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Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 8

NASA Panel for Data Evaluation:

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Jet Propulsion Laboratory
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16. Abstract

This is the eighth in a series of evaluated sets of rate constants and photochemical cross sections complied 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, Documentation Section, 111-116B, California Institute of Technology, Pasadena, California, 91109.

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This is the eighth 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, Documentation Section, 111-116B, 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 eighth 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)
7	JPL Publication 85-37 (DeMore *et al*., 1985)

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

W. B. DeMore, Chairman

D. M. Golden (three-body reactions, equilibrium constants)

R. F. Hampson (halogen chemistry)

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

M. J. Kurylo (SO_x chemistry)

M. J. Molina (photochemical data)

A. R. Ravishankara (hydrocarbon oxidation)

S. P. Sander (NO_x chemistry)

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 may 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, but only when it is expected that they will appear as published journal articles. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel considers the question of consistency of data with expectations based on the theory of reaction kinetics, and when 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 important rate constants for which no experimental data are available, the panel may provide estimates of rate constant parameters based on analogy to similar reactions for which data are available.

RECENT CHANGES AND CURRENT NEEDS OF LABORATORY KINETICS

Laboratory studies have produced no major changes in the kinetics and photochemistry used to model the normal stratosphere since the publication of our previous evaluation, JPL Publication 85-37. There are approximately thirty-seven changes in the rate constant recommendations in the present evaluation, but these are for the most part minor. Nonetheless, an important refinement has been made in the rate constant for OH + HO_2, and some significant changes in NO_x chemistry have also been made. Forty-two new reactions have been added, representing processes which play small but possibly significant roles in the stratosphere. Some reactions which are thought to be unimportant in the stratosphere are included for completeness and for possible applications to laboratory studies.

The recent emphasis on Antarctic chemistry, with its unusual characteristics of low temperature and the presence of polar stratospheric clouds, has focused attention on three areas of stratospheric chemistry not previously considered very important: (1) chemistry at temperatures as low as 180 K; (2) heterogeneous reactions, especially on ice particles; and (3) certain reactions such as ClO + ClO, which are normally not competitive in the stratosphere because of the low ClO concentration.

Very few laboratory studies of stratospheric chemistry have been conducted at temperatures below 220 K, partly because of difficulties with enhanced surface reactivity, and because such work has not been considered relevant to the stratosphere. It is now apparent that increased emphasis should be placed on the temperature regime of 180-220 K, especially since the simple Arrhenius temperature coefficients of several very important reactions, e.g., Cl + CH_4 and HO_2 + O_3, are not sufficiently reliable for extrapolation to very low temperatures. Indeed, the Arrhenius equation may prove to be unacceptable for wide temperature ranges, because of the more complex dependence shown by many reactions.

An additional aspect of low temperature chemistry is the possibly enhanced role of complex formation. Examples are the formation of O_2 complexes with species such as ClO and atomic chlorine. The kinetics and thermochemistry for these processes are not well known. In this connection, we have now provided uncertainty estimates in the tabulation of equilibrium constants, Table 3. The chemistry and photochemistry of complexes may also be significant in certain cases.

Heterogeneous chemistry on aerosol particles has previously been considered to be of marginal importance in the stratosphere (i.e., see the discussion on heterogeneous chemistry on page 16). It has nevertheless long been recognized that certain very slow gas phase processes, such as hydrolysis of chlorine nitrate, might be significantly accelerated on particle surfaces. It is now thought that such processes on ice particles are possibly of major importance in Antarctic ozone chemistry. The effects of volcanic emissions, which temporarily increase the stratospheric particle loading by large amounts, may also be important in short term (two to three year) ozone fluctuations.

Measurements in Antarctica show that unexpectedly high concentrations of ClO are present in certain regions within the polar vortex. As a consequence, reactions such as ClO + ClO may play a major role in the chlorine chemistry of that region. Very little is known about the chemistry of the Cl_2O_2 dimer, which may exist in more than one isomeric form. In the present evaluation, we have not attempted to make recommendations for the high chlorine chemistry because of the lack of information.

With regard to changes made in the present evaluation, it should also be mentioned that a table of enthalpy data has now been added as an Appendix.

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. Bair and coworkers (Locker et al., 1987) report formation of about 60% electronically excited $O_3(^3B_2)$ as an intermediate in the O + O_2 + M reaction. Based on their rate constant for quenching to the ground state, the ratio of excited O_3 to ground state O_3 is at most a few parts per thousand at 60 km, and decreases sharply at lower altitudes. Thus, unless the quenching process itself results in chemical change, the process may be insignificant.

$O(^1D)$ Reactions

The data base for $O(^1D)$ kinetics is in fairly good condition. There is good to excellent agreement among 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. The rate coefficient for the reaction of $O(^1D)$ with HCN should be measured since it may play a role in the atmospheric oxidation of this trace gas.

HO_x Reactions

Our knowledge of the kinetics of HO_x radicals has continued to improve. The most significant development with this report is on the $OH + HO_2$ reaction. This reaction is a key HO_x radical termination step throughout much of the atmosphere. New measurements by Keyser (1987) appear to explain a discrepancy between previous low pressure and high pressure measurements. Keyser has found a systematic error due to the presence of atomic H and O in the low pressure discharge flow experiments. The recommended rate coefficient for the $OH + HO_2$ reaction has been increased and the previous pressure dependence has been removed. The recommendation for $k(HO_2 + O_3)$ has also been revised, but the overall situation for this reaction is less satisfactory. All of the data for the temperature range 240-400 K cannot be fit satisfactorily with a single Arrhenius equation. The recommendation is weighted heavily toward the low temperature data for stratospheric applications. High quality measurements that avoid the limitations of the previous studies are still needed for both reactions.

