as reviewed by Lewis and Watson (1980) and with the recent measurements of Brune et al. (1983). The ratio $k(O + HO_2)/k(O + OH)$ measured by Keyser (1983) agrees with the rate constants recommended here.

B4. $O + HO_2$. The recommendation for the $O + HO_2$ reaction rate constant is the average of four studies at room temperature (Keyser, 1982, Sridharan et al., 1982, Ravishankara et al., 1983b and Brune et al., 1983) fitted to the temperature dependence given by Keyser (1982). Earlier studies by Hack et al. (1979a) and Burrows et al. (1977, 1979) are not considered, because the $OH + H_2O_2$ reaction was important in these studies and the value used for its rate constant in their analyses has been shown to be in error. Data from Lii et al. (1980c) is not considered, because it is based on only four experiments and involves a curve fitting procedure that appears to be insensitive to the desired rate constant. Data from Ravishankara et al. (1983b) at 298 K show no dependence on pressure between 10 and 500 Torr N_2. The ratio $k(O + HO_2)/k(O + OH)$ measured by Keyser (1983) agrees with the rate constants recommended here.

B5. $O + H_2O_2$. There are two direct studies of the $O + H_2O_2$ reaction: Davis et al. (1974c) and Wine et al. (1983). The recommended value is a fit to the combined data. Wine et al. suggest that the earlier measurements may be too high because of secondary chemistry. The A factor for both data sets is quite low compared to similar atom-molecule reactions. An indirect measurement of the E/R by Roscoe (1982) is consistent with the recommendation.

B6. $OH + HO_2$. Four measurements of the rate constant at low pressure (1-3 torr) in discharge-flow systems all give values near 7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}: Keyser (1981), Thrush and Wilkinson (1981a), Sridharan et al. (1981), and Temps and Wagner (1982). The latter two studies supersede earlier work which reported lower values from the same laboratories, Chang and Kaufman (1978) and Hack et al. (1978a). Separate studies at pressures near one atmosphere obtain consistently a larger rate constant, about 1.1

$\times 10^{-10}$; Lii et al. (1980a), Hochanadel et al. (1980), DeMore (1982), Cox et al. (1981) and Braun et al. (1982). Less definitive measurements by Burrows et al. (1981) and Kurylo et al. (1981) are in reasonable agreement. DeMore (1982) reports rate constants that increase from about 7×10^{-11} at 75 torr to about 1.2×10^{-10} at 730 torr. The present recommendation is for a rate constant that increases linearly with pressure from 7×10^{-11} at low pressure to 1.1×10^{-10} at one atmosphere and 298 K. The separate components are given different temperature coefficients. For the low pressure component the direct measurements of Sridharan et al. (1984) are adopted. For the pressure dependent component, a somewhat larger temperature coefficient is estimated by analogy to the $HO_2 + HO_2$ reaction. Although this recommendation incorporates the most reliable and thorough studies, it has not been reconciled in terms of the current models of reaction rate theory. Burrows et al. (1981) and DeMore (1982) did not observe any water vapor effect at 298 K. Further direct studies of the temperature and pressure dependences and products of this reaction are required.

B7. $OH + O_3$. The recommendation for the $OH + O_3$ rate constant is based on the room temperature measurements of Kurylo (1973) and Zahniser and Howard (1980) and the temperature dependence studies of Anderson and Kaufman (1973) and Ravishankara et al. (1979b). Kurylo's value was adjusted (-8%) to correct for an error in the ozone concentration measurement (Hampson and Garvin, 1977). The Anderson and Kaufman rate constants were normalized to $k = 6.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 295 K as suggested by Chang and Kaufman (1978).

B8. OH + OH. The recommendation for the OH + OH reaction is the average of six measurements near 298 K: Westenberg and de Haas (1973a), McKenzie et al. (1973), Clyne and Down (1974), Trainor and von Rosenberg (1974), Farquharson and Smith (1980) and Wagner and Zellner (1981). The rate constants for these studies all fall between $(1.4 \text{ and } 2.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The temperature dependence is from Wagner and Zellner, who reported rate constants for the range $T = 250\text{-}580$ K.

B9. $OH + H_2O_2$. There are extensive data on the $OH + H_2O_2$ reaction. The recommendation is a fit to the temperature dependence studies of

Keyser (1980b), Sridharan et al. (1980), Wine et al. (1981c) and Kurylo et al. (1982b). The first two references contain a discussion of some possible reasons for the discrepancies with earlier work and an assessment of the impact of the new value on other kinetic studies. A measurement at 298 K by Marinelli and Johnston (1982a) agrees with the recommendation. There is some evidence that the E/R decreases with temperature as discussed by Lamb et al. (1983), therefore the recommendation incorporates a large error limit on the temperature dependence.

B10. $OH + H_2$. The $OH + H_2$ reaction has been the subject of numerous studies (see Ravishankara et al. (1981b) for a review of experimental and theoretical work). The recommendation is fixed to the average of nine studies at 298 K: Greiner (1969), Stuhl and Niki (1972), Westenberg and de Haas (1973c), Smith and Zellner (1974), Atkinson et al. (1975), Overend et al. (1975), Tully and Ravishankara (1980), Zellner and Steinert (1981), and Ravishankara et al. (1981b). The E/R is an average of five temperature dependence studies: Greiner (1969), Westenberg and de Haas (1973c), Smith and Zellner (1974), Atkinson et al. (1975), and Ravishankara et al. (1981b).

B11. $HO_2 + HO_2$. Two separate expressions are given for the rate constant for the $HO_2 + HO_2$ reaction. The effective rate constant is given by the sum of these two equations. This reaction has been shown to have a pressure independent bimolecular component and a pressure dependent termolecular component. Both components have negative temperature coefficients. The bimolecular expression is obtained from data of Cox and Burrows (1979), Thrush and Tyndall (1982a,b), Kircher and Sander (1984), and Takacs and Howard (1984). Earlier results of Thrush and Wilkinson (1979) are inconsistent with these data. The termolecular expression is obtained from data of Sander et al. (1982), Simonaitis and Heicklen (1982) at room temperature and Kircher and Sander (1984) for the temperature dependence. This equation applies to M = air. On this reaction system there is general agreement among investigators on the following aspects of the reaction at high pressure ($P \sim 1$ atm): (a) the HO_2 uv absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel et al. (1980), and Sander et al. (1982); (b) the rate constant at 300 K: Paukert and Johnston (1972), Hamilton (1975), Hamilton and Lii (1977), Cox and Burrows (1979), Lii et al. (1979), Tsuchiya and Nakamura (1979), Sander et al. (1982), and Simonaitis and Heicklen (1982) (all values fall in the range (2.5 to 4.7) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}); (c) the rate constant temperature dependence: Cox and Burrows (1979), Lii et al. (1979), and Kircher and Sander (1984); (d) the rate constant water vapor dependence: Hamilton (1975), Hochanadel et al. (1972), Hamilton and Lii (1977), Cox and Burrows (1979), DeMore (1979), Lii et al. (1981), and Sander et al. (1982); (e) the H/D isotope effect: Hamilton and Lii (1977) and Sander et al. (1982); and (f) the formation of H_2O_2 + O_2 as the major products at 300 K: Su et al. (1979b), Niki et al. (1980), Sander et al. (1982), and Simonaitis and Heicklen (1982). Measurements by Sahetchian et al. (1982) give evidence for the formation of a small amount of H_2 near 500 K in this system, Glinski and Birks (1984) report an upper limit of 1% H_2 yield at a total pressure of about 50 torr and 298 K. For systems containing water vapor, the factors given by Lii et al. (1981) and Kircher and Sander (1984) can be incorporated: $[1 + 1.4 \times 10^{-21} \exp(2200/T)][H_2O]$.

B12. HO_2 + O_3. There is only one direct study of the HO_2 + O_3 reaction (Zahniser and Howard, 1980). This is the basis of the recommendation. Three indirect studies, all using HO_2 + HO_2 as the reference reaction, are in good agreement when the negative temperature dependence of the reference reaction is considered (Simonaitis and Heicklen, 1973; DeMore and Tschuikow-Roux, 1974; and DeMore, 1979). Another direct study would be valuable. The A factor is unusually low.

C1. N + O_2. The activation energy is based on Becker et al. (1969). The value and uncertainty at 298 K are assigned from the average of Clyne and Thrush (1961), Wilson (1967), Becker et al. (1969), Clark and Wayne (1970) and Westenberg et al. (1970b). Independent confirmation of the temperature dependence is needed.

C2. N + O_3. The recommendation is based on results of Stief et al. (1979). Note that this is an upper limit based on instrumental sensitivity. Results of Stief et al. and Garvin and Broida (1963) cast doubt on the fast rate reported by Phillips and Schiff (1962).

C3. N + NO. Recommendation is based on the results of Lee et al. (1978c). A recent study of Husain and Slater (1980) reports a room temperature rate constant 30 percent higher than the recommended value.

C4. N + NO_2. The Panel accepts the results of Clyne and Ono (1982) for the value of the rate constant at 298 K. This is a factor of 2 higher than that reported by Clyne and McDermid (1975). However, Clyne and Ono consider that the more recent study is probably more reliable. Husain and Slater (1980) reported a room temperature rate constant of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} which is a factor of 12 greater than the value reported by Clyne and Ono. This high value may indicate the presence of catalytic cycles as discussed by Clyne and McDermid, and Clyne and Ono. There are no studies of the temperature dependence of the rate constant. The reaction products are taken to be N_2O + O (Clyne and McDermid).

C5. O + NO_2. Based on results of Davis et al. (1973a), Bemand et al. (1974) and Slanger et al. (1973), there may be a slight negative temperature coefficient, but the evidence at low temperature is uncertain.

C6. O + NO_3. Based on the study of Graham and Johnston (1978) and 298 K and 329 K. While limited in temperature range, the data indicate no temperature dependence. Furthermore, by analogy with the reaction of O with NO_2, it is assumed that this rate constant is in fact independent of temperature. Clearly, temperature dependent studies are needed.

C7. O + N_2O_5. Based on Kaiser and Japar (1978).

C8. O + HNO_3. The upper limit reported by Chapman and Wayne (1974) is accepted.

C9. O + HO_2NO_2. The recommended value is based on the study of Chang et al. (1981). The large uncertainty in E/R and k at 298 K are due to the fact that this is a single study.

C10. O_3 + NO. The recommended Arrhenius expression is a least squares fit to the data reported by Birks et al. (1976), Lippmann et al. (1980), Ray and Watson (1981b), Michael et al. (1981) and Borders and Birks (1982) at and below room temperature, with the data at closely spaced temperatures reported in Lippmann et al. and Borders and Birks being grouped together so that these five studies are weighted equally. This expression fits all the data within the temperature range 195-304 K reported in these five studies to within 20 percent. Only the data between 195 and 304 K were used to derive the recommended Arrhenius expression due to the observed non-linear Arrhenius behavior (Clyne et al. (1964), Clough and Thrush (1967), Birks et al., Michael et al. and Borders and Birks). Clough and Thrush, Birks et al., Schurath et al. (1981), and Michael et al. have all reported individual Arrhenius parameters for each of the two primary reaction channels. The range of values for k at stratospheric temperatures is somewhat larger than would be expected for such an easy reaction to study. The measurements of Stedman and Niki (1973) and Bemand et al. (1974) of k at 298 K are in excellent agreement with the recommended value of k at 298 K.

C11. NO + HO_2. The recommendation for HO_2 + NO is based on the average of six measurements of the rate constant near room temperature: Howard and Evenson (1977), Leu (1979), Howard (1979), Glaschick-Schimpf et al. (1979), Hack et al. (1980), and Thrush and Wilkinson (1981a). All of these are in quite good agreement. An earlier study from the Thrush Laboratory, Burrows et al. (1979), has been dropped because of an error in the reference rate constant, k(OH + H_2O_2). The temperature dependence is from Howard (1980) and is in reasonable agreement with that given by Leu (1979). A high pressure study is needed in view of the many unusual effects seen in the HO_2 reactions.

C12. NO + NO_3. Changed from JPL 83-62. The values of Torabi and Ravishankara (1984) measured by fast flow (3.16×10^{-11}) and flash photolysis (2.95×10^{-11}) techniques are in excellent agreement with the value of 2.9×10^{-11} measured by Hammer et al. (1985). The recommendation is an average of these three direct studies. The T dependence is based on preliminary work from Hammer et al. (1985).

C13. OH + HNO_3. Changed from JPL 83-62. The intensive study of this reaction over the past few years has significantly reduced many of the apparent discrepancies among (a) the early studies yielding a low, temperature independent rate constant (Smith and Zellner, 1975 and Margitan et al., 1975); (b) more recent work (mostly flash photolysis) with a k(298) approximately 40% larger, and a strong negative T dependence below room temperature (Wine et al., 1981b; Kurylo et al., 1982a; Margitan and Watson, 1982; Marinelli and Johnston, 1982a; Ravishankara et al., 1982; Jourdain et al., 1982; C. A. Smith et al., 1984); and (c) recent discharge flow studies yielding the lower value for k(298) but showing substantial negative T dependence (Devolder et al., 1984; Connell and Howard, 1985). Major features of the data are (1) a strong negative T dependence below room temperature, (2) a much weaker temperature dependence above room temperature, possibly leveling off around 500 K, (3) a small, measurable pressure dependence which becomes greater at low temperatures. The pressure dependence has been determined by Margitan and Watson (1982) over the ranges 20-100 torr and 225-298 K and by Stachnik et al. (1985) at pressures of 10, 60 and 730 torr at 298 K and 248 K. The two studies are in excellent agreement. Their "low pressure limit" agrees well with the average k(298) = 1.0 x 10^{-13} cm^3 s^{-1} derived from the 4 low pressure discharge flow studies. The values measured for pressures typical of the other flash photolysis studies (20-50 torr) also agree well. The two pressure dependence studies indicate that the high pressure limit is approximately 50% greater than the low pressure limit at 298 K, and about a factor of 2 greater at 240 K. Thus, over the narrow pressure ranges explored in most flash photolysis studies, the P-dependence would escape notice. For temperatures below 300 K, the pressure and temperature dependence can be represented by combining a low pressure (bimolecular) limit, k_o, with a Lindemann-Hinshelwood expression for the P dependence:

$$k(M,T) = k_o + \frac{k_3[M]}{1 + \frac{k_3[M]}{k_2}} \qquad \text{with} \qquad \begin{aligned} k_o &= 7.2 \times 10^{-15} \exp(785/T) \\ k_2 &= 4.1 \times 10^{-16} \exp(1440/T) \\ k_3 &= 1.9 \times 10^{-33} \exp(725/T) \end{aligned}$$

where k_3 and k_2 are the termolecular and high pressure limits for the "association" channel. The value of k at high pressures is the sum k_o + k_2. The weak pressure dependence and weak T dependence above 300 K explain many of the apparent discrepancies for all the data (including the 1975 studies) except for a few minor features which are probably due to the normally encountered experimental scatter: The Smith and Zellner flash photolysis values are low compared to other flash systems (closer to the flow studies), although the difference is not unusual (~30%). Conversely, the Jourdain et al. flow study is high relative to the other ones. The Connell and Howard T dependence (below 300 K) is significantly weaker than the other studies. The failure of Smith et al. to observe a pressure effect between 50 and 760 torr, even at 240 K, is in sharp conflict with the effect seen by Stachnik et al. over the same range in a much more detailed study. Nelson et al. (1981), Jourdain et al. and Ravishankara et al. have all shown that within experimental error the yield of NO_3 (per OH removed) is unity at 298 K, with similar results at 250 K (Ravishankara et al.).

C14. $OH + HO_2NO_2$. The recommendation for both k at 298 K and the Arrhenius expression is based upon the data of Trevor et al. (1982), Barnes et al. (1981) and C. A. Smith et al. (1984). Trevor et al. studied this reaction over the temperature range 246-324 K and reported a temperature invariant value of 4.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, although a weighted least squares fit to their data yields an Arrhenius expression with an E/R value of (193 ± 193) K. In contrast, Smith et al. studied the reaction over the temperature range 240-300 K and observed a negative temperature dependence with an E/R value of -(650 ± 30) K. Barnes et al. only studied the reaction at room temperature. The values of k at 298 K from the three studies are in excellent agreement. An unweighted least squares fit to all the experimental data of Trevor et al., Barnes et al., and Smith et al. yields the recommended Arrhenius expression. The less precise value for k at 298 K reported by Littlejohn and Johnston (1980) is in fair agreement with the recommended value. The error limits on the recommended E/R are sufficient to encompass the results of both Trevor et al. and Smith et al. It should be noted that the values of k at 220 K deduced from the two studies differ by a factor of 2. Clearly additional studies of k as a function of temperature, and the identification of the reaction products are needed.

C15. $O_3 + NO_2$. Based on least squares fit to data in studies of Davis et al. (1974b), Graham and Johnston (1974) and Huie and Herron (1974).

C16. $O_3 + HNO_2$. Based on Kaiser and Japar (1977) and Streit et al. (1979).

C17. $N_2O_5 + H_2O$. New entry. Upper limit based on Tuazon et al. (1983), who suggest that this limit may be close to the true homogeneous rate constant.

C18. $OH + NH_3$. Minor change from JPL 83-62. The recommended value at 298 K is the average of the values reported by Stuhl (1973b), Smith and Zellner (1975), Perry et al. (1976b), Silver and Kolb (1980), and Stephens (1984). The values reported by Kurylo (1973), Hack et al. (1974), Pagsberg et al. (1979) and Cox et al. (1975) were not included. The temperature dependence is based on the results reported by Smith and Zellner, Perry et al., Silver and Kolb, and Stephens, and the pre-exponential factor has been selected to fit the recommended room temperature value.

C19. $NH_2 + HO_2$. There is fairly good agreement on the value of k at 298 K between the direct study of Kurasawa and Lesclaux (1980b), and the relative studies of Cheskis and Sarkisov (1979) and Pagsberg et al. (1979). The recommended value is the average of the values reported in these three studies. The identity of the products is not known; however, Kurasawa and Lesclaux suggest that the most probable reaction channels give either $NH_3 + O_2$ or $HNO + H_2O$ as products.

C20. $NH_2 + NO$. Minor change from JPL 83-62. The recommended value for k at 298 K is the average of the values reported by Gordon et al. (1971), Gehring et al. (1973), Lesclaux et al., (1975), Hancock et al., (1975), Sarkisov et al. (1978), Hack et al. (1979b), Stief et al. (1982), Silver and Kolb (1982), and Whyte and Phillips (1983). The values reported in these studies for k at 298 K range from 8.3 to 27.0 ($\times 10^{-12}$) cm^3 $molecule^{-1}$ s^{-1}, which is not particularly satisfactory. The results tend to separate into two groups. The flash photolysis results average 1.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, while those obtained using the discharge flow technique average 0.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The apparent discrepancy cannot simply be due to a pressure effect as the pressure ranges of the flash photolysis and discharge flow studies overlapped, and none of the studies observed a pressure dependence for k. There have been four studies of the temperature dependence of k. Each study reported k to decrease with increasing temperature, i.e $T^{-1.25}$ (Lesclaux et al. from 300-500 K), $T^{-1.85}$ (Hack et al. from 210-503 K), $T^{-1.67}$ (Stief et al. from 216-480 K) and $T^{-2.3}$ exp(-684/T) (Silver and Kolb from 294-1215 K). The recommended temperature dependence is taken to be a weighted average of the data below 500 K from all four studies. The expression is: $k = 1.6 \times 10^{-11} (T/298)^{-1.5}$ for the temperature range 210-500 K.

There are many possible product channels for this reaction. Strong evidence against the formation of H atoms exists. Both Silver and Kolb (1982) and Andresen et al. (1982) report substantial yields of OH of 40% and ≥ 65%, respectively, in disagreement with Stief et al. (1982) who set an upper limit of <22% for OH production. In addition, Andresen et al. set a lower limit of ≥ 29% for the channel $N_2 + H_2O$.

C21. $NH_2 + NO_2$. Minor change from JPL 83-62. There have been three studies of this reaction (Hack et al. (1979b), Kurasawa and Lesclaux (1979) and Whyte and Phillips (1983)). There is very poor agreement among these studies both for k and 298 K (factor of 2.3) and for the temperature dependence of k ($T^{-3.0}$ and $T^{-1.3}$). The recommended values of k at 298 K and the temperature dependence of k are averages of the results reported in these three studies. Hack et al. have shown that the predominant reaction channel (>95%) produces $N_2O + H_2O$. Just as for the $NH_2 + NO$ reaction, the data for this reaction seem to indicate a factor of two discrepancy between flow and flash techniques, although the data base is much smaller.

C22. $NH_2 + O_2$. Minor change from JPL 83-62. The recommendation is based on the reported upper limits of 2×10^{-18} (Lesclaux and Demissy, 1977), 8×10^{-15} (Pagsberg et al., 1979), 1.5×10^{-17} (Cheskis and Sarkisov, 1979), 3×10^{-18} (Lozovsky et al., 1984) and 1×10^{-17} (Patrick and Golden, 1984b), all expressed as bimolecular rate constants with units of $cm^3 s^{-1}$. The termolecular rate constant upper limit would be 2×10^{-36} $cm^6 s^{-1}$. The values reported by Hack et al. (1982), $k = 3.6 \times 10^{-33} (T/295)^{-2}$ $cm^6 s^{-1}$ and Jayanty et al. (1976), $k = 4 \times 10^{-15}$ $cm^3 s^{-1}$ are not used in arriving at the recommendation.

C23. $NH_2 + O_3$. Changed from JPL 83-62. There is poor agreement among the recent study of Patrick and Golden (1984b): k(298) = 3.25×10^{-13} cm^3 s^{-1} and the earlier studies by Hack et al. (1981), 1.84×10^{-13} cm^3 s^{-1}; Bulatov et al. (1980), 1.2×10^{-13} cm^3 s^{-1} and Kurasawa and Lesclaux (1980a), 0.63×10^{-13} cm^3 s^{-1}. The very low value of Kurasawa and Lesclaux may be due to regeneration of NH_2 from secondary reactions (see Patrick and Golden), and it is disregarded here. The discharge flow value of Hack et al. is nearly a factor of two less than the recent Patrick and Golden flash photolysis value. The large discrepancy between Bulatov et al. and Patrick and Golden eludes explanation. The recommendation is the k(298) average of these three studies, and E/R is an average of Patrick and Golden (1151 K) with Hack et al. (710 K).

D1. OH + CO. Changed from JPL 83-62. The recommendation allows for an increase in k with pressure. The zero pressure value was derived by averaging all direct low pressure determinations (those listed in Baulch et al. (1980) and the values reported by Dreier and Wolfrum (1980), Husain et al. (1981), Ravishankara and Thompson (1983), Paraskevopoulos and Irwin (1984), Hofzumahaus and Stuhl (1984), and Fritz and Zellner (private communication, 1984)). An increase in k with pressure has been observed by a large number of investigators (Overend and Paraskevopoulos (1977a), Perry et al. (1977), Chan et al. (1977), Bierman et al. (1978), Cox et al. (1976b), Butler et al. (1978) Paraskevopoulos and Irwin (1982b, 1984), DeMore (1984), Hofzumahaus and Stuhl (1984), Fritz and Zellner (private communication, 1984), Wine et al. (private communication, 1984)). In addition, Niki et al. (1984) have measured k relative to OH + C_2H_4 in one atmosphere of air by following CO_2 production using FTIR. The recommended value was obtained by using a weighted non-linear least squares analysis of all pressure dependent data in N_2 (Paraskevopoulos and Irwin (1984), DeMore (1984), Hofzumahaus and Stuhl (1984) and Wine et al. (private communication, 1984)) as well as those in air (Fritz and Zellner (private communcation, 1984), Wine et al. (private communication, 1984), and Niki et al. (1984)) to the form $k = (A+BP)/(C+DP)$ where P is pressure in atmospheres. The data were best fit with D = 0 and therefore a linear form is recommended.

Previous controversy regarding the effect of small amounts of O_2 (Bierman et al.) has been resolved and is attributed to secondary reactions (DeMore (1984), Hofzumahaus and Stuhl (1984)). The results of Butler et al. (1978) have to be reevaluated in the light of refinements in the rate coefficient for the OH + H_2O_2 reaction. The corrected rate coefficient is in approximate agreement with the recommended value.

Results of Paraskevopoulos and Irwin (1984), Hofzumahaus and Stuhl (1984), Fritz and Zellner (private communication, 1984) and Wine et al. (private communication, 1984) clearly show that k increases non-linearly with pressure in a manner that is typical of addition reactions. For example, a weighted non-linear least squares analysis of data from Fritz and Zellner, Wine et al., and Niki, all in air yield $k = (6.82 \times 10^{-4} + 2.88 \times 10^{-3} P)/(4.70 \times 10^{9} + 9.24 \times 10^{9} P)$ where P is in atmospheres. Similarly, the results of Paraskevopolos and Irwin and Hofzumahaus and Stuhl, in N_2, yield $k = (5.36 \times 10^{-4} + 7.12 \times 10^{-4} P)/(3.79 \times 10^{9} + 1.56 \times 10^{9} P)$. Further measurements are expected to allow better definition of k as a function of P, as well as the high pressure limit for k. Currently, there are no indications to suggest that the presence of O_2 has effects other than as a third body. The E/R value is assumed to be zero and requires further study. The uncertainty factor is for 1 atm of air. In the presence of O_2, the HOCO intermediate is converted to HO_2 + CO_2 (DeMore, 1984). Beno et al. (1984) observe an enhancement of k with water vapor which is in conflict with the flash photolysis studies, e.g. Ravishankara and Thompson (1983), Paraskevopoulos and Irwin (1984), and DeMore (1984).

D2. OH + CH_4. This is an extremely well characterized reaction. All temperature dependence studies are in good agreement (Greiner (1970a), Davis et al. (1974a), Margitan et al. (1974), Zellner and Steinert (1976), Tully and Ravishankara (1980), Jeong and Kaufman (1982)). Due to this good agreement, and the curved nature of the Arrhenius plot at higher temperatures, the value of Davis et al., obtained in the temperature interval $240 < T < 373$ K is recommended.

D3. OH + C_2H_6. Changed from JPL 83-62. There is good agreement among seven studies of this reaction at 298 K, i.e., Greiner (1970a), Howard and Evenson (1976b), Overend et al. (1975), Lee and Tang (1982), Leu (1979), Tully et al. (1983) and Jeong et al. (1984). k(298 K) is the average of these seven measurements. The temperature dependence was computed by using the data of Greiner (1970a), Tully et al. (1983), and Jeong et al. (1984). Higher temperature results of Baulch et al. (1983) are in agreement with the recommended value.

D4. OH + C_3H_8. There are five measurements of the rate coefficient at 298K; Greiner (1970a), Gorse and Volman (1974), Bradley et al. (1973), Overend et al. (1975), and Tully et al. (1983). Gorse and Volman measured k(OH + C_3H_8) relative to k(OH + CO) in the presence of O_2 and calculated k(OH + C_3H_8) assuming that k(OH + CO) = 1.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. If the current recommended value for k(OH + CO) at high pressure is used, k(OH + C_3H_8) will be approximately 3.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Therefore the results of Overend et al. (1975) (k = 2×10^{-12} cm^3 s^{-1}) and Gorse and Volman are in disagreement with the other values. The most probable cause for the discrepancy is the presence of secondary reactions in their system. The 298 K value is the average of the three studies. Only Greiner (1970a) and Tully et al. (1983) have measured the temperature dependence of this reaction, and the recommended E/R was obtained from a linear least squares analysis of the data below 500 K. The A factor was adjusted to reproduce k(298 K). This reaction has two possible channels, i.e., abstraction of the primary or the secondary H atom. Therefore, non-Arrhenius behavior may be exhibited over a wide temperature range, as seen by Tully et al. The branching ratios can be estimated from Greiner's (1970a) formula:

$$k_{primary} = 6.1 \times 10^{-12} \exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k_{secondary} = 4.6 \times 10^{-12} \exp(-430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

D5. OH + H_2CO. The value for k (298 K) is the average of those determined by Atkinson and Pitts (1978) and Stief et al. (1980), both using the flash photolysis-resonance fluorescence technique. The value reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al. (1978b) relative to OH + C_2H_4 is higher while the value of Smith (1978) relative to OH + OH is lower. The latter data are also at variance with the negligible temperature dependence observed in the two flash photolysis studies. Although Atkinson and Pitts assign a small energy barrier (E/R = 90 ± 150), their data at 356 K and 426 K and that of Stief et al. at 228 K, 257 K and 362 K are all within 10% of the k (298 K) value. Thus, the combined data set suggests E/R = 0. The abstraction reaction shown in the table is probably the major channel; other channels may contribute (Horowitz et al., 1978).

D6. OH + CH_3OOH. The recommended value is that of Niki et al. (1983). They measured the rate coefficient relative to that of OH with C_2H_4 by monitoring CH_3OOH disappearance using an FTIR system. This measured value is very fast and hence is not expected to show substantial temperature dependence. Niki et al. have determined that the rate coefficient for H atom abstraction from the CH_3 group is approximately 0.7 times that for H atom abstraction from the OH group. Independent, direct measurements of this rate coefficient are needed.

D7. OH + HCN. This reaction is pressure dependent. The recommended value is the high pressure limit measured by Fritz et al. (1984) using a laser photolysis-resonance fluorescence apparatus. Phillips (1978) studied this reaction using a discharge flow apparatus at low pressures and found the rate coefficient to have reached the high pressure limit at ~10 torr at 298 K. Fritz et al.'s results contradict this finding. They agree with Phillips's measured value, within a factor of two, at 7 torr but they find k to increase further with pressure. The products of the reaction are unknown. The measured A factor appears to be low.

D8. OH + CH_3CN. Changed from JPL 83-62. This rate coefficient has been measured as a function of temperature by Harris et al. (1981) between 298 and 424 K, Kurylo and Knable (1984) between 250 and 363, and Rhasa and Zellner (private communication, 1984) between 295 and 520 K. In addition, the 298 K value has been measured by Zetsch (private communication, 1983) and Poulet et al. (1984a). The 298 K results of Harris et al. are in disagreement with all other measurements and therefore have not been included. The recommended 298 K value is the average of all other studies. The temperature dependence was computed using the results of Kurylo and Knable (250-363 K) and the lower temperature values (i.e. 295-391 K) of Rhasa and Zellner. Two points are worth noting: (a) Rhasa and Zellner observe a curved Arrhenius plot even in the temperature range of 295-520 K and therefore extrapolation of the recommended expression could lead to large errors, and (b) Zetsch observed a pressure dependent increase at k(298 K) which levels off at about 1 atmosphere. This observation is contradictory to the results of other investigations. A complex reaction mechanism cannot be ruled out. The products of the reaction are unknown.

D9. HO_2 + CH_2O. There is a general consensus that this reaction proceeds through addition of HO_2 to CH_2O (Su et al., 1979b,c, Veyret et al. 1982). The value of the rate coefficient deduced by Su et al. (1979c) based on modeling a complex system involving the oxidation of CH_2O is approximately seven times lower than that obtained by Veyret et al. (1982), who also modeled a complex system. The recommended value is an average of the two measurements and is very uncertain. Su et al. (1979c) have deduced that lifetime of the adduct towards decomposition to CH_2O and HO_2 is ~1 sec at 298 K.

D10. O + C_2H_2. The value at 298 K is an average of nine measurements; Arrington et al. (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al. (1967), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), Westenberg and deHaas (1977) Aleksandrov et al. (1981). There is reasonably good agreement among these studies. Arrington et al. (1965) did not observe a temperature dependence, an observation which was later shown to be erroneous by Westenberg and deHaas (1969b). Westenberg and deHaas are the only ones who have measured the temperature dependence, and they observed a curved Arrhenius plot. In the range of 195-450 K, Arrhenius behavior provides an adequate description and the E/R obtained by them in this temperature range is recommended. The A factor was calculated to reproduce k(298 K). This reaction can have two sets of products, i.e., C_2HO + H or CH_2 + CO. Under molecular beam conditions C_2HO has been shown to be the major product. However, a recent study by Aleksandrov et al. using a discharge flow-resonance fluorescence method (under undefined pressure conditions) indicates that the CH_2O + H channel contributes no more than 7% to the net reaction at 298 K.

D11. $O + H_2CO$. The recommended values for A, E/R and k (298 K) are the averages of those determined by Klemm (1979) using flash photolysis-resonance fluorescence (250 to 498 K) by Klemm et al. (1980) using discharge flow-resonance fluorescence (298 to 748 K) and Chang and Barker (1979) using discharge flow-mass spectrometry (296 to 436 K). All three studies are in good agreement. The k (298 K) value is also consistent with the results of Niki et al. (1969), Herron and Penzhorn (1969), and Mack and Thrush (1973). Although the mechanism for $O + H_2CO$ has been considered to be the abstraction reaction yielding OH + HCO, Chang and Barker suggest that an addition channel yielding $H + HCO_2$ may be occurring to the extent of 30% of the total reaction. This conclusion is based on an observation of CO_2 as a product of the reaction under conditions where reactions such as $O + HCO \rightarrow H + CO_2$ and $O + HCO \rightarrow OH + CO$ apparently do not occur. This interesting suggestion needs independent confirmation.

D12. $O + CH_3$. The recommended k(298 K) is the weighted average of three measurements by Washida and Bayes (1976), Washida (1980), and Plumb and Ryan (1982b). The E/R value is based on the results of Washida and Bayes (1976) who found k to be independent of temperatures between 259 and 341 K.

D13. $CH_3 + O_2$. This bimolecular reaction is not expected to be important based on the results of Baldwin and Golden (1978a) who found $k < 5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} for temperatures up to 1200 K. Klais et al., (1979) failed to detect OH (via $CH_3 + O_2 \rightarrow CH_2O + OH$) at 368 K and placed an upper limit of 3×10^{-16} cm^3 $molecule^{-1}$ s^{-1} for this rate coefficient. Bhaskaran, Frank and Just (1979) measured $k = 1 \times 10^{-11} \exp(-12,900/T)$ cm^3 $molecule^{-1}$ s^{-1} for $1800 < T < 2200$ K. The latter two studies, thus, support the results of Baldwin and Golden. Recent studies by Selzer and Bayes (1983) and Plumb and Ryan (1982b) confirm the low value for this rate coefficient. Previous studies of Washida and Bayes (1976) are superseded by those of Selzer and Bayes. Plumb and Ryan have placed an upper limit of 3×10^{-16} cm^3 $molecule^{-1}$ s^{-1} based on their inability to find HCHO in their experiments.

D14. $CH_2OH + O_2$. The rate coefficient has been measured by Radford (1980) by detecting the HO_2 product in a laser magnetic resonance spectrometer. The effect of wall loss of CH_2OH could have introduced a large error in this measurement. Radford also showed that the previous measurement of Avramenko and Kolesnikova (1961) was in error.

D15. $CH_3O + O_2$. Changed from JPL 83-62. The recommended A factor and E/R are those obtained using the results of Gutman et al. (1982) and Lorenz, Rhasa and Zellner (private communication, 1984). These investigators have measured k directly under pseudo-first order conditions by following CH_3O via laser induced fluorescence. The temperature intervals were 413 to 608 K (by Gutman et al.) and 298 to 441 K (by Lorenz et al.). Cox et al. (1980) used an end product analysis technique to measure k down to 298 K. The previous high temperature measurements (Barker et al. (1977) and Batt and Robinson (1979)), are in reasonable agreement with the derived expression. k(298 K) is calculated from the recommended expression. The inclusion of the new data reduces the uncertainty from the previous evaluation. This value is consistent with the 298 K results of Cox et al. (1980) and with the upper limit measured by Sanders et al. (1980b). The A factor, shown above, appears to be too low for a hydrogen atom transfer reaction. The Arrhenius plot is likely to be curved at higher temperature. The reaction may be more complicated than a simple abstraction. The products of this reaction are HO_2 and CH_2O, as shown by Niki et al. (1981).

D16. $HCO + O_2$. The value of k(298 K) is the average of the determinations by Washida et al. (1974), Shibuya et al. (1977), Veyret and Lesclaux (1981), and Langford and Moore (1984). There are three measurements of k where HCO was monitored via the intracavity dye laser technique (Reilly et al. (1978), Nadtochenko et al. (1979), and Gill et al. (1981)). Even though there is excellent agreement between these three studies, they yield consistently lower values than those obtained by other techniques. There are several possible reasons for this discrepancy: (a) The relationship between [HCO] and laser attenuation might not be linear, (b) there could have been depletion of O_2 in the static systems that were used (as suggested by Veyret and Lesclaux), and (c) these experiments were designed more for the study of photochemistry than kinetics. Therefore, these values are not included in obtaining the recommended value. The recommended temperature dependence is essentially identical to that measured by Veyret and Lesclaux. We have expressed the temperature dependence in an Arrhenius form even though the authors preferred a T^n form ($k = 5.5 \times 10^{-11}\ T^{-(0.4 \pm 0.3)}$ cm^3 $molecule^{-1}$ s^{-1}).

D17. $CH_3 + O_3$. The recommended A factor and E/R are those obtained from the results of Ogryzlo et al. (1981). The results of Simonaitis and Heicklen (1975) based on an analysis of a complex system are not used. Washida et al. (1980b) used $O + C_2H_4$ as the source of CH_3. Recent results (Buss et al. (1981), Kleinermanns and Luntz (1981), Hunziker et al. (1981), and Inoue and Akimoto (1981)) have shown the $O + C_2H_4$ reaction to be a poor source of CH_3. Therefore, the results of Washida et al. are also not used.

D18. $CH_3O_2 + O_3$. There are no direct studies of this reaction. The quoted upper limit is based on indirect evidence obtained by Simonaitis and Heicklen (1975).