NO_x Reactions

The data base for NO_x reactions is relatively well established. The rate constant for the important $O + NO_2$ reaction has been revised resulting in a 20% increase at 220 K. Our understanding of the important $OH + HNO_3$ reaction 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 reactions 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 atomic chlorine 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 two 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 and (2) CH_3OOH + OH, which has been recently studied in a competitive system and found to be extremely rapid. Discrepancies in the absorption cross sections of CH_3O_2 and HO_2 have added to the uncertainty regarding the rate coefficient for the

$CH_3O_2 + HO_2$ reaction. Even though the rate constants for the two reactions mentioned above are not very well known, the effects of these uncertainties on stratospheric O_3 perturbation calculations are negligible.

One 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 $CH_3O_2 + CH_3O_2$ and $CH_3O_2 + HO_2$.

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.

Halogen Chemistry

The recommendations for the important ClO_x reactions have not changed significantly since the previous evaluation. This reflects the fact that most of the important homogeneous gas phase processes are well understood. There is a better upper limit to the rate of reaction of $ClONO_2$ with HCl and a new entry for the reaction of $ClONO_2$ with H_2O. The data indicate that these homogeneous gas phase reactions are too slow to be important in the chemistry of the stratosphere, but it is possible that the corresponding heterogeneous reactions may be important under certain conditions such as those in the atmosphere above Antarctica. There are new entries for the reactions of OH with seven potential alternative chlorofluorocarbons. There are still a number of questions regarding the important ClO + ClO reaction: the absolute rate as a function of T and P; the relative importance of bimolecular and termolecular reaction channels as a function of T and P; the dependence of product branching ratios on T and P; importance of the dimer and its reactions and photochemistry; possible role of complex formation with O_2. There are only minor changes in the data base for reactions of BrO_x and FO_x species apart from changes in the recommendations for the reactions of Br atoms with HO_2 and H_2O_2. There have been several recent studies of the important BrO + ClO reaction which have improved our knowledge of the rate constant at room temperature, but further work is required to determine the temperature dependence and product ratios.

SO_x Reactions

The data base 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 now have information on the temperature-dependence of several SH reactions important in the atmospheric oxidation of H_2S and first-time information on several HSO reactions. Nevertheless, our understanding of the reactivity of these radicals is still far from complete. Similar improvements have been seen in the data for the reactions of SO with several atmospheric molecules (notably ClO, BrO, and NO_2). Of particular interest are the first direct measurements of $HOSO_2$ which had been postulated by Stockwell and Calvert (1983) and Margitan (1984a) as an intermediate in the oxidation of SO_2 into sulfuric acid via the sequence

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

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

New data by Gleason et al. (1987) and by Gleason and Howard (1987) result in a direct determination of the rate constant for the second reaction and 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. Recent data for OH + OCS does not reveal a rate constant dependence on total pressure or O_2 pressure despite the observation of direct formation of SH in both the CS_2 and OCS reactions and the postulation 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

Twelve new 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.

The total flux of alkali metals through the atmosphere is relatively small, e.g., one or two orders of magnitude less than CFMs. Therefore extremely efficient catalytic cycles are required in order for Na to have a significant effect on stratospheric chemistry. There are no measurements of metals or metal compounds in the stratosphere which indicate a significant role.

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.

Some recent studies have shown that the polar species NaO and NaOH associate with abundant gases such as O_2 and CO_2 with very fast rates in the atmosphere. It has been proposed that reactions of this type will lead to the production of clusters with many molecules attached to the sodium compounds. Photolysis is expected to compete with the association reactions and to limit the cluster concentrations in daylight. If atmospheric sodium does form large clusters, it is unlikely that Na species can have a significant role in stratospheric ozone chemistry. In order to assess the importance of these processes, data are needed on the association rates and the photolysis rates involving the cluster species.

Photochemical Cross Sections

The absorption cross sections of O_2 around 200 nm -- 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.

The temperature dependence of the absorption cross sections of HO_2NO_2 and H_2O_2 in the 300 nm region might be significant and should be determined. The photochemistry of the ClO dimer, Cl_2O_2, must be studied in detail.

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_3Cl, CHF_2Cl, etc.) or C=C (C_2Cl_4, C_2HCl_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). As previously mentioned, Antarctic conditions require the consideration of even lower temperatures.

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 composition of this region of the atmosphere which may be due to inaccurate rate data or missing chemistry. In this region the composition of the atmosphere is predominantly photochemically controlled and the photolytic lifetimes of temporary reservoir species such as HOCl, HO_2NO_2, $ClONO_2$, 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 has 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 $Cl + O_3$, $NO + ClO$, $NO + O_3$, etc., have occurred in the last few years. 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 ClO_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 1.3 to 1.8 over the 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 ClO_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 K and lower) and the high total pressures (30-200 torr).

Heterogeneous Effects

A continuing question in stratospheric modeling is whether or not aerosols perturb the homogeneous chemistry to a significant degree. This question has assumed much greater importance in connection with the possible role of polar stratospheric clouds in Antarctic chemistry. 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 such as SO_2.

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 is 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 HCl by the Cl + 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 meteoritic 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 large changes that may occur 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 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 ClO + NO, which normally produces Cl + NO_2 as a bimolecular product, but which undoubtedly involves ClONO (chlorine nitrite) as an intermediate. This can be viewed as a chemical activation process forming $(ClONO)^*$ which decomposes 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 especially 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 $A + B \rightleftarrows [AB]^* \overset{M}{\rightarrow} AB$ are given in the form

$$k_o(T) = k_o^{300}(T/300)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

(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:

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

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:

$$k_o^x(T) = \beta_x k_{o,sc}^x(T)$$

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 $k_{o,sc}^x(T)$ 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 at 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 are to be extrapolated beyond 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 Limit 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 being 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 accurate, a "reasonable guess" of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is effective over the entire range of stratospheric conditions.

Temperature Dependence of High-Pressure Limit Rate Constants: m

There are 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 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 Cl-atoms with NO_2. These reactants may come together to form either $ClNO_2$ or ClONO. 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 case that we are sure about is the above example. In the past however, there was some thought that data on the reaction between ClO radicals and NO_2 could be understood only in terms of the formation of both chlorine nitrate ($ClONO_2$) and other isomers (ClOONO, OClONO). 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 16 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:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

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 ΔE/R are, respectively, the uncertainty in the rate constant at 298 K and in the Arrhenius temperature coefficient, as listed in Table 1. This approach is based on the fact that rate constants are almost always known with minimum uncertainty at room temperature. The overall uncertainty normally increases at other temperatures, because there are usually fewer data and it is almost always more difficult to make measurements at other temperatures. It is important to note that the uncertainty at a temperature T <u>cannot</u> be calculated from the expression exp(ΔE/RT). The above expression for f(T) must be used to obtain the correct result.

The uncertainty represented by f(298) is normally symmetric; i.e., the rate constant may be greater than or less than the central value, k(298), by the factor f(298). In a few cases in Table 1 asymmetric uncertainties are given in the temperature coefficient. Examples of symmetric and asymmetric error limits are shown in Figure 1.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_o 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 techniques, 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 form. 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 recommended rate constants for the reactions HO_2 + NO and Cl + $ClONO_2$ 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.

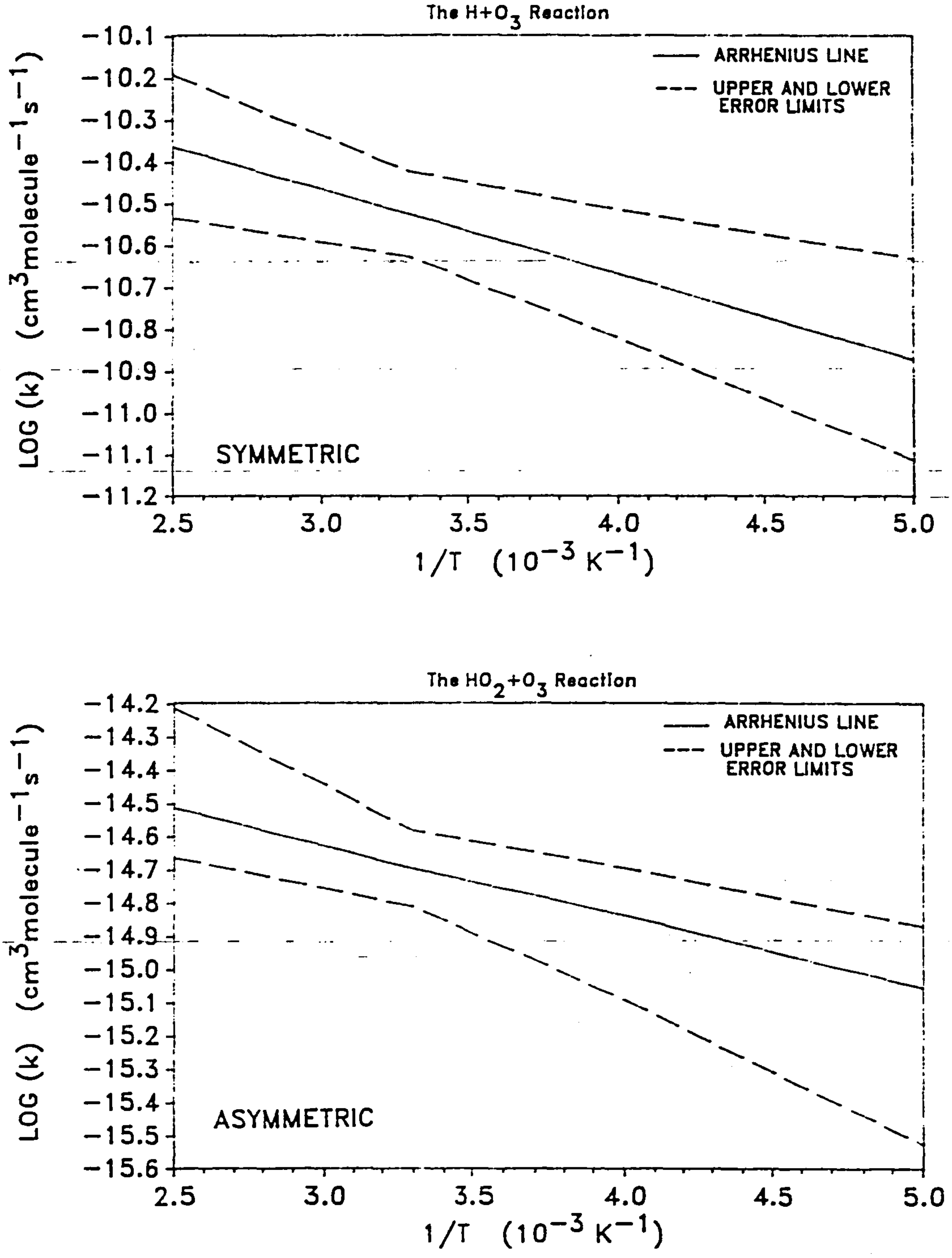

Fig. 1. Symmetric and Asymmetric Error Limits

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[a]

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	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
$O(^1D) + N_2 \rightarrow O + N_2$	$1.8\text{x}10^{-11}$	-(110±100)	$2.6\text{x}10^{-11}$	1.2	A2
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
$O(^1D) + O_2 \rightarrow O + O_2$	$3.2\text{x}10^{-11}$	-(70±100)	$4.0\text{x}10^{-11}$	1.2	A2
$O(^1D) + CO_2 \rightarrow O + CO_2$	$7.4\text{x}10^{-11}$	-(120±100)	$1.1\text{x}10^{-10}$	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
& $O(^1D) + HCl \rightarrow$ products	$1.5\text{x}10^{-10}$	0±100	$1.5\text{x}10^{-10}$	1.2	A2, A7
$O(^1D) + HF \rightarrow OH + F$	$1.4\text{x}10^{-10}$	0±100	$1.4\text{x}10^{-10}$	2.0	A8
# $O(^1D) + HBr \rightarrow$ products	$1.5\text{x}10^{-10}$	0±100	$1.5\text{x}10^{-10}$	2.0	A9
# $O(^1D) + Cl_2 \rightarrow$ products	$2.8\text{x}10^{-10}$	0±100	$2.8\text{x}10^{-10}$	2.0	A10
$O(^1D) + CCl_4 \rightarrow$ products	$3.3\text{x}10^{-10}$	0±100	$3.3\text{x}10^{-10}$	1.2	A2, A11