D19. $CH_3O_2 + CH_3O_2$. The recommended value for k(298 K) is the average of those reported by Hochanadel et al. (1977), Parkes (1977), Anastasi et al. (1978), Kan et al. (1979), Sanhueza et al. (1979), and Sander and Watson (1981c). All the above determinations used ultraviolet absorption techniques to monitor CH_3O_2 and hence measured k/σ where σ is the absorption cross section for CH_3O_2 at the monitored wavelength. To obtain a set of numbers that can be compared, the values of k have been recalculated using the absorption cross sections measured by Hochanadel et al. (1977). k(298 K) is the average of these numbers. The recommended temperature dependence is that measured by Sander and Watson (1981c).

This reaction has three possible sets of products, i.e.,

$$CH_3O_2 + CH_3O_2 \rightarrow \begin{cases} 2CH_3O + O_2 & k_a \\ CH_2O + CH_3OH + O_2 & k_b \\ CH_3OOCH_3 + O_2 & k_c \end{cases}$$

FTIR studies by Kan et al. (1980) and Niki et al. (1981) are in reasonable agreement on branching ratios at 298 K: $k_a/k \sim 0.35$, $k_b/k \sim 0.10$. Because of the existence of multiple pathways, the temperature dependence of k may be complex. Further work is required on both the temperature dependence and the variation of branching ratios with temperature.

D20. $CH_3O_2 + NO$. The value of k(298 K) is the average of those determined by Sander and Watson (1980), Ravishankara et al. (1981a), Cox and Tyndall (1980), Plumb et al. (1981), Simonaitis and Heicklen (1981) and Zellner (private communication, 1984). Values lower by more than a factor of two have been reported by Adachi and Basco (1979) and Simonaitis and Heicklen (1979). The former direct study was probably in error because of interference by CH_3ONO formation. The results of Simonaitis and Heicklen (1979) and Plumb et al. (1979) are assumed to be superseded by their more recent values. Ravishankara et al. (1981a) and Simonaitis and Heicklen (1981) have measured the temperature dependence of k over limited temperature ranges. The recommended A factor and E/R were obtained by a least squares analysis of the data from the two studies. The value of k(218 K) obtained by Simonaitis and Heicklen (1981) is not included; however, the large error bounds allow the calculated value of k at 218 K to overlap that measured by Simonaitis and Heicklen. Ravishankara et al. (1981a) find that the reaction channel leading to NO_2 accounts for at least 80% of the reaction. Zellner (private communication, 1984) has measured the yield of CH_3O to be 1.0 ± 0.1. These results in conjunction with the indirect evidence obtained by Pate et al. (1974), confirm that NO_2 formation is the major, if not the only, reaction path.

D21. $CH_3O_2 + HO_2$. The room temperature value is that of Cox and Tyndall (1979, 1980). This study also reports a large negative E/R value over a temperature range 274-338 K, which is similar to that found for the $HO_2 + HO_2$ reaction by many groups (see note on $HO_2 + HO_2$). The measurement has been carried out only at 1 atmosphere pressure. The rate coefficient needs independent verification at one atmosphere, and measurements as functions of pressure, water vapor concentration, and temperature.

D22. $NO_3 + CO$. New entry. The upper limit is based on the results of Ridley and McFarland (private communication, 1984) and Ravishankara (private communication, 1984). Ridley and McFarland estimated an upper limit of 1

$\times 10^{-20}$ cm^3 molecule^{-1} s^{-1} based on their measurements of NO_3 loss in excess CO. Ravishankara estimated an upper limit of 1×10^{-15} cm^3 molecule^{-1} s^{-1} based on discharge flow-long path laser absorption measurements. The higher limit is indicated to be conservative. Products are expected to be $NO_2 + CO_2$.

D23. $NO_3 + CH_2O$. New entry. There are two measurements of this rate coefficient at 298 K, Atkinson et al. (1984) and Cantrell et al. (1985). The value reported by Atkinson et al. (1984), $k = (3.23 \pm 0.26) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, is corrected to 5.8×10^{-16}cm^3 molecule^{-1} s^{-1} to account for the different value of the equilibrium constant for the $NO_3 + NO_2 \rightleftarrows N_2O_5$ reaction that was measured subsequent to this study by the same group using the same apparatus. This correction is in accordance with their suggestion (Tuazon et al. 1984). The value reported by Cantrell et al., $k = 6.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, is in good agreement with the corrected value of Atkinson et al. The recommended value is the average of these two studies. Cantrell et al. have good evidence to suggest that HNO_3 and CHO are the products of this reaction. The temperature dependence of this rate coefficient is unknown.

E1. $C\ell + O_3$. The results reported for k(298 K) by Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205-300 K. In this temperature range, the rate constants at any particular temperature agree to within 30-40%. Although the values of the activation energy obtained by Watson et al. and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consisently (~17%) lower than that of Watson et al. This may suggest a systematic underestimate of the rate constant, as the values from the other three studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (528-831 cal mole^{-1}). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298 K. Inclusion of higher temperature (≤ 466 K) experimental data would yield the following Arrhenius expression: $k = (3.4 \pm 1.0) \times 10^{-11} \exp(-310 \pm 76)/T$).

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1-0.5%) of O_2 $(^1\Sigma_g^+)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981), in connection with the $C\ell_2$ photosensitized decomposition of ozone.

E2. $C\ell + H_2$. This Arrhenius expression is based on the data below 300 K reported by Watson et al. (1975), Lee et al. (1977) and Miller and Gordon (1981). The results of these three studies are in excellent agreement below 300 K; the data at higher temperatures are in somewhat poorer agreement. The results of Watson et al. and those of Miller and Gordon agree well (after extrapolation) with the results of Benson et al. (1969) and Steiner and Rideal (1939) at higher temperatures. For a discussion of the large body of rate data at high temperatures see the review by Baulch et al. (1980). Miller and Gordon also measured the rate of the reverse reaction, and the ratio was found to be in good agreement with equilibrium constant data. Results of a new study by Kita and Stedman (1982) are in excellent agreement with this recommendation. They also measured the rate of the reverse reaction and found the ratio to be in good agreement with equilibrium constant data.

E3. $C\ell + CH_4$. The values reported from the thirteen absolute rate coefficient studies for k at 298 K fall in the range $(0.99 \text{ to } 1.48) \times 10^{-13}$, with a mean value of 1.15×10^{-13}. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.04×10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weighting to the values reported in Lin et al. (1978a), Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), Zahniser et al. (1978), Michael and Lee (1977), Keyser (1978), and Ravishankara and Wine (1980). The values derived for k at 298 K from the competitive chlorination studies of Pritchard et al. (1954), Knox (1955), Pritchard et al. (1955), Knox and Nelson (1959), and Lin et al. (1978a) range from

(0.95-1.13) x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value of 1.04 x 10^{-13} was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been nine absolute studies of the temperature dependence of k. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported studies it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three resonance fluorescence studies have been performed over the temperature range ~200-500 K (Whytock et al. (1977), Zahniser et al. (1978) and Keyser (1978)) and in each case a strong nonlinear Arrhenius behavior was observed. Ravishankara and Wine (1980) also noted nonlinear Arrhenius behavior over a more limited temperature range. This behavior tends to explain partially the large variance in the values of E/R reported between those other investigators who predominantly studied this reaction below 300 K (Watson et al. (1976) and Manning and Kurylo (1977)) and those who only studied it above 300 K (Clyne and Walker (1973), Poulet et al. (1974), and Lin et al. (1978a)). The agreement between all studies below 300 K is good, with values of (a) E/R ranging from 1229-1320 K, and (b) k(230 K) ranging from (2.64-3.32) x 10^{-14}. The mean of the two discharge flow values (Zahniser et al. (1978) and Keyser (1978)) is 2.67 x 10^{-14}, while the mean of the four flash photolysis values (Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), and Ravishankara and Wine (1980)) is 3.22 x 10^{-14} at 230 K. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Ravishankara and Wine (1980) have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures (<240 K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. Ravishankara and Wine observed that at temperatures below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture; i.e., if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine is proven it is assumed that the discharge flow and competitive chlorination results are reliable.

Above 300 K the three resonance fluorescence studies reported (a) "averaged" values of E/R ranging from 1530-1623 K, and (b) values for k (500 K) ranging from (7.74-8.76) x 10^{-13}. Three mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409-1790 K. The data of Poulet et al. (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k(298 K) is ~20% higher than the preferred value at 298 K, while that of Lin et al. (1978a) is in fair agreement with the resonance fluorescence results.

In conclusion, it should be stated that the best values of k from the absolute studies, both above and below 300 K, are obtained from the resonance fluorescence studies. The competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k(230 K) from (2.11-2.54) x 10^{-14} with a mean value of 2.27 x 10^{-14}. It can be seen from the above discussion that the average values at 230 K are: 3.19 x 10^{-14} (flash photolysis), 2.67 x 10^{-14} (discharge flow) and 2.27 x 10^{-14} (competitive chlorination). These differences increase at lower temperatures. Until the hypothesis of Ravishankara and Wine (1980) is re-examined, the preferred Arrhenius expression attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04 x 10^{-13}, and at 230 K is 2.71 x 10^{-14} (this is a simple mean of the three average values). The preferred Arrhenius expression is 9.6 x 10^{-12} exp(-1350/T). This expression yields values similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used then an alternate expression of 6.4 x 10^{-12} (exp(-1200/T)) can be obtained (k(298 K) = 1.07 x 10^{-13}, and k(230 K) = 3.19 x 10^{-14}).

A recent study (Heneghan et al. (1981)) using very low pressure reactor techniques reports results from 233 to 338 K in excellent agreement with the other recent measurements. They account for the curvature in the Arrhenius plot at higher temperatures by transition state theory. Measured equilibrium constants are used to derive a value of the heat of formation of the methyl radical at 298 K of 35.1 ± 0.1 kcal/mol.

E4. $Cl + C_2H_6$. The absolute rate coefficients reported in all four studies (Davis et al. (1970), Manning and Kurylo (1977), Lewis et al. (1980), and Ray et al. (1980)) are in good agreement at 298 K. The value reported by Davis et al. was probably overestimated by ~10% (the authors assumed that I_f was proportional to $[Cl]^{0.9}$, whereas a linear relationship between I_f and [Cl] probably held under their experimental conditions). The preferred value at 298 K was taken to be a simple mean of the four values (the value reported by Davis et al. was reduced by 10%), i.e., 5.7×10^{-11}. The two values reported for E/R are in good agreement; E/R = 61 K (Manning and Kurylo) and E/R = 130 K (Lewis et al.). A simple least squares fit to all the data would unfairly weight the data of Lewis et al. due to the larger temperature range covered. Therefore, the preferred value of $7.7 \times 10^{-11} \exp(-90/T)$ is an expression which best fits the data of Lewis et al. and Manning and Kurylo between 220 and 350 K.

E5. $Cl + C_3H_8$. This recommendation is based on results over the temperature range 220-607 K reported in the recent discharge flow-resonance fluorescence study of Lewis et al. (1980). These results are consistent with these obtained in the competitive chlorination studies of Pritchard et al. (1955) and Knox and Nelson (1959).

E6. $Cl + C_2H_2$. Since abstraction would be endothermic by 9 kcal/mol, the initial step must be addition to give an excited C_2H_2Cl radical which either will be stabilized or will decompose to give the original reactants. Lee and Rowland (1977), in a high pressure study using radioactive tracer techniques, concluded that the initial addition must occur once in not more than 5 collisions. They calculated that under conditions corresponding to the stratosphere at 30 km the overall conversion of Cl to stabilized C_2H_2Cl proceeds with a rate coefficient of about 1 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Poulet et al. (1977) discuss their own earlier work using the discharge flow-mass spectrometric technique at 1 torr helium in which they report a value of (2.0 ± 0.5) x 10^{-13} independent of temperature from 295-500 K. They point out that these results can be reconciled with those of Lee and Rowland if the efficiency of stabilization of excited C_2H_2Cl is 1/500 at 1 torr helium. The rate constant given in the table is for the overall rate of conversion of Cl to a stabilized C_2H_2Cl radical under conditions of the stratosphere at 30 km. The probable fate of this radical is reaction with O_2.

E7. Cl + CH_3OH. This recommendation is based on results obtained over the temperature range 200-500 K using the flash photolysis-resonance fluorescence technique in the only reported study of this reaction, Michael et al. (1979b). This reaction has been used as a source of CH_2OH and as a source of HO_2 by the reaction of CH_2OH with O_2. See Radford (1980) and Radford et al. (1981).

E8. Cl + CH_3Cl. The results reported by both groups (Clyne and Walker (1973), and Manning and Kurylo (1977)) are in good agreement at 298 K. However, the value of the activation energy measured by Manning and Kurylo is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the Cl + CH_4 and, similarly, the activation energy measured by Manning and Kurylo was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique was in this case subject to a systematic error, and it is recommended that the flash photolysis results be used for stratospheric calculations in the 200-300 K temperature range (see discussion of the Cl + CH_4 studies). In the discussion of the Cl + CH_4 reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A-factor (as measured in the flash photolysis studies) is already ~3.5 x 10^{-11} and the significant curvature which would be required in the Arrhenius plot to make the data compatible would result in an unreasonably high value for A (> 2 x 10^{-10}).

E9. $C\ell + CH_3CC\ell_3$. There has been only one study of this rate, that by Wine *et al.* (1982) using a laser flash photolysis-resonance fluorescence technique. It was concluded that the presence of a reactive impurity accounted for a significant fraction of the $C\ell$ removal, and therefore only upper limits to the rate were reported for the temperature range 259-356 K. This reaction is too slow to be of any importance in atmospheric chemistry.

E10. $C\ell + H_2CO$. The results from five of the six published studies (Michael *et al.* (1979a), Anderson and Kurylo (1979), Niki *et al.* (1978a), Fasano and Nogar (1981) and Poulet *et al.* (1981)) are in good agreement at ~298 K, but ~50% greater than the value reported by Foon *et al.* (1979). The preferred value at 298 K (7.3×10^{-11}) was obtained by combining the absolute values reported by Michael *et al.*, Anderson and Kurylo, and Fasano and Nogar, with the values obtained by combining the ratio of $k(C\ell + H_2CO)/k(C\ell + C_2H_6)$ reported by Niki *et al.* (1.3 ± 0.1) and by Poulet *et al.* (1.16 ± 0.12) with the preferred value of 5.7×10^{-11} for $k(C\ell + C_2H_6)$ at 298 K. The preferred value of E/R was obtained from a least squares fit to all the data reported in Michael *et al.* and in Anderson and Kurylo. The A-factor was adjusted to yield the preferred value at 298 K.

E11. $C\ell + H_2O_2$. The absolute rate coefficients determined at ~298 K by Watson *et al.* (1976), Leu and DeMore (1976), Michael *et al.* (1977), Poulet *et al.* (1978a) and Keyser (1980a) range in value from $(3.6\text{-}6.2) \times 10^{-13}$. The studies of Michael *et al.*, Keyser, and Poulet *et al.* are presently considered to be the most reliable. The preferred value for the Arrhenius expression is taken to be that reported by Keyser. The A-factor reported by Michael *et al.* is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300 K. The data of Michael *et al.* at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well established. Results of a recent study by Heneghan and Benson (1983) using mass spectrometry confirmed that this reaction proceeds only by the abstraction mechanism shown to give $HC\ell$ and HO_2 as products.

E12. Cℓ + HOCℓ. This recommendation is based on results over the temperature range 243-365 K using the discharge flow-mass spectrometric technique in the only reported study of this reaction, Cook et al. (1981a). In a subsequent paper, Cook et al. (1981b) argue that $C\ell_2$ + OH are the major products of this reaction, even though the reaction channel giving HCℓ + CℓO is more exothermic.

E13. Cℓ + HNO_3. There are two recent studies of this rate, in which the decay of Cℓ atoms in excess HNO_3 was monitored by resonance fluorescence (Kurylo et al., 1983b) or by resonance absorption (Clark et al., 1982). Both report values higher than those obtained in earlier discharge flow-mass spectrometric studies by Leu and DeMore (1976) and by Poulet et al. (1978a) which monitored the decay of HNO_3 in excess Cℓ. Kurylo et al. report a value for E/R of 1700 K for the temperature range 243-298 K. Poulet et al. report a value for E/R of 4380 K for the temperature range 439-633 K. The higher temperature data of Poulet et al. are not directly applicable to stratospheric conditions, and extrapolation to room temperature may not be valid. The preferred value is based on assuming that the room temperature data of Kurylo et al. represents an upper limit. The higher value reported by Clark et al. is based on data which exhibit significant scatter and is not considered in deriving the preferred value.

E14. Cℓ + HO_2. The recommendations for the two reaction channels are based upon the recent results by Lee and Howard (1982) using a discharge flow system with laser magnetic resonance detection of HO_2, OH and CℓO. The total rate constant is temperature independent with a value of (4.2 ± 0.7) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250-420 K. This value for the total rate constant is in agreement with the value recommended in JPL 81-3, which was based on indirect studies relative to Cℓ + H_2O_2 (Leu and DeMore (1976), Poulet et al. (1978a), Burrows et al. (1979)) or to Cℓ + H_2 (Cox (1980)). The contribution of the reaction channel producing OH + CℓO (21% at room temperature) is much higher than the upper limit reported by Burrows et al. (1% of total reaction). The value of the rate constant for this channel, when combined with the rate constant for the reaction CℓO + OH (assuming the products are Cℓ + HO_2), yields an equilibrium constant of 1.0. This gives a value for the heat of formation of HO_2 at 298 K of 3.3 kcal/mole, in reasonably good agreement with the Howard (1980) value of 2.5 ± 0.6 kcal/mole. Weissman et al. (1981) propose that the reaction proceeds by radical combination to give an excited HOOCℓ intermediate whose stabilization may become important at stratospheric temperatures.

E15. $Cl + Cl_2O$. The preferred value of 9.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} was determined from two independent absolute rate coefficient studies reported by Ray et al. (1980), using the discharge flow-resonance fluorescence and discharge flow-mass spectrometric techniques. This value has been confirmed by Burrows and Cox (1981) who determined the ratio $k(Cl + Cl_2O)/k(Cl + H_2) = 6900$ in modulated photolysis experiments. The earlier value reported by Basco and Dogra (1971a) has been rejected. The Arrhenius parameters have not been experimentally determined; however, the high value of k at 298 K precludes a substantial positive activation energy.

E16. $Cl + OClO$. Data reported by Bemand, Clyne and Watson (1973).

E17. $Cl + ClONO_2$. Recent flash photolysis/resonance fluorescence studies by Margitan (1983a) and by Kurylo et al. (1983a) which are in good agreemment show that the rate constant for this reaction is almost two orders of magnitude faster than that indicated by the previous work of Kurylo and Manning (1977) and Ravishankara et al. (1977b). It is probable that the slower reaction observed by Kurylo and Manning was actually $O + ClNO_3$, not $Cl + ClNO_3$. The preferred value averages the results of the two new studies.

E18. $Cl + ClNO$. This value is based on the discharge flow-resonance fluorescence study of Clyne and Cruse (1972) and the flash photolysis-resonance fluorescence study of Nelson and Johnston (1981). Grimley and Houston (1980) reported a value which is lower than this preferred value by a factor of four. This low value may be due to adsorption of ClNO on the vessel walls in their static experiment. There are no reliable data on the temperature dependence. A new study by Kita and Stedman (1982) using the same technique as that of Clyne and Cruse (1972) reports a value which is a factor of three higher than the preferred value. However, there are insufficient data reported to assess the reliability of this result, and the preferred value has therefore been left unchanged.

E19. $C\ell + C\ell OO$. Values of 1.56×10^{-10}, 9.8×10^{-11}, and 1.67×10^{-10} have been reported for $k_a(C\ell + C\ell OO \rightarrow C\ell_2 + O_2)$ by Johnston *et al*. (1969), Cox *et al*. (1979), and Ashford *et al*. (1978), respectively. Values of 108, 20.9, 17, and 15 have been reported for $k_a(C\ell + C\ell OO \rightarrow C\ell_2 + O_2)/k(C\ell + C\ell OO \rightarrow 2\ C\ell O)$ by Johnston *et al*., Cox *et al*., Ashford *et al*., and Nicholas and Norrish (1968). Obviously the value of 108 by Johnston *et al*. is not consistent with the others, and the preferred value of 17.6 was obtained by averaging the other three values (this is in agreement with a value that can be derived from a study by Porter and Wright (1953)). The absolute values of k_a and k_b are dependent upon the choice of ΔH_f° ($C\ell OO$) (the values of ΔH_f° ($C\ell OO$) reported by Cox *et al*. and Ashford *et al*. are in excellent agreement, i.e. 22.7 and 22.5 kcal/mol, respectively). The preferred value of $k_a(C\ell + C\ell OO \rightarrow C\ell_2 + O_2)$ is taken to be the average of the three reported values, i.e. 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Consequently, the preferred value of $k_b(C\ell + C\ell OO \rightarrow 2\ C\ell O)$ is $k_a/17.6$, i.e. 8.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The E/R values are estimated to be zero, which is consistent with other experimentally determined E/R values for atom-radical reactions.

E20. $O + C\ell O$. Changed from JPL 83-62. There have been four recent studies of this rate coefficient, three of which covered an extended temperature range. The recommendation is based on a least-squares fit to all data below 370 K reported in the new studies by Leu (1984b), Margitan (1984b), Schwab *et al*. (1984), and Ongstad and Birks (1984) and in the earlier studies by Bemand *et al*. (1973), Clyne and Nip (1976b), and Zahniser and Kaufman (1977). Values reported in the newer studies are lower than those reported in the 1973 and 1976 studies. Inclusion of the new studies results in a lowering of the recommended room temperature value by twenty percent.

E21. $C\ell O + NO$. The absolute rate coefficients determined in the four discharge flow mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978), Ray and Watson (1981a) and Clyne and MacRobert (1980)) and the discharge flow laser magnetic resonance study Lee *et al*. (1982) are in excellent agreement at 298 K, and are averaged to yield the preferred value. The value reported by Zahniser and Kaufman (1977) from a competitive study is not used in the derivation of the preferred value as it is about 33% higher. The magnitudes of the temperature dependences reported by Leu and DeMore (1978) and Lee <u>et al</u>. are in excellent agreement. Although the E/R value reported by Zahniser and Kaufman (1977) is in fair agreement with the other values, it is not considered as it is dependent upon the E/R value assumed for the $C\ell + O_3$ reaction. The Arrhenius expression was derived from a least squares fit to the data reported by Clyne and Watson, Leu and DeMore, Ray and Watson, Clyne and MacRobert and Lee <u>et al</u>.

$C\ell O + HO_2$. There have been four low pressure discharge flow studies, each using a different experimental detection technique, and one high pressure molecular modulation study (Burrows and Cox, 1981) at 298 K. The values reported at 298 K, in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, are 0.85 ± 0.19 (Poulet <u>et al</u>., 1978b), 3.8 ± 0.5 (Reimann and Kaufman, 1978), 4.5 ± 0.9 (Leck <u>et al</u>., 1980), 6.3 ± 1.3 (Stimpfle <u>et al</u>., 1979), and 5.4^{+4}_{-2} (Burrows and Cox, 1981). The value of Poulet <u>et al</u>. was disregarded and the preferred value taken to be the mean of the other four values, i.e. $k = 5.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} The agreement between the low pressure values and the one atmosphere value suggests the absence of a third order complex forming process. The only temperature dependence study (Stimpfle <u>et al</u>.) resulted in a non-linear Arrhenius behavior. The data were best described by a four parameter equation of the form $k = Ae^{-B/T} + CT^n$, possibly suggesting that two different mechanisms may be occurring. The expression forwarded by Stimpfle <u>et al</u>. was $3.3 \times 10^{-11} \exp(-850/T) + 4.5 \times 10^{-12} (T/300)^{-3.7}$. Two possible preferred values can be suggested for the temperature dependence of k; (a) an expression of the form suggested by Stimpfle <u>et al</u>., but where the values of A and C are adjusted to yield a value of 5.0×10^{-12} at 298 K, or (b) a simple Arrhenius expression which fits the data obtained at and below 300 K (normalized to 5.0×10^{-12} at 298 K), i.e., $4.6 \times 10^{-13} \exp(710/T)$. The latter expression is preferred. The two most probable pairs of reaction products are, (1) $HOC\ell + O_2$ and (2) $HC\ell + O_3$. Both Leu (1980b) and Leck <u>et al</u>. used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K), 3.0% (248 K) and 2.0% (298 K), respectively, on k_2/k. Burrows and Cox report an upper limit of 0.3% for k_2/k at 300 K.

E23. $ClO + H_2CO$. Poulet et al. (1980) have determined an upper limit of 10^{-15} cm^3 molecule^{-1} s^{-1} for k at 298 K using the discharge flow-EPR technique.

E24. $ClO + OH$. Changed from JPL 83-62. Since the previous evaluation there have been two studies of this reaction. The results of Burrows et al. (1984a) show a temperature-independent value. The results of Hills and Howard (1984) are fifty percent higher at room temperature and exhibit a slight negative temperature dependence. The recommendation is based on a fit to the data reported in these two new studies. Effects due to secondary chemistry in the studies of Ravishankara et al. (1983a) and Leu and Lin (1979) preclude using rate data from these studies in the derivation of the recommended value. The fraction of total reaction yielding $HO_2 + Cl$ as products has been determined by Leu and Lin (1979), Burrows et al. (1984a), and Hills and Howard (1984); they report values at 298 K of >0.65, 0.85 ± 0.2, and 0.85 ± 0.14 respectively. No product HCl has been observed, and it is entirely possible that the HCl yield is indeed zero.

E25. ClO Reactions. These upper limits are based on the data of Walker (reported in Clyne and Watson (1974a)). The upper limits shown for k (298) were actually determined from data collected at either 587 or 670 K. The Arrhenius expressions were estimated based on this ~600 K data.

E26. $ClO + ClO$. No recommendation at present. For a discussion of the $ClO + ClO$ reactions the reader is referred to Watson (1977, 1980).

E27. $ClO + O_3$. The branching ratio between the two channels is not known, but, for the present discussion, is assumed to be unity. The Arrhenius parameters were estimated, and the upper limit rate constants are based on data reported by DeMore, Lin and Jaffe (1976) and by Wongdontri-Stuper et al. (1979).

E28. $OH + HCl$. Changed from JPL 83-62. Since the previous evaluation five studies of this rate have been published. Husain et al. (1984) and Cannon et al. (1984) report a room temperature value in good agreement with the previous recommendation which was based on six studies in good agreement: Takacs and Glass (1973a), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), Hack et al. (1977), and Husain et al. (1981). However, new studies by Molina et al. (1984), Keyser (1984), and Ravishankara (private communication, 1984) report room temperature values about twenty percent higher than the previous recommendation. In these latter studies particular attention was paid to the determination of the absolute concentration of HCℓ by UV and IR spectrophotometry. The recommended value is based on a least-squares fit to the data reported in these three new studies.

E29. OH + HOCℓ. There are no experimental data for this reaction. This is an estimated value based on the OH + H_2O_2 reaction, which should have roughly similar E/R and A values.

E30. OH + Substituted Methanes. There have been several studies of each of the OH + $CH_xF_yX_{(4-x-y)}$ (X = Cℓ or Br) reactions, i.e. OH + $CH_3Cℓ$, $CH_2Cℓ_2$, $CHCℓ_3$, $CHFCℓ_2$, $CHF_2Cℓ$, $CH_2CℓF$, and CH_3Br. In each case there has been quite good agreement between the reported results (except for Clyne and Holt, (1979b)), both at ~298 K and as a function of temperature. However, in certain cases it can be noted that the E/R values obtained from studies performed predominantly above 298 K were greater than the E/R values obtained from studies performed over a lower temperature range, e.g. the E/R value for OH + $CH_3Cℓ$ reported by Perry et al. (1976a) is significantly higher than that reported by Davis et al. (1976). These small but significant differences could be attributed to either experimental error or non-linear Arrhenius behavior. The recent results of Jeong and Kaufman (1982) have shown a non-linear Arrhenius behavior for each reaction studied. They found that their data could best be represented by a three parameter equation of the form $AT^2\exp(-B/T)$. The experimental $AT^2\exp(-B/T)$ fit is stated by the authors to be in agreement with that expected from transition state theory.

The preferred values shown in this review were obtained by first fitting all of the absolute rate data for each reaction (except Clyne and Holt (1979b)) to the three parameter equation $AT^2\exp(-B/T)$, and then simplifying these equations to a set of "derived Arrhenius expressions" centered at 265 K. The derived Arrhenius expressions were centered at 265 K as a temperature representative of the mid-troposphere. The $AT^2\exp(-B/T)$ expressions are given for each reaction in the individual notes, while the "derived Arrhenius expressions" are entered in the table of preferred values. Obviously "derived" Arrhenius expressions can be centered at any temperature from the three parameter equations (these should be restricted to within the temperature range studied). Transforming $k = AT^2\exp(-B/T)$ to the form $k = A'\exp(-E/T)$: $E' = B + 2T$ and $A' = A \times e^2 \times T^2$.

$OH + CH_3C\ell$. The preferred values were obtained using only absolute rate coefficient data. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976a), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation $3.49 \times 10^{-18}\ T^2\exp(-582/T)$ over the temperature range (247-483)K. This results in a preferred value of 4.40×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.81 \times 10^{-12}\exp(-1112/T)$.

$OH + CH_2C\ell_2$. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the $OH + CH_4/OH + CH_2C\ell_2$ study (Cox et al., 1976a)) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976a), and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred value (the values of Davis et al. are somewhat lower (20%) than those reported in the other studies but are included in the evaluation). Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation $8.58 \times 10^{-18}\ T^2\exp(-502/T)$ over the temperature range 245-455 K. This results in a preferred value of 1.41×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $4.45 \times 10^{-12}\exp(-1032/T)$.

$OH + CHC\ell_3$. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the $OH + CH_4/OH + CHC\ell_3$ study (Cox et al. (1976a)) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis et al. (1976) and Jeong and Kaufman

(1982) are in good agreement and were used to determine the preferred values. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation 6.3×10^{-18} $T^2\exp(-504/T)$ over the temperature range 245-487 K. This results in a preferred value of 1.03×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $3.27 \times 10^{-12}\exp(-1034/T)$.

$OH + CHFCl_2$. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Perry et al. (1976a), Watson et al. (1977), Chang and Kaufman (1977a), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982). The data of Clyne and Holt (1979b) was not considered as it is in rather poor agreement with the other data within the temperature range studied, e.g. there is a difference of ~65% at 400 K. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation 1.71×10^{-18} $T^2\exp(-483/T)$ over the temperature range 241-483 K. This results in a preferred value of 3.0×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $0.89 \times 10^{-12}\exp(-1013/T)$.

$OH + CHF_2Cl$. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Atkinson et al. (1975), Watson et al. (1977), Chang and Kaufman (1977a), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982), which are in good agreement. The data of Clyne and Holt (1979b) was not considered as it is in rather poor agreement with the other data within the temperature range studied, except at 298 K (the reported A-factor of $\sim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is inconsistent with that expected theoretically). Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation 1.51×10^{-18} $T^2\exp(-1000/T)$ over the temperature range 250-482 K. This results in a preferred value of 4.68×10^{-15} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $0.78 \times 10^{-12}\exp(-1530/T)$.

$OH + CH_2FCl$. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Watson et al. (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982) which are in fair agreement. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation $3.77 \times 10^{-18}\ T^2\exp(-604/T)$ over the temperature range 245-486 K. This results in a preferred value of 4.41×10^{-14} cm^3 molecule^{-1} s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.96 \times 10^{-12}\exp(-1134/T)$.

E31. $OH + CH_3CC\ell_3$. This evaluation is based on the recent data of Jeong and Kaufman (1979) and Kurylo et al. (1979). Their results are in excellent agreement over the temperature range 250-460 K. The earlier results of Howard and Evenson (1976b), Watson et al. (1977), Chang and Kaufman (1977a) and Clyne and Holt (1979a) were discounted in favor of the recent results. The earlier results showed higher values of the rate constant, and lower E/R values. This may be indicative of the $CH_3CC\ell_3$ used in the early studies being contaminated with small amounts of a reactive olefinic impurity.

E32. $OH + C_2C\ell_4$. The preferred value at 298 K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a). The value reported by Winer et al. (1976), which is more than a factor of 10 greater, is rejected. The preferred Arrhenius parameters are those of Chang and Kaufman.

E33. $OH + C_2HC\ell_3$. The preferred value at 298 K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a). The value derived from a relative rate coefficient study by Winer et al. (1976) is a factor of about ~2 greater than the other values and is not considered in deriving the preferred value at 298 K. The Arrhenius parameters are based on those reported by Chang and Kaufman (the A-factor is reduced to yield the preferred value at 298 K).

E34. $OH + CFC\ell_3$ and $OH + CF_2C\ell_2$. The A-factor was estimated, and a lower limit was derived for E/R by using the upper limits reported for the rate constants by Chang and Kaufman (1977b) at about ~480 K. These expressions are quite compatible with the upper limits reported for these rate constants by Atkinson et al. (1975), Howard and Evenson (1976a), Cox et al. (1976a) and Clyne and Holt (1979b). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes.

E35. OH + $ClONO_2$. The results reported by Zahniser et al. (1977) and Ravishankara et al. (1977b) are in good agreement at ~245 K (within 25%), considering the difficulties associated with handling $ClONO_2$. The preferred value is that of Zahniser et al. Neither study reported any data on the reaction products.

E36. O + HCl. Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Ravishankara et al. (1977a), Hack et al. (1977) and Singleton and Cvetanovic (1981) at 300 K (some of the values for k (300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~7 lower than that of Balakhnin et al. (1971). Unfortunately, the values reported for E/R are in complete disagreement, ranging from 2260-3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Ravishankara et al., Hack et al. and Singleton and Cvetanovic but not those reported by Balakhnin et al.

E37. O + HOCl. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

E38. O + $ClONO_2$. The results reported by Molina et al. (1977b) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara et al. (1977b) at 245 K is a factor of 2 greater than those from the other studies, and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in the $ClONO_2$, or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products. The recent room temperature result of Adler-Golden and Wiesenfeld (1981) is in good agreement with the recommended value.

E39. O + Cl_2O. The recommendation averages the results of Miziolek and Molina (1978) for 236-295 K with the approximately 30 percent lower values of Wecker et al. (1982) over the same temperature range. Earlier results by Basco and Dogra (1971a) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in both studies.

E40. O + OCℓO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E41. NO + OCℓO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E42. Cℓ + CH_3CN. New entry. The recommendation accepts the upper limit at room temperature reported by Kurylo and Knable (1984) using flash photolysis-resonance fluorescence. Poulet et al. (1984a) used discharge flow-mass spectrometry and reported the expression $k = 3.5 \times 10^{-11} \exp(-2785/T)$ over the temperature range 478-723 K. They also reported a room temperature value of 9×10^{-15}, which is a factor of 3 greater than that calculated from their expression. It appears likely that their room temperature observations were strongly influenced by heterogeneous processes. It should be noted that their extrapolated room temperature value is approximately equal to Kurylo and Knable's upper limit. Olbregts et al. (1984) reported values near 400 K that agree with results of Poulet et al.

E43. Cℓ + NO_3 and CℓO + NO_3. New entry. The recommended values are based on results reported by Cox et al (1984a) in the only reported study of these reactions. $Cℓ_2$ was photolyzed in the presence of $CℓONO_2$ and the kinetic growth and decay of NO_3 were determined using time-resolved absorption at 662 nm.

E44. OH + $Cℓ_2$. New entry. The recommended value is based on the room temperature results reported by Loewenstein and Anderson (1984), Ravishankara et al. (1983a), and Leu and Lin (1979). Loewenstein and Anderson also determined that the exclusive products are Cℓ + HOCℓ.

E45. HCℓ + $CℓONO_2$. New entry. This upper limit is based on results of static cell-long path UV absorption experiments by M. J. Molina (private communication, 1985). Earlier unpublished results from the same laboratory have been shown to include significant heterogeneous effects. New results of J. H. Goble, R. Friedl, S. P. Sander and J. J. Margitan (private communication, 1985) are in agreement with this upper limit. At present the only published information on this rate constant is a much less sensitive upper limit reported by Birks et al. (1977). This new sensitive upper limit precludes this homogeneous reaction from having any significant effect in atmospheric chemistry. All of the above investigators found the reaction to be catalyzed by surfaces.

E46. $HCl + HO_2NO_2$. New entry. This upper limit is based on results of static photolysis - FTIR experiments (M. T. Leu, private communication, 1985).

F1. $Br + O_3$. The results reported for k (298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978) and Michael and Payne (1979) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these four values. The temperature dependences reported for k by Leu and DeMore, Michael et al. and Michael and Payne can only be considered to be in fair agreement. There is a spread of 25% in k at 200 K and 50% at 360 K. Although the results reported by Michael et al. and Michael and Payne are in good agreement, there is no reason at present to discard the results of Leu and DeMore. Therefore, until further results are reported, the preferred value was synthesized to best fit all the data reported from these four studies.

F2. $Br + H_2O_2$. Using the discharge flow-mass spectrometric technique Leu (1980a), and Posey et al. (1981) determined an upper limit for k of $\sim 2 \times 10^{-15}$ at ~298 K. Leu also reported an upper limit for k of 3×10^{-15} at 417 K. An estimate of the Arrhenius expression would be $<1 \times 10^{-11}\exp(-2500/T)$. The A-factor was chosen to be consistent with that determined for the $Cl + H_2O_2$ reaction, and the E/R value was calculated to yield the upper limit at 298 K. However, since the previous evaluation a study of this reaction has been reported by Heneghan and Benson (1983). They report a room temperature value which is an order of magnitude greater than the upper limit reported in the two previous studies. Until this discrepancy is resolved, we have chosen to leave the recommendation unchanged.