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}	0±100	2.3×10^{-10}	1.2	A2, A11
$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}	0±100	1.4×10^{-10}	1.3	A2, A11
$O(^1D) + CF_4 \rightarrow CF_4 + O$	1.8×10^{-13}	0±100	1.8×10^{-13}	2.0	A2, A11
$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0±100	3.6×10^{-10}	2.0	A2, A12
$O(^1D) + CFClO \rightarrow$ products	1.9×10^{-10}	0±100	1.9×10^{-10}	2.0	A2, A12
$O(^1D) + CF_2O \rightarrow$ products	7.4×10^{-11}	0±100	7.4×10^{-11}	2.0	A2, A12
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0±100	2.5×10^{-10}	1.3	A2, A13
<u>HO_x Reactions</u>					
$H + O_2 \xrightarrow{M} HO_2$	(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	8.1×10^{-11}	0±200	8.1×10^{-11}	1.3	B2
$O + OH \rightarrow O_2 + H$	2.2×10^{-11}	-(120±100)	3.3×10^{-11}	1.2	B3
& $O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-(200±100)	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
* $OH + HO_2 \rightarrow H_2O + O_2$	4.6×10^{-11}	-(230±200)	1.0×10^{-10}	1.3	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}	240±240	1.9×10^{-12}	1.4	B8
$\xrightarrow{M} H_2O_2$	(See Table 2)				
$OH + H_2O_2 \rightarrow H_2O + HO_2$	3.3×10^{-12}	$200\pm^{100}_{300}$	1.7×10^{-12}	1.3	B9
$OH + H_2 \rightarrow H_2O + H$	5.5×10^{-12}	2000±400	6.7×10^{-15}	1.2	B10

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
& $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3\text{x}10^{-13}$	-(600±200)	$1.7\text{x}10^{-12}$	1.3	B11
$\xrightarrow{M} H_2O_2 + O_2$	$1.7\text{x}10^{-33}$[M]	-(1000±400)	$4.9\text{x}10^{-32}$[M]	1.3	B11
* $HO_2 + O_3 \rightarrow OH + 2O_2$	$1.1\text{x}10^{-14}$	$500\pm^{500}_{100}$	$2.0\text{x}10^{-15}$	1.3	B12
		NO_x Reactions			
$N + O_2 \rightarrow NO + O$	$4.1\text{x}10^{-12}$	3200±400	$8.9\text{x}10^{-17}$	1.25	C1
$N + O_3 \rightarrow NO + O_2$	-	-	$<1.0\text{x}10^{-15}$	-	C2
$N + NO \rightarrow N_2 + O$	$3.4\text{x}10^{-11}$	0±100	$3.4\text{x}10^{-11}$	1.3	C3
& $N + NO_2 \rightarrow N_2O + O$	-	-	$3.0\text{x}10^{-12}$	3.0	C4
$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
* $O + NO_2 \rightarrow NO + O_2$	$6.5\text{x}10^{-12}$	-(120±120)	$9.7\text{x}10^{-12}$	1.1	C5
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	$1.0\text{x}10^{-11}$	0±150	$1.0\text{x}10^{-11}$	1.5	C6
$O + N_2O_5 \rightarrow$ products	-	-	$<3.0\text{x}10^{-16}$	-	C7
$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0\text{x}10^{-17}$	-	C8
$O + HO_2NO_2 \rightarrow$ products	$7.8\text{x}10^{-11}$	3400±750	$8.6\text{x}10^{-16}$	3.0	C9
$O_3 + NO \rightarrow NO_2 + O_2$	$2.0\text{x}10^{-12}$	1400±200	$1.8\text{x}10^{-14}$	1.2	C10
& $NO + HO_2 \rightarrow NO_2 + OH$	$3.7\text{x}10^{-12}$	-(240±80)	$8.3\text{x}10^{-12}$	1.2	C11
* $NO + NO_3 \rightarrow 2NO_2$	$1.7\text{x}10^{-11}$	-(150±100)	$2.9\text{x}10^{-11}$	1.3	C12
$OH + NO \xrightarrow{M} HONO$	(See Table 2)				
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
& $OH + HNO_3 \rightarrow H_2O + NO_3$	(See Note C13 and ≠ below)			1.3	C13
& $OH + HO_2NO_2 \rightarrow$ products	$1.3x10^{-12}$	$-(380\pm^{270}_{500})$	$4.6x10^{-12}$	1.5	
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				
$O_3 + NO_2 \rightarrow NO_3 + O_2$	$1.4x10^{-13}$	2500±140	$3.2x10^{-17}$	1.15	C15
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0x10^{-19}$	-	C16
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
& $N_2O_5 + H_2O \rightarrow 2HNO_3$	-	-	$<2.0x10^{-21}$	-	C17
& $OH + NH_3 \rightarrow H_2O + NH_2$	$3.6x10^{-12}$	930±200	$1.6x10^{-13}$	1.4	C18
$NH_2 + HO_2 \rightarrow$ products	-	-	$3.4x10^{-11}$	2.0	C19
& $NH_2 + NO \rightarrow$ products	$3.8x10^{-12}$	-(450±150)	$1.7x10^{-11}$	2.0	C20
& $NH_2 + NO_2 \rightarrow$ products	$2.1x10^{-12}$	-(650±250)	$1.9x10^{-11}$	3.0	C21
& $NH_2 + O_2 \rightarrow$ products	-	-	$<3.0x10^{-18}$	-	C22
$NH_2 + O_3 \rightarrow$ products	$4.8x10^{-12}$	930±500	$2.1x10^{-13}$	3.0	C23
		Hydrocarbon Reactions			
* $OH + CO \rightarrow CO_2 + H$	$1.5x10^{-13}(1+0.6P_{atm})$	0±300	$1.5x10^{-13}(1+0.6P_{atm})$	1.3	D1
$OH + CH_4 \rightarrow CH_3 + H_2O$	$2.3x10^{-12}$	1700±200	$7.7x10^{-15}$	1.2	D2
# $OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O$	(See Note)				D3
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	$1.1x10^{-11}$	1100±200	$2.8x10^{-13}$	1.2	D4

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

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

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

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* $OH + C_3H_8 \rightarrow H_2O + C_3H_7$	1.4×10^{-11}	750±200	1.1×10^{-12}	1.3	D5
$OH + C_2H_4 \rightarrow$ 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	D6
# $OH + CH_3CHO \rightarrow CH_3CO + H_2O$	6.0×10^{-12}	-(250±200)	1.4×10^{-11}	1.4	D7
$OH + CH_3OOH \rightarrow$ products	1.0×10^{-11}	0±200	1.0×10^{-11}	2.0	D8
$OH + HCN \rightarrow$ products	1.2×10^{-13}	400±150	3.1×10^{-14}	3.0	D9
$OH + CH_3CN \rightarrow$ products	4.5×10^{-13}	900±400	2.2×10^{-14}	2.0	D10
$HO_2 + CH_2O \rightarrow$ adduct	-	-	4.5×10^{-14}	10.0	D11
# $O + HCN \rightarrow$ products	1.0×10^{-11}	4000±1000	1.5×10^{-17}	10.0	D12
$O + C_2H_2 \rightarrow$ products	3.0×10^{-11}	1600±250	1.4×10^{-13}	1.3	D13
$O + H_2CO \rightarrow$ products	3.4×10^{-11}	1600±250	1.6×10^{-13}	1.25	D14
# $O + CH_3CHO \rightarrow CH_3CO + OH$	1.8×10^{-11}	1100±200	4.5×10^{-13}	1.25	D15
$O + CH_3 \rightarrow$ products	1.1×10^{-10}	0±250	1.1×10^{-10}	1.3	D16
$CH_3 + O_2 \rightarrow$ products	-	-	$<3.0\times10^{-16}$	-	D17
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(See Table 2)				
* $CH_2OH + O_2 \rightarrow CH_2O + HO_2$	9.6×10^{-12}	0±500	9.6×10^{-12}	1.3	D18
* $CH_3O + O_2 \rightarrow CH_2O + HO_2$	3.9×10^{-14}	900±300	1.9×10^{-15}	1.5	D19
$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	-(140±140)	5.5×10^{-12}	1.3	D20
$CH_3 + O_3 \rightarrow$ products	5.4×10^{-12}	220±150	2.6×10^{-12}	2.0	D21
* $CH_3O_2 + O_3 \rightarrow$ products	-	-	$<3.0\times10^{-17}$	-	D22

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* $CH_3O_2 + CH_3O_2 \rightarrow$ products	1.9×10^{-13}	-(220±220)	4.0×10^{-13}	1.5	D23
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	-(180±180)	7.6×10^{-12}	1.2	D24
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	7.7×10^{-14}	$-(1300\pm^{500}_{1300}$	6.0×10^{-12}	3.0	D25
* $NO_3 + CO \rightarrow$ products	-	-	$<4.0\times10^{-19}$	-	D26
$NO_3 + CH_2O \rightarrow$ products	-	-	6.0×10^{-16}	1.5	D27
# $NO_3 + CH_3CHO \rightarrow$ products	1.4×10^{-12}	1900±300	2.4×10^{-15}	1.3	D28
		ClO_x Reactions			
& $Cl + O_3 \rightarrow ClO + O_2$	2.9×10^{-11}	260±100	1.2×10^{-11}	1.15	E1
$Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	E2
$Cl + CH_4 \rightarrow HCl + CH_3$	1.1×10^{-11}	1400±150	1.0×10^{-13}	1.1	E3
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	7.7×10^{-11}	90±90	5.7×10^{-11}	1.1	E4
$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}	-(40±250)	1.6×10^{-10}	1.5	E5
$Cl + C_2H_2 \rightarrow$ products	(See Table 2)				
* $Cl + CH_3OH \rightarrow CH_2OH + HCl$	5.7×10^{-11}	0±250	5.7×10^{-11}	1.5	E6
$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.3×10^{-11}	1250±200	4.9×10^{-13}	1.2	E7
$Cl + CH_3CN \rightarrow$ products	-	-	$<2.0\times10^{-15}$	-	E8
$Cl + CH_3CCl_3 \rightarrow CH_2CCl_3 + HCl$	-	-	$<4.0\times10^{-14}$	-	E9
$Cl + H_2CO \rightarrow HCl + HCO$	8.1×10^{-11}	30±100	7.3×10^{-11}	1.15	E10
$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	E11
& $Cl + HOCl \rightarrow Cl_2 + OH$	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	E12