F3. Br + H_2CO. There have been two studies of this rate constant as a function of temperature; Nava et al. (1981), using the flash photolysis-resonance fluorescence technique, and Poulet et al. (1981), using the discharge flow-mass spectrometric technique. These results are in reasonably good agreement. The Arrhenius expression was derived from a least squares fit to the data reported in these two studies. The higher room temperature value of LeBras et al. (1980) using the discharge flow - EPR technique has been shown to be in error due to secondary chemistry (Poulet et al.).

F4. Br + HO_2. Changed from JPL 83-62. The preferred room temperature value is based on results of the recent study by Poulet et al. (1984b) using LIF and MS techniques. This value is a factor of four larger than the only other reported value by Posey et al. (1981), which seemed much too low for an atom-radical reaction. However, even this new value seems quite small, and therefore a large uncertainty factor has been assigned. It should be noted that the reactions of Br atoms with H_2O_2, HCHO, and HO_2 are all slower than the corresponding reactions of Cℓ atoms by one to two orders of magnitude.

F5. BrO + O. The preferred value is based on the value reported by Clyne et al. (1976). This value appears to be quite reasonable in light of the known reactivity of CℓO radicals with atomic oxygen. The temperature dependence of k is expected to be small for an atom-radical process, e.g., O + CℓO.

F6. BrO + CℓO. The results reported by Clyne and Watson (1977) and Basco and Dogra (1971b) differ not only in the magnitude of the rate constants, but also in the interpretation of the reaction mechanism. The preferred value is that reported by Clyne and Watson. The temperature dependence for such processes is expected to be small, as for BrO + BrO. Although the second reaction channel is shown proceeding directly to Br + Cℓ + O_2, it may proceed through Br + CℓOO ($\Delta H° = -6.6$ kcal/mol^{-1}) or Cℓ + BrOO ($\Delta H°$ unknown).

F7. BrO + NO. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1981a) and Leu (1979)) and the high pressure uv absorption study (Watson et al. (1979)), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure uv absorption study (Clyne and Cruse (1970b)). The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in the four recent studies. By combining the data reported by Watson et al. with that from the three mass spectrometric studies, it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependences of k for the analogous $C\ell O$ and HO_2 reactions are also negative, and are similar in magnitude.

F8. BrO + BrO. There are two possible bimolecular channels for this reaction: $BrO + BrO \rightarrow 2Br + O_2$ (k_1) and $BrO + BrO \rightarrow Br_2 + O_2$ (k_2). The total rate constant for disappearance of BrO ($k = k_1 + k_2$) has been studied by a variety of techniques, including discharge flow-ultraviolet absorption (Clyne and Cruse, 1970a), discharge flow-mass spectrometry (Clyne and Watson, 1975) and flash photolysis-ultraviolet absorption (Basco and Dogra, 1971b; Sander and Watson, 1981b). Since this reaction is second order in [BrO], those studies monitoring [BrO] by ultraviolet absorption required the value of the cross section σ to determine k. There is substantial disagreement in the reported values of σ. Although the magnitude of σ is dependent upon the particular spectral transition selected and instrumental parameters such as spectral bandwidth, the most likely explanation for the large differences in the reported values of σ is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies were used incorrectly (see discussion by Clyne and Watson). The recent study of Sander and Watson used totally independent methods to determine the values of σ and (σ/k). The recommendations for k_1 and k_2 are consistent with a recommendation of $k = 1.14 \times 10^{-12} \exp(+255/T)$ cm^3 $molecule^{-1}$ s^{-1}. This temperature dependence is the corrected value from Sander and Watson, and the pre-exponential factor has been chosen to fit the value of $k(298\ K) = 2.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, which is the average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required) and by Sander and Watson (the recent absorption study). There was no observable pressure dependence from 50 to 475 torr in the latter study. In a recent study, Cox et al. (1982) used the molecular modulation technique with ultraviolet absorption to derive a temperature independent value of k_2 which is 50 percent greater than the 298 K value recommended here.

The partitioning of the total rate constant into its two components, k_1 and k_2, has been measured by Sander and Watson at 298 K, by Jaffe and Mainquist (1980) from 258 to 333 K, and by Cox et al. (1982) from 278 to 348 K. All are in agreement that $k_1/k = 0.84 \pm 0.03$ at 298 K. In the temperature dependent studies the quantum yield for the bromine photosensitized decomposition of ozone was measured. Jaffe and Mainquist observed a strong, unexplained dependence of the quantum yield at 298 K on $[Br_2]$, and their results were obtained at much higher $[Br_2]$ values than were those of Cox et al. This makes a comparison of results difficult. From an analysis of both sets of temperature dependent data, the following expressions for k_1/k were derived: 0.98 exp(-44/T) (Jaffe and Mainquist); 1.42 exp(-163/T) (Cox et al.); and 1.18 exp(-104/T) (mean value). This mean value has been combined with the expression for k given above to yield the expression for k_1 shown in the table. The expression for k_2 results from the numerical values of k_2 at 200 K and 300 K derived from the evaluation of these expressions for k_1 and for $k(=k_1 + k_2)$.

F9. $BrO + O_3$. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) also reported an upper limit of 8×10^{-14} cm^3 molecule^{-1} s^{-1} for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $<10^{-18}$ cm^3 molecule^{-1} s^{-1}.

F10. $BrO + HO_2$. The preferred value was based on the value of $k(ClO + HO_2)$. Cox and Sheppard (1982) have studied the rate of this reaction in an investigation of the photolysis of O_3 in the presence of Br_2, H_2, and O_2 using the molecular modulation - ultraviolet absorption technique. Although the reported value is not very precise, it does show that this reaction occurs and at a rate comparable to that for $ClO + HO_2$. By analogy with the $ClO + HO_2$ system, the products may be expected to be HOBr

+ O_2.

F11. BrO + OH. Value chosen to be consistent with k(ClO + OH), due to the absence of any experimental data.

F12. OH + HBr. The preferred value at room temperature averages the values reported by Ravishankara et al. (1979a) using FP-RF, by Jourdain et al. (1981) using DF-EPR, and by Cannon et al. (1984) using FP-LIF. The data of Ravishankara et al. (1979a) show no dependence on temperature over the range 249-416 K. Values reported by Takacs and Glass (1973a) and by Husain et al. (1981) are a factor of two lower and were not included in the derivation of the preferred value.

F13. OH + CH_3Br. The absolute rate coefficients determined by Howard and Evenson (1976a) and Davis et al. (1976) are in excellent agreement at 298 K. The same approach has been used to determine the preferred Arrhenius parameters as was used for the OH + $CH_xF_yCl_{4-x-y}$ reactions. Fitting the data to an expression of the form $AT^2\exp(-B/T)$ results in the equation $1.17 \times 10^{-18}\ T^2\exp(-295/T)$ over the temperature range 244-350 K. This results in a preferred value of 3.86×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is 6.09×10^{-13} $\exp(-825/T)$.

F14. O + HBr. Results of the recent flash photolysis-resonance fluorescence study of Nava et al. (1983) for 221-455 K provide the only data at stratospheric temperatures. Results have also been reported by Singleton and Cvetanovic (1978) for 298-554 K by a phase-shift technique, and on discharge flow results of Brown and Smith (1975) for 267-430 K and of Takacs and Glass at 298 K. The preferred value is based on the results of Nava et al. and those of Singleton and Cvetanovic over the same temperature range, since these results are less subject to complications due to secondary chemistry than are the results using discharge flow techniques. The uncertainty at 298 K has been set to encompass these latter results.

F15. OH + Br_2. New entry. The recommended value is based on the room temperature results reported by Loewenstein and Anderson (1984) and by

Poulet et al. (1983). Loewenstein and Anderson also determined that the exclusive products are Br + HOBr.

G1. $F + O_3$. The only experimental data is that reported by Wagner et al. (1972). The value appears to be quite reasonable in view of the well known reactivity of atomic chlorine with O_3.

G2. $F + H_2$. Changed from JPL 83-62. The value of k at 298 K seems to be well established with the results reported by Zhitneva and Pshezhetskii (1978), Heidner et al. (1979, 1980), Wurzberg and Houston (1980), Dodonov et al. (1971), Clyne et al. (1973), Bozzelli (1973), and Igoshin et al. (1974), being in excellent agreement (range of k being $2.3\text{-}3.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}). The preferred value at 298 K is taken to be the mean of the values reported in these references. Values of E/R range from 433-595 K (Heidner et al., Wurzberg and Houston, Igoshin et al.). The preferred value of E/R is taken to be the mean of the results from all of the studies. The A-factor was calculated by taking E/R to be 525 K, and k at 298 K to be 2.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

G3. $F + CH_4$. The three absolute rate coefficients determined by Wagner et al. (1971), Clyne et al. (1973) and Kompa and Wanner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0×10^{-11} for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al., and Foon and Reid, and the preferred Arrhenius parameters of the $F + H_2$ reaction. This reaction has recently been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). The A-factor may be too high. Since the earlier evaluation there has been another study of this reaction, by Fasano and Nogar (1982). The reported value at 298 k is 30% lower than the preferred value, well within the stated uncertainty limits. The preferred value is based on results of five studies and the inclusion of this new result does not change the preferred value.

G4. F + H_2O. Changed from JPL 83-62. The recommended expression is based on the recent results of Walther and Wagner (1983). These are the only published results and are selected in preference to earlier unpublished results of Zetzsch (1971) which were quoted in the review of Jones and Skolnik (1976).

G5. NO + FO. This is the value reported by Ray and Watson (1981a) for k at 298 K using the discharge flow-mass spectrometric technique. The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous CℓO and BrO reactions have been reported to be negative, with E/R preferred values of -294 K and -265 K, respectively.

G6. FO + FO. Although the value of k (FO + FO) reported by Clyne and Watson (1974b) was obtained in a more direct manner than that of Wagner et al. (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions and thus would normally be preferred, the value to be recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al. it can be seen that the dominant reaction channel is that producing 2F + O_2. However, their data base is not adequate to conclude that it is the only process.

G7. FO + O_3. The FO + O_3 reaction has two possible pathways which are exothermic, resulting in the production of F + 2 O_2 or FO_2 + O_2. Although this reaction has not been studied in a simple, direct manner, two studies of complex chemical systems have reported some kinetic information about it. Starrico et al. (1962) measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2 F + O_2$ (the latter reaction has been studied twice (Wagner et al. (1972), Clyne and Watson (1974b)), and although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al. whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2\ O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al. utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or the $FO + O_3$ reactions being not of negligible importance in their study. Consequently, it is not possible to determine a value for the $FO + O_3$ reaction rate constant from existing experimental data. It is worth noting the the analogous $C\ell O + O_3$ reactions are extremely slow ($<10^{-18}$ cm^3 molecule^{-1} s^{-1}) (DeMore et al. (1976)), and upper limits of 8×10^{-14} (Clyne and Cruse (1970a)) and 5×10^{-15} cm^3 molecule^{-1} s^{-1} (Sander and Watson (1981b)) have been reported for $BrO + O_3$.

G8. O + FO. This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of FO is similar to that of $C\ell O$ and BrO. The recommended rate constants for the $C\ell O$ and BrO reactions at ~298 K are 4.0×10^{-11} and 3.0×10^{-11}, respectively. The temperature dependence of the rate constant is expected to be small. The temperature dependence of the analogous $C\ell O$ reaction is $E/R = 50 \pm 100$ K.

G9. $O + FO_2$. No experimental data. The rate constant for such a radical-atom process is expected to approach the gas collision frequency, and is not expected to exhibit a strong temperature dependence.

G10. CX_3O_2 + NO. New entry. These recommended values for the reactions of NO with the perhalogenated methylperoxy radicals are based on the results reported by Dognon et al. (1985) for the temperature range 230-430 K. They are in good agreement with the room temperature values reported for the reaction of CF_3O_2 (Plumb and Ryan (1982a)), $CFCl_2O_2$ (Lesclaux and Caralp (1984)), and CCl_3O_2 (Ryan and Plumb (1984)). Dognon et al. have shown that NO_2 is the major product in these reactions.

H1. OH + H_2S. The value of k(298) is an average of the rate constants reported by Perry et al. (1976b), Cox and Sheppard (1980), Wine et al. (1981a), Leu and Smith (1982a), and Michael et al. (1982). The value of E/R is taken from a composite unweighted least squares fit to the individual data points from these same five studies. The study of Leu and Smith (1982a) shows a slight parabolic temperature dependence of k with a minimum occurring near room temperature. Within the error limits stated in this evaluation, all data are fit reasonably well with an Arrhenius expression. The data from the very recent study by Lin (1982) are in excellent agreement with the present recommendation. They also show a slight non-Arrhenius behavior. The weight of evidence from these recent measurements suggests that the earlier study by Westenberg and deHaas (1973b) was in error (quite possibly due to secondary reactions). The room temperature value of Stuhl (1974) lies just outside the 2σ error limit set for k(298). A very recent study by Friedl et al. (1984a) using OH resonance fluorescence and SD laser-induced fluorescence detection yields a value of $k(298\ K) = 2.3 \times 10^{-12}$ for the reaction OH + $D_2S \rightarrow HDO + SD$. This slower rate constant is consistent with the expected kinetic isotope effect. The quantitative relationship between the OH consumed and the SD formed confirms the reaction products as written.

H2. OH + OCS. Changed from JPL 83-62. This recommendation averages the results of Leu and Smith (1981) with the recent data of Friedl et al. (1984a). Although the latter experiments involved OD rather than OH, one would not expect a significant isotope effect for this reaction. Both of these studies report nearly identical values of k at 400 K but differ by a factor of two at 298 K. Hence, over this temperature range they are approximately one order of magnitude lower than the results of Ravishankara et al. (1980b) who were thought to have minimized the complications due to secondary and/or excited state reactions present in the studies of Atkinson et al. (1978) and Kurylo (1978). The upper limit for k(298 K) reported by Cox and Sheppard (1980) is too insensitive to permit comparison with the more recent studies. The similarity between the E/R value of 2000 K calculable from the data of Ravishankara et al. (1980b) and that recommended here suggests that the interfering reaction responsible for the OH removal in the experiments of Ravishankara et al. has the same temperature dependence as the OH + OCS reaction (E/R ~ 1800 K). Such a suggestion, however, is not consistent with the identity of the most common impurities in OCS (namely H_2S and CO) since both species have near zero activation energies for their OH reactions. This would have led to a considerably lower observed temperature dependence in the Ravishankara et al. work. The possibility of a pressure effect has not been totally resolved although Ravishankara et al. observed no change in k with pressure between 20 and 100 Torr (for both Ar and SF_6). The Leu and Smith (1981) and Friedl et al. (1984a) experiments were performed at pressures less than 10 Torr. Pending further experimental results we have set the uncertainty factor on k(298) to encompass all three studies. The value chosen for $\Delta E/R$ covers the reported E/R values from both Leu and Smith (1981) and Friedl et al. (1984a).

Product observations by Leu and Smith (1981) and Friedl et al. (1984a) indicate that SH (or SD) is a primary product of the OH (or OD) reaction with OCS and tentatively confirm the suggestion of Kurylo and Laufer (1979) that the reaction produces predominantly SH + CO_2 through a complex (adduct) mechanism. This mechanism is similar to the adduct formation seen in the OH + CO_2 and OH + CS_2 reactions. There are, however, no measurements exploring a possible O_2 effect for this reaction at high pressures. Such an effect has been observed in the OH + CS_2 reaction (see following note).

H3. OH + CS_2. There is a consensus of experimental evidence indicating that this reaction proceeds very slowly as a direct bimolecular process. Wine et al. (1980) set an upper limit on k(298 K) of 1.5×10^{-15}. More recently, Friedl et al. (1984a) have measured a value of k(298 K) = 3.0 x

10^{-16} for the OD reaction. A consistent upper limit is also reported by Iyer and Rowland (1980) for the rate of direct production of OCS in an OH + CS_2 reaction system suggesting that OCS and SH are the primary products of the bimolecular process. Time-resolved detection of SD produced in the OD + CS_2 reaction led Friedl et al. (1984a) to similarly conclude that SD is a primary homogeneous reaction product of the OD reaction. This mechanistic interpretation is further supported by the studies of Leu and Smith (1982b) and Biermann et al. (1982) which set upper limits on k(298) somewhat higher than Wine et al. (1980). The more rapid reaction rates observed by Atkinson et al. (1978), Kurylo (1978), and Cox and Sheppard (1980) may be attributed to severe complications arising from excited state and secondary chemistry in their photolytic systems. The Cox and Sheppard study in particular may have been affected by the reaction of electronically excited CS_2 (produced via the 350 nm photolysis) with O_2 (in the 1 atmosphere synthetic air mix). The importance of this reaction in the tropospheric photooxidation of CS_2 to OCS has been suggested by Wine et al. (1981d).

Investigations by Wine et al. (1984b), Jones et al. (1982), and Barnes et al. (1983) have demonstrated a marked acceleration of the OH + CS_2 reaction in the presence of O_2 with a one to one relationship between the SO_2 and OCS produced and the CS_2 consumed. In the Barnes study the effective bimolecular reaction rate was found to be a function of total pressure (O_2 + N_2) as well, and exhibited an appreciable negative temperature dependence. These observations are consistent with the formation of a long-lived collision adduct postulated by Kurylo (1978) and Kurylo and Laufer (1979), followed by its reaction with O_2:

$$OH + CS_2 + M \underset{k_b}{\overset{k_a}{\rightleftarrows}} HOCS_2 + M$$

$$HOCS_2 + O_2 \xrightarrow{k_c} \text{Products}$$

Wine et al. (1984b) have in fact directly observed the approach to equilibrium in this reversible adduct formation. The rearrangement of such an adduct followed by dissociation into OCS and SH corresponds to the low k (bimolecular) channel referred to earlier. Friedl et al. (1984a)

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observe a slight negative temperature dependence of this reaction in contrast to OH + OCS which is characterized by a normal activation energy. Further information is needed regarding the microscopic aspects of the reaction mechanisms of both reactions in order to interpret these differences in Arrhenius parameters.

The effective second order rate constant of CS_2 or OH removal in the above-written scheme can be expressed as

$$1/k_{eff} = \frac{k_b}{k_a k_c P_{O_2}} + \frac{1}{k_a P_M}$$

where P_{O_2} is the partial pressure of O_2 and P_M equals $P_{O_2} + P_{N_2}$. The validity of this expression requires that k_a and k_b are invariant with the P_{O_2}/P_{N_2} ratio. A 1/k vs $1/P_{O_2}$ plot of the data of Jones et al. taken at atmospheric pressure exhibits marked curvature, suggesting a more complex mechanistic involvement of O_2. The more extensive data base of Barnes et al., however, appears to be fit quite satisfactorily by the above analysis. Nevertheless several inconsistencies arise. First, under the same conditions of P_{O_2} and P_{N_2}, the Barnes et al. rate constants lie ~60% higher than those of Jones et al. Secondly, two fits of the Barnes data can be made: one at fixed P_M and varying P_{O_2}, and the other at fixed P_{O_2} and varying P_M (i.e. varying added N_2). While both fits converge for mole fractions of O_2 near 0.2 (the common data point) their differences approach more than a factor of 2 for a pure O_2 system. Finally, the temperature dependence of the k_{eff} values from Barnes et al. varies systematically from an E/R or ~1300 K for runs in pure O_2 (at 700 torr total pressure) to ~2900 K in a 50 torr O_2 plus 650 torr N_2 mixture. These last two observations suggest that k_a and k_b are not independent of the identity of M.

The present recommendation was derived by averaging the two above mentioned fits of the Barnes et al. room temperature data and incorporating the temperature dependence calculated from an Arrhenius analysis of the $1/k_{eff}$ vs. P_{O_2} fits of the constant P_M data at 264, 278, and 293 K. This leads to the following equation:

$$k(298) = 3.7 \times 10^{-15}\ P\ \mathrm{cm}^3\ \mathrm{molec}^{-1}\ \mathrm{s}^{-1}$$

for air mixtures (i.e. $P_{O_2}/P_{N_2} = 0.25$) where P (the total pressure) is expressed in torr. The uncertainty factor at 298 K ($f_{298} = 1.5$) encompasses the synthetic air data of Jones et al. It also includes the $SF_6 + O_2$ data of Wine et al. (1984b).

Values of k at temperatures below 298 K can be calculated from the expression

$$k = 2.0 \times 10^{-18} \exp[(2200 \pm 500)/T] \times P\ \mathrm{cm}^3\ \mathrm{molec}^{-1}\ \mathrm{s}^{-1}$$

Again, this expression is valid for oxygen-nitrogen mixtures at a total pressure P (in torr) having an oxygen mole fraction of 0.2. The $\Delta E/R$ has been set to account for (within 2σ) the range of E/R found as a function of the P_{O_2}/P_{N_2} ratio.

No recommendation is given for $N_2 + O_2$ mixtures with mole fractions differing from air since, as mentioned, the fits to the two sets of Barnes et al. room temperature data diverge at high O_2 mole fractions. Additional work is needed to understand more fully the complex details of this reaction.

H4. $O + H_2S$. This recommendation is derived from an unweighted least squares fit of the data of Singleton et al. (1979) and Whytock et al. (1976). The results of Slagle et al. (1978) show very good agreement for E/R in the temperature region of overlap (300-500 K) but lie systematically higher at every temperature. The uncertainty factor at 298 K has been chosen to encompass the values of k(298 K) determined by Slagle et al. (1978) and Hollinden et al. (1970). Other than the 263 K data point of Whytock et al. (1976) and the 281 K point of Slagle et al. (1978) the main body of rate constant data below 298 K comes from the study of Hollinden et al. (1970), which indicates a dramatic change in E/R in this temperature region. Thus, $\Delta E/R$ was set to account for these observations. Such a non-linearity in the Arrhenius plot might indicate a change in the reaction mechanism from abstraction (as written) to addition. An additional channel (resulting in H atom displacement) has been proposed for this reaction by Slagle et al. (1978), Singleton et al. (1979), and Singleton et al. (1982). In the two Singleton studies an upper limit of 20% is placed on the displacement channel. Direct observation of product HSO was made in the recent reactive scattering experiments of Clemo et al. (1981) and Davidson et al. (1982). A threshold energy of 3.3 Kcal/mole was observed (similar to the activation energy measured in earlier studies) suggesting the importance of this direct displacement channel. Addition products from this reaction have been seen in a matrix by Smardzewski and Lin (1977). Further kinetic study in the 200 to 300 K range as well as quantitative direct mechanistic information could clarify these issues. This reaction is thought to be of limited stratospheric importance, however.

H5. O + OCS. The value for k(298 K) is the average of five different studies of this reaction: Westenberg and de Haas (1969a), Klemm and Stief (1974), Wei and Timmons (1975), Manning et al. (1976) and Breckenridge and Miller (1972). The recommended value for E/R is the average of those determined in the temperature studies reported in the first three references. Hsu et al. (1979) report that this reaction proceeds exclusively by a stripping mechanism.

H6. O + CS_2. The value of k(298 K) is the average of seven determinations: Wei and Timmons (1975), Westenberg and de Haas (1969a), Slagle et al. (1974a), Callear and Smith (1967), Callear and Hedges (1970), Homman et al. (1968), and Graham and Gutman (1977). The E/R value is an average of those determined by Wei and Timmons (1975) and Graham and Gutman (1977). E/R has been set to encompass the limited temperature data of Westenberg and de Haas (1969a). The principal reaction products are thought to be CS + SO. However, Hsu et al. (1979) report that 1.4% of the reaction at 298 K proceeds through the channel yielding CO + S_2 and calculate a rate constant for the overall process in agreement with that recommended. Graham and Gutman (1977) have found that 9.6% of the reaction proceeds to yield OCS + S at room temperature.

H7. O + SH. This recommendation accepts the results of Cupitt and Glass (1975). The large uncertainty reflects the fact that there is only one study of the reaction.

H8. S + O_2. This recommendation is based primarily on the study of Davis et al. (1972). Modest agreement at 298 K is provided by the studies of Fair and Thrush (1969), Fair et al. (1971), Donovan and Little (1972) and Clyne and Townsend (1975). A more recent study by Clyne and Whitefield (1979) indicates a slightly negative E/R between 300 and 400 K. Their data are encompassed by the error limits of the present recommendation.

H9. S + O_3. This recommendation accepts the only available experimental data by Clyne and Townsend (1975). In the same study these authors report a value for S + O_2 in reasonable agreement with that recommended. The error limit cited reflects both the agreement and the need for independent confirmation.

H10. S + OH. This recommendation is based on the single study by Jourdain et al. (1979). Their measured value for k(298) compares favorably with the recommended value of k(O + OH) when one considers the slightly greater exothermicity of the present reaction.

H11. SO + O_2. This recommendation is based on the recent low temperature measurements of Black et al. (1982a, 1982b). The room temperature value accepts the latter results as recommended by the authors. The uncertainties cited reflect the need for further confirmation and the fact that these results lie significantly higher than an extrapolation of the higher temperature data of Homann et al. (1968) upon which the previous recommendation was based. A room temperature upper limit on k set by Breckenridge and Miller (1972) is in good agreement with the Black et al. data.

H12. SO + O_3. The value of k(298) is an average of the determinations by Halstead and Thrush (1966), Robertshaw and Smith (1980), and Black et al. (1982a, 1982b) using widely differing techniques. The value of E/R is an average of the values reported by Halstead and Thrush (1966) and Black et al. (1982b) with the A-factor calculated to fit the value recommended for k(298).

H13. $SO + OH$. The value recommended for k(298) is an average of the determinations by Fair and Thrush (1969) and Jourdain et al. (1979). Both sets of data have been corrected using the present recommendation for the $O + OH$ reaction.

H14. $SO + NO_2$. The value of k(298) is an average of the measurements by Clyne and MacRobert (1980) and Black et al. (1982a) which agree quite well with the rate constant calculated from the relative rate measurements of Clyne et al. (1966).

H15. $SO + ClO$, $OClO$, and BrO. These recommendations are based on the single investigation by Clyne and MacRobert (1981). Uncertainties for both the ClO and $OClO$ reactions reflect the absence of any confirming investigations. In the BrO reaction (performed in excess SO), the BrO decay was too rapid to permit quantitative analysis. The lower limit for k(298) was therefore obtained from the measurement of SO_2 production.

H16. $SO_2 + HO_2$. This upper limit is based on the atmospheric pressure study of Graham et al. (1979). A more recent low pressure laser magnetic resonance study by Burrows et al. (1979) places a slightly higher upper limit on k(298) of 4×10^{-17} (determined relative to $OH + H_2O_2$). Their limit is based on the assumption that the products are $OH + SO_3$. The weight of both these studies suggests an error in the earlier determination by Payne et al. (1973).

H17. $CH_3O_2 + SO_2$. This recommendation accepts results from the study of Sander and Watson (1981a), which is believed to be the most appropriate study for stratospheric modeling purposes among those which have been conducted. Their experiments were conducted using much lower CH_3O_2 radical concentrations than in the earlier studies of Sanhueza et al. (1979) and Kan et al. (1979), both of which resulted in k(298) values approximately 100 times larger. A more recent report by Kan et al. (1981) postulates that these differences are due to the reactive removal of the $CH_3O_2SO_2$ adduct at high CH_3O_2 radical concentrations, prior to its reversible decomposition into $CH_3O_2 + SO_2$. They suggest that such behavior of $CH_3O_2SO_2$ or its equilibrated adduct with O_2 ($CH_3O_2SO_2O_2$) would be expected in the studies yielding high k values, while decomposition of $CH_3O_2SO_2$

into reactants would dominate in the Sander and Watson experiments. It does not appear likely that such secondary reactions involving CH_3O_2, NO, or other radical species, if they occur, would be rapid enough under normal stratosphere conditions to complete with the adduct decomposition.

H18. $SH + O_2$. Changed from JPL 83-62. This new upper limit for k(298 K) is based on a recent study by Friedl et al. (1984b) employing resonance fluorescence detection for the measurement of product OH. A slightly more conservative upper limit of 4×10^{-17} is reported by Black (1984) based on the lack of SH decay (detected by laser-induced fluorescence). However, the expected regeneration of SH by the reaction of OH with H_2S (the SH source) could complicate Black's measurement. The present recommendation supercedes much higher upper limits set in the studies of Tiee et al. (1981), Nielsen (1979), and Cupitt and Glass (1975). Even at the recommended upper limit for k, however, this reaction is of atmospheric importance. Further study is therefore needed.

H19. $C\ell + H_2S$. This recommendation is based on the laser-initiated, time-resolved infrared chemiluminescence study by Nesbitt and Leone (1980) which refines the measurements of Braithwaite and Leone (1978). The uncertainty factor at 298 K has been set to encompass (within 2σ) the discharge flow results of Clyne and Ono (1983) which may have been complicated by heterogeneous effects or by wall loss of the very low concentrations of H_2S used.

H20. $C\ell + OCS$; $C\ell O + OCS$; $C\ell O + SO_2$. These recommendations are based on the discharge flow mass spectrometer data of Eibling and Kaufman (1983). The upper limit on k(298) for the $C\ell + OCS$ reaction is calculated from their minimum detectable decrease in atomic chlorine. Based on the observation of product $SC\ell$, a lower limit for k(298) for the reaction as written can be set at 10^{-18} cm^3 $molec^{-1}$ s^{-1}.

Similarly, the upper limit on k(298) for the $C\ell O + OCS$ reaction was set from the minimum detectable decrease of $C\ell O$ in this reaction system. No products were observed.

The recommended upper limit on k(298) for the $ClO + SO_2$ reaction is based on the authors' estimate of their detectability for SO_3. Other estimates of k at 298 K and 200 K, based on the minimum detectable decrease in ClO, have not been used because of the potential problem of ClO reformation from the $Cl + O_3$ source reaction.

H21. $SH + H_2O_2$. New entry. This recommended upper limit for k(298 K) is based on the single study of Friedl et al. (1984b). Their value is calculated from the lack of SH decay (measured by laser-induced fluorescence) and the lack of OH production (measured by resonance fluorescence). The three possible product channels are: $H_2S + HO_2$, $HSOH + OH$, and $HSO + H_2O$.

H22. $SH + O_3$; $HSO + O_3$. New entry. These recommendations are based on the room temperature measurements of Friedl et al. (1984b) employing laser-induced fluorescence detection of SH in a discharge flow reactor. The $SH + O_3$ reaction rate was determined from SH decays at low O_3 concentrations since at the higher O_3 concentrations (higher HSO concentrations) SH approached a steady state due to regeneration via the $HSO + O_3$ reaction. The rate constant for the latter was determined relative to the rate constant for the SH reaction from measurements of the steady state SH concentration relative to initial SH. Based on the observation of no isotope effect for either reaction when SD was employed, the authors interpret the products of the HSO reaction to be $SH + 2O_2$ (analaogous to that for the $HO_2 + O_3$ reaction).

H23. $SH + NO_2$. New entry. This recommendation is an average of the two room temperature LIF studies of Black (1984) and Friedl et al. (1984b) which are in excellent agreement. While no products were observed, the reaction as written reflects the most exothermic channel and quite possibly explains the rapid reaction rate observed in comparison with the $OH + NO_2$ bimolecular reaction which is endothermic. In neither of the above two studies was evidence found for a three-body combination reaction. Black (1984) sets an upper limit of 7×10^{-31} for this third body rate constant based on a pressure independence from 30 to 300 Torr.

H24. $HOSO_2 + O_2$. New entry. This room temperature value for k is based on the single study by Margitan (1984a) which is supported by the preliminary measurements of Bando and Howard (private communication, 1984). The Margitan results are derived from a modeling fit of OH radical decays in the $OH + SO_2 + M$ reaction system in the presence of varying amounts of O_2 and NO. In this system the HO_2 generated by this reaction reacts with NO to regenerate OH. The Bando and Howard investigation employs laser magnetic resonance detection of HO_2 and chemical ionization detection of SO_3 to obtain a preliminary value of k(298 K) similar to that of Margitan.

H25. $SO_2 + NO_2$; $SO_3 + NO_2$. New entry. The recommendations for both of these reactions are based on the recent study of Penzhorn and Canosa (1983) using second derivative uv spectroscopy. The upper limit given for k(298 K) in the SO_2 reaction is actually their measured value. However, their observations of strong heterogeneous and water vapor catalyzed effects prompt us to accept their measurement as an upper limit. This value is approximately two orders of magnitude lower than that for a dark reaction observed by Jaffe and Klein (1966) in $NO_2 + SO_2$ mixtures (much of which may have been due to heterogeneous processes). Penzhorn and Canosa suggest the products of the SO_2 reaction to be $NO + SO_3$. They observe a white aerosol produced in the reaction of NO_2 with SO_3 and interpret it to be the adduct NSO_5. This claim is supported by ESCA spectra.

H26. $SO_2 + O_3$. New entry. This recommendation is based on the limited data of Davis et al. (1974b) at 300 K and 360 K in a stopped-flow investigation using mass spectrometric and uv spectroscopic detection.

H27. $CS + O_2$. New entry. The recommendation given for k(298 K) is based on the work of Black et al. (1983) using LIF to monitor CS decays. This value agrees with the somewhat less precise determination by Richardson (1975) using OCS formation rates suggesting the validity of the reaction products as written. The latter author presents evidence that this reaction channel dominates the one producing SO + CO by more than a factor of 10. Measurements by Richardson at 293 K and 495 K yield an E/R value of 1860 K. However, use of this activation energy with the recommended value of k(298 K) results in an unusually low Arrhenius A factor of 1.5×10^{-16}. In view of this, no recommendation is presently given for the temperature dependence.

H28. $CS + O_3$; $CS + NO_2$. New entry. The k(298 K) recommendations for both reactions accept the results of Black et al. (1983) who used LIF real-time detection of CS in a laser photolysis experiment at room temperature. The uncertainty factor reflects the absence of any confirming measurements.

J1. $Na + O_3$. The recommendation is the average of measurements of Silver et al. (1985) and Ager et al. (1985). The latter place an upper limit on the path forming NaO_2 and O.

J2. $NaO + HC\ell$. There is only one indirect measurement of the rate coefficient for this reaction from the study of Silver et al. (1984a). They indicate that the products are $NaC\ell$ and OH, although some NaOH and $C\ell$ production is not ruled out.

J3. $NaOH + HC\ell$. The recommendation is based on the study of Silver et al. (1984a), which is the only published study of this reaction.

Table 2. Rate Constants for Three-Body Reactions

Reaction	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
$O + O_2 \xrightarrow{M} O_3$	(6.0±0.5)(-34)	2.3±0.5	- -	-	1
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0)(-37)	$0.6^{+2}_{-.6}$	- -	-	2
*$H + O_2 \xrightarrow{M} HO_2$	(5.5±0.5)(-32)	1.6±0.5	(7.5±4.0)(-11)	0±1	3
$OH + OH \xrightarrow{M} H_2O_2$	(6.9±3.0)(-31)	$0.8^{+2.0}_{-0.8}$	(1.0±0.5)(-11)	1.0±1.0	4
*$O + NO \xrightarrow{M} NO_2$	(9.0±2.0)(-32)	1.5±0.3	(3.0±1.0)(-11)	0±1	5
$O + NO_2 \xrightarrow{M} NO_3$	(9.0±1.0)(-32)	2.0±1.0	(2.2±0.3)(-11)	0±1	6
$OH + NO \xrightarrow{M} HONO$	(7.0±2.0)(-31)	2.6±1.0	(1.5±1.0)(-11)	0.5±0.5	7
$OH + NO_2 \xrightarrow{M} HNO_3$	(2.6±0.3)(-30)	3.2±0.7	(2.4±1.2)(-11)	1.3±1.3	8
*$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(2.0±0.5)(-31)	2.7±1.5	(4.2±1.0)(-12)	2.0±2.0	9
*$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.2±0.5)(-30)	4.3±1.3	(1.5±0.8)(-12)	0.5±0.5	10
$C\ell + NO \xrightarrow{M} C\ell NO$	(9.0±2.0)(-32)	1.6±0.5	- -	-	11
*$C\ell + NO_2 \xrightarrow{M} C\ell ONO$	(1.3±0.2)(-30)	2.0±1.0	(1.0±0.5)(-10)	1.0±1.0	12
$\xrightarrow{M} C\ell NO_2$	(1.8±0.3)(-31)	2.0±1.0	(1.0±0.5)(-10)	1.0±1.0	12
$C\ell + O_2 \xrightarrow{M} C\ell OO$	(2.0±1.0)(-33)	1.4±1.4	- -	-	13
$C\ell O + NO_2 \xrightarrow{M} C\ell ONO_2$	(1.8±0.3)(-31)	3.4±1.0	(1.5±0.7)(-11)	1.9±1.9	14
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.0±2.0)(-31)	2.0±2.0	(1.0±0.5)(-11)	1.0±1.0	15

Note: $k(Z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

*Indicates a change from the previous Panel evaluation (JPL 83-62).