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$Cl + HNO_3 \rightarrow$ products	-	-	$<1.7\times10^{-14}$	-	E13
& $Cl + HO_2 \rightarrow HCl + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	E14
$\rightarrow OH + ClO$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	E14
$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	E15
$Cl + OClO \rightarrow ClO + ClO$	5.9×10^{-11}	0±250	5.9×10^{-11}	1.25	E16
$Cl + ClONO_2 \rightarrow$ products	6.8×10^{-12}	-(160±200)	1.2×10^{-11}	1.3	E17
$Cl + NO \xrightarrow{M} NOCl$	(See Table 2)				
$Cl + NO_2 \xrightarrow{M} ClONO\ (ClNO_2)$	(See Table 2)				
* $Cl + NO_3 \rightarrow ClO + NO_2$	5.2×10^{-11}	0±400	5.2×10^{-11}	2.0	E18
# $Cl + N_2O \rightarrow ClO + N_2$	(See Note)				E19
* $Cl + ClNO \rightarrow NO + Cl_2$	6.0×10^{-11}	$0\pm^{500}_{250}$	6.0×10^{-11}	2.0	E20
$Cl + O_2 \xrightarrow{M} ClOO$	(See Table 2)				
$Cl + ClOO \rightarrow Cl_2 + O_2$	1.4×10^{-10}	0±250	1.4×10^{-10}	3.0	E21
$\rightarrow ClO + ClO$	8.0×10^{-12}	0±250	8.0×10^{-12}	3.0	E21
* $ClO + O \rightarrow Cl + O_2$	3.0×10^{-11}	-(70±70)	3.8×10^{-11}	1.2	E22
$ClO + NO \rightarrow NO_2 + Cl$	6.4×10^{-12}	-(290±100)	1.7×10^{-11}	1.15	E23
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(See Table 2)				
$ClO + NO_3 \rightarrow$ products	4.0×10^{-13}	0±400	4.0×10^{-13}	2.0	E24
& $ClO + HO_2 \rightarrow HOCl + O_2$	4.8×10^{-13}	$-(700\pm^{250}_{700})$	5.0×10^{-12}	1.4	E25
$ClO + H_2CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>2100	$<1.0\times10^{-15}$	-	E26
* $ClO + OH \rightarrow$ products	1.1×10^{-11}	-(120±150)	1.7×10^{-11}	1.5	E27

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$ClO + CH_4 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	E28
$ClO + H_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>4800	$<1.0\times10^{-19}$	-	E28
$ClO + CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	E28
$ClO + N_2O \rightarrow$ products	$\sim1.0\times10^{-12}$	>4300	$<6.0\times10^{-19}$	-	E28
* $ClO + ClO \rightarrow$ products	8.0×10^{-13}	1250±500	1.2×10^{-14}	2.0	E29
$ClO + O_3 \rightarrow ClOO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	E30
$\rightarrow OClO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	E30
* $OH + Cl_2 \rightarrow HOCl + Cl$	1.4×10^{-12}	900±400	6.7×10^{-14}	1.2	E31
& $OH + HCl \rightarrow H_2O + Cl$	2.6×10^{-12}	350±100	8.0×10^{-13}	1.3	E32
* $OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	500±500	5.0×10^{-13}	3.0	E33
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	1.7×10^{-12}	1100±200	4.3×10^{-14}	1.2	E34
$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	4.7×10^{-12}	1050±200	1.4×10^{-13}	1.2	E34
$CH + CHCl_3 \rightarrow CCl_3 + H_2O$	3.4×10^{-12}	1050±200	1.0×10^{-13}	1.2	E34
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	8.6×10^{-13}	1000±200	3.0×10^{-14}	1.3	E34
$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	8.3×10^{-13}	1550±200	4.6×10^{-15}	1.2	E34
$OH + CH_2ClF \rightarrow CHClF + H_2O$	2.1×10^{-12}	1150±150	4.4×10^{-14}	1.2	E34
$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$	5.0×10^{-12}	1800±200	1.2×10^{-14}	1.3	E35
# $OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$	1.5×10^{-12}	1800±200	3.6×10^{-15}	1.3	E36
# $OH + CH_3CHF_2 \rightarrow$ products	1.9×10^{-12}	1200±300	3.4×10^{-14}	1.3	E37
# $OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$	1.1×10^{-12}	1050±300	3.2×10^{-14}	1.3	E38
# $OH + CHClFCF_3 \rightarrow CClFCF_3 + H_2O$	7.2×10^{-13}	1250±300	1.1×10^{-14}	1.3	E39

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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Table-1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
# $OH + CH_2ClCClF_2 \rightarrow CHClCClF_2 + H_2O$	3.4×10^{-12}	1600±300	1.6×10^{-14}	2.0	E40
# $OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$	6.6×10^{-13}	1300±300	8.4×10^{-15}	1.5	E41
# $OH + CH_3CCl_2F \rightarrow CH_2CCl_2F + H_2O$	3.4×10^{-12}	1800±500	8.0×10^{-15}	3.0	E42
$OH + C_2Cl_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	E43
$OH + C_2HCl_3 \rightarrow$ products	4.9×10^{-13}	-(450±200)	2.2×10^{-12}	1.25	E44
$OH + CFCl_3 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<5.0\times10^{-18}$	-	E45
$OH + CF_2Cl_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3600	$<6.0\times10^{-18}$	-	E45
$OH + ClONO_2 \rightarrow$ products	1.2×10^{-12}	330±200	3.9×10^{-13}	1.5	E46
$O + HCl \rightarrow OH + Cl$	1.0×10^{-11}	3300±350	1.5×10^{-16}	2.0	E47
$O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10.0	E48
$O + ClONO_2 \rightarrow$ products	2.9×10^{-12}	800±200	2.0×10^{-13}	1.5	E49
$O + Cl_2O \rightarrow ClO + ClO$	2.9×10^{-11}	630±200	3.5×10^{-12}	1.4	E50
$O + OClO \rightarrow ClO + O_2$	2.8×10^{-11}	1200±300	5.0×10^{-13}	2.0	E51
# $OH + OClO \rightarrow HOCl + O_2$	4.5×10^{-13}	-(800±200)	6.8×10^{-12}	2.0	E52
$NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600±300	3.4×10^{-13}	2.0	E53
* $HCl + ClONO_2 \rightarrow$ products	-	-	$<1.0\times10^{-20}$	-	E54
$HCl + HO_2NO_2 \rightarrow$ products	-	-	$<1.0\times10^{-20}$	-	E55
# $H_2O + ClONO_2 \rightarrow$ products	-	-	$<2.0\times10^{-21}$	-	E56
		BrO_x Reactions			
* $Br + O_3 \rightarrow BrO + O_2$	1.7×10^{-11}	800±200	1.2×10^{-12}	1.2	F1
* $Br + H_2O_2 \rightarrow HBr + HO_2$	1.0×10^{-11}	>3000	$<5.0\times10^{-16}$	-	F2

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298)\exp\left|\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{298}\right)\right|$. Note that the exponent is absolute value.

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Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	F3
* $Br + HO_2 \rightarrow HBr + O_2$	1.5×10^{-11}	600±600	2.0×10^{-12}	2.0	F4
# $Br + Cl_2O \rightarrow BrCl + ClO$	-	-	3.8×10^{-12}	2.0	F5
$BrO + O \rightarrow Br + O_2$	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	F6
& $BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}	0±250	6.7×10^{-12}	1.5	F7
$\rightarrow Br + ClOO$	6.7×10^{-12}	0±250	6.7×10^{-12}	1.5	F7
$BrO + NO \rightarrow NO_2 + Br$	8.8×10^{-12}	-(260±130)	2.1×10^{-11}	1.15	F8
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(See Table 2)				
$BrO + BrO \rightarrow 2\ Br + O_2$	1.4×10^{-12}	-(150±150)	2.3×10^{-12}	1.25	F9
$\rightarrow Br_2 + O_2$	6.0×10^{-14}	-(600±600)	4.4×10^{-13}	1.25	F9
$BrO + O_3 \rightarrow Br + 2O_2$	$\sim 1.0 \times 10^{-12}$	>1600	$<5.0 \times 10^{-15}$	-	F10
$BrO + HO_2 \rightarrow$ products	-	-	5.0×10^{-12}	3.0	F11
$BrO + OH \rightarrow$ products	-	-	1.0×10^{-11}	5.0	F12
* $OH + Br_2 \rightarrow HOBr + Br$	4.2×10^{-11}	0±600	4.2×10^{-11}	1.3	F13
& $OH + HBr \rightarrow H_2O + Br$	1.1×10^{-11}	0±250	1.1×10^{-11}	1.2	F14
$OH + CH_3Br \rightarrow CH_2Br + H_2O$	6.0×10^{-13}	820±200	3.8×10^{-14}	1.25	F15
$O + HBr \rightarrow OH + Br$	6.7×10^{-12}	1550±200	3.7×10^{-14}	1.3	F15
		FO_x Reactions			
$F + O_3 \rightarrow FO + O_2$	2.8×10^{-11}	230±200	1.3×10^{-11}	2.0	G1
$F + H_2 \rightarrow HF + H$	1.5×10^{-10}	520±250	2.7×10^{-11}	1.3	G2
$F + CH_4 \rightarrow HF + CH_3$	3.0×10^{-10}	400±300	8.0×10^{-11}	1.5	G3

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
* $F + H_2O \rightarrow HF + OH$	4.6×10^{-11}	400±200	1.2×10^{-11}	1.5	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)				
$NO + FO \rightarrow NO_2 + F$	2.6×10^{-11}	0±250	2.6×10^{-11}	2.0	G5
$FO + FO \rightarrow 2\,F + O_2$	1.5×10^{-11}	0±250	1.5×10^{-11}	3.0	G6
$FO + O_3 \rightarrow F + 2\,O_2$	(See Note)				G7
$\rightarrow FO_2 + O_2$	(See Note)				G7
$FO + NO_2 \xrightarrow{M} FONO_2$	(See Table 2)				
$O + FO \rightarrow F + O_2$	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
$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$	3.1×10^{-12}	-(500±200)	1.6×10^{-11}	1.3	G10
$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$	3.5×10^{-12}	-(430±200)	1.5×10^{-11}	1.3	G10
$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2$	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}	70±70	4.7×10^{-12}	1.2	H1
* $OH + OCS \rightarrow$ products	1.1×10^{-13}	1200±500	1.9×10^{-15}	2.0	H2
& $OH + CS_2 \rightarrow$ products	(See Note)	-	-	-	H3
$OH + SO_2 \xrightarrow{M} HOSO_2$	(See Table 2)				
$O + H_2S \rightarrow OH + SH$	9.2×10^{-12}	1800±550	2.2×10^{-14}	1.7	H4

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

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Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$O + OCS \rightarrow CO + SO$	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
$S + O_2 \rightarrow SO + O$	2.3×10^{-12}	0±200	2.3×10^{-12}	1.2	H7
$S + O_3 \rightarrow SO + O_2$	-	-	1.2×10^{-11}	2.0	H8
$S + OH \rightarrow SO + H$	-	-	6.6×10^{-11}	3.0	H9
$SO + O_2 \rightarrow SO_2 + O$	2.6×10^{-13}	2400±500	8.4×10^{-17}	2.0	H10
$SO + O_3 \rightarrow SO_2 + O_2$	3.6×10^{-12}	1100±200	9.0×10^{-14}	1.2	H11
$SO + OH \rightarrow SO_2 + H$	-	-	8.6×10^{-11}	2.0	H12
$SO + NO_2 \rightarrow SO_2 + NO$	1.4×10^{-11}	0±50	1.4×10^{-11}	1.2	H13
* $SO + ClO \rightarrow SO_2 + Cl$	2.8×10^{-11}	0±50	2.8×10^{-11}	1.3	H14
$SO + OClO \rightarrow SO_2 + ClO$	-	-	1.9×10^{-12}	3.0	H15
* $SO + BrO \rightarrow SO_2 + Br$	-	-	5.7×10^{-11}	1.4	H16
$SO_2 + HO_2 \rightarrow$ products	-	-	$<1.0 \times 10^{-18}$	-	H17
$SO_2 + CH_3O_2 \rightarrow$ products	-	-	$<5.0 \times 10^{-17}$	-	H18
$SO_2 + NO_2 \rightarrow$ products	-	-	$<2.0 \times 10^{-26}$	-	H19
$SO_3 + NO_2 \rightarrow$ products	-	-	1.0×10^{-19}	10.0	H19
# $SO_2 + NO_3 \rightarrow$ products	-	-	$<7.0 \times 10^{-21}$	-	H20
$SO_2 + O_3 \rightarrow SO_3 + O_2$	3.0×10^{-12}	>7000	$<2.0 \times 10^{-22}$	-	H21
* $Cl + H_2S \rightarrow HCl + SH$	5.7×10^{-11}	0±50	5.7×10^{-11}	1.3	H22
& $Cl + OCS \rightarrow SCl + CO$	-	-	$<1.0 \times 10^{-16}$	-	H23
$ClO + OCS \rightarrow$ products	-	-	$<2.0 \times 10^{-16}$	-	H24