Table 2. (Continued)

	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		
Reaction	k_o^{300}	n	k_∞^{300}	m	Notes
$F + O_2 \xrightarrow{M} FO_2$	(1.6±0.8)(-32)	1.4±1.0	- -	-	16
$F + NO \xrightarrow{M} FNO$	(5.9±3.0)(-32)	1.7±1.7	- -	-	17
*$F + NO_2 \xrightarrow{M}$ Products	(1.1±0.6)(-30)	2.0±2.0	(3.0±2.0)(-11)	1.0±1.0	18
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0)(-31)	1.3±1.3	(2.0±1.0)(-11)	1.5±1.5	19
*$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5)(-31)	2.0±1.0	(1.8±0.2)(-12)	1.7±1.7	20
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8)(-30)	4.0±2.0	(6.5±3.2)(-12)	2.0±2.0	21
*$OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.0)(-31)	3.3±1.5	(1.5±0.5)(-12)	0^{+0}_{-2}	22
*$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.5±0.6)(-28)	0.8±2.0	(8.8±0.9)(-12)	0^{+0}_{-2}	23
*$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0)(-30)	0.0±0.2	(8.3±1.0)(-13)	$-2.0^{+2.0}_{-1.0}$	24
#$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(4.5±1.0)(-29)	2±2	(8±6)(-12)	1±1	25
#$CFC\ell_2 + O_2 \xrightarrow{M} CFC\ell_2O_2$	(5.0±0.8)(-30)	2±2	(6.0±1.0)(-12)	1±1	26
#$CC\ell_3 + O_2 \xrightarrow{M} CC\ell_3O_2$	(1.0±0.7)(-30)	2±2	(2.5±2)(-12)	1±1	27
#$CFC\ell_2O_2 + NO_2 \xrightarrow{M} CFC\ell_2O_2NO_2$	(3.5±0.5)(-29)	4±2	(6.0±1.0)(-12)	2±2	28
#$HS + NO \xrightarrow{M} HSNO$	(2.4±0.4)(-31)	3±1	(2.7±0.5)(-11)	0^{+0}_{-2}	29
#$Na + O_2 \xrightarrow{M} NaO_2$	(1.9±1)(-30)	1.1±0.5	(2.0±1.8)(-10)	0±1	30

Note: $k(Z) = k(M,T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)}\right) 0.6^{\{1 + [\log_{10}(k_o(T)[M]/k_\infty(T))]^2\}^{-1}}$

The values quoted are suitable for air as the third body, M.

*Indicates a change from the previous Panel evaluation (JPL 83-62).

#Indicates a new entry that was not in the previous evaluation.

NOTES TO TABLE 2

1. $O + O_2$. Low-pressure limit and T-dependence are an average of Klais, Anderson, and Kurylo (1980a), and Lin and Leu (1982). The result is in agreement with most previous work (see references therein).

2. $O(^1D) + N_2$. Low-pressure limit from Kajimoto and Cvetanovic (1976). The T-dependence is obtained by assuming a constant β. Rate constant is extremely low in this special system due to electronic curve crossing.

3. $H + O_2$. Kurylo (1972), Wong and Davis (1974) averaged. Both studies include T-dependence; the recommended value is chosen with constant $\langle \Delta E \rangle_{N_2}$ ~.05 kcal mole^{-1}. This very low number reflects rotational effects. The high pressure limit is from Cobos et al. (1985). The temperature dependence is estimated. Cobos et al. estimate $m = -0.6$, which is within our uncertainty.

4. OH + OH. Zellner (private communication, 1982) reports pressure and T-dependence in N_2 for $253 < T < 353$. Their values are in rough agreement with those of Kijewsky and Troe (1972), who report low-pressure values in Ar for $950 < T < 1450$. Trainor and von Rosenberg (1974) also report a value.

5. O + NO. Changed from JPL 83-62. Low-pressure limit and n from direct measurements of Schieferstein et al. (1983) and their reanalysis of the data of Whytock et al. (1976). Error limits encompass other studies. High-pressure limit and m from Baulch et al. (1980) and Baulch et al. (1982), slightly modified.

6. $O + NO_2$. Values of rate constants and temperature dependences from the evaluations of Baulch et al. (1980). They use $F_c = 0.8$ to fit the measured data at 298 K, but our value of $F_c = 0.6$ gives a similar result. In a supplementary review, Baulch et al. (1982) suggest a slight temperature dependence for F_c, which would cause their suggested value to rise to $F_c = 0.85$ at 200 K.

7. OH + NO. The low-pressure limit rate constant has been reported by Anderson and Kaufman (1972), Stuhl and Niki (1972), Morley and Smith (1972), Westenberg and de Haas (1972), Anderson et al. (1974), Howard and Evenson (1974), Harris and Wayne (1975), Atkinson et al. (1975), Overend et al. (1976), Anastasi and Smith (1978), and Burrows et al. (1983). The general agreement is good, and the recommended value is a weighted average, with heavy weighting to the work of Anastasi and Smith. The reported high pressure limit rate constant is generally obtained from extrapolation. The recommended value is a weighted average of the reports in Anastasi and Smith (1978) and Anderson et al. (1974). [Both cis and trans - HONO are expected to be formed.]

8. OH + NO_2. The low-pressure limit is from Anderson et al. (1974), who report n = 2.5 ($240 < T/K < 450$); Howard and Evenson (1974); Anastasi and Smith (1976), who report n = 2.6 ($220 < T/K < 550$) and Wine et al. (1979) who support these values over the range ($247 < T/K < 352$). The recommended value of n = 3.2 comes from $\langle \Delta E \rangle_{N_2}$ = 0.55 kcal $mole^{-1}$. (This value is consistent with the experiments.) Burrows et al. (1983) confirm the value of k at 295 K. The high-pressure limit and T-dependence come from RRKM model of Smith and Golden (1978), although the error limits have been expanded to encompass m = 0.

Robertshaw and Smith (1982) have measured k up to 8.6 atmospheres of CF_4. Their work suggests that k_∞ might be higher than suggested here (~50%). This might also be due to other causes (i.e., isomer formation or involvement of excited electronic states). The recommendation here fits all data over the range of atmospheric interest.

9. HO_2 + NO_2. Changed from JPL 83-62. The previous recommendation was taken from Sander and Peterson (1984) and was their preferred fit to all of their data over their complete temperature and pressure ranges. This fit is poorest for the low temperature, 100 torr data. The new recommendation gives a better fit to all their data, particularly at low temperature. These parameters also yield a k_0(200 K) in better agreement with the calculations of Patrick and Golden (1983). The recommended k_0(300 K) is

consistent with Howard (1977). More data are needed, particularly at stratospheric temperatures and pressures and on the temperature dependence of the low pressure limit. Other studies by Simonaitis and Heicklen (1978) and Cox and Patrick (1979) are in reasonable agreement with the recommendations.

10. NO_2 + NO_3. Changed from JPL 83-62. Data on the reverse reaction are from Connell and Johnston (1979) and Viggiano et al. (1981). (These data are used in this analysis by multiplying by the equilibrium constant given in Table 3.) A very thorough analysis of this data and a more complicated fit than presented in JPL 83-62 can be found in Malko and Troe (1982). Recent experiments by Kircher et al. (1984), Croce de Cobos et al. (1984), Smith et al. (1985), and Moortgat (private communication, 1984), have verified the equilibrium constant within 50% and extended the room temperature data to 200 atm.

The values in Table 2 yield a curve that perfectly matches all the data up to 5 atm. This includes the two lowest pressure points of Croce de Cobos et al. The values from this latter work above 10 atm are 30% higher than the curve. The value of $n = 4.3$ is from Kircher et al. (1984). The value of $m = 0.5 \pm 0.5$ is from Kircher et al. The study of Fowles et al. (1982) is noted but not used in the analysis.

11. Cl + NO. Low-pressure limit from Lee et al., (1978a), Clark et al. (1966), Ashmore and Spencer (1959), and Ravishankara et al. (1978). Temperature dependence from Lee et al. (1978a) and Clark et al. (1966).

12. Cl + NO_2. Low-pressure limit and T-dependence from Leu (1984a). (The T-dependence by assuming not much difference between N_2 and He.) Leu confirms the observation of Niki et al. (1978c) that both $ClONO$ and $ClNO_2$ are formed with the former dominating. This has been explained by Chang et al. (1979a) with detailed calculations in Patrick and Golden (1983). The temperature dependence is as predicted in Patrick and Golden (1983). Leu's (1984a) results are in excellent agreement with the report of Ravishankara et al. (private communication, 1978). The latter work extends to 200 torr and the high pressure limit was chosen to fit these measurements. The

temperature dependence of the high pressure limit is estimated.

13. $Cl + O_2$. Stedman et al. (1968) and Nicholas and Norrish (1968) measured this process in Ar. Recommended value based on $k(N_2)/k(Ar) = 1.8$. T-dependence from constant $\langle \Delta E \rangle$.

14. $ClO + NO_2$. The available kinetics data for this reaction fall into two sets, which are in substantial disagreement. Several independent low-pressure determinations (Zahniser et al., 1977; Birks et al., 1977; Leu et al., 1977; Lee et al., 1982) of the rate of ClO disappearance via the $ClO + NO_2 + M$ reaction are in excellent agreement and give an average $k_o(300)$ near 1.8×10^{-31} cm^6 s^{-1}. No product identification was carried out, and it was assumed that the reaction gave chlorine nitrate, $ClONO_2$. In contrast, direct measurements of the rate of thermal decomposition of $ClONO_2$ (Knauth, 1978; Schonle et al., 1979), combined with the equilibrium constant, give $k_o(300) = 4.5 \times 10^{-32}$ cm^6 s^{-1} for the three-body reaction forming $ClONO_2$. Since the measured rate of ClO disappearance seems well established by four groups, the Knauth results can be reconciled with the higher number by three different explanations: (1) the measured thermal decomposition rate is incorrect; (2) the equilibrium constant is in error by a factor of three (requiring that the ΔH_f's are off by ~1 kcal/mole, which, while small, is outside the stated error limits); (3) all the data are correct, and the low-pressure ClO disappearance studies measured not only a reaction forming $ClONO_2$, but another channel forming an isomer, such as $OClNO_2$, ClOONO, or OClONO (Chang et al., 1979a; Molina et al., 1980a).

Recent work by Margitan (1983b), Cox et al. (1984b), and Burrows et al. (1985) indicate that there are no isomers of $ClONO_2$ formed. Thus, either explanation (1) and/or (2) above must be invoked.

The high-pressure limit rate constants and their temperature dependence are from the model of Smith and Golden (1978). The rate constants above fit measured rate data for the disappearance of reactants (Cox and Lewis, 1979; Dasch et al., 1981). Data from Handwerk and Zellner (1984) indicate a slightly lower k_∞.

15. $BrO + NO_2$. Data at 300 K are from Sander et al. (1981). They suggest k_o = (5.0 ± 1.0)(-31) k_∞ = $(2.0^{+0.5}_{-1.0})$(-11) and F_c = $0.4^{+0.1}_{-0.05}$. The temperature dependences are simple estimates.

Even though isomer formation seems to have been ruled out for the $C\ell O + NO_2$ reaction (i.e. the isomer stability is too low to make a significant contribution to the measured rate constant), this does not eliminate the possibility that $BrO + NO_2$ leads to more than one stable compound. In fact, if the measured value of k_o is accepted, it can only be theoretically reconciled with a single isomer, $BrONO_2$, which would have a 6-7 kcal mole^{-1} stronger bond than $C\ell ONO_2$! This would fix the heat of formation of $BrONO_2$ to be the same as $C\ell ONO_2$, an unlikely possibility.

16. $F + O_2$. Low-pressure limit from Baulch et al. (1982), who averaged the results of Zetzsch (1973), Arutyunov et al. (1976), Chen et al. (1977), and Shamonima and Ketov (1979). Temperature dependence is calculated (Patrick and Golden (1983)).

Calculated values of the strong-collision rate constant yield a more physically meaningful value of β when the JANAF value of the heat of formation of FO_2 is adopted. See notes to Table 3 and Patrick and Golden (1983).

17. F + NO. Parameters estimated from strong collision calculations with $\langle \Delta E \rangle$ set at .42 kcal/mole^{-1}, yielding β = .30 at 300 K and β = .38 at 200 K. T-dependence as per text.

18. $F + NO_2$. Changed from JPL 83-62. Experimental data of Fasano and Nogar (1983) were used to determine both the high and low pressure limits at 300 K. They fit their data to an expression such as recommended here.

Treatment of the data for this system requires knowledge of the relative stabilities of FNO_2 and FONO. Patrick and Golden (1983) assumed that the difference between these would be the same as between the $C\ell NO_2$ isomers. Thus, they concluded that $k^{0}_{300}(FNO_2) = 8.9 \times 10^{-31}$ and $k^{0}_{300}(FONO) =$ 2.4×10^{-30}, and that FONO would be formed ~3 times more favorably than

FNO_2. We have found an error of a factor of four in their calculations, which would predict $k^0_{300}(FONO) \approx 1.06 \times 10^{-29}$, and thus an overwhelming amount of FONO. The measured value is $k \approx 1.06 \times 10^{-30}$, which is one-tenth of the predicted value.

A calculation at the MP-3/6-31G* level by Evleth (private communication, 1984) indicates that the FONO is much more than 10 kcal mol^{-1} less stable than FNO_2 and that its rate of formation can be ignored. Thus, we have $k(exp) = k(FNO_2) = 1.06 \times 10^{-30}$.

The value of $n = 2$ is from Patrick and Golden, and the value of m is a rough estimate from similar reactions.

19. $FO + NO_2$. Low-pressure limit from strong collision calculation and $\beta = 0.33$. T-dependence from resultant $\langle \Delta E \rangle = .52$ kcal $mole^{-1}$. High-pressure limit and T-dependence estimated.

Once again (see Note 15) multiple channels could be important here, which would mean that the reaction between FO and NO_2 could be much faster, since these values consider only $FONO_2$ formation.

20. $CH_3 + O_2$. Changed from JPL 83-62. Low-pressure limit from Seltzer and Bayes (1983). (These workers determined the rate constants as a function of pressure in N_2, Ar, O_2, and He. Only the N_2 points were used directly in the evaluation, but the others are consistent.) Plumb and Ryan (1982b) report a value in He which is consistent within error limits with the work of Seltzer and Bayes. The work of Laguna and Baughcum (1982) seems to be in the fall off region. Results of Pratt and Wood (1984) in Ar are consistent with this recommendation, although the measurements are indirect. Their T-dependence is within our estimate. As can be seen from Patrick and Golden (1983), the above value leads to a very small $\beta \sim .02$, and thus temperature dependence is hard to calculate. The suggested value is an estimate. Ryan and Plumb (1984) suggest that the same type of calculation as employed by Patrick and Golden yields a reasonable value of β. We have not been able to reproduce their results. The high pressure rate constant is from work of Hippler et al. (private communication, 1984).

(Data of ven den Bergh and Callear (1971), Hochanadel et al. (1977), Basco et al. (1972), Washida and Bayes (1976), Laufer and Bass (1975), and Washida (1980) are also considered.) The temperature dependence is estimated.

21. $CH_3O_2 + NO_2$. Parameters from a reasonable fit to the temperature and pressure-dependent data in Sander and Watson (1980) and Ravishankara et al. (1980a). The former reference reports their room-temperature data in the same form as herein, but they allow F_c to vary. They report:

$$k_o = 2.33 \times 10^{-30},\ k_\infty = 7 \times 10^{-12}(T/300)^{-3.5},\ F_c = 0.4.$$

These parameters are a better fit at all temperatures than those recommended here. We do not adopt them since they are not much better in the stratospheric range, and they would require both a change in our F_c = 0.6 format, and the adoption of a quite large negative activation energy for k_∞.

The CODATA recommendations (Baulch et al., 1982) are: $k_o = 2.3 \times 10^{-30}(T/300)^{-4}$, $k_\infty = 8 \times 10^{-12}$ and $F_c = e^{-T/320} + e^{-1280/T}$; yielding F_c = .41 at 300 K and .54 at 200 K. These values do not fit the data as well as the current recommendations. It is interesting to note that the data require a negative T-dependence for k_∞, similar to our new $HO_2 + NO_2$ recommendation, and that the value of β at 300 K is ~.2.

22. $OH + SO_2$. Changed from JPL 83-62. Values of the rate constant as a function of pressure of 298 K from Leu (1982), Paraskovopoulos et al. (1983), and Wine et al. (1984a). The value of the low pressure limit is from Leu (1982), corrected for fall off. The high pressure limit is from a fit to all the data.

The value of n comes from the above data combined with calculations such as those of Patrick and Golden (1983), except that the heat of formation of $HOSO_2$ is raised by 4 kcal mol^{-1}, as suggested by the work of Margitan (1984a). The value of m is estimated. This is not a radical-radical reaction and is unlikely to have a positive value of m. The limit of m = -2 corresponds to a real activation energy of ~1 kcal mol^{-1}. Earlier data listed in Baulch et al. (1980) and Baulch et al. (1982) are noted.

23. OH + C_2H_4. Changed from JPL 83-62. Experimental data of Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970a), Morris et al. (1971), and Overend and Paraskevopolous (1977b) in helium, Atkinson et al. (1977) in argon, and Lloyd et al. (1976) and Cox (1975) and Klein et al. (1984) in nitrogen/oxygen mixtures, have been considered in the evaluation. This well-studied reaction is considerably more complex than most others in this table. The parameters recommended here fit exactly the same curve proposed by Klein et al. (1984) at 298 K. Discrepancies remain and the effect of multiple product channels is not well understood. The temperature dependence of the low-pressure limit has not been determined experimentally. Calculations of the type in Patrick and Golden (1983) yield the recommended value.

The high-pressure limit temperature dependence has been determined by several workers. Almost all obtain negative activation energes, the Zellner and Lorenz (1984) value being equivalent to m = + 0.8 over the range (296 < T/K < 524) at about 1 atmosphere. Although this could theoretically arise as a result of reversibility, the equilibrium contant is too high for this possibility. If there is a product channel that proceeds wth a low barrier via a tight transition state, a complex rate constant may yield the observed behavior. The actual addition process (OH + C_2H_4) may even have a small positive barrier. The recommended limits encompass the reported values.

24. OH + C_2H_2. Changed from JPL 83-62. The rate constant for this complex process has recently been re-examined by G. P. Smith et al. (1984) in the temperature range from 228 to 1400 K, and in the pressure range 1 to 760 torr. Their analysis, which is cast in similar terms to those used here, is the source of the rate constants and temperature dependences at both limits. The negative value of m reflects the fact that their analysis includes a 1.2 kcal/mole barrier for the addition of OH to C_2H_2.

The data analyzed include those of Pastrana and Carr (1974), Perry et al. (1977), Michael et al. (1980), and Perry and Williamson (1982). Other data of Wilson and Westenberg (1967), Breen and Glass (1971), Smith and Zellner (1973), and Davis et al. (1975) were not included.

Calculations of k_o via the methods of Patrick and Golden (1983) yield values compatible with those of Smith et al.

25. $CF_3 + O_2$. New entry. Low-pressure limit from Caralp and Lesclaux (1983) who made a few measurements with $M = N_2$. Their more extensive values with $M = He$ agree with those of Ryan and Plumb (1982). The ratio $k(N_2)/k(He)$ is ~2.5. The high-pressure limit is from Ryan and Plumb (1982). Temperature dependences are rough estimates based on similar reactions.

26. $CFCl_2 + O_2$. New entry. Values for both low- and high-pressure limits at 300 K are from Caralp and Lesclaux (1983). Temperature dependences are rough estimates based on similar reactions.

27. $CCl_3 + O_2$. New entry. Values for both low- and high-pressure limits are from Ryan and Plumb (1984). They use the same format as recommended here and report:

$$k_o^{300}(He) = (5.8 \pm 0.6) \times 10^{-31},\ k_\infty^{300} = 2.5 \times 10^{-12} \text{ with } F = 0.25.$$

We find a good fit to their data using $F = 0.6$ to yield

$$k_o^{300}(He) = 4 \times 10^{-31}, \text{ keeping } k_\infty^{300} = 2.5 \times 10^{-12}.$$

The recommended value of $k_o^{300}(N_2)$ is $2.5\ k_o^{300}(He) = 1 \times 10^{-30}$.

Temperature dependences are rough estimates based on similar reactions. A value of $k_\infty^{300} = 5 \times 10^{-12}$ has been reported by Cooper et al. (1980).

28. $CFCl_2O_2 + NO_2$. New entry. Values for both low- and high-pressure limits at 300 K from Lesclaux and Caralp (1984). Their bath gas was O_2 which is assumed to be equal to N_2 in energy transfer characteristics. Temperature dependences are rough estimates based on similar reactions.

29. HS + NO. New entry. Data and analysis are from the recent work of Black et al. (1984). The temperature dependence of k_∞ has been estimated.

30. $Na + O_2$. New entry. The low-pressure limit and temperature dependence are taken from the recent paper of Silver et al. (1984b). The error limits are

broadened somewhat. Patrick and Golden (1984a) have performed calculations in the manner of Patrick and Golden (1983) which yield $\beta_{N_2}^{300} = 0.3$. The high-pressure limiting rate constant is an estimate by Silver et al. (1984b). The error limits and temperature dependence are estimated.

EQUILIBRIUM CONSTANTS

Format

Some of the three-body reactions in Table 2 form products which are thermally unstable at atmospheric temperatures. In such cases the thermal decomposition reaction may compete with other loss processes, such as photodissociation or radical attack. Table 3 lists the equilibrium constants, K(T), for six reactions which may fall into this category. The table has three column entries, the first two being the parameters A and B which can be used to express K(T):

$$K(T)/\mathrm{cm}^3\ \mathrm{molecule}^{-1} = A\ \exp(B/T)\ (200 < T < 300\ \mathrm{K})$$

The third column entry in Table 3 is the calculated value of K at 300 K.

The data sources for K(T) are described in the individual notes to Table 3. When values of the heats of formation and entropies of all species are known at the temperature T, we note that:

$$\log[K(T)/\mathrm{cm}^3\ \mathrm{molecule}^{-1}] = \frac{\Delta S^o_T}{2.303R} - \frac{\Delta H^o_T}{2.303RT} + \log T - 21.87$$

where the superscript "o" refers to a standard state of one atmosphere. In some cases K values were calculated from this equation, using thermochemical data. In other cases the K values were calculated directly from kinetic data for the forward and reverse reactions. When available, JANAF values were used for the equilibrium constants. The following equations were then used to calculate the parameters A and B:

$$B/^{\circ}K = 2.303 \left[\log \frac{K_{200}}{K_{300}} \right] \left(\frac{300 \cdot 200}{300 - 200} \right)$$

$$= 1382 \log(K_{200}/K_{300})$$

$$\log A = \log K(T) - B/2.303\ T$$

Table 3. Equilibrium Constants

Reaction	$A/cm^3\ molecule^{-1}$	$B/^{o}K$	$\log K_{eq}(300)$	Note
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.33×10^{-27}	10,870	-10.90	1
*$NO_2 + NO_3 \rightarrow N_2O_5$	1.52×10^{-27}	11,153	-10.68	2
$Cl + O_2 \rightarrow ClOO$	2.43×10^{-25}	2,979	-20.30	3
$ClO + O_2 \rightarrow ClO \cdot O_2$	$<1.3 \times 10^{-26}$	<5,230	<-18.30	4
$F + O_2 \rightarrow FOO$	5.32×10^{-25}	7,600	-13.27	5a
	1.15×10^{-25}	3,582	-19.75	5b
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.30×10^{-28}	11,192	-11.68	6

$K/cm^3\ molecule^{-1} = A\ \exp(B/T)$ $[200 < T/K < 300]$

NOTES TO TABLE 3

1. The value was obtained by combining the data of Sander and Peterson (1984) for the rate constant of the reaction as written and that of Graham et al. (1977) for the reverse reaction.

   From the equilibrium constant, it may be inferred that the thermal decomposition of HO_2NO_2 is unimportant in the stratosphere, but is important in the troposphere.

2. Recent measurements led us to choose a slightly altered value. The previous value using thermochemical parameters from JANAF was $K_{298}^{-1} = 5.24 \times 10^{10}$ molec cm^{-3}. The current values yield $K_{298}^{-1} = 4.7 \times 10^{10}$ molec cm^{-3}, to accommodate reports by Perner et al. (1985), Graham and Johnston (1978), Kircher et al. (1984), Tuazon et al. (1983) and Smith et al. (1985).

   The parameters were derived by changing the value of ΔH for the reaction by 1.00 kJ $mole^{-1}$ and using the same entropy change as before (see Patrick and Golden (1983)).

3. Cox et al. (1979) measured K at 298 K. Their reported value of K, $(5.4 \pm 2.6) \times 10^{-21}$ cm^3 $molecule^{-1}$, when combined with JANAF values for the entropy change, gives $\Delta H_f(298)(C\ell O_2) = 22.5$ kcal/$mole^{-1}$. This is in excellent agreement with Ashford et al. (1978), who suggest $\Delta H_f(298)(C\ell O_2) = 22.5 \pm .5$ kcal/$mole^{-1}$. The expression of Cox et al. is:

$$k = 3.71 \times 10^{-28}\ T \exp(3217/T).$$

4. Zellner (private communication, 1982) suggests $K < 12\ atm^{-1}$ and $\Delta H \geq -11$ kcal/mole. The corresponding value of A leads to $S^o300(C\ell O \cdot O_2) \sim 73$ cal $mole^{-1}$ K^{-1}. A higher value of K has been proposed by Prasad (1980), but it requires $S^o(C\ell O \cdot O_2)$ to be about 83 cal $mole^{-1}$ K^{-1}, which seems unreasonably high. Carter and Andrews (1981) found no experimental evidence for $C\ell O \cdot O_2$.

5. (a) From JANAF thermochemical values. (This value favored by k_o

calculation, see Note 16, Table 2.) (b) From Benson's (1976) thermochemical values.

6. Thermochemical values at 300 K for $CH_3O_2NO_2$ and CH_3O_2 are from Baldwin (1982). In the absence of data, ΔH^o and ΔS^o were assumed to be independent of temperature. Bahta et al. (1982) have measured k(dissociation) at 263 K. Using the values of k(recombination) suggested in this evaluation, they compute $K(263) = (2.68 \pm 0.26) \times 10^{-10}$ cm^3. Our values predict 3.94×10^{-10} cm^3, in good agreement.

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

In Table 4 we present a list of photochemical reactions considered to be of stratospheric interest. The absorption cross sections of O_2 and O_3 largely determine the extent of penetration of solar radiation into the stratosphere and troposphere. Some comments and references to these cross sections are presented in the text, but the data are not listed here. (See, for example, WMO Report #11, 1982; WMO-NASA, 1985.) The photodissociation of NO in the O_2 Schumann-Runge band spectral range is another important process requiring special treatment and is not discussed in this evaluation (see, for example, Frederick and Hudson, 1979; Allen and Frederick, 1982; and WMO Report #11, 1982).

For some other species having highly structured spectra, such as CS_2, SO_2 and $OC\ell O$, some comments are given in the text, but the photochemical data are not presented. The species CH_2O, NO_2 and NO_3 also have complicated spectra, but in view of their importance for atmospheric chemistry a sample of the data is presented in the evaluation; for more detailed information on their high-resolution spectra and temperature dependence, the reader is referred to the original literature.

Table 5 gives recommended reliability factors for some of the more important photochemical reactions. These factors represent the combined uncertainty in cross sections and quantum yields, taking into consideration the atmospherically important wavelength regions, and they refer to the total dissociation rate regardless of product identity (except in the case of $O(^1D)$ production from photolysis of O_3).

The absorption cross sections are defined by the following expression of Beer's Law:

$$I = I_0 \exp(-\sigma n l),$$

where: I_0, I are the incident and transmitted light intensity, respectively, σ is the absorption cross section in cm^2 $molecule^{-1}$, n is the concentration in molecule cm^{-3}, and l is the pathlength in cm. The cross sections are room temperature values at the specific wavelengths listed in the tables, and the expected photodissociation quantum yields are unity, unless otherwise stated.

Table 4. Photochemical Reactions of Stratospheric Interest

$O_2 + h\nu \rightarrow O + O$

$O_3 + h\nu \rightarrow O_2 + O$

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

$HO_2 + h\nu \rightarrow$ products

$H_2O + h\nu \rightarrow H + OH$ (1)

$H_2O_2 + h\nu \rightarrow OH + OH$

$NO + h\nu \rightarrow N + O$

$NO_2 + h\nu \rightarrow NO + O$

$NO_3 + h\nu \rightarrow$ products

$N_2O + h\nu \rightarrow N_2 + O(^1D)$

$N_2O_5 + h\nu \rightarrow$ products

$NH_3 + h\nu \rightarrow NH_2 + H$ (1)

$HNO_2 + h\nu \rightarrow OH + NO$

$HNO_3 + h\nu \rightarrow OH + NO_2$

$HNO_4 + h\nu \rightarrow$ products

$C\ell_2 + h\nu \rightarrow C\ell + C\ell$

$C\ell O + h\nu \rightarrow C\ell + O$

$C\ell OO + h\nu \rightarrow$ products

$OC\ell O + h\nu \rightarrow O + C\ell O$

$C\ell O_3 + h\nu \rightarrow$ products

$HC\ell + h\nu \rightarrow H + C\ell$

$HOC\ell + h\nu \rightarrow OH + C\ell$

$C\ell NO + h\nu \rightarrow C\ell + NO$

$C\ell NO_2 + h\nu \rightarrow$ products

$C\ell ONO + h\nu \rightarrow$ products

$C\ell ONO_2 + h\nu \rightarrow$ products

$CC\ell_4 + h\nu \rightarrow$ products

$CC\ell_3F + h\nu \rightarrow$ products

$CC\ell_2F_2 + h\nu \rightarrow$ products

$CHC\ell F_2 + h\nu \rightarrow$ products

$CH_3C\ell + h\nu \rightarrow$ products

$CC\ell_2O + h\nu \rightarrow$ products

$CC\ell FO + h\nu \rightarrow$ products

$CF_2O + h\nu \rightarrow$ products

$CH_3CC\ell_3 + h\nu \rightarrow$ products

$BrO + h\nu \rightarrow Br + O$

$BrONO_2 + h\nu \rightarrow$ products

$HF + h\nu \rightarrow H + F$

$CO + h\nu \rightarrow C + O$ (1)

$CO_2 + h\nu \rightarrow CO + O$ (1)

$CH_4 + h\nu \rightarrow$ products (2)

$CH_2O + h\nu \rightarrow$ products

$CH_3OOH + h\nu \rightarrow$ products

$HCN + h\nu \rightarrow$ products

$CH_3CN + h\nu \rightarrow$ products

$SO_2 + h\nu \rightarrow SO + O$

$H_2S + h\nu \rightarrow HS + H$ (2)

$COS + h\nu \rightarrow CO + S$

$CS_2 + h\nu \rightarrow$ products

#$NaC\ell + h\nu \rightarrow Na + C\ell$

#$NaOH + h\nu \rightarrow Na + OH$

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(1) Hudson and Kieffer (1975)

(2) Turco (1975)

New entry

Table 5. Combined Uncertainties for Cross Sections and Quantum Yields

Species	Uncertainty
O_2 (Schumann-Runge bands)	1.4
O_2 (Continua)	1.3
O_3	1.1
$O_3 \rightarrow O(^1D)$	1.4
NO_2	1.3
NO_3	2.0
N_2O	1.2
N_2O_5	2.0
H_2O_2	1.4
HNO_3	1.3
HO_2NO_2	2.0
CH_2O	1.4
HCl	1.1
$HOCl$	1.4
$ClONO_2$	1.3
CCl_4	1.1
CCl_3F	1.1
CCl_2F_2	1.1
CH_3Cl	1.1
CF_2O	2.0
CH_3OOH	1.4
$BrONO_2$	1.4

$O_2 + h\nu \rightarrow O + O$

The photodissociation of molecular oxygen in the stratosphere is due primarily to absorption of solar radiation in the 200-220 nm wavelength region, i.e., within the Herzberg continuum. The 185-200 nm region -- the O_2 Schumann-Runge band spectral range -- is also very important, since solar radiation penetrates efficiently into the stratosphere at those wavelengths.

Frederick and Mentall (1982) and Herman and Mentall (1982) have estimated O_2 absorption cross sections from balloon measurements of solar irradiance in the stratosphere. The latter authors find the cross sections in the 200-210 nm range to be ~35% smaller than the smallest of the older laboratory results, which are those of Shardanand and Prasad Rao (1977). There is considerable disagreement among the cross section values measured in the laboratory in this wavelength range. Hasson and Nicholls (1971) report the largest values: $\sim 1.4 \times 10^{-23}$ cm^2 at 200 nm and $\sim 1.1 \times 10^{-23}$ cm^2 at 210 nm. Shardanand and Prasad Rao (1977) obtain the smallest cross sections among the older data set, 1.0×10^{-23} cm^2 at 200 nm and 7.7×10^{-24} cm^2 at 210 nm. Other investigators (Ditchburn and Young, 1962; Ogawa, 1971) report values lying between the two extremes. There are two recent laboratory studies (Johnston et al., 1984; Chueng et al., 1984) which tend to confirm the lower values obtained from solar irradiance measurements. There is also, however, a recent study of the penetration of stellar UV radiation into the stratosphere which agrees better with the higher O_2 cross section values (Pirre et al., 1984).

The attenuation of solar radiation in the Schumann-Runge wavelength region is a problem requiring special treatment due to the rotational structure of the bands; see, for example, Nicolet and Peetermans (1980); Frederick and Hudson (1980); and Allen and Frederick (1982). The effective O_2 cross sections obtained from solar irradiance measurements in the stratosphere by Herman and Mentall (1982) are in good agreement between 187 and 195 nm with the values reported by Allen and Frederick (1982), which were obtained by an empirical fit to the effective cross sections appropriate for stratospheric conditions. Between 195 and 200 nm the fit yielded values which are somewhat larger than those estimated by Herman and Mentall.

The studies of the penetration of solar radiation in the atmosphere in the Schumann-Runge wavelength region have been based so far on laboratory measurements of cross sections which were affected by instrumental parameters due to insufficient spectral resolution. Yoshino et al. (1983) have reported high resolution O_2 cross section measurements at 300 K, between 179 and 202 nm, obtaining presumably the first set of results which is independent of the instrumental width. The Schumann-Runge cross sections are temperature-dependent, so that additional studies will be required in order to carry out detailed atmospheric modeling calculations. Furthermore, for estimates of the solar irradiance in the stratosphere the cross section values which need to be accurately known are those at the wings of the rotational lines and in the underlying continuum, and these are several orders of magnitude smaller than the peak values.

$O_3 + h\nu \rightarrow O + O_2$

The O_3 absorption cross sections and their temperature dependency have been remeasured recently by several groups. For a review see WMO-NASA, 1985; Table 6 lists a sample of the data taken from this review, namely the 273 K cross section values averaged over the wavelength intervals commonly employed in modeling calculations. The temperature effect is negligible for wavelengths shorter than ~260 nm.

The quantum yields for $O(^1D)$ production, $\Phi(O^1D)$, for wavelengths near 310 nm--i.e., the energetic threshold or fall-off region--have been measured mostly relative to quantum yields for wavelengths shorter than 300 nm, which were assumed to be unity. There are several studies which indicate that this assumption is not correct: Fairchild et al. (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is, $\Phi(O^3P) \approx 0.1$, at 274 nm; Sparks et al. (1980) also report $\Phi(O^3P) \approx 0.1$, at 266 nm; according to Brock and Watson (1980b) $\Phi(O^1D) = 0.88$ at 266 nm; Amimoto et al. (1980) report $\Phi(O^1D) = 0.85$ at 248 nm, and Wine and Ravishankara (1982) measured directly $\Phi(O^1D) = 0.9$ at 248 nm. There are also some indications that $\Phi(O^1D)$ decreases slightly between 304 and 275 nm (see Brock and Watson, 1980 a, b).

The recommendation for the quantum yields in the fall-off region is given in Table 7, and is taken from the mathematical expression given by Moortgat and Kudzus (1978), scaled down by a factor of 0.9 to account for the absolute magnitude of $\Phi(O^1D)$ at short wavelengths. The relative values are in good agreement with those reported by Brock and Watson (1980a).

Table 6. Absorption Cross Sections of O_3 at 273 K

λ (nm)	$10^{20}\sigma(cm^2)$ average	λ (nm)	$10^{20}\sigma(cm^2)$ average
175.439-176.991	81.1	238.095-240.964	797
176.991-178.571	79.9	240.964-243.902	900
178.571-180.180	78.6	243.902-246.914	1000
180.180-181.818	76.3	246.914-250.000	1080
181.818-183.486	72.9	250.000-253.165	1130
183.486-185.185	68.8	253.165-256.410	1150
185.185-186.916	64.0	256.410-259.740	1120
186.916-188.679	58.8	259.740-263.158	1060
188.679-190.476	53.1	263.158-266.667	965
190.476-192.308	48.0	266.667-270.270	834
192.308-194.175	43.8	270.270-273.973	692
194.175-196.078	41.1	273.973-277.778	542
196.078-198.020	36.9	277.778-281.690	402
198.020-200.000	33.0	281.690-285.714	277
200.000-202.020	32.6	285.714-289.855	179
202.020-204.082	32.6	289.855-294.118	109
204.082-206.186	35.1	294.118-298.507	62.4
206.186-208.333	41.1	298.507-303.030	34.3
208.333-210.526	48.4	303.030-307.692	18.5
210.526-212.766	62.6	307.692-312.5	9.80
212.766-215.054	85.7	312.5-317.5	5.01
215.054-217.391	117	317.5-322.5	2.49
217.391-219.780	152	322.5-327.5	1.20
219.780-222.222	197	327.5-332.5	0.617
222.222-224.719	255	332.5-337.5	0.274
224.719-227.273	324	337.5-342.5	0.117
227.273-229.885	400	342.5-347.5	0.0588
229.885-232.558	483	347.5-352.5	0.0266
232.558-235.294	579	352.5-357.5	0.0109
235.294-238.095	686	357.5-362.5	0.00549

Table 7. Mathematical Expression for $O(^1D)$ Quantum Yields, Φ, in the Photolysis of O_3

$$\Phi(\lambda,T) = A(\tau)\ \arctan[B(\tau)(\lambda-\lambda_o(\tau))] + C(\tau)$$

Where $\tau = T - 230$ is a temperature function with T given in Kelvin, λ is expressed in nm, and arctan in radians.

The coefficients $A(\tau)$, $B(\tau)$, $\lambda_o(\tau)$ and $C(\tau)$ are expressed as interpolation polynomials of the third order:

$$A(\tau) = 0.332 + 2.565 \times 10^{-4}\tau + 1.152 \times 10^{-5}\tau^2 + 2.313 \times 10^{-8}\tau^3$$
$$B(\tau) = -0.575 + 5.59 \times 10^{-3}\tau - 1.439 \times 10^{-5}\tau^2 - 3.27 \times 10^{-8}\tau^3$$
$$\lambda_o(\tau) = 308.20 + 4.4871 \times 10^{-2}\tau + 6.9380 \times 10^{-5}\tau^2 - 2.5452 \times 10^{-6}\tau^3$$
$$C(\tau) = 0.466 + 8.883 \times 10^{-4}\tau - 3.546 \times 10^{-5}\tau^2 + 3.519 \times 10^{-7}\tau^3.$$

In the limit where $\Phi(\lambda,T) > 0.9$, the quantum yield is set $\Phi = 0.9$, and similarly for $\Phi(\lambda,T) < 0$, the quantum yield is set $\Phi = 0$.

$HO_2 + h\nu \rightarrow OH + O$

The absorption cross sections of the hydroperoxyl radical, HO_2, in the 200-250 nm region have been measured at room temperature by Paukert and Johnston (1972), Hochanadel et al. (1972) and Cox and Burrows (1979). Hochanadel et al. (1980) give a cross section value of $4.0 \pm 0.5 \times 10^{-18}$ cm^2 at 205 nm, and Sander et al. (1982) a value of $3.0 \pm 0.4 \times 10^{-18}$ cm^2 at 227.5 nm.

The shape of the spectrum reported by the first three groups cited above is in reasonable agreement. The recommended absorption cross sections, listed in Table 8, are computed from the mean of the three after normalization of each spectrum to the value at 227.5 nm reported by Sander et al. (1982). This latter study gives the most direct measurement of an absolute cross section value for HO_2.

Lee (1982) has detected $O(^1D)$ as a primary photodissociation product at 193 and at 248 nm, with a quantum yield which is about 15 times larger at the longer wavelength. The absolute quantum yield for $O(^1D)$ production has not been reported yet.

Table 8. Absorption Cross Sections of HO_2

λ(nm)	$10^{20}\sigma(cm^2)$
190	430
200	480
210	490
220	400
230	260
240	120
250	50

$H_2O_2 + h\nu \rightarrow OH + OH$

The recommended absorption cross section values, listed in Table 9, are the mean of the data of Lin et al. (1978b) and of Molina and Molina (1981). The latter work supersedes the earlier results of Molina et al. (1977a).

Table 9. Absorption Cross Sections of H_2O_2 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	67.2	270	3.2
195	56.3	275	2.5
200	47.5	280	2.0
205	39.8	285	1.5
210	34.9	290	1.13
215	29.9	295	0.87
220	25.4	300	0.66
225	21.3	305	0.49
230	17.9	310	0.37
235	14.8	315	0.28
240	12.2	320	0.20
245	10.0	325	0.15
250	8.3	330	0.12
255	6.7	335	0.09
260	5.2	340	0.07
265	4.2	345	0.05
		350	0.03

$NO_2 + h\nu \rightarrow NO + O$

Table 10 lists a sample of the the recommended absorption cross sections of nitrogen dioxide, taken from the work of Bass et al. (1976), who report extinction coefficients every 1/8 nm between 185 and 410 nm at 298 K, and between 290 and 400 nm at 235 K. For atmospheric photodissociation calculations which require cross section values averaged over appropriate wavelength intervals the original literature report should be consulted; Table 9 lists the values only at the indicated wavelengths.

Recent cross section measurements by Schneider et al. (1985) give results which are 2-3% smaller than those of Bass et al. around 375-395 nm, which is the most important wavelength region for atmospheric photodissociation, but which are larger by as much as 20-25% around 270 nm and around 200 nm, where the experimental measurements are more difficult.

Harker et al. (1977) have reported measurements of absorption cross sections and quantum yields in the 375-420 nm region. Their cross sections are 4-10% larger than the values reported by Bass et al. (1976), and their quantum yields are, on the average, about 15% smaller than those measured by Jones and Bayes (1973). The measurements of the quantum yields by Davenport (1978) at six different wavelengths agree very well with those of Harker et al., and they indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced.

Direct measurements of the solar photodissociation rate of NO_2 in the troposphere by Parrish et al. (1983) agree better with theoretical calculations that incorporate the quantum yield values of Jones and Bayes (1973) rather than those of Harker et al. (1977).

Table 11 presents the recommended quantum yield values ϕ, which are computed using the recommended cross sections σ (Bass et al., 1976) and the measurements of Harker et al. (1977), which to a reasonable approximation yield the product $\phi\sigma$. In the atmospherically important 375-395 nm wavelength region the currently recommended quantum yield values are about 10% larger than those in the previous recommendation, which listed the quantum yields reported by Harker _et al_. without adjustments. Additional self consistent quantum yield and cross section measurements are in order.

For quantum yields in the 295-365 nm region the recommendation is to use the expression given by Jones and Bayes (1973), listed at the bottom of Table 11. More accurate values should be established in this wavelength region, although their contribution to the overall atmospheric photodissociation rate is not of major importance.

Table 10. NO_2 Absorption Cross Sections at 235 and 298 K

λ	$10^{20}\sigma(cm^2)$		λ	$10^{20}\sigma(cm^2)$	
(nm)	235 K	298 K	(nm)	235 K	298 K
185		26.0	300	10.9	11.7
190		29.3	305	16.7	16.6
195		24.2	310	18.3	17.6
200		25.0	315	21.9	22.5
205		37.5	320	23.5	25.4
210		38.5	325	25.4	27.9
215		40.2	330	29.1	29.9
220		39.6	335	31.4	34.5
225		32.4	340	32.3	38.8
230		24.3	345	34.3	40.7
235		14.8	350	31.1	41.0
240		6.70	355	43.7	51.3
245		4.35	360	39.0	45.1
250		2.83	365	53.7	57.8
255		1.45	370	48.7	54.2
260		1.90	375	50.0	53.5
265		2.05	380	59.3	59.9
270		3.13	385	57.9	59.4
275		4.02	390	54.9	60.0
280		5.54	395	56.2	58.9
285		6.99	400	66.6	67.6
290	6.77	8.18	405	59.6	63.2
295	8.52	9.67	410	53.2	57.7

Table 11. Quantum Yields for NO_2 Photolysis

λ,nm	Φ	λ,nm	Φ	λ,nm	Φ
375	0.77	389	0.78	400	0.68
376	0.78	390	0.80	401	0.65
377	0.92	391	0.88	402	0.62
378	0.82	392	0.84	403	0.57
379	0.87	393	0.90	404	0.42
380	0.90	394	0.90	405	0.32
381	0.81	394.5	0.86	406	0.33
382	0.70	395	0.84	407	0.25
383	0.68	395.5	0.81	408	0.20
384	0.70	396	0.83	409	0.19
385	0.77	396.5	0.88	410	0.15
386	0.84	397	0.82	411	0.10
387	0.75	398	0.77	415	0.067
388	0.81	399	0.78	420	0.023

295-365 nm: $\Phi(\lambda) = 1.0 - 0.0008\ (\lambda(\mathrm{nm})-275)$

$$NO_3 + h\nu \rightarrow NO + O_2 \quad (\Phi_1)$$

$$\rightarrow NO_2 + O \quad (\Phi_2)$$

The absorption cross sections of the nitrate free radical, NO_3, have been studied by (1) Johnston and Graham (1974); (2) Graham and Johnston (1978); (3) Mitchell et al. (1980); (4) Marinelli et al. (1982); and (5) Ravishankara and Wine (1983). The 1st and 4th studies required calculation of the NO_3 concentration by modeling a complex kinetic system. The 2nd, 3rd and 5th studies are more direct and the results in terms of integrated absorption coefficients are in good agreement. A sample of the absorption cross sections is presented in Table 12. These values are taken from the study of Ravishankara and Wine (1983), which gives a peak cross section value around 662 nm of 1.8×10^{-17} cm^2. Note, however, that there are some very recent flash photolysis measurements by Sander (private communication, 1985) which indicate that the cross sections might be about 25% larger. Furthermore, the cross sections for the 662 nm band appear to be strongly temperature dependent (Sander, private communication, 1985; Ravishankara, private communication, 1985).

The quantum yields Φ_1 and Φ_2 have been measured by Graham and Johnston (1978) and under higher resolution by Magnotta and Johnston (1980), who report the product of the cross section times the quantum yield in the 400 to 630 nm range. The total quantum yield value $\Phi_1 + \Phi_2$ computed from the results of this latter study and the cross sections of Graham and Johnston (1978) are above unity for $\lambda < 610$ nm, which is, of course, impossible; hence, there is some systematic error and it is most likely in the primary quantum yield measurements. Magnotta and Johnston (1980) and Marinelli et al. (1982) have discussed the probable sources of this error, but the question remains to be resolved and further studies are in order. At present, the recommendation remains unchanged, namely, to use the following photodissociation rates estimated by Magnotta and Johnston (1980) for overhead sun at the earth's surface:

$$J_1(NO + O_2) = 0.022\ s^{-1}$$

$$J_2(NO_2 + O) = 0.18\ s^{-1}.$$

Table 12. Absorption Cross Sections of NO_3 at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
571	226	605	365	639	157
572	224	606	291	640	111
573	220	607	194	641	92
574	221	608	143	642	85
575	240	609	125	643	83
576	270	610	116	644	84
577	288	611	139	645	80
578	286	612	166	646	65
579	263	613	203	647	65
580	277	614	213	648	55
581	305	615	180	649	46
582	259	616	157	650	46
583	231	617	153	651	46
584	213	618	162	652	47
585	203	619	185	653	48
586	263	620	236	654	65
587	319	621	342	655	83
588	407	622	795	656	122
589	504	623	1238	657	162
590	490	624	998	658	185
591	434	625	698	659	278
592	397	626	628	660	522
593	397	627	628	661	1063
594	323	628	619	662	1756
595	351	629	601	663	1618
596	368	630	555	664	1017
597	351	631	425	665	615
598	305	632	342	666	397
599	250	633	157	667	185
600	222	634	110	668	125
601	222	635	102	669	92
602	251	636	139	670	70
603	296	637	162		
604	360	638	171		

$N_2O + h\nu \rightarrow N_2 + O(^1D)$

The recommended values are taken from the work of Selwyn et al. (1977), who measured the temperature dependence of the absorption cross sections in the atmospherically relevant wavelength region. They have fitted their data with the expression shown in Table 13; Table 14 presents the room temperature data. Hubrich and Stuhl (1980) remeasured the N_2O cross sections at 298 K and 208 K, and their results are in very good agreement with those of Selwyn et al.

Table 13. Mathematical Expression for Absorption Cross Sections of N_2O as a Function of Temperature

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$$\ln \sigma(\lambda,T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4$$
$$+ (T-300)\exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

Where: T: temperature, Kelvin λ : nm

$A_1 = 68.21023$

$A_2 = -4.071805$

$A_3 = 4.301146 \times 10^{-2}$

$A_4 = -1.777846 \times 10^{-4}$

$A_5 = 2.520672 \times 10^{-7}$

$B_1 = 123.4014$

$B_2 = -2.116255$

$B_3 = 1.111572 \times 10^{-2}$

$B_3 = -1.881058 \times 10^{-5}$

Range: 173 to 240 nm; 194 to 320 K

Table 14. Absorption Cross Sections of N_2O at 298 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
173	11.3	196	6.82	219	0.115
174	11.9	197	6.10	220	0.0922
175	12.6	198	5.35	221	0.0739
176	13.4	199	4.70	222	0.0588
177	14.0	200	4.09	223	0.0474
178	13.9	201	3.58	224	0.0375
179	14.4	202	3.09	225	0.0303
180	14.6	203	2.67	226	0.0239
181	14.6	204	2.30	227	0.0190
182	14.7	205	1.95	228	0.0151
183	14.6	206	1.65	229	0.0120
184	14.4	207	1.38	230	0.00955
185	14.3	208	1.16	231	0.00760
186	13.6	209	0.980	232	0.00605
187	13.1	210	0.755	233	0.00478
188	12.5	211	0.619	234	0.00360
189	11.7	212	0.518	235	0.00301
190	11.1	213	0.421	236	0.00240
191	10.4	214	0.342	237	0.00191
192	9.75	215	0.276	238	0.00152
193	8.95	216	0.223	239	0.00123
194	8.11	217	0.179	240	0.00101
195	7.57	218	0.142		

$N_2O_5 + h\nu \rightarrow$ products

The absorption cross sections of dinitrogen pentoxide, N_2O_5, have been measured at room temperature by Jones and Wulf (1937) between 285 and 380 nm, by Johnston and Graham (1974) between 210 and 290 nm, by Graham (1975) between 205 and 310 nm; and for temperatures in the 223 to 300 K range by Yao et al. (1982), between 200 and 380 nm. The agreement is good particularly considering the difficulties in handling N_2O_5. The recommended cross section values, listed in Table 15, are taken from Yao et al. (1982); for wavelengths shorter than 280 nm there is little or no temperature dependence, and between 285 and 380 nm the temperature effect is best computed with the expression listed at the bottom of Table 15.

There are now several studies on the primary photolysis products of N_2O_5: Swanson et al. (1984) have measured the quantum yield for NO_3 production at 249 and at 350 nm obtaining a value close to unity, a result consistent with the observations of Burrows et al. (1984b) for photolysis at 254 nm. Barker et al. (1985) report a quantum yield for $O(^3P)$ production at 290 nm of less than 0.1, and near unity for NO_3. For O-atom production Margitan (private communication, 1985) measures a quantum yield value of 0.35 at 266 nm, and Ravishankara (private communication, 1985) reports values of 0.7, 0.35, 0.22 and 0.15 at 248, 266, 287 and 291 nm respectively with a quantum yield near unity for NO_3 production at all these wavelengths. It appears, then, that NO_3 is produced with unit quantum yield while the O-atom and hence the NO yield increases at shorter wavelengths with a consequent decrease in the NO_2 yield.

Table 15. Absorption Cross Sections of N_2O_5

λ(nm)	$10^{20}\sigma$(cm^2)	λ(nm)	$10^{20}\sigma$(cm^2)
200	920	245	52
205	820	250	40
210	560	255	32
215	370	260	26
220	220	265	20
225	144	270	16.1
230	99	275	13.0
235	77	280	11.7
240	62		

For 285 nm $< \lambda <$ 380 nm; 300 K $> T >$ 225 K:

$$10^{20}\sigma = \exp[2.735 + ((4728.5 - 17.127\ \lambda)/T)]$$

Where σ/cm^2; λ/nm; T/K.

$HONO + h\nu \rightarrow OH + NO$

The ultraviolet spectrum of HONO between 300 and 400 nm has been studied by Stockwell and Calvert (1978) by examination of its equilibrium mixtures with NO, NO_2, H_2O, N_2O_3 and N_2O_4; the possible interferences by these compounds were taken into account. The recommended cross sections, taken from this work, are listed in Table 16.

Table 16. HONO Absorption Cross Sections

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
310	0.0	339	16.3	368	45.0
311	0.0	340	10.5	369	29.3
312	0.2	341	8.70	370	11.9
313	0.42	342	33.5	371	9.46
314	0.46	343	20.1	372	8.85
315	0.42	344	10.2	373	7.44
316	0.3	345	8.54	374	4.77
317	0.46	346	8.32	375	2.7
318	3.6	347	8.20	376	1.9
319	6.10	348	7.49	377	1.5
320	2.1	349	7.13	378	1.9
321	4.27	350	6.83	379	5.8
322	4.01	351	17.4	380	7.78
323	3.93	352	11.4	381	11.4
324	4.01	353	37.1	382	14.0
325	4.04	354	49.6	383	17.2
326	3.13	355	24.6	384	19.9
327	4.12	356	11.9	385	19.0
328	7.55	357	9.35	386	11.9
329	6.64	358	7.78	387	5.65
330	7.29	359	7.29	388	3.2
331	8.70	360	6.83	389	1.9
332	13.8	361	6.90	390	1.2
333	5.91	362	7.32	391	0.5
334	5.91	363	9.00	392	0.0
335	6.45	364	12.1	393	0.0
336	5.91	365	13.3	394	0.0
337	4.58	366	21.3	395	0.0
338	19.1	367	35.2	395	0.0

$HNO_3 + h\nu \rightarrow OH + NO_2$

The recommended absorption cross sections, listed in Table 17, are taken from the work of Molina and Molina (1981). These data are in good agreement throughout the 190-330 nm range with the values reported by Biaume (1973). They are also in very good agreement with the data of Johnston and Graham (1973) except towards both ends of the wavelength range. Okabe (1980) has measured the cross sections in the 110-190 nm range; his results are 20-30% lower than those of Biaume and of Johnston and Graham around 185-190 nm.

The temperature dependence of these cross sections has not been measured yet; it might be significant in the 300 nm region and hence for estimates of the atmospheric photodissociation rate.

Johnston et al. (1974) measured a quantum yield value of ~1 for the $OH + NO_2$ channel in the 200-315 nm range, using end product analysis. The quantum yield for O-atom production at 266 nm has been measured to be 0.03, and that for H-atom production less than 0.002, by Margitan and Watson (1982), who looked directly for these products using atomic resonance fluorescence.

Table 17. Absorption Cross Sections of HNO_3 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1560	260	1.88
195	1150	265	1.71
200	661	270	1.59
205	293	275	1.35
210	105	280	1.10
215	35.6	285	0.848
220	15.1	290	0.607
225	8.62	295	0.409
230	5.65	300	0.241
235	3.72	305	0.146
240	2.57	310	0.071
245	2.10	315	0.032
250	1.91	320	0.012
255	1.90	325	0.005
		330	0.002

$HO_2NO_2 + h\nu \rightarrow$ products

There are four studies of the UV spectrum of HO_2NO_2 vapor: Cox and Patrick (1979), Morel et al., (1980), Graham et al. (1978b) and Molina and Molina (1981). The latter two studies are the only ones covering the gas phase spectrum in the critical wavelength range for atmospheric photodissociation, that is, wavelengths longer than 290 nm. The recommended values, listed in Table 18 are taken from the work of Molina and Molina (1981), which is the more direct study. The temperature dependence of the cross sections at these longer wavelengths and the identity of the photodissociation products remain to be determined.

Table 18. Absorption Cross Sections of HO_2NO_2 Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	1010	260	27.8
195	816	265	22.4
200	563	270	17.8
205	367	275	13.4
210	241	280	9.3
215	164	285	6.3
220	120	290	4.0
225	95.2	295	2.6
230	80.8	300	1.6
235	69.8	305	1.1
240	59.1	310	0.7
245	49.7	315	0.4
250	41.8	320	0.3
255	35.1	325	0.2
		330	0.1

$Cl_2 + h\nu \rightarrow Cl + Cl$

The absorption cross sections of Cl_2, listed in Table 19, are taken from the work of Seery and Britton (1964). These results are in good agreement with those reported by Gibson and Bayliss (1933), and Fergusson et al. (1936).

Table 19. Absorption Cross Sections of Cl_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
240	0.08	350	18.9
250	0.12	360	13.1
260	0.23	370	8.3
270	0.88	380	4.9
280	2.7	390	3.3
290	6.5	400	1.9
300	12.0	410	1.3
310	18.5	420	0.99
320	23.6	430	0.73
330	25.6	440	0.53
340	23.6	450	0.34

$C\ell O + h\nu \rightarrow C\ell O + O$

The absorption cross sections of chlorine monoxide, $C\ell O$, have been reviewed by Watson (1977). There are more recent measurements yielding results in reasonable agreement with the earlier ones, by Mandelman and Nicholls (1977) in the 250-310 nm region; by Wine *et al*. (1977) around 283 nm; and by Rigaud *et al*. (1977) and Jourdain *et al*. (1978) in the 270-310 nm region.

The calculations of Coxon *et al*. (1976) and Langhoff *et al*. (1977) indicate that photodecomposition of $C\ell O$ accounts for at most 2 to 3 percent of the total destruction rate of $C\ell O$ in the stratosphere, which occurs predominantly by reaction with oxygen atoms and nitric oxide.

$ClOO + h\nu \rightarrow ClO + O$

Johnston *et al.* (1969) measured the absorption cross sections of the ClOO radical using a molecular-modulation technique which required interpretation of a complex kinetic scheme. The values listed in Table 20 are taken from their work.

Table 20. Absorption Cross Sections of ClOO

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
225	260	255	1240
230	490	260	1000
235	780	265	730
240	1050	270	510
245	1270	275	340
250	1230	280	230

$OC\ell O + h\nu \rightarrow O + C\ell O$

The spectrum of $OC\ell O$ is characterized by a series of well developed progressions of bands extending from ~280 to 480 nm. The spectroscopy of this molecule has been studied extensively, and the quantum yield for photodissociation appears to be unity throughout the above wavelength range--see, for example, the review by Watson (1977).

Birks *et al*. (1977) have estimated a half-life against atmospheric photodissociation of $OC\ell O$ of a few seconds.

ClO_3 + hν → products

Table 21 lists absorption cross sections of chlorine trioxide, ClO_3, for the 200 to 350 nm range obtained by graphical interpolation between the data points of Goodeve and Richardson (1937). Although the quantum yield for decomposition has not been measured, the continuous nature of the spectrum indicates that it is likely to be unity.

Table 21. ClO_3 Absorption Cross Sections

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
200	530	280	460
210	500	290	430
220	480	300	400
230	430	310	320
240	350	320	250
250	370	330	180
260	430	340	110
270	450	350	76

$HCl + h\nu \rightarrow H + Cl$.

The absorption cross sections of HCl, listed in Table 22, are taken from the work of Inn (1975).

Table 22. Absorption Cross Sections of HCl Vapor

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
140	211	185	31.3
145	281	190	14.5
150	345	195	6.18
155	382	200	2.56
160	332	205	0.983
165	248	210	0.395
170	163	215	0.137
175	109	220	0.048
180	58.8		

$HOCl + h\nu \rightarrow OH + Cl$

Knauth et al. (1979) have measured absorption cross sections of HOCl using essentially the same technique as Molina and Molina (1978) except for a higher temperature, which allowed them to obtain a more accurate value for the equilibrium constant Keq for the H_2O-Cl_2O-HOCl system. The cross section values from Molina and Molina's measurements recalculated using the new Keq are in excellent agreement with the results of Knauth et al. The recommended values, taken from this later work, are presented in Table 23.

Molina et al. (1980b), by monitoring directly OH radicals produced by laser photolysis of HOCl, obtain an absorption cross section value of ~6 x 10^{-20} cm^2 around 310 nm, again in excellent agreement with the data of Knauth et al. (1979).

In contrast, the theoretical predictions of Jaffe and Langhoff (1978) indicate negligible absorption at those wavelengths. The reason is not known, although it should be pointed out that no precedent exists to validate the theoretical approach for this particular type of problem.

Butler and Phillips (1983) found no evidence for O-atom production at 308 nm, and placed an upper limit of ~0.02 for the primary quantum yield for the HCl + O channel.

Table 23. Absorption Cross Sections of HOCℓ

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
200	5.2	310	6.2
210	6.1	320	5.0
220	11.0	330	3.7
230	18.6	340	2.4
240	22.3	350	1.4
250	18.0	360	0.8
260	10.8	370	0.45
270	6.2	380	0.24
280	4.8	390	0.15
290	5.3	400	0.05
300	6.1	420	0.04

$C\ell NO + h\nu \rightarrow C\ell + NO$

Nitrosyl chloride has a continuous absorption extending beyond 650 nanometers. There is good agreement between the work of Martin and Gareis (1956) for the 240 to 420 nm wavelength region, of Ballash and Armstrong (1974) for the 185 to 540 nm region, and of Illies and Takacs (1976) for the 190 to 400 nm region. These results indicate that the early data of Goodeve and Katz (1939) were seriously in error between 186 and 300 nm, whereas, at longer wavelengths, they are in good agreement with the most recent measurements.

The recommended absorption cross sections, listed in Table 24, are obtained by taking the mean of the results of Ballash and Armstrong (1974) and of Illies and Takacs (1976). The two sets of measurements agree within 20 percent, except in the region near 240 nm, where the values of Ballash and Armstrong are about 60 percent higher.

The quantum yield for the primary photolytic process has been reviewed by Calvert and Pitts (1966a); it is unity over the entire visible and near-ultraviolet bands.

Table 24. CℓNO Absorption Cross Sections

λ(nm)	$10^{20}\sigma(\mathrm{cm}^2)$
190	5270
200	6970
210	3180
220	1170
230	377
240	134
260	18.0
280	10.3
300	9.5
320	12.1
340	13.7
360	12.2
380	8.32
400	5.14

$C\ell NO_2 + h\nu \rightarrow$ products

The absorption cross sections of nitryl chloride, $C\ell NO_2$, have been measured between 230 and 330 nm by Martin and Gareis (1956), between 185 and 400 nm by Illies and Takacs (1976), and between 270 and 370 nm by Nelson and Johnston (1981). The results are in good agreement below 300 nm. Table 25 lists the recommended values which are taken from Illies and Takacs (1976) between 190 and 270 nm, and from Nelson and Johnston (1981) between 270 and 370 nm. These latter authors showed that an approximate 6% $C\ell_2$ impurity in the samples used by Illies and Takacs could explain the discrepancy in the results above 300 nm.

Nelson and Johnston (1981) report a value of one (within experimental error) for the quantum yield for production at $C\ell$ atoms; they also report a negligible quantum yield for the production of oxygen atoms.

Table 25. Absorption Cross Sections of $C\ell NO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	2690	290	18.1
200	455	300	15.5
210	339	310	12.5
220	342	320	8.70
230	236	330	5.58
240	140	340	3.33
250	98.5	350	1.78
260	63.7	360	1.14
270	37.2	370	0.72
280	22.3		

ClONO + hν → products

Measurements in the near-ultraviolet of the cross sections of chlorine nitrite (ClONO) have been made by Molina and Molina (1977). Their results are listed in Table 26. The characteristics of the spectrum and the instability of ClONO strongly suggest that the quantum yield for decomposition is unity. The Cl-O bond strength is only about 20 kilocalories, so that chlorine atoms are likely photolysis products.

Table 26. ClONO Absorption Cross Sections at 231 K

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

$ClONO_2$ + hν → products

The recommended cross section values, listed in Table 27, are taken from the work of Molina and Molina (1979), which supersedes the earlier work of Rowland, Spencer and Molina (1976).

The identity of the primary photolytic fragments has been investigated by several groups. Smith et al. (1977) report O + ClONO as the most likely products, using end product analysis and steady-state photolysis. The results of Chang et al. (1979a), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are Cl + NO_3. Adler-Golden and Wiesenfeld (1981), using a flash photolysis atomic absorption technique, find O-atoms to be the predominant photolysis product, and report a quantum yield for Cl-atom production of less than 4%. Marinelli and Johnston (1982b) report a quantum yield for NO_3 production at 249 nm between 0.45 and 0.85 with a most likely value of 0.55; they monitored NO_3 by tunable dye-laser absorption at 662 nm. Margitan (1983a) used atomic resonance fluorescence detection of O- and Cl-atoms and find the quantum yield at 266 and at 355 nm to be 0.9 ± 0.1 for Cl-atom production, and ~0.1 for O-atom production, with no discernible difference at the two wavelengths.

The preferred quantum yield values are 0.9 for the Cl + NO_3 channel, and a complementary value of 0.1 for the O + ClONO channel. The recommendation is based on Margitan (1983a), whose direct study is the only one with results at a wavelength longer than 290 nm, which is where atmospheric photodissociation will predominantly occur. The reason for the discrepancy with the studies by Adler-Golden and Weisenfeld (1981) and by Marinelli and Johnston (1982b) is almost surely that the rate constant for Cl + $ClNO_3$ is much faster (two orders of magnitude) than previously thought (Margitan, 1983a; Kurylo et al., 1983a).

Table 27. Absorption Cross Sections of $C\ell ONO_2$

λ	$10^{20}\sigma(cm^2)$			λ	$10^{20}\sigma(cm^2)$		
(nm)	227K	243K	296K	(nm)	227K	243K	296K
190	555	-	589	325	0.463	0.502	0.655
195	358	-	381	330	0.353	0.381	0.514
200	293	-	307	335	0.283	0.307	0.397
205	293	-	299	340	0.246	0.255	0.323
210	330	-	329	345	0.214	0.223	0.285
215	362	-	360	350	0.198	0.205	0.246
220	348	-	344	355	0.182	0.183	0.218
225	282	-	286	360	0.170	0.173	0.208
230	206	-	210	365	0.155	0.159	0.178
235	141	-	149	370	0.142	0.140	0.162
240	98.5	-	106	375	0.128	0.130	0.139
245	70.6	-	77.0	380	0.113	0.114	0.122
250	52.6	50.9	57.7	385	0.098	0.100	0.108
255	39.8	39.1	44.7	390	0.090	0.083	0.090
260	30.7	30.1	34.6	395	0.069	0.070	0.077
265	23.3	23.1	26.9	400	0.056	0.058	0.064
270	18.3	18.0	21.5	405	-	-	0.055
275	13.9	13.5	16.1	410	-	-	0.044
280	10.4	9.98	11.9	415	-	-	0.035
285	7.50	7.33	8.80	420	-	-	0.027
290	5.45	5.36	6.36	425	-	-	0.020
295	3.74	3.83	4.56	430	-	-	0.016
300	2.51	2.61	3.30	435	-	-	0.013
305	1.80	1.89	2.38	440	-	-	0.009
310	1.28	1.35	1.69	445	-	-	0.007
315	0.892	0.954	1.23	450	-	-	0.005
320	0.630	0.681	0.895				

Halocarbon Absorption Cross Sections and Quantum Yields

The primary process in the photodissociation of chlorinated hydrocarbons is well established: absorption of ultraviolet radiation in the lowest frequency band is interpreted as an n-σ^* transition involving excitation to a repulsive electronic state (antibonding in $C-C\ell$), which dissociates by breaking the carbon-chlorine bond (Majer and Simons, 1964). As expected, the chlorofluoromethanes--which are just a particular type of chlorinated hydrocarbons--behave in this fashion (Sandorfy, 1976). Hence, the quantum yield for photodissociation is expected to be unity for these compounds. There are several studies which show specifically that this is the case for $CF_2C\ell_2$, $CFC\ell_3$ and $CC\ell_4$. These studies--which have been reviewed in CODATA (1982)--also indicate that at shorter wavelengths two halogen atoms can be released simultaneously in the primary process.

Several authors have reinvestigated the absorption cross sections for $CC\ell_4$, $CC\ell_3F$, $CC\ell_2F_2$, $CHC\ell F_2$, and $CH_3C\ell$--e.g., Hubrich et al. (1977); Hubrich and Stuhl (1980); Vanlaethem-Meuree et al. (1978a,b); Green and Wayne (1976-1977)--and their results are in general in very good agreement with our earlier recommendations. Tables 28, 29 and 30 list the present recommendations for the cross sections of $CC\ell_4$, $CC\ell_3F$ and $CC\ell_2F_2$ respectively; these data are given by the mean of the values reported by various groups--those cited above as well as those referred to in earlier evaluations--as reviewed by CODATA (1982). For atmospheric photodissociation calculations the change in the cross section values with temperature is negligible for $CC\ell_4$ and $CFC\ell_3$; for $CF_2C\ell_2$ the temperature dependence is given by the expression at the bottom of Table 28.

The species $CHC\ell F_2$, $CH_3C\ell$ and $CH_3CC\ell_3$ are discussed individually; their absorption cross sections are listed in Tables 31, 32 and 34, respectively.

The absorption cross sections for various other halocarbons not listed in this evaluation have also been investigated: for $CC\ell F_3$, $CC\ell_2FCC\ell F_2$, $CC\ell F_2CC\ell F_2$ and $CC\ell F_2CF_3$ the values given by Hubrich and Stuhl (1980) at 298 K are in very good agreement with the earlier results of Chou *et al*. (1978) and of Robbins (1977); Hubrich and Stuhl also report values of 208 K for these species. Other absorption cross section measurement include the following: $CHC\ell_2F$ by Hubrich *et al*. (1977); $CHC\ell_3$, $CH_2C\ell_2$, $CH_2C\ell F$, $CF_3CH_2C\ell$, $CH_3CC\ell F_2$ and $CH_3CH_2C\ell$ by Hubrich and Stuhl (1980); $CHC\ell_3$, CH_3Br, $CHFC\ell_2$, $C_2F_4Br_2$, $C_2HC\ell_3$ and $C_2H_3C\ell_3$ by Robbins (1977); $CH_2C\ell_2$ and $CHC\ell_3$ by Vanlaethem-Meuree *et al*. (1978a); $CHC\ell_2F$, $CC\ell F_2CH_2C\ell$, $CF_3CH_2C\ell$, $CF_3CHC\ell_2$ and $CH_3CF_2C\ell$ by Green and Wayne (1976-1977); and CH_3Br, CH_2Br_2, $CBrF_3$, CBr_2F_2, $CBrC\ell F_2$, $CBrF_2CBrF_2$ and $CBrF_2CF_3$ by Molina *et al*. (1982).

As before, the recommendation for the photodissociation quantum yield value is unity for all these species.

Table 28. Absorption Cross Sections of CCl_4

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
174	995	218	21.8
176	1007	220	17.0
178	976	222	13.0
180	772	224	9.61
182	589	226	7.19
184	450	228	5.49
186	318	230	4.07
188	218	232	3.01
190	144	234	2.16
192	98.9	236	1.51
194	74.4	238	1.13
196	68.2	240	0.784
198	66.0	242	0.579
200	64.8	244	0.414
202	62.2	246	0.314
204	60.4	248	0.240
206	56.5	250	0.183
208	52.0	255	0.0661
210	46.6	260	0.0253
212	39.7	265	0.0126
214	33.3	270	0.0061
216	27.2	275	0.0024

Table 29. Absorption Cross Sections of $CC\ell_3F$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	316	208	21.2
172	319	210	15.4
174	315	212	10.9
176	311	214	7.52
178	304	216	5.28
180	308	218	3.56
182	285	220	2.42
184	260	220	1.60
186	233	224	1.10
188	208	226	0.80
190	178	228	0.55
192	149	230	0.35
194	123	235	0.126
196	99	240	0.0464
198	80.1	245	0.0173
200	64.7	250	0.00661
202	50.8	255	0.00337
204	38.8	260	0.00147
206	29.3		

Table 30. Absorption Cross Sections of CCl_2F_2

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
170	124	200	8.84
172	151	202	5.60
174	171	204	3.47
176	183	206	2.16
178	189	208	1.32
180	173	210	0.80
182	157	212	0.48
184	137	214	0.29
186	104	216	0.18
188	84.1	218	0.12
190	62.8	220	0.068
192	44.5	225	0.022
194	30.6	230	0.0055
196	20.8	235	0.0016
198	13.2	240	0.00029

$$\sigma_T = \sigma_{298}\exp[4.1 \times 10^{-4}(\lambda-184.9)(T-298)]$$

Where: σ_{298} : cross section at 298 K

λ : nm

T : temperature, Kelvin

$CHCℓF_2$ + hν → products

The preferred absorption cross sections, listed in Table 31, are the mean of the values reported by Robbins and Stolarski (1976) and Chou et al. (1976), which are in excellent agreement with each other. Hubrich et al. (1977) have reported cross sections for $CHCℓF_2$ at 298 K and 208 K. Their results indicate a significant temperature dependence for $\lambda > 200$ nm, and their room temperature values are somewhat higher than those of the former two groups.

Photolysis of $CHCℓF_2$ is rather unimportant throughout the atmosphere; reaction with OH radical is the dominant destruction process.

Table 31. Absorption Cross Sections of $CHCℓF_2$

λ(nm)	$10^{20}\sigma(cm^2)$
174	5.94
176	4.06
178	2.85
180	1.99
182	1.30
184	0.825
186	0.476
188	0.339
190	0.235
192	0.157
194	0.100
196	0.070
198	0.039
200	0.026
202	0.022
204	0.013

$CH_3C\ell + h\nu \rightarrow$ products

The preferred absorption cross sections, listed in Table 32, are those given by Vanlaethem-Meuree et al. (1978b). These values are in very good agreement with those reported by Robbins (1976) at 298 K, as well as with those given by Hubrich et al. (1977) at 298 K and 208 K, if the temperature trend is taken into consideration.

Table 32. Absorption Cross Sections of $CH_3C\ell$

λ (nm)	$10^{20}\sigma(cm^2)$ 296 K	279 K	255 K
186	24.7	24.7	24.7
188	17.5	17.5	17.5
190	12.7	12.7	12.7
192	8.86	8.86	8.86
194	6.03	6.03	6.03
196	4.01	4.01	4.01
198	2.66	2.66	2.66
200	1.76	1.76	1.76
202	1.09	1.09	1.09
204	0.691	0.691	0.691
206	0.483	0.475	0.469
208	0.321	0.301	0.286
210	0.206	0.189	0.172
212	0.132	0.121	0.102
214	0.088	0.074	0.059
216	0.060	0.048	0.033

$CCl_2O + h\nu \rightarrow$ products, $CClFO + h\nu \rightarrow$ products, and $CF_2O + h\nu \rightarrow$ products

Table 33 shows the absorption cross sections of CCl_2O (phosgene) and $CFClO$ given by Chou et al. (1977a), and of CF_2O taken from the work of Molina and Molina (1982). The spectrum of CF_2O shows considerable structure; the values listed in Table 33 are averages over each 50-wave number interval. The spectrum of $CFClO$ shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1966a).

The quantum yield for the photodissociation of CF_2O at 206 nm appears to be ~0.25 (Molina and Molina, 1982); additional studies of the quantum yield in the 200 nm region are required in order to establish the atmospheric photodissociation rate.

Table 33. Absorption Cross Sections of CCl_2O, $CClFO$, and CF_2O

λ (nm)	$10^{20}\sigma(cm^2)$		
	CCl_2O	$CClFO$	CF_2O
184.9	204.0	-	-
186.0	189.0	15.6	5.5
187.8	137.0	14.0	4.8
189.6	117.0	13.4	4.2
191.4	93.7	12.9	3.7
193.2	69.7	12.7	3.1
195.1	52.5	12.5	2.6
197.0	41.0	12.4	2.1
199.0	31.8	12.3	1.6
201.0	25.0	12.0	1.3
203.0	20.4	11.7	0.95
205.1	16.9	11.2	0.69
207.3	15.1	10.5	0.50
209.4	13.4	9.7	0.34
211.6	12.2	9.0	0.23
213.9	11.7	7.9	0.15
216.2	11.6	6.9	0.10
218.6	11.9	5.8	0.06
221.0	12.3	4.8	0.04
223.5	12.8	4.0	0.03
226.0	13.2	3.1	-

CH_3CCl_3 + hν → products

The absorption cross sections have been measured by Robbins (1977), by Vanlaethem-Meuree et al. (1979) and by Hubrich and Stuhl (1980). These latter authors corrected the results to account for the presence of a UV-absorbing stabilizer in their samples, a correction which might account for the rather large discrepancy with the other measurements. The results of Robbins (1977) and of Vanlaethem-Meuree et al. (1979) are in good agreement. The recommended values are taken from this latter work (which reports values at 210 K, 230 K, 250 K, 270 K and 295 K, every 2 nm, and in a separate table at wavelengths corresponding to the wavenumber intervals generally used in stratospheric photodissociation calculations). Table 34 lists the values at 210 K, 250 K and 295 K, every 5 nm; the odd wavelength values were computed by linear interpolation.

Table 34. Absorption Cross Sections of CH_3CCl_3

λ (nm)	$10^{20}\sigma(cm^2)$ 295 K	250 K	210 K
185	265	265	265
190	192	192	192
195	129	129	129
200	81.0	81.0	81.0
205	46.0	44.0	42.3
210	24.0	21.6	19.8
215	10.3	8.67	7.47
220	4.15	3.42	2.90
225	1.76	1.28	0.97
230	0.700	0.470	0.330
235	0.282	0.152	0.088
240	0.102	0.048	0.024

$BrO + h\nu \rightarrow Br + O$

The BrO radical has a banded spectrum in the 290-380 nm range, the strongest absorption feature lying around 338 nm. The photodissociation quantum yield in this wavelength range is expected to be unity due to extensive predissociation.

The recommended absorption cross sections averaged over 5 nm wavelength intervals are taken from the work of Cox et al. (1982), and are listed in Table 35. These authors estimate a BrO lifetime against atmospheric photodissociation of ~20 seconds at the earth's surface, for a solar zenith angle of 30°.

The earlier BrO cross section measurements were carried out mostly around 338 nm, and have been reviewed by CODATA (1980; 1982).

Table 35. Absorption Cross Sections of BrO

λ (nm)	$10^{20}\sigma(cm^2)$ average
300 - 305	200
305 - 310	259
310 - 315	454
315 - 320	391
320 - 325	600
325 - 330	753
330 - 335	628
335 - 340	589
340 - 345	515
345 - 350	399
350 - 355	228
355 - 360	172
360 - 365	161
365 - 370	92
370 - 375	51

$BrONO_2 + h\nu \rightarrow$ products

The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm; their results are given in Table 36. The photolysis products are not known.

Table 36. Absorption Cross Sections of $BrONO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.9

$HF + h\nu \rightarrow H + F$

The ultraviolet absorption spectrum of HF has been studied by Safary et al. (1951). The onset of absorption occurs at $\lambda < 170$ nm, so that photodissociation of HF should be unimportant in the stratosphere.

$H_2CO + h\nu \rightarrow H + HCO \quad (\Phi_1)$

$\rightarrow H_2 + CO \quad (\Phi_2)$

Bass et al. (1980) have measured the absorption cross sections of formaldehyde with a resolution of 0.05 nm at 296 K and 223 K. The cross sections have also been measured by Moortgat et al. (1980; 1983) with a resolution of 0.5 nm in the 210-360 K temperature range; their values are ~30% larger than those of Bass et al. for wavelengths longer than 300 nm. The recommended cross section values, listed in Table 37, are the mean of the two sets of data (as computed in CODATA, 1982).

The quantum yields have been reported with good agreement by Horowitz and Calvert (1978), Clark et al. (1978a), Tang et al. (1979), Moortgat and Warneck (1979), and Moortgat et al. (1980; 1983). The recommended values listed in Table 37 are based on the results of all of these investigators. The quantum yield Φ_2 is pressure dependent for wavelengths longer than 329 nm, and is given by the expression at the bottom of Table 37, which is based on the values reported by Moortgat et al. (1980; 1983) for 300 K.

Additional work is needed to determine Φ_1 and the cross sections around 330 nm, which is the important wavelength region for atmospheric photodissociation of CH_2O to yield H + HCO; only a few scattered measurements of Φ_1 have been carried out around this wavelength. At present the recommendation for the 320-340 nm wavelength interval is to calculate Φ_1 by linear interpolation assuming a value of $\Phi_1 = 0.62$ at 320 nm and $\Phi_1 = 0$ at 340 nm.

Table 37. Absorption Cross Sections and Quantum Yields for Photolysis of CH_2O.

λ	$10^{20}\sigma(cm^2)$		Φ_1	Φ_2
(nm)	290 K	220 K	(H + HCO)	(H_2 + CO)
240	0.03	0.08	0.21	0.42
250	0.13	0.08	0.24	0.46
260	0.47	0.47	0.30	0.48
270	0.86	0.85	0.40	0.46
280	1.86	1.93	0.59	0.35
290	2.51	2.47	0.71	0.26
300	2.62	2.58	0.78	0.22
310	2.45	2.40	0.77	0.23
320	1.85	1.71	0.62	0.38
330	1.76	1.54	0.31	0.69
340	1.18	1.10	0	0.69*
350	0.42	0.39	0	0.40*
360	0.06	0.02	0	0.12*

Note: The values are averaged for 10 nm intervals centered on the indicated wavelength.

* : at P = 760 torr

For $\lambda > 329$ nm, Φ_2 at a given wavelength (not averaged over 10 nm intervals) is given by the following expression:

$$\Phi_2 = \frac{1 - \exp(112.8 - 0.347\lambda)}{1 + \frac{P}{760}\left(\frac{\lambda - 329}{364 - \lambda}\right)}$$

λ : nm

P : torr

$CH_3OOH + h\nu \rightarrow$ products

Molina and Arguello (1979) have measured the absorption cross sections of CH_3OOH vapor. Their results are listed in Table 38.

Table 38. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
210	37.5	290	0.90
220	22.0	300	0.58
230	13.9	310	0.34
240	8.8	320	0.19
250	5.8	330	0.11
260	3.8	340	0.06
270	2.5	350	0.04
280	1.5		

$HCN + h\nu \rightarrow$ products and $CH_3CN + h\nu \rightarrow$ products

Herzberg and Innes (1957) have studied the spectroscopy of hydrogen cyanide, HCN, which starts absorbing weakly at $\lambda < 190$ nm. McElcheran et al. (1958) have reported the spectrum of methyl cyanide, CH_3CN; the first absorption band appears at $\lambda < 216$ nm.

The solar photodissociation rates for these molecules should be rather small, even in the upper stratosphere; estimates of these rates would require additional studies of the absorption cross sections and quantum yields in the 200 nm region.

$SO_2 + h\nu \rightarrow$ products

The UV absorption spectrum of SO_2 is highly structured, with a very weak absorption in the 340-390 nm region, a weak absorption in the 260-340 nm, and a strong absorption extending from 180 to 235 nm; the threshold wavelength for photodissociation is ~220 nm. The atmospheric photochemistry of SO_2 has been reviewed by Heicklen et al. (1980) and by Calvert and Stockwell (1983). Direct photo-oxidation at wavelengths longer than ~300 nm by way of the electronically excited states of SO_2 appears to be relatively unimportant.

$OCS + h\nu \rightarrow CO + S$

The absorption cross sections of OCS have been measured by Breckenridge and Taube (1970), who presented their 298 K results in graphical form, between 200 and 260 nm; by Rudolph and Inn (1981) between 200 and ≈300 nm (see also Turco et al., 1981), at 297 and 195 K; by Leroy et al. (1981) at 294 K, between 210 and 260 nm, using photographic plates; and by Molina et al. (1981) between 180 and 300nm, at 295 and 225 K. The results are in good agreement in the regions of overlap, except for λ > 280 nm, where the cross section values reported by Rudolph and Inn (1981) are significantly larger than those reported by Molina et al. (1981). The latter authors concluded that solar photodissociation of OCS in the troposphere occurs only to a negligible extent.

The recommended cross sections, given in Table 39, are taken from Molina et al. (1981). (The original publication also lists a table with cross sections values averaged over 1 nm intervals, between 185 and 300 nm.)

The recommended quantum yield for photodissociation is 0.72. This value is taken from the work of Rudolph and Inn (1981), who measured the quantum yield for CO production in the 220-254 nm range.

Table 39. Absorption Cross Sections of OCS

λ	$10^{20}\sigma(cm^2)$		λ	$10^{20}\sigma(cm^2)$	
(nm)	295 K	225 K	(nm)	295 K	225 K
186.1	18.9	13. 0	228.6	26.8	23.7
187.8	8.33	5.63	231.2	22.1	18.8
189.6	3.75	2.50	233.9	17.1	14.0
191.4	2.21	1.61	236.7	12.5	9.72
193.2	1.79	1.53	239.5	8.54	6.24
195.1	1.94	1.84	242.5	5.61	3.89
197.0	2.48	2.44	245.4	3.51	2.29
199.0	3.30	3.30	248.5	2.11	1.29
201.0	4.48	4.50	251.6	1.21	0.679
203.1	6.12	6.17	254.6	0.674	0.353
205.1	8.19	8.27	258.1	0.361	0.178
207.3	10.8	10.9	261.4	0.193	0.0900
209.4	14.1	14.2	264.9	0.0941	0.0419
211.6	17.6	17.6	268.5	0.0486	0.0199
213.9	21.8	21.8	272.1	0.0248	0.0101
216.2	25.5	25.3	275.9	0.0119	0.0048
218.6	28.2	27.7	279.7	0.0584	0.0021
221.5	30.5	29.4	283.7	0.0264	0.0009
223.5	31.9	29.5	287.8	0.0012	0.0005
226.0	30.2	27.4	292.0	0.0005	0.0002
			296.3	0.0002	-

Photodissociation quantum yield Φ = 0.72

$CS_2 + h\nu \rightarrow CS + S$

The CS_2 absorption spectrum is rather complex. Its photochemistry has been reviewed by Okabe (1978). There are two distinct regions in the near UV spectrum: a strong absorption extending from 185 to 230 nm, and a weaker one in the 290-380 nm range. The threshold wavelength for photodissociation is ~280 nm.

The photo-oxidation of CS_2 in the atmosphere has been discussed by Wine _et al_. (1981d), who report that electronically excited CS_2 may react with O_2 to yield eventually OCS.

$NaC\ell + h\nu \rightarrow Na + C\ell$

$NaOH + h\nu \rightarrow Na + OH$

There are several studies on the UV absorption spectra of NaCℓ vapor; for a review see Rowland and Rogers (1982). These spectra have been inferred from high temperature studies, and the absorption cross section values at stratospheric temperatures are uncertain. The recommendation is to use the solar photodissociation rates estimated by Rowland and Rogers.

The spectrum of NaOH vapor is poorly characterized. Rowland and Makide (1982) inferred the absorption cross section values and the average solar photodissociation rate from the flame measurements of Daidoji (1979). Additional measurements are required.

REFERENCES

Adachi, H., and N. Basco, 1979, Chem. Phys. Lett. 63, p. 490.

Adler-Golden, S. M., and J. R. Wiesenfeld, 1981, Chem. Phys. Lett. 82, p. 281.

Ager, J. W., III, C. L. Talcott, and C. J. Howard, 1985, J. Phys. Chem. (to be submitted).

Aleksandrov, E. N., V. S. Arutyunov, and S. N. Kozlov, 1981, Kinetics and Catalysis 22, pp. 391-394.

Allen, M., and J. E. Frederick, 1982, J. Atmos. Sci. 39, pp. 2066-2075.

Amimoto, S. T., A. P. Force and J. R. Wiesenfeld, 1978, Chem. Phys. Lett. 60, pp. 40-43.

Amimoto, S. T., A. P. Force, R. G. Gulotty, Jr. and J. R. Wiesenfeld, 1979, J. Chem. Phys. 71, pp. 3640-3647.

Amimoto, S. T., A. P. Force, J. R. Wiesenfeld and R. H. Young, 1980, J. Chem. Phys. 73, pp. 1244-1247.

Anastasi, C., and I. W. M. Smith, 1976, J. Chem. Soc., Faraday Trans. II 72, pp. 1459-1468.

Anastasi, C., and I. W. M. Smith, 1978, J. Chem. Soc., Faraday Trans. II 74, p. 1056.

Anastasi, C., I. W. M. Smith and D. A. Parkes, 1978, J. Chem. Soc., Faraday Trans. I 74, pp. 1693-1701.

Anderson, J. G., and F. Kaufman, 1972, Chem. Phys. Lett. 16, 375-379.

Anderson, J. G., and F. Kaufman, 1973, Chem. Phys. Lett. 19, 483-486.

Anderson, J. G., J. J. Margitan and F. Kaufman, 1974, J. Chem. Phys. 60, p. 3310.

Anderson, P. C., and M. J. Kurylo, 1979, J. Phys. Chem. 83, p. 2055.

Andresen, P., A. Jacobs, C. Kleinermanns and J. Wolfrum, 1982, 19th Symp. (Intl.) Combustion, p. 11.

Arnold, I., and F. J. Comes, 1979, J. Chem. Phys. 42, p. 231.

Arrington, C. A., W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, 1965, J. Chem. Phys. 43, p. 525.

Arutyunov, V. S., L. S. Popov, and A. M. Chaikin, 1976, Kinet. Katal. 17, p. 286.

Ashford, R. D., N. Basco and J. E. Hunt, 1978, Int. J. Chem. Kinet. 10, pp. 1233-1244.

Ashmore, P. G., and M. S. Spencer, 1959, Trans. Faraday Soc. 55, p. 1868.

Atkinson, R., and S. M. Aschmann, 1984, Int. J. Chem. Kinetics 16, 1175-1186.

Atkinson, R., and J. N. Pitts, Jr., 1978, J. Chem. Phys. 68, p. 3581.

Atkinson, R., D. A. Hansen and J. N. Pitts, Jr., 1975, J. Chem. Phys. 63, pp. 1703-1706.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., 1977, J. Chem. Phys. 66, p. 1197.

Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., 1978, Chem. Phys. Lett. 54, p. 14.

Atkinson, R., C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., 1984, J. Phys. Chem. 88, pp. 1210-15.

Avramenko, L. I., and R. V. Kolesnikova, 1961, Bull. Acad. Sci. USSR Div. Chem. Sci., p. 545.

Bahta, A., R. Simonaitis, and J. Heicklen, 1982, J. Phys. Chem. 86, p. 1849.

Balakhnin, V. P., V. I. Egorov and E. I. Intezarova, 1971, Kinetics and Catalysis 12, p. 299.

Baldwin, A. C., 1982, "Thermochemistry of Peroxides," in Chemistry of Functional Groups (ed. S. Patai), John Wiley and Sons, Inc., New York.

Baldwin, A. C., and D. M. Golden, 1978a, Chem. Phys. Lett. 55, p. 350.

Baldwin, A. C., and D. M. Golden, 1978b, J. Phys. Chem. 82, p. 644.

Ballash, N. M., and D. A. Armstrong, 1974, Spectrochim. Acta 30A, pp. 941-944.

Barker, J. R., S. W. Benson and D. M. Golden, 1977, Int. J. Chem. Kinet. 9, p. 31.

Barker, J. R., M. J. Rossi, P. L. Trevor and D. M. Golden, 1985, Int. J. Chem. Kinet., in press.

Barnes, I., V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, 1981, Chem. Phys. Lett. 83, pp. 459-464.

Barnes, I., K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, 1983, Int. J. Chem. Kinet. 15, pp. 631-645.

Basco, N., and S. K. Dogra, 1971a, Proc. Roy. Soc. A. 323, p. 401.

Basco, N., and S. K. Dogra, 1971b, Proc. Roy. Soc. A. 323, p. 417.

Basco, N., and S. K. Dogra, 1971c, Proc. Roy. Soc. A. 323, p. 29.

Basco, N., D. G. L. James and F. C. James, 1972, Int. J. Chem. Kinet. 4, p. 129.

Bass, A. M., and A. E. Ledford, 1978, pp. 282-284 in 12th Informal Conference on Photochemistry, M. J. Kurylo and W. Braun, Eds., NBS, Spec. Publ. 526, National Bureau of Standards, Guithersburg, MD.

Bass, A. M., A. E. Ledford and A. H. Laufer, 1976, J. Res. NBS 80A, pp. 143-166.

Bass, A. M., L. C. Glasgow, C. Miller, J. P. Jesson, and D. L. Filken, 1980, Planet. Space Sci. 28, p. 675.

Batt, L., and G. N. Robinson, 1979, Int. J. Chem. Kinet. 11, p. 1045.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe and R. T. Watson, 1980, J. Phys. Chem. Ref. Data 9, p. 295.

Baulch, D. L., R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, 1982, J. Phys. Chem. Ref. Data 11, pp. 327-496.

Baulch, D. L., R. J. B. Craven, M. Din, D. D. Drysdale, S. Grant, D. J. Richardson, A. Walker, and G. Watling, 1983, J. Chem. Soc. Faraday Trans., 1, 79, pp. 689-698.

Becker, K. H., W. Groth and D. Z. Kley, 1969, Z. Naturforsch A24, p. 1280.

Bemand, P. P., M. A. A. Clyne and R. T. Watson, 1973, J. Chem. Soc., Faraday Trans. I. 69, p. 1356.

Bemand, P. P., M. A. A. Clyne and R. T. Watson, 1974, J. Chem. Soc., Faraday Trans. II 70, p. 564.

Beno, M. F., C. D. Jonah and W. A. Mulac, 1984, Int. J. Chem. Kinet. (submitted).

Benson, S. W., 1976, Thermochemical Kinetics, John Wiley and Sons, Inc., New York, p. 292.

Benson, S. W., F. R. Cruickshank and R. Shaw, 1969, Int. J. Chem. Kinet. 1, p. 29.

Bhaskaran, K. A., P. Frank and Th. Just, 1979, paper presented at 12th International Shock Tube Symposium, Jerusalem.

Biaume, F., 1973, J. Photochem. 2, p. 139.

Biermann, H. W., C. Zetzsch and F. Stuhl, 1978, Ber. Bunsenges. Phys. Chem. 82, p. 633.

Biermann, H. W., G. W. Harris and J. N. Pitts, Jr., 1982, J. Phys. Chem. 86, pp. 2958-2964.

Birks, J. W., B. Shoemaker, T. J. Leck and D. M. Hinton, 1976, J. Chem. Phys. 65, p. 5181.

Birks, J. W., B. Schoemaker, T. J. Leck, R. A. Borders and L. J. Hart, 1977, J. Chem. Phys. 66, p. 4591.

Black, G., 1984, J. Chem. Phys. 80, pp. 1103-1107.

Black, G., R. L. Sharpless, and T. G. Slanger, 1982a, Chem. Phys. Lett. 90, pp. 55-58.

Black, G., R. L. Sharpless, and T. G. Slanger, 1982b, Chem. Phys. Lett. 93, pp. 598-602.

Black, G., L. E. Jusinski, and T. G. Slanger, 1983, Chem. Phys. Lett. 102, pp. 64-68.

Black, G., R. Patrick, L. E. Jusinski, and T. G. Slanger, 1984, J. Chem. Phys. 80, 4065.

Borders, R. A., and J. W. Birks, 1982, J. Phys. Chem. 86, pp. 3295-3302.

Bozzelli, J. W., 1973, Ph.D. Thesis, Dept. of Chemistry, Princeton University, (Diss. Abstr. Int. B, 34(2), p. 608).

Bradley, J. N., W. Hack, K. Hoyermann, and H. Gg. Wagner, 1973, J. Chem. Soc., Faraday Trans. I. 69, p. 1889.

Braithwaite, M., and S. R. Leone, 1978, J. Chem. Phys. 69, pp. 839-845.

Braun, M., A. Hofzumahaus, and F. Stuhl, 1982, Ber. Bunsenges. Phys. Chem. 86, pp. 597-602.

Breckenridge, W. H., and T. A. Miller, 1972, J. Chem. Phys. 56, p. 465.

Breckenridge, W. H., and H. Taube, 1970, J. Chem. Phys. 52, pp. 1713-1715.

Breen, J. E., and G. P. Glass, 1971, Int. J. Chem. Kinet. 3, p. 145.

Brock, J. C., and R. T. Watson, 1980a, Chem. Phys. 46, pp. 477-484.

Brock, J. C., and R. T. Watson, 1980b, Chem. Phys. Lett. 71, pp. 371-375.

Brown, J. M., and B. A. Thrush, 1967, Trans. Faraday Soc. 63, p. 630.

Brown, R. D., and I. W. M. Smith, 1975, Int. J. Chem. Kinet. 7, p. 301.

Brune, W. H., J. J. Schwab, and J. G. Anderson, 1983, J. Phys. Chem. 87, 4503-4514.

Bulatov, V. P., A. A. Buloyan, S. G. Cheskis, M. Z. Kozliner, O. M. Sarkisov, and A. I. Trostin, 1980, Chem. Phys. Lett. 74, p. 288.

Burrows, J. P., and R. A. Cox, 1981, J. Chem. Soc., Faraday Trans. I 77, p. 2465.

Burrows, J. P., G. W. Harris and B. A. Thrush, 1977, Nature 267, pp. 233-234.

Burrows, J. P., D. I. Cliff, G. W. Harris, B. A. Thrush and J. P. T. Wilkinson, 1979, Proc. Roy. Soc. (London) A368, p. 463-481.

Burrows, J. P., R. A. Cox and R. G. Derwent, 1981, J. Photochem. 16, pp. 147-168.

Burrows, J. P., T. J. Wallington, and R. P. Wayne, 1983, J. Chem. Soc., Faraday Trans. II 79, pp. 111-122.

Burrows, J. P., T. J. Wallington, and R. P. Wayne, 1984a, J. Chem. Soc., Faraday Trans. 2, 80, pp. 957-971.

Burrows, J. P., G. S. Tyndall, and G. K. Moortgat, 1984b, paper presented at the 16th Informal Conf. on Photochemistry, Boston, August 1984.

Burrows, J. P., D. W. T. Griffith, G. K. Moortgat, and G. S. Tyndall, 1985, J. Phys. Chem. 89, 266-271.

Buss, R. J., R. J. Baseman, G. He, and Y. T. Lee, 1981, J. Photochem. 17, p. 389.

Butler, P. J. D., and L. F. Phillips, 1983, J. Phys. Chem. 87, pp. 183-184.

Butler, R., I. J. Solomon and A. Snelson, 1978, Chem. Phys. Lett. 54, p. 19.

Callear, A. B., and R. E. M. Hedges, 1970, Trans. Faraday Soc. 66, p. 605.

Callear, A. B., and I. W. M. Smith, 1967, Nature 213, p. 382.

Calvert, J. G., and J. N. Pitts, 1966a, Photochemistry, John Wiley & Sons, Inc., New York, pp. 230-231.

Calvert, J. G., and J. N. Pitts, 1966b, op. cit., p. 783.

Calvert, J. G., and W. R. Stockwell, 1983, in Acid Precipitation: SO_2, NO and NO_2 Oxidation Mechanisms: Atmospheric Considerations, Ann Arbor Sci. Publishers, Ann Arbor, Michigan.

Cannon, B. D., J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, 1984, Chem. Phys. Lett. 105, pp. 380-385.

Cantrell, C. A., W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekopf, J. G. Calvert, and H. S. Johnston, 1985, J. Phys. Chem. 89, pp. 139-146.

Caralp, F. and R. Lesclaux, 1983, Chem. Phys. Lett. 102, pp. 54-58.

Carter, R. O., and L. Andrews, 1981, J. Phys. Chem. 85, p. 2351.

Casavecchia, P., R. J. Buss, S. J. Sibener and Y. T. Lee, 1980, J. Chem. Phys. 73, pp. 6351-6332.

Chan, W. H., W. M. Huselman, J. G. Calvert, and J. H. Shaw, 1977, Chem. Phys. Lett. 45, p.240.

Chang, J. S., and J. R. Barker, 1979, J. Phys. Chem. 84, p. 3059.

Chang, J. S., and F. Kaufman, 1977a, J. Chem. Phys. 66, p. 4989.

Chang, J. S., and F. Kaufman, 1977b, Geophys. Res. Lett. 4, p. 192.

Chang, J. S., and F. Kaufman, 1978, J. Phys. Chem. 82, pp. 1683-1686.

Chang, J. S., A. C. Baldwin and D. M. Golden, 1979a, J. Chem. Phys. 71, p. 2021.

Chang, J. S., J. R. Barker, J. E. Davenport and D. M. Golden, 1979b, Chem. Phys. Lett. 60, pp. 385-390.

Chang, J. S., P. L. Trevor, and J. R. Barker, 1981, Int. J. Chem. Kinet. 13, pp. 1151-1161.

Chapman, C. J., and R. P. Wayne, 1974, Int. J. Chem. Kinet. 6, pp. 617-630.

Chen, H. L., D. W. Trainor, R. E. Cender, and W. T. Fyfe, 1977, J. Chem. Phys. 66, p. 5513.

Cheskis, S. G., and O. M. Sarkisov, 1979, Chem. Phys. Lett. 62, p. 72.

Chou, C. C., R. J. Milstein, W. S. Smith, H. Vera-Ruiz, M. J. Molina and F. S. Rowland, 1978, J. Phys. Chem. 82, p. 1.

Chueng, A. S. C., K. Yoshino, W. H. Parkinson, and D. E. Freeman, 1984, Geophys. Res. Lett. 11, p. 580

Clark, I. D., and R. P. Wayne, 1970, Proc. Roy. Soc. A316, p. 539.

Clark, J. H., C. B. Moore and N. S. Nogar, 1978a, J. Chem. Phys. 68, p. 1264.

Clark, J. H., C. B. Moore and J. B. Reilly, 1978b, Int. J. Chem. Kinet. 10, p. 427.

Clark R. H., D. Husain and J. Y. Jezequel, 1982, J. Photochem. 18, pp. 39-46.

Clark, T. C., M. A. A. Clyne and D. H. Stedman, 1966, Trans. Faraday Soc. 62, p. 3354.

Clemo, A. R., F. E. Davidson, G. L. Duncan, and R. Grice, 1981, Chem. Phys. Lett. 84, pp. 509-511.

Clough, P. N., and B. A. Thrush, 1967, Trans. Faraday Soc. 63, p. 915.

Clyne, M. A. A., and J. A. Coxon, 1968, Proc. Roy. Soc. A., 303, p. 207.

Clyne, M. A. A., and H. W. Cruse, 1970a, Trans. Faraday Soc. 66, p. 2214.

Clyne, M. A. A., and H. W. Cruse, 1970b, Trans. Faraday Soc. 66, p. 2227.

Clyne, M. A. A., and H. W. Cruse, 1972, J. Chem. Soc., Faraday Trans. II 68, p. 1281.

Clyne, M. A. A., and S. Down, 1974, J. Chem. Soc., Faraday Trans. II 70, pp. 253-266.

Clyne, M. A. A., and P. M. Holt, 1979a, J. Chem. Soc., Faraday Trans. II 75, pp. 564-581

Clyne, M. A. A., and P. M. Holt, 1979b, J. Chem. Soc., Faraday Trans. II 75, pp. 582-591.

Clyne, M. A. A., and A. J. MacRobert, 1980, Int. J. Chem. Kinet. 12, pp. 79-96.

Clyne, M. A. A., and A. J. MacRobert, 1981, Int. J. Chem. Kinet. 13, pp. 187-197.

Clyne, M. A. A., and I. S. McDermid, 1975, J. Chem. Soc., Faraday Trans. I 71, p. 2189.

Clyne, M. A. A., and P. Monkhouse, 1977, J. Chem. Soc., Faraday Trans. II 73, pp. 298-309.

Clyne, M. A. A., and W. S. Nip, 1976a, J. Chem. Soc., Faraday Trans. II 72, p. 838.

Clyne, M. A. A., and W. S. Nip, 1976b, J. Chem. Soc., Faraday Trans. I 72, p. 2211.

Clyne, M. A. A., and Y. Ono, 1982, Chem. Phys. 69, pp. 381-388.

Clyne, M. A. A., and Y. Ono, 1983, Chem. Phys. Lett. 94, pp. 597-602.

Clyne, M. A. A., and L. W. Townsend, 1975, Int. J. Chem. Kinet. Symp. 1, pp. 73-84.

Clyne, M. A. A., and B. A. Thrush, 1961, Proc. Roy. Soc. A261, p. 259.

Clyne, M. A. A., and R. F. Walker, 1973, J. Chem. Soc., Faraday trans. I 69, p. 1547.

Clyne, M. A. A., and R. T. Watson, 1974a, J. Chem. Soc., Faraday Trans. I. 70, p. 2250.

Clyne, M. A. A., and R. T. Watson, 1974b, J. Chem. Soc., Faraday Trans. I 70, p. 1109.

Clyne, M. A. A., and R. T. Watson, 1975, J. Chem. Soc., Faraday Trans. I 71, p. 336.

Clyne, M. A. A., and R. T. Watson, 1977, J. Chem. Soc., Faraday Trans. I 73, p. 1169.

Clyne, M. A. A., and P. D. Whitefield, 1979, J. Chem. Soc., Faraday Trans. II 75, p. 1327.

Clyne, M. A. A., B. A. Thrush, and R. P. Wayne, 1964, Trans. Faraday Soc. 60, p. 359.

Clyne, M. A. A., C. J. Halstead, and B. A. Thrush, 1966, Proc. Soc. London, Ser. A, 295, p. 355.

C-3

Clyne, M. A. A., D. J. McKenney, and R. F. Walker, 1973, Can. J. Chem. 51, p. 3596.

Clyne, M. A. A., P. B. Monkhouse, and L. W. Townsend, 1976, Int. J. Chem. Kinet. 8, p. 425.

Cobos, C. J., H. Hippler, and J. Troe, 1985, J. Phys. Chem. 89, 342-9.

CODATA, 1980, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. J. Phys. Chem. Ref. Data 9, pp. 295-471.

CODATA, 1982, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement I. J. Phys. Chem. Ref. Data 11, pp. 327-496.

Connell, P. S., and C. J. Howard, 1985, Int. J. Chem. Kinet. 17, p. 17.

Connell, P. S., and H. S. Johnston, 1979, Geophys. Rev. Lett. 6, p. 553.

Cook, J. L., C. A. Ennis, T. J. Leck, and J. W. Birks, 1981a, J. Chem. Phys. 74, p. 545.

Cook, J. L., C. A. Ennis, T. J. Leck, and J. W. Birks, 1981b, J. Chem. Phys. 75, p. 497.

Cooper, R., J. B. Cumming, S. Gordon, and W. A. Mulac, 1980, Radiat. Phys. Chem. 16, 169.

Cox, R. A., 1975, Int. J. Chem. Kinet., Symp. 1, p. 379.

Cox, R. A., 1980, Int. J. Chem. Kinet. 12, p. 649.

Cox, R. A., and J. P. Burrows, 1979, J. Phys. Chem. 83, p. 2560-2568.

Cox, R. A., and R. Lewis, 1979, J. Chem. Soc., Faraday Trans. I 75, p. 2649.

Cox, R. A., and R. Patrick, 1979, Int. J. Chem. Kinet. 11, p. 635.

Cox, R. A., and D. Sheppard, 1980, Nature 284, pp. 330-331.

Cox, R. A., and D. W. Sheppard, 1982, J. Chem. Soc., Faraday Trans. II 78, pp. 1383-1389.

Cox, R. A., and G. Tyndall, 1979, Chem. Phys. Lett. 65, p. 357.

Cox, R. A., and G. S. Tyndall, 1980, J. Chem. Soc., Faraday Trans. II 76, p. 153.

Cox, R. A., R. G. Derwent, and P. M. Holt, 1975, Chemosphere 4, p. 201.

Cox, R. A., R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, 1976a, Atmos. Environ. 10, p. 305.

Cox, R. A., R. G. Derwent, and P. M. Holt, 1976b, J. Chem. Soc., Faraday Trans. I 72, p. 2031.

Cox, R. A., R. G. Derwent, A. E. J. Eggleton and H. J. Read, 1979, J. Chem. Soc., Faraday Trans. I 75, pp. 1648-1666.

Cox, R. A., R. G. Derwent, S. V. Kearsey, L. Batt, and K. G. Patrick, 1980, J. Photochem. 13, p. 149.

Cox, R. A., J. P. Burrows, and T. J. Wallington, 1981, Chem. Phys. Lett. 84, p. 217-221.

Cox, R. A., D. W. Sheppard, and M. P. Stevens, 1982, J. Photochem. 19, pp. 189-207.

Cox, R. A., R. A. Barton, E. Ljungstrom, and D. W. Stocker, 1984a, Chem. Phys. Lett. 108, pp. 228-232.

Cox, R. A., J. P. Burrows, and G. B. Coker, 1984b, Int. J. Chem. Kinet. 16, pp. 445-67.

Coxon, J. A., W. E. Jones and D. A. Ramsey, 1976, 12th International Symposium on Free Radicels, Laguna Beach, California.

Croce de Cobos, A. E., H. Hippler, and J. Troe, 1984, J. Phys. Chem. 88, pp. 5083-5086.

Cupitt, L. T. and G. P. Glass, 1975, Int. J. Chem. Kinet., Symp. 1, pp. 39-50.

Daidoji, H., 1979, Bunseki Kagaku 28, p. 77.

Dasch, W., K.-H. Steinberg, and R. N,. Schindler, 1981, Ber. Bunsenges. Phys. Chem., 85, p. 611.

Davenport, J. E., 1978, "Determination of NO_2 Photolysis Parameters for Stratospheric Modeling," Report No. FAA-EQ-78-14, FAA, Washington, D.C.

Davenport, J. E., B. Ridley, H. I. Schiff, and K. H. Welge, 1972, J. Chem. Soc., Faraday Discussion, 53, pp. 230-231.

Davidson, F. E., A. R. Clemo, G. L. Duncan, R. J. Browett, J. H. Hobson, and R. Grice, 1982, Molec. Phys. 46, pp. 33-40.

Davidson, J. A., H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, 1977, J. Chem. Phys. 67, pp. 5021-5025.

Davidson, J. A., H. I. Schiff, T. J. Brown, and C. J. Howard, 1978, J. Chem. Phys. 69, pp. 4277-4279.

Davidson, J. A., C. J. Howard, H. I. Schiff, and F. C. Fehsenfeld, 1979, J. Chem. Phys. 70, pp. 1697-1704.

Davis, D. D., W. Braun, and A. M. Bass, 1970, Int. J. Chem. Kinet. 2, p. 101.

Davis, D. D., R. B. Klemm, and M. Pilling, 1972, Int. J. Chem. Kinet. 4, pp. 367-382.

Davis, D. D., J. T. Herron, and R. E. Huie, 1973a, J. Chem. Phys. 58, p. 530.

Davis, D. D., W. Wong, and J. Lephardt, 1973b, Chem. Phys. Lett. 22, pp. 273-278.

Davis, D. D., S. Fischer, and R. Schiff, 1974a, J. Chem. Phys. 61, pp. 2213-2219.

Davis, D. D., J. Prusazcyk, M. Dwyer, and P. Kim., 1974b, J. Phys. Chem. 78, p. 1775-9.

Davis, D. D., W. Wong, and R. Schiff, 1974c, J. Phys. Chem. 78, pp. 463-464.

Davis, D. D., S. Fischer, R. Schiff, R. T. Watson, and W. Bollinger, 1975, J. Chem. Phys. 63, p. 1707.

Davis, D. D., G. Machado, B. Conaway, Y. Oh, and R. T. Watson, 1976, J. Chem. Phys. 65, p. 1268.

DeMore, W. B., 1979, J. Phys. Chem. 83, pp. 1113-1118.

DeMore, W. B., 1981, results presented at 182nd National Meeting, American Chemical Society, New York, August, 1981.

DeMore, W. B., 1982, J. Phys. Chem. 86, pp. 121-126.

DeMore, W. B., 1984, Int. J. Chem. Kinet. 16, pp. 1187-1200.

DeMore, W. B., and E. Tschuikow-Roux, 1974, J. Phys. Chem. 78, pp. 1447-1451.

DeMore, W. B., C. L. Lin, and S. Jaffe, 1976, "12th Informal Conference on Photochemistry", M. J. Kurylo and W. Braun, Eds., NBS Spec. Publ. 526 (1978), pp. 287-289.

DeMore, W. B., L. J. Stief, F. Kaufman, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, 1979, JPL Publication 79-27, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

DeMore, W. B., D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, L. J. Stief, and R. T. Watson, 1981, JPL Publication 81-3, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

DeMore, W. B., D. M. Golden, R. F. Hampson, C. J. Howard, M. J. Kurylo, M. J. Molina, A. R. Ravishankara, and R. T. Watson, 1982, JPL Publication 82-57, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Devolder, P., M. Carlier, J. F. Pauwels and L. R. Sochet, 1984, Chem. Phys. Lett. 111, pp. 94-9.

Dickerson, R. R., and D. H. Stedman, 1980, Environ. Sci. Technol. 14, p. 1261.

Ditchburn, R. W., and P. A. Young, 1962, J. Atmos. Terrest. Phys. 24, pp. 127-139.

Dodonov, A. F., G. K. Lavrovskaya, I. I. Morozov, and V. L. Tal'Roze, 1971, Dokl. Adak. Nauk USSR, 198, 662; Dokl. Phys. Chem. (Engl. Trans), 198, p. 440.

Dognon, A. M., F. Caralp, and R. Lesclaux, 1985, J. Chim. Phys. Phys.-Chim. Biol., in press.

Donovan, R. J., and D. J. Little, 1972, Chem. Phys. Lett. 13, p. 488.

Dreier, T., and J. Wolfrum, 1980, 18th International Symposium on Combustion, pp. 801-809.

Eibling, R. E., and M Kaufman, 1983, Atmos. Environ. 17, pp. 429-431.

Fair, R. W., and B. A. Thrush, 1969, Trans. Faraday Soc. 65, p. 1557.

Fair, R. W., A. van Roodaelaar, and O. P. Strausz, 1971, Can. J. Chem. 49, p. 1659.

Fairchild, C. E., E. J. Stone, and G. M. Lawrence, 1978, J. Chem. Phys. 69, pp. 3632-3638.

Farquharson, G. K., and R. H. Smith, 1980, Aust. J. Chem. 33, pp. 1425-1435.

Fasano, D. M., and N. S. Nogar, 1981, Int. J. Chem. Kinet. 13, p. 325.

Fasano, D. M., and N. S. Nogar, 1982, Chem. Phys. Lett. 92, pp. 411-414.

Fergusson, W. C., L. Slotin, and W. G. Style, 1936, Trans. Far. Soc. 32, p. 956.

Finlayson-Pitts, B. J., and T. E. Kleindienst, 1979, J. Chem. Phys. 70, pp. 4804-4806.

Finlayson-Pitts, B. J., T. E. Kleindienst, J. J. Ezell, and D. W. Toohey, 1981, J. Chem. Phys. 74, pp. 4533-4543.

Fletcher, I. S., and D. Husain, 1976a, Can. J. Chem. 54, pp. 1765-1770.

Fletcher, I. S., and D. Husain, 1976b, J. Phys. Chem. 80, pp. 1837-1840.

Fletcher, I. S., and D. Husain, 1978, J. Photochem. 8, pp. 355-361.

Foon, R., and G. P. Reid, 1971, Trans. Faraday Soc. 67, p. 3513.

Foon, R., and M. Kaufman, 1975, Progress Reaction Kinetics 8, p. 81.

Foon, R., G. LeBras, and J. Combourieu, 1979, C.R. Acad. Sci. Paris, Series C, 288, p. 241.

Force, A. P., and J. R. Wiesenfeld, 1981a, J. Phys. Chem. 85, pp. 782-785.

Force, A. P., and J. R. Wiesenfeld, 1981b, J. Chem. Phys. 74, pp. 1718-1723.

Fowles, M., D. N. Mitchell, J. W. L. Morgan, and R. P. Wayne, 1982, J. Chem. Soc., Faraday Trans. II 78, p. 1239.

Frederick, J. E., and R. D. Hudson, 1979, J. Atmos. Sci. 36, pp. 737-745.

Frederick, J. E., and R. D. Hudson, 1980, J. Atmos. Sci. 37, pp. 1099-1106.

Frederick, J. E., and J. E. Mentall, 1982, Geophys. Res. Lett. 9, pp. 461-464.

Freeman, C. G., and L. F. Phillips, 1968, J. Phys. Chem. 72, p. 3025.

Friedl, R. R., W. H. Brune, and J. G. Anderson, 1984a, "Kinetic and SD Product Measurements for the Reactions OD + CS_2, OD + OCS, and OH + H_2S", manuscript in preparation.

Friedl, R. R., W. H. Brune, and J. G. Anderson, 1984b, "Kinetics of the Reactions of SH with O_2, O_3, NO_2, and H_2O_2", manuscript in preparation.

Fritz, B., K. Lorenz, W. Steinert and R. Zellner, 1984, Oxidation Communications, Vol. 6, pp. 363-370.

Garvin, D., and H. P. Broida, 1963, 9th Symposium on Combustion, p. 678.

Gehring, M., K. Hoyermann, H. Schaeke, and J. Wolfrum, 1973, 14th Int. Symposium on Combustion, p. 99.

Gericke, K.-H., and F. J. Comes, 1981, Chem. Phys. Lett. 81, pp. 218-222.

Gibson, G. E., and N. S. Bayliss, 1933, Phys. Rev. 44, p. 188.

Gill, R. J., W. D. Johnson, and G. H. Atkinson, 1981, Chem. Phys., 58, p. 29.

Glaschick-Schimpf, I., A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker, and E. H. Fink, 1979, Chem. Phys. Lett. 67, pp. 318-323.

Glinski, R. J., and J. W. Birks, 1984, J. Phys. Chem., submitted.

Goodeve, C. F., and S. Katz, 1939, Proc. Roy. Soc. 172A, pp. 432-444.

Goodeve, C. F., and F. D. Richardson, 1937, Trans. Faraday. Soc. 33, pp. 453-457.

Gordon, S., W. Mulac, and P. Nangia, 1971, J. Phys. Chem. 75, p. 2087.

Gorse, R. A., and D. H. Volman, 1974, J. Photochem. 3, p. 115.

Graham, R. A., 1975, "Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," Ph.D. Thesis, University of California, Berkeley.

Graham, R. A., and D. J. Gutman, 1977, J. Phys. Chem. 81, p. 207.

Graham, R. A., and H. S. Johnston, 1974, J. Chem. Phys. 60, p. 4628.

Graham, R. A., and H. S. Johnston, 1978, J. Phys. Chem. 82, pp. 254-268.

Graham, R. A., A. M. Winer, and J. N. Pitts, Jr., 1977, Chem. Phys. Lett. 51, p. 215.

Graham, R. A., A. M. Winer, and J. N. Pitts, Jr., 1978a, J. Chem. Phys. 68, pp. 4505-4510.

Graham, R. A., A. M. Winer, and J. N. Pitts, Jr., 1978b, Geophys. Res. Lett. 5, p. 909.

Graham, R. A., A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., 1979, J. Phys. Chem. 83, p. 1563.

Green, R. G., and R. P. Wayne, 1976/77, J. Photochem. 6, pp. 375-377.

Greiner, N. R., 1969, J. Chem. Phys. 51, pp. 5049-5051.

Greiner, N. R., 1970a, J. Chem. Phys. 53, p. 1284.

Greiner, N. R., 1970b, J. Chem. Phys. 53, pp. 1070-1076.

Grimley, A. J., and P. L. Houston, 1980, J. Chem. Phys. 72, pp. 1471-1475.

Gutman, D., N. Sanders, and J. E. Butler, 1982, J. Phys. Chem. 86, p. 66.

Hack, W., K. Hoyermann, and H. Gg. Wagner, 1974, Ber. Bunsenges. Phys. Chem. 78, p. 386.

Hack, W., G. Mex, and H. G. Wagner, 1977, Ber. Bunsenges. Phys. Chem. 81, pp. 677-684.

Hack, W., A. W. Preuss, and H. Gg. Wagner, 1978a, Ber Bunsenges. Phys. Chem. 82, pp. 1167-1171.

Hack, W., H. Gg. Wagner, and K. Hoyermann, 1978b, Ber. Bunsenges. Phys. Chem. 82, pp. 713-719.

Hack, W., A. W. Preuss, F. Temps and H. Gg. Wagner, 1979a, Ber. Bunsenges. Phys. Chem. 83, pp. 1275-1279.

Hack, W., H. Schacke, M. Schroter, and H. Gg. Wagner, 1979b, 17th Int. Symp. on Combustion, p. 505.

Hack, W., A. W. Preuss, H. Gg. Wagner, and K. Hoyermann, 1979c, Ber. Bunsenges. Phys. Chem. 83, pp. 212-217.

Hack, W., A. W. Preuss, F. Temps, H. Gg. Wagner, and K. Hoyermann, 1980, Int. J. Chem. Kinet. 12, pp. 851-860.

Hack, W., O. Horie, and H. Gg. Wagner, 1981, Ber. Bunsenges. Phys. Chem. 85, p. 72.

Halstead, C. J. and B. A. Thrush, 1966, Proc. Roy. Soc. London, Ser. A, 295, p. 380.

Hamilton, E. J., Jr., 1975, J. Chem. Phys. 63, pp. 3682-3683.

Hamilton, E. J., Jr., and R.-R. Lii, 1977, Int. J. Chem. Kinet. 9, pp. 875-885.

Hammer, P. D., E. J. Dlugokencky, and C. J. Howard, 1985, J. Phys. Chem., to be submitted.

Hampson, R. F., Jr., and D. Garvin, Eds., 1977, Reaction Rate and Photochemical Data for Atmospheric Chemistry, National Bureau of Standards Special Publication 513, p. 33, Washington, D.C.

Hancock, G., W. Lang, M. Lenzi, and K. H. Welge, 1975, Chem. Phys. Lett. 33, p. 168.

Handwerk, V., and R. Zellner, 1978, Ber. Bunsenges. Phys. Chem. 82, pp. 1161-1166.

Handwerk, V., and R. Zellner, 1984, Ber. Bunsenges. Phys. Chem. 88, p. 405.

Harker, A. B., W. Ho, and J. J. Ratto, 1977, Chem. Phys. Lett. 50, pp. 394-397.

Harris, G. W., and R. P. Wayne, 1975, J. Chem. Soc., Faraday Trans. I 71, p. 610.

Harris, G. W., T. E. Kleindienst, and J. N. Pitts, Jr., 1981, Chem. Phys. Lett. 80, pp. 479-483.

Hasson, V., and R. W. Nicholls, 1971, J. Phys. B.: Atom. Molec. Phys. 4, pp. 1789-1797.

Heicklen, J., N. Kelly, and K. Partymiller, 1980, Rev. Chem. Intermediates 3, pp. 315-404.

Heidner, R. F., III, and D. Husain, 1973, Int. J. Chem. Kinet. 5, pp. 819-831.

Heidner, R. F., III, D. Husain, and J. R. Weisenfeld, 1973, J. Chem. Soc., Faraday Trans. II 69, pp. 927-938.

Heidner, R. F., J. F. Bott, C. E. Gardner, and J. E. Melzer, 1979, J. Chem. Phys. 70, p. 4509.

Heidner, R. F., J. F. Bott, C. E. Gardner, and J. E. Melzer, 1980, J. Chem. Phys. 72, p. 4815.

Heneghan, S. P., and S. W. Benson, 1983, Int. J. Chem. Kinet. 15, pp. 1311-1319.

Heneghan, S. P., P. A. Knoot, and S. W. Benson, 1981, Int. J. Chem. Kinet. 13, p. 677.

Herman, J. R., and J. E. Mentall, 1982, J. Geophys. Res. 87, pp. 8967-8975.

Herron, J. T., and R. D. Penzhorn, 1969, J. Phys. Chem. 73, p. 191.

Herzberg, G., and K. K. Innes, 1957, Canad. J. Phys. 35, p. 842.

Hills, A. J., and C. J. Howard, 1984, J. Chem. Phys. 81, pp. 4458-65.

Hislop, J. R., and R. P. Wayne, 1977, J.C.S. Faraday II 73, pp. 506-516.

Hochanadel, C. J., J. A. Ghormley, and P. J. Ogren, 1972, J. Chem. Phys. 56, pp. 4426-4432.

Hochanadel, C. J., J. A. Ghormley, J. W. Boyle, and P. J. Ogren, 1977, J. Phys. Chem. 81, p. 3.

Hochanadel, C. J., T. J. Sworski and P. J. Ogren, 1980, J. Phys. Chem. 84, pp. 3274-3277.

Hofmann-Sievert R., and A. W. Castleman, 1984, J. Phys. Chem. 88, pp. 3329-3333.

Hofzumahaus, A., and F. Stuhl, 1984, Ber. Bunsenges. Phys. Chem. 88, pp. 557-561.

Hollinden, G. A., M. J. Kurylo, and R. B. Timmons, 1970, J. Chem. Phys. 74, pp. 988-991.

Homann, K. H., G. Krome, and H. Gg. Wagner, 1968, Ber. Bunsenges. Phys. Chem. 72, p. 998.

Homman, K. H., W. C. Solomon, J. Warnatz, H. Gg. Wagner, and C. Zetzsch, 1970, Ber. Bunsenges. Phys. Chem. 74, p. 585.

Horowitz, A., and J. G. Calvert, 1978, Int. J. Chem. Kinet. 10, p. 805.

Horowitz, A., F. Su, and J. G. Calvert, 1978, Int. J. Chem. Kinet. 10, p. 1099.

Howard, C. J., 1976, J. Chem. Phys. 65, p. 4771.

Howard, C. J., 1977, J. Chem. Phys. 67, p. 5258.

Howard, C. J., 1979, J. Chem. Phys. 71, pp. 2352-2359.

Howard, C. J., 1980, J. Am. Chem. Soc. 102, pp. 6937-6941.

Howard, C. J., and K. M. Evenson, 1974, J. Chem. Phys, 61, p. 1943.

Howard, C. J., and K. M. Evenson, 1976a, J. Chem. Phys. 64, p. 197.

Howard, C. J., and K. M. Evenson, 1976b, J. Chem. Phys. 64, p. 4303.

Howard, C. J., and K. M. Evenson, 1977, Geophys. Res. Lett. 4, pp. 437-440.

Howard, C. J., and B. J. Finlayson-Pitts, 1980, J. Chem. Phys. 72, pp. 3842-3843.

Howard, M. J., and I. W. M. Smith, 1981, J. Chem. Soc., Faraday Trans. II 77, pp. 997-1008.

Hoyermann, K., H. G. Wagner, and J. Wolfrum, 1967, Z. Phys. Chem. 55, p. 72.

Hsu, D. S. Y., W. M. Shaub, T. L. Burks, and M. C. Lin, 1979, Chem. Phys. 44, pp. 143-150.

Hubrich, C., and F. Stuhl, 1980, J. Photochem. 12, pp. 93-107.

Hubrich, C., C. Zetzsch, and F. Stuhl, 1977, Ber. Bunsenges. Phys. Chem. 81, p. 437.

Hudson, R. D., Editor, 1977, Chlorofluoromethanes and the Stratosphere, NASA Reference Publication 1010, NASA, Washington, D.C.

Hudson, R. D., and L. J. Kieffer, 1975, "Absorption Cross Sections of Stratospheric Molecules," The Natural Stratosphere of 1974, CIAP Monograph 1, pp. (5-156)-(5-194).

Hudson, R. D., and E. I. Reed, Editors, 1979, The Stratosphere: Present and Future, NASA Reference Publication 1049, NASA, Washington, D.C.

Huie, R. E., and J. T. Herron, 1974, Chem. Phys. Lett. 27, p. 411.

Huie, R. E., and P. Neta, 1984, J. Phys. Chem. 88, pp. 5665-5669.

Hunziker, H. E., H. Kneppe, and H. R. Wendt, 1981, J. Photochem. 17, p. 377.

Husain, D., and N. K. H. Slater, 1980, J. Chem. Soc., Faraday Trans. II 76, pp. 606-619.

Husain, D., J. M. C. Plane, and N. K. H. Slater, 1981, J. Chem. Soc. Faraday Trans. II 77, p. 1949.

Husain, D., J. M. C. Plane, and C. C. Xiang, 1984, J. Chem. Soc. Faraday Trans. 2, 80, pp. 713-728.

Igoshin, V. I., L. V. Kulakov, and A. I. Nikitin, 1974, Sov. J. Quant. Electron. 3, p. 306.

Illies, A. J., and G. A. Takacs, 1976, J. Photochem. 6, pp. 35-42.

Inn, E. C. Y., 1975, Atmospheric Sciences 32, p. 2375.

Inoue, G., and H. Akimoto, 1981, J. Chem. Phys. 84, pp. 425-433.

Iyer, R. S., and F. S. Rowland, 1980, Geophys. Res. Lett. 7, pp. 797-800.

Jaffe, R. L., and S. R. Langhoff, 1978, J. Chem. Phys. 68, p. 1638.

Jaffe, S., and F. S. Klein, 1966, Trans. Faraday Soc. 62, pp. 2150-2157.

Jaffe, S., and W. K. Mainquist, 1980, J. Phys. Chem. 84, p. 3277.

James, G. S. and G. P. Glass, 1970, J. Chem. Phys. 50, p. 2268.

Jayanty, R. K. M., R. Simonaitis, and J. Heicklen, 1976, J. Phys. Chem. 80, p. 443.

Jeong, K. M., and F. Kaufman, 1979, Geophys. Res. Lett. 6, pp. 757-759.

Jeong, K. M., and F. Kaufman, 1982, J. Phys. Chem. 86, pp. 1808-1815.

Jeong, K. M., K. J. Hsu, J. B. Jeffries, and F. Kaufman, 1984, J. Phys. Chem. 88, pp. 122-26.

Johnston, H. S., and R. Graham, 1973, J. Chem. Phys. 77, p. 62.

Johnston, H. S., and R. Graham, 1974, Can. J. Chem. 52, pp. 115-1423.

Johnston, H. S., E. D. Morris, Jr., and J. Van den Bogaerde, 1969, J. Am. Chem. Soc. 91, p. 7712.

Johnston, H. S., S. Chang, and G. Whitten, 1974, J. Phys. Chem. 78, pp. 1-7.

Johnston, H. S., M. Paige, and F. Yao, 1984, J. Geophys. Res. 89, p. 11, 661.

Jones, B. M. R., J. P. Burrows, R. A. Cox, and S. A. Penkett, 1982, Chem. Phys. Lett. 88, pp. 372-376.

Jones, E. L., and O. R. Wulf, 1937, J. Chem. Phys. 5, p. 873.

Jones, I. T. N., and K. Bayes, 1973, J. Chem. Phys. 59, pp. 4836-4844.

Jones, W. E., and E. G. Skolnik, 1976, Chemical Reviews 76, p. 563.

Jourdain, J. L., G. Le Bras, G. Poulet, J. Combourieu, P. Rigaud, and B. LeRoy, 1978, Chem. Phys. Lett. 57, p. 109.

Jourdain, J. L., G. Le Bras, and J. Combourieu, 1979, Int. J. Chem. Kinet. 11, pp. 569-577.

Jourdain, J. L., G. Le Bras, and J. Combourieu, 1981, Chem. Phys. Lett. 78, p. 483.

Jourdain, J. L., G. Poulet, and G. Le Bras, 1982, J. Chem. Phys. 76, pp. 5827-5833.

Kaiser, E. W., and S. M. Japar, 1977, Chem. Phys. Lett. 52, p. 121.

Kaiser, E. W., and S. M. Japar, 1978, Chem. Phys. Lett. 54, p. 265.

Kajimoto, O., and R. J. Cvetanovic, 1976, J. Chem. Phys. 64, p. 1005.

Kan, C. S., R. D. McQuigg, M. R. Whitbeck, and J. G. Calvert, 1979, Int. J. Chem. Kinet. 11, p. 921.

Kan, C. S., J. G. Calvert, and J. H. Shaw, 1980, J. Phys. Chem. 84, p. 3411.

Kan, C. S., J. G. Calvert, and J. H. Shaw, 1981, J. Phys. Chem. 85, pp. 1126-1132.

Keyser, L. F., 1978, J. Chem. Phys. 69, p. 214.

Keyser, L. F., 1979, J. Phys. Chem. 83, pp. 645-648.

Keyser, L. F., 1980a, J. Phys. Chem. 84, pp. 11-14.

Keyser, L. F., 1980b, J. Phys. Chem. 84, pp. 1659-1663.

Keyser, L. F., 1981, J. Phys. Chem. 85, pp. 3667-3673.

Keyser, L. F., 1982, J. Phys. Chem. 86, pp. 3439-3446.

Keyser, L. F., 1983, J. Phys. Chem. 87, pp. 837-841.

Keyser, L. F., 1984, J. Phys. Chem. 88, pp. 4750-4758.

Kijewski, H., and J. Troe, 1972, Helv. Chim. Acta 55, p. 205.

Kircher, C. C., and S. P. Sander, 1984, J. Phys. Chem., 88, pp. 2082-91.

Kircher, C. C., J. J. Margitan, and S. P. Sander, 1984, J. Phys. Chem. 88, pp. 4370-4375.

Kita, D., and D. H. Stedman, 1982, J. Chem. Soc. Faraday Trans. II 78, pp. 1249-1259.

Klais, O., P. C. Anderson, A. H. Laufer and M. J. Kurylo, 1979, Chem. Phys. Lett. 66, p. 598.

Klais, O., P. C. Anderson, and M. J. Kurylo, 1980a, Int. J. Chem. Kinet. 12, p. 469.

Klais, O., A. H. Laufer, and M. J. Kurylo, 1980b, J. Chem. Phys. 73, pp. 2696-2699.

Klein, Th., I. Barnes, K. H. Becker, E. H. Fink, and F. Zabel, 1984, J. Phys. Chem. 88, pp. 5020-5025.

Kleinermanns, K., and A. C. Luntz, 1981, J. Phys. Chem. 85, p. 1966.

Klemm, R. B., 1979, J. Chem. Phys. 71, p. 1987.

Klemm, R. B., and L. J. Stief, 1974, J. Chem. Phys. 61, p. 4900.

Klemm, R. B., E. G. Skolnik, and J. V. Michael, 1980, J. Chem. Phys. 72, p. 1256.

Knauth, H. D., 1978, Ber. Bunsenges. Phys. Chem. 82, p. 212.

Knauth, H. D., H. Alberti, and H. Clausen, 1979, J. Phys. Chem. 83, pp. 1604-1612.

Knox, J. H., 1955, Chemistry and Industry, p. 1631. See also Lin et al., 1978a.

Knox, J. H., and R. L. Nelson, 1959, Trans. Far. Soc. 55, p. 937.

Kompa, K. L., and J. Wanner, 1972, Chem. Phys. Lett. 12, p. 560.

Kurasawa, H., and R. Lesclaux, 1979, Chem. Phys. Lett. 66, p. 602.

Kurasawa, H., and R. Lesclaux, 1980a, Chem. Phys. Lett. 72, p. 437.

Kurasawa, H., and R. Lesclaux, 1980b, 14th Informal Photochemistry Conference, Newport Beach, CA, April 1980.

Kurylo, M. J., 1972, J. Phys. Chem. 76, p. 3518.

Kurylo, M. J., 1973, Chem. Phys. Lett. 23, pp. 467-471.

Kurylo, M. J., 1977, Chem. Phys. Lett. 49, p. 467.

Kurylo, M. J., 1978, Chem. Phys. Lett. 58, pp. 238-242.

Kurylo, M. J., and W. Braun, 1976, Chem. Phys. Lett. 37, p. 232.

Kurylo, M. J., and G. L. Knable, 1984, J. Phys. Chem. 88, pp. 3305-3308.

Kurylo, M. J., and A. H. Laufer, 1979, J. Chem. Phys. 70, pp. 2032-2033.

Kurylo, M. J. and R. Manning, 1977, Chem. Phys. Lett. 48, p. 279.

Kurylo, M. J., P. C. Anderson, and O. Klais, 1979, Geophys. Res. Lett. 6, pp. 760-762.

Kurylo, M. J., O. Klais, and A. H. Laufer, 1981, J. Phys. Chem. 85, pp. 3674-3678.

Kurylo, M. J., K. D. Cornett, and J. L. Murphy, 1982a, J. Geophys. Res. 87, pp. 3081-3085.

Kurylo, M. J., J. L. Murphy, G. S. Haller, and K. D. Cornett, 1982b, Int. J. Chem. Kinet. 14, pp. 1149-1161.

Kurylo, M. J., G. L. Knable, and J. L. Murphy, 1983a, Chem. Phys. Lett. 95, pp. 9-12.

Kurylo, M. J., J. L. Murphy, and G. L. Knable, 1983b, Chem. Phys. Lett. 94, pp. 281-284.

Laguna, G. A. and S. L. Baughcum, 1982, Chem. Phys. Lett. 88, 568-71.

Lam, L., D. R. Hastie, B. A. Ridley, and H. I. Schiff, 1981, J. Photochem. 15, pp. 119-130.

Lamb, J. J., L. T. Molina, C. A. Smith, and M. J. Molina, 1983, J. Phys. Chem. 87, pp.4467-4470.

Langford, A. O., and C. B. Moore, 1984, J. Phys. Chem. 80, 4211.

Langhoff, S. R., L. Jaffe, and J. O. Arnold, 1977, J. Quant. Spectrosc. Radiat. Transfer 18, p. 227.

Laufer, A. H., and A. M. Bass, 1975, Int. J. Chem. Kinet. 7, p. 639.

Le Bras, G., R. Foon, and J. Combourieu, 1980, Chem. Phys. Lett. 73, p. 357.

Leck, T. J., J. E. Cook, and J. W. Birks, 1980, J. Chem. Phys. 72, pp. 2364-2373.

Lee, F. S. C., and F. S. Rowland, 1977, J. Phys. Chem. 81, p. 684.

Lee, J. H., I. N. Tang, 1982, J. Chem. Phys. 77, pp. 4459-63.

Lee, J. H., J. V. Michael, W. A. Payne, Jr., and L. J. Stief, 1977, J. Chem. Soc. Faraday Trans. I 73, pp. 1530-1536.

Lee, J. H., J. V. Michael, W. A. Payne, Jr., and L. J. Stief, 1978a, J. Chem. Phys. 68, pp. 5410-5413.

Lee, J. H., J. V. Michael, W. A. Payne, Jr., and L. J. Stief, 1978b, J. Chem. Phys. 69, pp. 350-353.

Lee, J. H., J. V. Michael, W. A. Payne, Hr., and L. J. Stief, 1978c, J. Chem. Phys. 69, pp. 3069-3076.

Lee, L. C., 1982, J. Chem. Phys. 76, pp. 4909-4915.

Lee, L. C., and T. G. Slanger, 1978, J. Chem. Phys. 69, pp. 4053-4060.

Lee, L. C., and T. G. Slanger, 1979, Geophys. Res. Lett. 6, pp. 165-166.

Lee, Y-P., and C. J. Howard, 1982, J. Chem. Phys. 77, pp. 756-763.

Lee, Y-P., R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, 1982, Int. J. Chem. Kinet. 14, pp. 711-732.

Leroy, B., G. LeBras, and P. Riguad, 1981, Ann. Geophys. 37, pp. 297-302.

Lesclaux, R., and F. Caralp, 1984, Int. J. Chem. Kinet. 16, pp. 1117-1128.

Lesclaux, R., and M. Demissy, 1977, Nouv. J. Chim. 1, p. 443.

Lesclaux, R., P. V. Khe, P. Dezauzier, and J. C. Soulignac, 1975, Chem. Phys. Lett. 35, p. 493.

Leu, M. T., 1979, J. Chem. Phys. 70, pp. 1662-1666.

Leu, M. T., 1980a, Chem. Phys. Lett. 69, pp. 37-39.

Leu, M. T., 1980b, Geophys. Res. Lett. 7, pp. 173-175.

Leu, M. T., 1982, J. Phys. Chem. 86, p. 4558.

Leu, M. T., 1984a, Int. J. Chem. Kinetics 16, pp. 1311-1320.

Leu, M. T., 1984b, J. Phys. Chem. 88, pp. 1394-1398.

Leu, M. T., and W. B. DeMore, 1976, Chem. Phys. Lett. 41, pp. 121-124.

Leu, M. T., and W. B. DeMore, 1977, Chem. Phys. Lett. 48, p. 317.

Leu, M. T., and W. B. DeMore, 1978, J. Phys. Chem. 82, p. 2049.

Leu, M. T., and C. L. Lin, 1979, Geophys. Res. Lett. 6, pp. 425-428.

Leu, M. T., and R. H. Smith, 1981, J. Phys. Chem. 85, pp. 2570-2575.

Leu, M. T., and R. H. Smith, 1982a, J. Phys. Chem. 86, pp. 73-81.

Leu, M. T., and R. H. Smith, 1982b, J. Phys. Chem. 86, pp. 958-961.

Leu, M. T., C. L. Lin, and W. B. DeMore, 1977, J. Phys. Chem. 81, p. 190.

Lewis, R. S., and R. T. Watson, 1980, J. Phys. Chem. 84, p. 3495-3503.

Lewis, R. S., S. P. Sander, S. Wagner, and R. T. Watson, 1980, J. Phys. Chem. 84, pp. 2009-2015.

Lii, R.-R., R. A. Gorse, Jr., M. C. Sauer, Jr., and S. Gordon, 1979, J. Phys. Chem. 83, pp. 1803-1804.

Lii, R.-R., R. A. Gorse, Jr., M. C. Sauer, Jr., and S. Gordon, 1980a, J. Phys. Chem. 84, pp. 819-821.

Lii, R.-R., R. A. Gorse, Jr., M. C. Sauer, Jr., and S. Gordon, 1980b, J. Phys. Chem. 84, pp. 813-817.

Lii, R.-R., M. C. Sauer, Jr., and S. Gordon, 1980c, J. Phys. Chem. 84, pp. 817-819.

Lii, R.-R., M. C. Sauer, Jr., and S. Gordon, 1981, J. Phys. Chem. 85, pp. 2833-2834.

Lin, C. L., 1982, Int. J. Chem. Kinet. 14, pp. 593-598.

Lin, C. L., and W. B. DeMore, 1973, J. Phys. Chem. 77, pp. 863-869.

Lin, C. L., and M. T. Leu, 1982, Int. J. Chem. Kinet. 14, p. 417.

Lin, C. L., M. T. Leu, and W. B. DeMore, 1978a, J. Phys. Chem. 82, p. 1772.

Lin, C. L., N. K. Rohatgi, and W. B. DeMore, 1978b, Geophys. Res. Lett. 5, pp. 113-115.

Lippmann, H. H., B. Jesser, and U. Schurath, 1980, Int. J. Chem. Kinet. 12, pp. 547-554.

Littlejohn, D., and H. S. Johnston, 1980, EOS 61, p. 966.

Lloyd, A. C., K. R. Darnall, A. M. Winer, and J. N. Pitts, Jr., 1976, J. Phys. Chem. 80, p. 789.

Loewenstein, L. M., and J. G. Anderson, 1984, J. Phys. Chem. 88, pp. 6277-6286.

Lozovsky, V. A., M. A. Ioffe, and O. M. Sarkisov, 1984, Chem. Phys. Lett. 110, pp. 651-4.

Mack, G. P. R., and B. Thrush, 1973, J. Chem. Soc., Faraday Trans. I 69, p. 208.

Magnotta, F., and H. S. Johnston, 1980, Geophys. Res. Lett. 7, pp. 769-772.

Majer, J. R., and J. P. Simons, 1964, "Photochemical Processes in Halogenated Compounds," J. Pitts, G. Hammond, and W. A. Noyes, ed., Advances in Photochemistry, 2, Interscience, New York, pp. 137-181.

Malko, M. W., and J. Troe, 1982, Int. J. Chem. Kinet. 14, p. 399.

Mandelman, M., and R. W. Nicholls, 1977, J. Quant. Spectrosc. Radiat. Transfer 17, p. 483.

Manning, R., and M. J. Kurylo, 1977, J. Phys. Chem. 81, p. 291.

Manning, R. G., W. Braun, and M. J. Kurylo, 1976, J. Chem. Phys. 65, p. 2609.

Margitan, J. J., 1983a, J. Phys. Chem. 87, pp. 674-679.

Margitan, J. J., 1983b, J. Geophys. Res. 88, pp. 5416-5420.

Margitan, J. J., 1984a, J. Phys. Chem. 88, pp. 3314-3318.

Margitan, J. J., 1984b, J. Phys. Chem. 88, pp. 3638-3643.

Margitan, J. J., and R. T. Watson, 1982, J. Phys. Chem. 86, pp. 3819-3824.

Margitan, J. J., F. Kaufman, and J. G. Anderson, 1974, Geophys. Res. Lett. 1, pp. 80-81.

Margitan, J. J., F. Kaufman, and J. G. Anderson, 1975, Int. J. Chem. Kinet. Symp. No. 1, p. 281.

Marinelli, W. J., and H. S. Johnston, 1982a, J. Chem. Phys. 77, pp. 1225-1234.

Marinelli, W. J., and H. S. Johnston, 1982b, Chem. Phys. Lett. 93, pp. 127-132.

Marinelli, W. J., D. M. Swanson, and H. S. Johnston, 1982, J. Chem. Phys. 76, pp. 2864-2870.

Martin, H., and R. Gareis, 1956, Z. Elektrochemie 60, pp. 959-964.

Marx, W., F. Bahe, and U. Schurath, 1979, Ber. Bunsenges. Phys. Chem. 83, pp. 225-230.

McCrumb, J. L., and F. Kaufman, 1972, J. Chem. Phys. 57, pp. 1270-1276.

McElcheran, D. E., M. H. J. Wijnen, and E. W. R. Steacie, 1958, Can. J. Chem. 36, p. 321.

McKenzie, A., M. F. R. Mulcahy, and J. R. Steven, 1973, J. Chem. Phys. 59, pp. 3244-3254.

Michael, J. V., and J. H. Lee, 1977, Chem. Phys. Letters 51, p. 303.

Michael, J. V., and W. A. Payne, 1979, Int. J. Chem. Kinet. 11, p. 799.

Michael, J. V., D. A. Whytock, J. H. Lee, W. A. Payne, and L. J. Stief, 1977, J. Chem. Phys. 67, p. 3533.

Michael, J. V., J. H. Lee, W. A. Payne, and L. J. Stief, 1978, J. Chem. Phys. 68, p. 4093.

Michael, J. V., D. F. Nava, W. A. Payne, and L. J. Stief, 1979a, J. Chem. Phys. 70, p. 1147.

Michael, J. V., D. F. Nava, W. A. Payne, and L. J. Stief, 1979b, J. Chem. Phys. 70, p. 3652.

Michael, J. V., D. F. Nava, R. P. Borkowski, W. A. Payne, and L. J. Stief, 1980, J. Chem. Phys. 73, p. 6108.

Michael, J. V., J. E. Allen, Jr., and W. D. Brobst, 1981, J. Phys. Chem. 85, p. 4109.

Michael, J. V., D. F. Nava, W. Brobst, R. P. Borkowski, and L. J. Stief, 1982, J. Phys. Chem. 86, pp. 81-84.

Miller, J. C., and R. J. Gordon, 1981, J. Chem. Phys. 75, p. 5305.

Mitchell, D. N., R. P. Wayne, P. J. Allen, R. P. Harrison, and R. J. Twin, 1980, J. Chem. Soc. Faraday Trans. II 76, p. 785.

Miziolek, A. W., and M. J. Molina, 1978, J. Phys. Chem. 82, p. 1769.

Molina, L. T., and M. J. Molina, 1977, Geophys. Res. Lett. 4, pp. 83-86.

Molina, L. T., and M. J. Molina, 1978, J. Phys. Chem. 82, pp. 2410-2414.

Molina, L. T., and M. J. Molina, 1979, J. Photochem. 11, pp. 139-144.

Molina, L. T., and M. J. Molina, 1981, J. Photochem. 15, p. 97.

Molina, L. T., and M. J. Molina, 1982, "Chemistry of Fluorine in the Stratosphere," 182nd American Chemical Society National Meeting, New York, August 1982.

Molina, L. T., S. D. Schinke, and M. J. Molina, 1977a, Geophys. Res. Lett. 4, pp. 580-582.

Molina, L. T., J. E. Spencer, and M. J. Molina, 1977b, Chem. Phys. Lett. 45, pp. 158-162.

Molina, L. T., J. J. Lamb, and M. J. Molina, 1981, Geophys. Res. Lett. 8, p. 1008.

Molina, L. T., M. J. Molina, and F. S. Rowland, 1982, J. Phys. Chem. 86, pp. 2672-2676.

Molina, M. J., and G. Arguello, 1979, Geophys. Res. Lett. 6, pp. 953-955.

Molina, M. J., L. T. Molina and T. Ishiwata, 1980a, J. Phys. Chem. 84, p. 3100.

Molina, M. J., T. Ishiwata, and L. T. Molina, 1980b, J. Phys. Chem. 84, pp. 821-826.

Molina, M. J., L. T. Molina, and C. A. Smith, 1984, Int. J. Chem. Kinet. 16, pp. 1151-1160.

Moortgat, G. K., and E. Kudzus, 1978, Geophys. Res. Lett. 5, p. 191.

Moortgat, G. K., and P. Warneck, 1979, J. Chem. Phys. 70, pp. 3639-3651.

Moortgat, G. K., W. Klippel, K. H. Mobius, W. Seiler, and P. Warneck, 1980, "Laboratory Measurements of Photolytic Parameters for Formaldehyde," Report No. FAA-EE-80-47.

Moortgat, G. K., W. Seiler, and P. Warneck, 1983, J. Chem. Phys. 78, pp. 1185-1190.

Morel, O., R. Simonaitis, and J. Heicklen, 1980, Chem. Phys. Lett. 73, p. 38.

Morley, C., and I. W. M. Smith, 1972, J. Chem. Soc. Faraday Trans. II 66, p. 1016.

Morris, E. D., and H. Niki, 1971, J. Chem. Phys. 55, p. 1991.

Morris, E. D., D. H. Stedman, and H. Niki, 1971, J. Am. Chem. Soc. 93, p. 3570.

Nadtochenko, V. A., O. M. Sarkisov, and V. I. Vedeneev, 1979, Doklady Akademii Nauk SSSR, 244, p. 152.

Nava, D. F., J. V. Michael, and L. J. Stief, 1981, J. Phys. Chem. 85, p. 1896.

Nava, D. F., S. R. Bosco, and L. J. Stief, 1983, J. Chem. Phys. 78, pp. 2443-2448.

Nelson, H. H., and H. S. Johnston, 1981, J. Phys. Chem. 85, p. 3891.

Nelson, H., W. J. Marinelli, and H. S. Johnston, 1981, Chem. Phys. Lett. 78, pp. 495-499.

Nesbitt, D. J., and S. R. Leone, 1980, J. Chem. Phys. 72, pp. 1722-1732.

Nicholas, J. E., and R. G. W. Norrish, 1968, Proc. Roy. Soc. A 307, p. 391.

Nicolet, M., and W. Peetermans, 1980, Planet. Space Sci. 28, pp. 85-103.

Nielsen, O. J., 1979, "Chemical Kinetics in the Gas Phase Pulse Radiolysis of Hydrogen Sulfide Systems," Riso National Laboratory Publication, Riso-M-2216, Roskilde, Denmark.

Niki, H., E. E. Daby and B. Weinstock, 1969, Data reported at Twelfth Symposium (International) on Combustion, The Combustion Institute, p. 277.

Niki, H., P. D. Maker, L. P. Breitenbach, and C. M. Savage, 1978a, Chem. Phys. Lett. 57, p. 596.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1978b, J. Phys. Chem. 82, p. 132.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1978c, Chem. Phys. Lett. 59, p. 78.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1980, Chem. Phys. Lett. 73, pp. 43-46.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1981, J. Phys. Chem. 85, p. 877.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1983, J. Phys. Chem. 87, pp. 2190-2193.

Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, 1984, J. Phys. Chem. 88, pp. 2116-2119.

Ogawa, M., 1971, J. Chem. Phys. 54, pp. 2550-2556.

Ogryzlo, E. A., R. Paltenghi, and K. D. Bayes, 1981, Int. J. Chem. Kinet. 13, pp. 667-675.

Okabe, H., 1978, *Photochemistry of Small Molecules*, John Wiley and Sons, Inc., New York, p. 217.

Okabe, H., 1980, J. Chem. Phys. 72, p. 6642.

Olbregts, J., G. Brasseur, and E. J. Arijs, 1984, J. Photochem. 24, pp. 315-322.

Ongstad, A. P., and J. W. Birks, 1984, J. Chem. Phys. 81, pp. 3922-3930.

Overend, R. P., and G. Paraskevopoulos, 1977a, Chem. Phys. Lett. 49, p. 109.

Overend, R. P., and G. Paraskevopoulos, 1977b, J. Chem. Phys. 67, p. 674.

Overend, R. P., G. Paraskevopoulos, and R. J. Cvetanovic, 1975, Can. J. Chem. 53, p. 3354-3382.

Overend, R. P., G. Paraskevopoulos, and C. Black, 1976, J. Chem. Phys. 64, p. 4149.

Pagsberg, P. B., J. Erikson, and H. C. Christensen, 1979, J. Phys. Chem. 83. p. 582.

Paraskevopoulos, G., and R. S. Irwin, 1982a, Chem. Phys. Lett. 93, pp. 138-143.

Paraskevopoulos, G., and R. S. Irwin, 1982b, XV Informal Conference on Photochemistry, Stanford, CA June 27-July 1.

Paraskevopoulos, G., and R. S. Irwin, 1984, J. Chem. Phys. 80, pp. 259-266.

Paraskevopoulos, G., D. L. Singleton, and R. S. Irwin, 1981, J. Phys. Chem. 85, p. 561.

Paraskevopoulos, G., D. L. Singleton, and R. S. Irwin, 1983, Chem. Phys. Lett. 100, pp. 83-87.

Parkes, D. A., 1977, Int. J. Chem. Kinet. 9, p. 451.

Parrish, D. D., P. C. Murphy, D. L. Albritton, and F. C. Fehsenfeld, 1983, Atmos. Environ. 17, p. 1365.

Pastrana, A. V., and R. W. Carr, Jr., 1974, Int. J. Chem. Kinet. 6, p. 587.

Pate, C. T., B. J. Finlayson, and J. N. Pitts, Jr., 1974, J. Am. Chem. Soc. 96, p. 6554.

Patrick, R., and D. M. Golden, 1983, Int. J. Chem. Kinetics 15, pp. 1189-1227.

Patrick, R., and D. M. Golden, 1984a, Int. J. Chem. Kinet. 16, pp. 1567-74.

Patrick, R., and D. M. Golden, 1984b, J. Phys. Chem. 88, pp. 491-5.

Paukert, T. T., and H. S. Johnston, 1972, J. Chem. Phys. 56, pp. 2824-2838.

Payne, W. A., L. J. Stief, and D. D. Davis, 1973, J. Am. Chem. Soc. 95, p. 7614.

Penzhorn, R. D., and C. E. Canosa, 1983, Ber. Bunsenges. Phys. Chem. 87, pp. 648-654.

Perner, D., A. Schmeltekopf, R. H. Winkler, H. S. Johnston, J. G. Calvert, C. A. Cantrell, and W. R. Stockwell, 1985, J. Geophys. Res. 90, 3807-3812.

Perry, R. A., and D. Williamson, 1982, Chem. Phys. Lett. 93, pp. 331-334.

Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., 1976a, J. Chem. Phys. 64, p. 1618.

Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., 1976b, J. Chem. Phys. 64, p. 3237.

Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., 1977, J. Chem. Phys. 67, p. 5577.

Phillips, L. F., 1978, Chem. Phys. Lett. 57, pp. 538-539.

Phillips, L. F., and H. I. Schiff, 1962, J. Chem. Phys. 36, p. 1509.

Pirre, M., P. Rigaud, and D. Huguenin, 1984, Geophys. Res. Lett. 11, p. 1199.

Plumb, I. C., and K. R. Ryan, 1982a, Chem. Phys. Lett. 92, pp. 236-238.

Plumb, I. C., and K. R. Ryan, 1982b, Int. J. Chem. Kinet. 14, p. 861-874.

Plumb, I. C., K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, 1979, Chem. Phys. Lett. 63, p. 255.

Plumb, I. C., K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, 1981, J. Phys. Chem. 85, p. 3136.

Porter, G., and F. G. Wright, 1953, Disc. Faraday Soc. 14, p. 23.

Posey, J., J. Sherwell, and M. Kaufman, 1981, Chem. Phys. Lett. 77, p. 476.

Poulet, G., G. Le Bras, and J. Combourieu, 1974, J. Chim. Physique 71, p. 101.

Poulet, G., G. Le Bras, and J. Combourieu, 1977, J. Phys. Chem. 81, p. 2303.

Poulet, G., G. Le Bras, and J. Combourieu, 1978a, J. Chem. Phys. 69, p. 767.

Poulet, G., G. Le Bras, and J. Combourieu, 1978b, Proceedings of the World Meteorological Organization Symposium on the Geophysical Aspects and Consequences of Changes in the Composition of the Stratosphere. Toronto, 26-30 June 1978. WMO-#511, p. 289.

Poulet, G., G. Le Bras, and J. Combourieu, 1980, Geophys. Res. Lett. 7, pp. 413-414.

Poulet, G., G. Laverdet, and G. Le Bras, 1981, J. Phys. Chem. 85, p. 1892.

Poulet, G., G. Laverdet, and G. Le Bras, 1983, Chem. Phys. Lett. 94, pp. 129-132.

Poulet, G., G. Laverdet, J. L. Jourdain, and G. Le Bras, 1984a, J. Phys. Chem. 88, pp. 6259-6263.

Poulet, G., G. Laverdet, and G. Le Bras, 1984b, J. Chem. Phys. 80, pp. 1922-1928.

Prasad, S. S., 1980, Nature 285, p. 152.

Pratt, G. L., and S. W. Wood, 1984, J. Chem. Soc. Faraday Trans. I, 80, 3419-27.

Pritchard, H. O., J. B. Pyke, and A. F. Trotman-dickenson, 1954, J. Amer. Chem. Soc. 76, p. 1201.

Pritchard, H. O., J. B. Pyke, and A. F. Trotman-dickensen, 1955, J. Amer. Chem. Soc. 77, p. 2629.

Radford, H. E., 1980, Chem. Phys. Lett. 71, p. 195.

Radford, H. E., K. M. Evenson, and D. A. Jennings, 1981, Chem. Phys. Lett. 78, p. 589.

Ravishankara, A. R., and R. L. Thompson, 1983, Chem. Phys. Letts., 99, p. 377.

Ravishankara, A. R., and P. H. Wine, 1980, J. Chem. Phys. 72, pp.25-30.

Ravishankara, A. R., and P. H. Wine, 1983, Chem. Phys. Lett. 101, p. 73.

Ravishankara, A. R., G. Smith, R. T. Watson, and D. D. Davis, 1977a, J. Phys. Chem. 81, p. 2220.

Ravishankara, A. R., D. D. Davis, G. Smith, G. Tesi, and J. Spencer, 1977b, Geophys. Res. Lett. 4, p. 7.

Ravishankara, A. R., G. Smith, and D. D. Davis, 1978, 13th Informal Photochemistry Conference, Clearwater Beach, Florida, January 1978.

Ravishankara, A. R., P. H. Wine, and A. O. Langford, 1979a, Chem. Phys. Lett. 63, p. 479.

Ravishankara, A. R., P. H. Wine, and A. O. Langford, 1979b, J. Chem. Phys. 70, pp. 984-989.

Ravishankara, A. R., F. L. Eisele, and P. H. Wine, 1980a, J. Chem.. Phys. 73, p. 3743.

Ravishankara, A. R., N. M. Kreutter, R. C. Shah, and P. H. Wine, 1980b, Geophys. Res. Lett. 7, pp. 861-864.

Ravishankara, A. R., F. L. Eisele, N. M. Kreutter, and P. H. Wine, 1981a, J. Chem. Phys. 74, p. 2267.

Ravishankara, A. R., J. M. Nicovich, R. L. Thompson, and F. P. Tully, 1981b, J. Phys. Chem. 85, pp. 2498-2503.

Ravishankara, A. R., F. L. Eisele, and P. H. Wine, 1982, J. Phys. Chem. 86, pp. 1854-1858.

Ravishankara, A. R., F. L. Eisele, and P. H. Wine, 1983a, J. Chem. Phys. 78, pp. 1140-1144.

Ravishankara, A. R., P. H. Wine, and J. M. Nicovich, 1983b, J. Chem. Phys. 78, pp. 6629-6639.

Ray, G. W., and R. T. Watson, 1981a, J. Phys. Chem. 85, pp. 2955-2960.

Ray, G. W., and R. T. Watson, 1981b, J. Phys. Chem. 85, pp. 1673-1676.

Ray, G. W., L. F. Keyser, and R. T. Watson, 1980, J. Phys. Chem. 84, pp. 1674-1681.

Reilly, J. D., J. H. Clark, C. B. Moore, and G. C. Pimentel, 1978, J. Chem. Phys. 69, p. 4381.

Reimann, B., and F. Kaufman, 1978, J. Chem. Phys,. 69, p. 2925.

Richardson, R. J., 1975, J. Phys. Chem. 79, pp. 1153-1158.

Rigaud, P., B. Leroy, G. Le Bras, G. Poulet, J. L. Jourdain, and J. Combourieu, 1977, Chem. Phys. Lett. 46, p. 161.

Robbins, D. E., 1976, Geophys. Res. Lett. 3, p. 213; Erratum, op. cit. 3, p. 757.

Robbins, D. E., 1977, "International Conference on Problems Related to the Stratosphere," W. Huntress, Jr., and D. Maple, Eds., JPL Publication 77-12, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Robbins, D. E., and R. S. Stolarski, 1976, Geophys. Rev. Lett. 3, pp. 603-606.

Robertshaw, J. S., and I. W. M. Smith, 1980, Int. J. Chem. Kinet. 12, p. 729.

Robertshaw, J. S., and I. W. M. Smith, 1982, J. Phys. Chem. 86, p. 785.

Roscoe, J. M., 1982, Int. J. Chem. Kinet. 14, pp. 471-478.

Rowland, F. S., and Y. Makide, 1982, Geophys. Res. Lett. 9, p. 473.

Rowland, F. S., and P. J. Rogers, 1982, Proc. Natl. Acad. Sci. USA 79, p. 2737.

Rowland, F. S., and J. E. Spencer, and M. J. Molina, 1976, J. Phys. Chem. 80, pp. 2711-2713.

Rudolph, R. N., and E. C. Y. Inn, 1981, J. Geophys. Res. 86, p. 9891.

Ryan, K. R., and I. C. Plumb, 1982, J. Phys. Chem. 86, pp. 4678-4683.

Ryan, K. R., and I. C. Plumb, 1984, Int. J. Chem. Kinet. 16, pp. 591-602.

Safary, E., J. Romand, and B. Vodar, 1951, J. Chem. Phys. 19, p. 379.

Sahetchian, K. A., A. Heiss, and R. Rigny, 1982, Can. J. Chem. 60, pp. 2896-2902.

Sander, S. P., and M. Peterson, 1984, J. Phys. Chem. 88, pp. 1566-71.

Sander, S. P., and R. T. Watson, 1980, J. Phys. Chem. 84, p. 1664.

Sander, S. P., and R. T. Watson, 1981a, Chem. Phys. Lett. 77, pp. 473-475.

Sander, S. P., and R. T. Watson, 1981b, J. Phys. Chem. 85, p. 4000.

Sander, S. P., and R. T. Watson, 1981c, J. Phys. Chem. 85, p. 2960.

Sander, S. P., G. W. Ray, and R. T. Watson, 1981, J. Phys. Chem. 85, p. 199.

Sander, S. P., M. Peterson, R. T. Watson, and R. Patrick, 1982, J. Phys. Chem. 86, pp. 1236-1240.

Sanders, N. D., J. E. Butler, and J. R. McDonald, 1980a, J. Chem. Phys. 73, pp. 5381-5383.

Sanders, N. D., J. E. Butler, L. R. Pasternack, and J. R. McDonald, 1980b, Chem. Phys. Lett. 48, p. 203.

Sandorfy, C., 1976, Atmos. Environ. 10, pp. 343-351.

Sanhueza, E., R. Simonaitis, and J. Heicklen, 1979, Int. J. Chem. Kinet. 11, p. 907.

Sarkisov, O. M., S. G. Cheskis, and E. A. Sviridenkov, 1978, Bull. Acad. Sci. USSR Chem. Ser. 27, p. 2336.

Schieferstein, M., K. Kohse-Hölnghaus, F. Stuhl, 1983, Ber. Bunsenges. Phys. Chem. 87, pp. 361-366.

Schneider, W., J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, 1985, manuscript in preparation.

Schonle, G., H. D. Knauth, and R. N. Schindler, 1979, J. Phys. Chem. 83, p. 3297.

Schurath, U., H. H. Lippmann, and B. Jesser, 1981, Ber. Bunsenges, Phys. Chem. 85, pp. 807-813.

Schwab, J. J., D. W. Toohey, W. H. Brune, and J. G. Anderson, 1984, J. Geophys. Res. 89, pp. 9581-9587.

Seery, D. J., and D. Britton, 1964, J. Phys. Chem. 68, p. 2263.

Selwyn, G., J. Podolske, H. S. Johnston, 1977, Geophys. Res. Lett. 4, pp. 427-430.

Selzer, E. A., and K. D. Bayes, 1983, J. Phys. Chem. 87, p. 392-394.

Shamonima, N. F., and A. G. Ketov, 1979, Kinet. Katal. 20, p. 233.

Shardanand, and A. D. Prasad Rao, 1977, J. Quant. Spectrosc. Radiat. Transfer 17, pp.433-439.

Shibuya, K., T. Ebatu, K. Obi, and I. Tanaka, 1977, J. Phys. Chem. 81, p. 2292.

Silver, J. A., and C. E. Kolb, 1980, Chem. Phys. Lett. 75, p. 191.

Silver, J. A., and C. E. Kolb, 1982, J. Phys. Chem. 86, pp. 3240-3246.

Silver, J. A., A. C. Stanton, M. S. Zahniser, and C. E. Kolb, 1984a, J. Phys. Chem. 88, pp. 312[illegible] 3129.

Silver, J. A., M. S. Zahniser, A. C. Stanton, and C. E. Kolb, 1984b, Twentieth International Symposium on Combustion, Pittsburgh, PA (preprint).

Silver, J. A., M. S. Zahniser, and C. E. Kolb, 1985, J. Phys. Chem. (to be submitted).

Simonaitis, R., and J. Heicklen, 1973, J. Phys. Chem. 77, pp. 1932-1935.

Simonaitis, R., and J. Heicklen, 1975, J. Phys. Chem. 79, p. 298.

Simonaitis, R., and J. Heicklen, 1978, Int. J. Chem. Kinet. 10, pp. 67-87.

Simonaitis, R., and J. Heicklen, 1979, Chem. Phys. Lett. 65, p. 361.

Simonaitis, R., and J. Heicklen, 1981, J. Phys. Chem. 85, p. 2946.

Simonaitis, R., and J. Heicklen, 1982, J. Phys. Chem. 86, pp. 3416-3418.

Singleton, D. L., and R. J. Cvetanovic, 1978, Can. J. Chem. 56, p. 2934.

Singleton, D. L., and R. J. Cvetanovic, 1981, Int. J. Chem. Kinet. 13, p. 945.

Singleton, D. L., R. S. Irwin, W. S. Nip, and R. J. Cvetanovic, 1979, J. Phys. Chem. 83, pp. 2195-2200.

Singleton, D. L., G. Paraskevopoulos, and R. S. Irwin, 1982, J. Phys. Chem. 86, pp. 2605-2609.

Slagle, I. R., J. R. Gilbert, and D. Gutman, 1974a, J. Chem. Phys. 61, p. 704.

Slagle, I. R., J. F. Pruss, Jr., and D. Gutman, 1974b, Int. J. Chem. Kinet. 6, p. 111.

Slagle, I. R., F. Baiocchi, and D. Gutman, 1978, J. Phys. Chem. 82, p. 1333.

Slanger, T. G., B. J. Wood, and G. Black, 1973, Int. J. Chem. Kinet. 5, p. 615.

Smardzewski, R. R., and M. C. Lin, 1977, J. Chem. Phys. 66, pp. 3197-3204.

Smith, C. A., and L. T. Molina, J. J. Lamb, and M. J. Molina, 1984, Int. J. Chem. Kinet. 16, p. 41.

Smith, C. A., A. R. Ravishankara, and P. H. Wine, 1985, J. Phys. Chem. 89, pp. 1423-1427.

Smith, G. P., and D. M. Golden, 1978, Int. J. Chem. Kinet. 10, p. 489.

Smith, G. P., P. W. Fairchild, and D. R. Crosley, 1984, J. Chem. Phys 81, pp. 2667-

Smith, I. W. M., and R. Zellner, 1973, J. Chem. Soc., Faraday Trans. II 69, p. 1617.

Smith, I. W. M., and R. Zellner, 1974, J. Chem. Soc., Faraday Trans. II 70, pp. 1045-1056.

Smith, I. W. M., and R. Zellner, 1975, Int. J. Chem. Kinet., Symp. 1, p. 341.

Smith, R. D., 1978, Int. J. Chem. Kinet. 10, p. 519.

Smith, W. S., C. C. Chou, and F. S. Rowland, 1977, Geophys. Res. Lett. 4, pp. 517-519.

Sparks, R. K., L. R. Carlson, K. Shobatake, M. L. Kowalczyk, and Y. T. Lee, 1980, J. Chem. Phys. 72, pp. 1401-1402.

Spencer, J. E., and F. S. Rowland, 1978, J. Phys. Chem. 82, pp. 7-10.

Sridharan, U. C., B. Reimann, and F. Kaufman, 1980, J. Chem. Phys. 73, pp. 1286-1293.

Sridharan, U. C., L. X. Qiu, and F. Kaufman, 1981, J. Phys. Chem. 85, pp. 3361-3363.

Sridharan, U. C., L. X. Qiu, and F. Kaufman, 1982, J. Phys. Chem. 86, pp. 4569-4574.

Sridharan, U. C., L. X. Qiu, and F. Kaufman, 1984, J. Phys. Chem. 88, pp. 1281-1282.

Stachnik, R. A., M. J. Molina, and L. T. Molina, 1985, "Pressure and Temperature Dependences of the OH and HNO_3 Reaction," J. Phys. Chem., to be submitted.

Staricco, E. H., S. E. Sicre, and H. J. Schumacher, 1962, Z. Phys. Chem. N.F. 31, p. 385.

Stedman, D. H., and H. Niki, 1973, J. Phys. Chem. 77, p. 2604.

Stedman, D. H., M. A. A. Clyne, and J. A. Coxon, 1968, quoted in Clyne and Coxon (1968).

Steiner, H., and E. K. Rideal, 1939, Proc. Roy. Soc. (London) Sec. A. 173, p. 503.

Stephens, R. D., 1984, J. Phys. Chem. 88, pp. 3308-13.

Stief, L. J., W. A. Payne, J. H. Lee, and J. V. Michael, 1979, J. Chem. Phys. 70, pp. 5241-5243.

Stief, L. J., D. F. Nava, W. A. Payne, and J. V. Michael, 1980, J. Chem. Phys. 73, p. 2254-2258.

Stief, L. J., W. D. Brobst, D. F. Nava, R. P. Borkowski, and J. V. Michael, 1982, J. Chem. Soc. Faraday Trans. II 78, pp. 1391-1401.

Stimpfle, R., R. Perry, and C. J. Howard, 1979, J. Chem. Phys. 71, pp. 5183-5190.

Stockwell, W. R., and J. G. Calvert, 1978, J. Photochem. 8, pp. 193-203.

Stockwell, W. R., and J. G. Calvert, 1983, Atmospheric Environment 17, pp. 2231-2235.

Streit, G. E., C. J. Howard, A. L. Schmeltekopf, J. A. Davison, and H. I. Schiff, 1976, J. Chem. Phys. 65, pp. 4761-4764.

Streit, G. E., J. S. Wells, F. C. Fehsenfeld, and C. J. Howard, 1979, J. Chem. Phys. 70, pp. 3439-3443.

Stuhl, F., 1973a, Ber. Bunsenges. Phys. Chem. 77, p. 674.

Stuhl, F., 1973b, J. Chem. Phys. 59, p. 635.

Stuhl, F., 1974, Ber. Bunsenges. Phys. Chem. 78, p. 230.

Stuhl, F., and H. Niki, 1971, J. Chem. Phys. 55, p. 3954.

Stuhl, F., and H. Niki, 1972, J. Chem. Phys. 57, pp. 3671-3677.

Su, F., J. G. Calvert, C. R. Lindley, W. M. Uselman, and J. H. Shaw, 1979a, J. Phys. Chem. 83, pp. 912-920.

Su, F., J. G. Calvert, J. H. Shaw, H. Niki, P. D. Maker, C. M. Savage, and L. D. Breitenbach, 1979b, Chem. Phys. Lett. 65, pp. 221-225.

Su, F., J. G. Calvert, and J. H. Shaw, 1979c, J. Phys. Chem. 83, pp. 3185-91.

Sullivan, J. O., and P. Warneck, 1965, J. Phys. Chem. 69, p. 1749.

Swanson, D., B. Kan, and H. S. Johnston, 1984, J. Phys. Chem. 88, p. 3115.

Takacs, G. A., and G. P. Glass, 1973a, J. Phys. Chem. 77, p. 1060.

Takacs, G. A., and G. P. Glass, 1973b, J. Phys. Chem. 77, p. 1182.

Takacs, G. A., and G. P. Glass, 1973c, J. Phys. Chem. 77, p. 1948.

Takacs, G. A., and C. J. Howard, 1984, J. Phys. Chem. 88, p. 2110.

Tang, K. Y., P. W. Fairchild, and E. K. C. Lee, 1979, J. Phys. Chem. 83, p. 569.

Temps, F., and H. Gg. Wagner, 1982, Ber. Bunsenges. Phys. Chem. 86, p. 119.

Thrush, B. A., and G. S. Tyndall, 1982a, J. Chem. Soc. Faraday II 78, pp. 1469-1475.

Thrush, B. A., and G. S. Tyndall, 1982b, Chem. Phys. Lett. 92, pp. 232-235.

Thrush, B. A., and J. P. T. Wilkinson, 1979, Chem. Phys. Lett. 66, pp. 441-443.

Thrush, B. A., and J. P. T. Wilkinson, 1981a, Chem. Phys. Lett. 81, pp. 1-3.

Thrush, B. A., and J. P. T. Wilkinson, 1981b, Chem. Phys. Lett. 84, pp. 17-19.

Tiee, J. J., F. B. Wampler, R. C. Oldenborg, and W. W. Rice, 1981, Chem. Phys. Lett. 82, pp. 80-84.

Torabi, A., and A. R. Ravishankara, 1984, paper presented at the 16th Informal Conference on Photochemistry, Harvard University, Cambridge, MA, August 1984.

Trainor, D. W., and C. W. von Rosenberg, Jr., 1974, J. Chem. Phys. 61, pp. 1010-1015.

Trevor, P. L., G. Black, and J. R. Barker, 1982, J. Phys. Chem. 86, p. 1661.

Troe, J., 1977, J. Chem. Phys. 66, p. 4745.

Tsuchiya, S., and T. Nakamura, 1979, Bull. Chem. Soc. Japan 52, pp. 1527-1528.

Tuazon, E. C., R. Atkinson, C. N. Plum, A. M. Winer and J. N. Pitts, 1983, Geophys. Res. Lett. 10, pp. 953-6.

Tuazon, E. C., E. Sanhueza, R. Atkinson, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., 1984, J. Phys. Chem. 88, pp. 3095-98.

Tully, F. P., 1983, Chem. Phys. Lett. 96, pp. 148-153.

Tully, F. P., and A. R. Ravishankara, 1980, J. Phys. Chem. 84, pp. 3126-3130.

Tully, F. P., A. R. Ravishankara, and K. Carr, 1983, Inter. J. Chem. Kinet. 15, pp. 1111-1118.

Turco, R. P., 1975, Geophys. Surveys 2, pp. 153-192.

Turco, R. P., R. J. Cicerone, E. C. Y. Inn, and L. A. Capone, 1981, J. Geophys. Res. 86, p. 5373.

van den Bergh, H. E., and A. B. Callear, 1971, Trans. Faraday Soc. 67, p. 2017.

Vanderzanden, J. W., and J. W. Birks, 1982, Chem. Phys. Lett. 88, pp. 109-114.

Vanlaethem-Meuree, N., J. Wisemberg, and P. C. Simon, 1978a, Bull. Acad. Roy. Belgique, Cl. Sci. 64, p. 31.

Vanlaethem-Meuree, N., J. Wisemberg, and P. C. Simon, 1978b, Bull. Acad. Roy. Belgique, Cl. Sci. 64, p. 42.

Vanlaethem-Meuree, N., J. Wisemberg, and P. C. Simon, 1979, Geophys. Res. Lett. 6, pp. 451-454.

Veyret, B., and R. Lesclaux, 1981, J. Phys. Chem. 85, p. 1918.

Veyret, B., J. C. Rayez, and R. Lesclaux, 1982, J. Phys. Chem. 86, pp. 3424-3430.

Viggiano, A. A., J. A. Davison, F. C. Fehsenfeld, and E. E. Ferguson, 1981, J. Chem. Phys. 74, p. 6113.

Volltrauer, H. N., W. Felder, R. J. Pirkle, and A. Fontijn, 1979, J. Photochem. 11, pp. 173-181.

Wagner, G., and R. Zellner, 1981, Ber. Bunsenges. Phys. Chem. 85, pp. 1122-1128.

Wagner, H. Gg., J. Warnatz, and C. Zetzsch, 1971, Anales Assoc. Quim. Argentina, 59, pp. 169-177.

Wagner, H. Gg., C. Zetzsch, and J. Warnatz, 1972, Ber. Bunsenges. Phys. Chem. 76, p. 526.

Walther, C.-D., and H. Gg. Wagner, 1983, Ber. Bunsenges. Phys. Chem. 87, pp. 403-409.

Warnatz, J., H. Gg. Wagner, and C. Zetzsch, 1972, Report 7-0240/92410/01017 Frankhofer Gesellchaft, Germany.

Washida, N., 1980, J. Chem. Phys. 73, p. 1665.

Washida, N., and K. D. Bayes, 1976, Int. J. Chem. Kinet. 8, p. 777.

Washida, N., R. J. Martinez, and K. D. Bayes, 1974, Z. Naturforsch. 29A, p. 251.

Washida, N., H. Akimoto, and M. Okuda, 1980a, J. Chem. Phys. 72, pp. 5781-5783.

Washida, N., H. Akimoto, and M. Okuda, 1980b, J. Phys. Chem. 73, p. 1673.

Washida, N., H. Akimoto, and M. Okuda, 1980c, Bull. Chem. Soc. Japan 53, pp. 3496-3503.

Watson, R. T., 1977, J. Phys. Chem. Reference Data 6, pp. 871-917.

Watson, R. T., 1980, Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report #FAA-EE:80:20, pp. 429-466, Dept. of Transportation, Washington, D.C.

Watson, R. T., E. S. Machado, R. L. Schiff, S. Fischer, and D. D. Davis, 1975, Proceedings of the 4th CIAP Conference. DOT-TSC-OST-75-38. Cambridge, Mass., February 1975. Dept. of Transportation, Washington, D.C.

Watson, R. T., G. Machado, S. Fischer, and D. D. Davis, 1976, J. Chem. Phys. 65, p. 2126.

Watson, R. T., G. Machado, B. C. Conaway, S. Wagner, and D. D. Davis, 1977, J. Phys. Chem. 81, p. 256.

Watson, R. T., S. P. Sander, and Y. L. Yung, 1979, J. Phys. Chem. 83, p. 2936.

Wecker, D., R. Johanssen, and R. N. Schindl , 1982, Ber. Bunsenges. Phys. Chem. 86, pp. 532-538.

Wei, C. N., and R. B. Timmons, 1975, J. Chem. Phys. 62, p. 3240.

Weissman, M., L. G. S. Shum, S. P. Heneghan, and S. W. Benson, 1981, J. Phys. Chem. 85, p. 2863.

West, G. A., R. E. Weston, Jr., and G. W. Flynn, 1978, Chem. Phys. Lett. 56, p. 429.

Westenberg, A. A., and N. de Haas, 1969a, J. Chem. Phys. 50, p. 707.

Westenberg, A. A., and N. de Haas, 1969b, J. Phys. Chem. 73, p. 1181.

Westenberg, A. A., and N. de Haas, 1972, J. Chem. Phys. 57, p. 5375.

Westenberg, A. A., and N. de Haas, 1973a, J. Chem. Phys. 58, pp. 4066-4071.

Westenberg, A. A., and N. de Haas, 1973b, J. Chem. Phys. 59, p. 6685.

Westenberg, A. A., and N. de Haas, 1973c, J. Chem. Phys. 58, pp. 4061-4065.

Westenberg, A. A., and N. de Haas, 1977, J. Chem. Phys. 66, p. 4900.

Westenberg, A. A., N. de Haas, and J. M. Roscoe, 1970a, J. Phys. Chem. 74, p. 3431.

Westenberg, A. A., J. M. Roscoe, and N. de Haas, 1970b, Chem. Phys. Lett. 7, pp. 597-599.

Whyte, A. R., and L. F. Phillips, 1983, Chem. Phys. Lett. 102, pp. 451-4.

Whytock, D. A., R. B. Timmons, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, 1976, J. Chem. Phys. 65, pp. 2052-2055.

Whytock, D. A., J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, 1977, J. Chem. Phys. 66, p. 2690.

Wilson, W. E., Jr., 1967, J. Chem. Phys. 46, p. 2017.

Wilson, W. E., and A. A. Westenberg, 1967, 11th Sumposium on Combustion (The Combustion Institute, Pittsburgh), p. 1143.

Wine, P. H., and A. R. Ravishankara, 1981, Chem. Phys. Lett. 77, pp. 103-109.

Wine, P. H., and A. R. Ravishankara, 1982, Chem. Phys. 69, pp. 365-373.

Wine, P. H., and A. R. Ravishankara, 1983, Chem. Phys. Lett. 96, pp. 129-132.

Wine, P. H., A. R. Ravishankara, D. L. Philen, D. D. Davis, and R. T. Watson, 1977, Chem. Phys. Lett. 50, p. 101.

Wine, P. H., N. M. Kreutter and A. R. Ravishankara, 1979, J. Phys. Chem. 83, p. 3191.

Wine, P. H., R. C. Shah, and A. R. Ravishankara, 1980, J. Phys. Chem. 84, pp. 2499-2503.

Wine, P. H., N. M. Kreutter, C. A. Gump, and A. R. Ravishankara, 1981a, J. Phys. Chem. 85, pp. 2660-2665.

Wine, P. H., A. R. Ravishankara, N. M. Kreutter, R. C. Shah, J. M. Nicovich, R. L. Thompson, and D. J. Wuebbles, 1981b, J. Geophys. Res. 86, pp. 1105-1112.

Wine, P. H., D. H. Semmes, and A. R. Ravishankara, 1981c, J. Chem. Phys. 75, pp. 4390-4395.

Wine, P. H., W. L. Chameides, and A. R. Ravishankara, 1981d, Geophys. Res. Lett. 8, pp. 543-546.

Wine, P. H., D. H. Semmes, and A. R. Ravishankara, 1982, Chem. Phys. Lett. 90, pp. 128-132.

Wine, P. H., J. M. Nicovich, R. J. Thompson, and A. R. Ravishankara, 1983, J. Phys. Chem. 87, pp. 3948-54.

Wine, P. H., R. J. Thomspon, A. R. Ravishankara, D. H. Semmes, C. A. Gump, A. Torabi, and J. M. Nicovich, 1984a, J. Phys. Chem. 80, p. 2095.

Wine, P. H., J. M. Nicovich, and A. R. Ravishankara, 1984b, "The Reaction of OH with CS_2. Direct Observation of Reversible Adduct Formation and Kinetics of OH Removal in the Presence of O_2", manuscript in preparation.

Winer, A. M., A. C. Lloyd, K. R. Darnell, and J. N. Pitts, Jr., 1976, J. Phys. Chem. 80, p. 1635.

WMO Global Ozone Research and Monitoring Project, 1982, Report No. 11, The Stratosphere 1981: Theory and Measurements.

WMO-NASA Global Ozone Research and Monitoring Project, 1985 (in preparation).

Wolfram, J., 1981, as quoted in Stief et al., 1982.

Wong, E. L., and F. R. Belles, 1971, NASA Tech. Note, NASA TN D-6495, NASA, Washington, D. C.

Wong, W., and D. D. Davis, 1974, Int. J. Chem. Kinet. 6, p. 401.

Wongdontri-Stuper, W., R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, 1979, J. Photochem. 10, p. 163.

Wurzburg, E., and P. L. Houston, 1980, J. Chem. Phys. 72, p. 4811.

Yao, F., I. Wilson, and H. Johnston, 1982, J. Phys. Chem. 86, p. 3611.

Yoshino, K., D. F. Freeman, J. R. Esmond, and W. H. Parkinson, 1983, Planet. Space Sci. 31, pp. 339-353.

Zahniser, M. S., and C. J. Howard, 1980, J. Chem. Phys. 73, pp. 1620-1626.

Zahniser, M. S., and F. Kaufman, 1977, J. Chem. Phys. 66, p. 3673.

Zahniser, M. S., F. Kaufman, and J. G. Anderson, 1974, Chem. Phys. Lett. 27, p. 507.

Zahniser, M. S., F. Kaufman, and J. G. Anderson, 1976, Chem. Phys. Lett. 37, p. 226.

Zahniser, M. S., J. Chang, and F. Kaufman, 1977, J. Chem. Phys. 67, p. 997.

Zahniser, M. S., B. M. Berquist, and F. Kaufman, 1978, Int. J. Chem. Kinet. 10, p. 15.

Zellner, R., 1978, Ber. Bunsenges. Phys. Chem. 82, p. 1172.

Zellner, R., and K. Lorenz, 1984, J. Phys. Chem. 88, pp. 984-989.

Zellner, R., and W. Steinert, 1976, Int. J. Chem. Kinet. 8, pp. 397-409.

Zellner, R., and W. Steinert, 1981, Chem. Phys. Lett. 81, pp. 568-572.

Zellner, R., G. Wagner, and B. Himme, 1980, J. Phys. Chem. 84, pp. 3196-3198.

Zetsch, C., 1971, Ph.D. dissertation, Georg-August University, Gottingen, Germany.

Zetsch, C., 1973, First European Sym. on Combust. (ed. Weinberg, F. S., Academic Press, London), p. 35.

Zhitneva, G. P., and S. Ya. Pshezhetskii, 1978, Kinetika i Kataliz 19, p. 296.