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
$ClO + SO_2 \rightarrow Cl + SO_3$	-	-	$<4.0\times10^{-18}$	-	H24
$SH + H_2O_2 \rightarrow$ products	-	-	$<5.0\times10^{-15}$	-	H25
$SH + O \rightarrow H + SO$	-	-	1.6×10^{-10}	5.0	H26
* $SH + O_2 \rightarrow OH + SO$	-	-	$<4.0\times10^{-19}$	-	H27
* $SH + O_3 \rightarrow HSO + O_2$	9.7×10^{-12}	280±200	3.8×10^{-12}	1.3	H28
* $SH + NO_2 \rightarrow HSO + NO$	2.9×10^{-11}	-(240±100)	6.5×10^{-11}	1.3	H29
$SH + NO \xrightarrow{M} HSNO$	(See Table 2)				
# $HSO + NO \rightarrow$ products	-	-	$<1.0\times10^{-15}$	-	H30
# $HSO + NO_2 \rightarrow HSO_2 + NO$	-	-	9.6×10^{-12}	2.0	H30
# $HSO + O_2 \rightarrow$ products	-	-	$<2.0\times10^{-17}$	-	H30
$HSO + O_3 \rightarrow$ products	-	-	1.0×10^{-13}	5.0	H31
# $HSO_2 + O_2 \rightarrow HO_2 + SO_2$	-	-	3.0×10^{-13}	3.0	H32
* $HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	1.3×10^{-12}	330±200	4.4×10^{-13}	1.2	H33
# $H_2S + NO_3 \rightarrow$ products	-	-	$<3.0\times10^{-14}$	-	H34
$CS + O_2 \rightarrow OCS + O$	-	-	2.9×10^{-19}	2.0	H35
$CS + O_3 \rightarrow OCS + O_2$	-	-	3.0×10^{-16}	3.0	H36
$CS + NO_2 \rightarrow OCS + NO$	-	-	7.6×10^{-17}	3.0	H36
Metal Reactions					
$Na + O_2 \xrightarrow{M} NaO_2$	(See Table 2)				
& $Na + O_3 \rightarrow NaO + O_2$	5×10^{-10}	0±400	5.0×10^{-10}	1.5	J1
$\rightarrow NaO_2 + O$	$<3\times10^{-11}$	0±400	$<3.0\times10^{-11}$	-	J1

[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

Table 1. (Continued)

Reaction	A-Factor[a]	E/R±(ΔE/R)	k(298 K)	f(298)[b]	Notes
# $Na + N_2O \rightarrow NaO + N_2$	2.4×10^{-10}	1600±400	1.1×10^{-12}	1.3	J2
# $Na + Cl_2 \rightarrow NaCl + Cl$	7.3×10^{-10}	0±200	7.3×10^{-10}	1.3	J3
# $NaO + O \rightarrow Na + O_2$	3.7×10^{-10}	0±400	3.7×10^{-10}	3.0	J4
# $NaO + O_2 \xrightarrow{M} NaO_3$	(See Table 2)				
# $NaO + O_3 \rightarrow NaO_2 + O_2$	1.6×10^{-10}	0±400	1.6×10^{-10}	2.0	J5
$\rightarrow Na + 2O_2$	6×10^{-11}	0±800	6.0×10^{-11}	3.0	J5
# $NaO + H_2 \rightarrow NaOH + H$	2.6×10^{-11}	0±600	2.6×10^{-11}	2.0	J6
# $NaO + H_2O \rightarrow NaOH + OH$	2.2×10^{-10}	0±400	2.2×10^{-10}	2.0	J7
# $NaO + NO \rightarrow Na + NO_2$	1.5×10^{-10}	0±400	1.5×10^{-10}	4.0	J8
# $NaO + CO_2 \xrightarrow{M} NaCO_3$	(See Table 2)				
$NaO + HCl \rightarrow$ products	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J9
# $NaO_2 + NO \rightarrow NaO + NO_2$			$<10^{-14}$		J10
# $NaO_2 + HCl \rightarrow$ products	2.3×10^{-10}	0±400	2.3×10^{-10}	3.0	J11
$NaOH + HCl \rightarrow NaCl + H_2O$	2.8×10^{-10}	0±400	2.8×10^{-10}	3.0	J12
# $NaOH + CO_2 \xrightarrow{M} NaHCO_3$	(See Table 2)				

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[a] Units are cm^3/molecule-sec.

[b] f(298) is the uncertainty at 298K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$. Note that the exponent is absolute value.

* Indicates a change from the previous Panel evaluation (JPL 85-37). Small round-off changes have been made for several entries in the table; these are not marked by asterisks.

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

& Indicates a change in the Note.

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, HCl, CCl_4, $CFCl_3$, CF_2Cl_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, CCl_4, $CFCl_3$, CF_2Cl_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 measurements 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 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 of the $O_2 + H_2$ product yield were made by Zellner *et al*. (1980) (1+0.5 or -1)% and by Glinski and Birks (1985) (0.006 + 0.007 or -0.006)%. 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*. (1986). Product studies by the latter indicate: $O(^3P)$ + HCl(9±5)%; H + ClO(24±5)%; and OH + Cl(67±10)%.

A8. $O(^1D)$ + HF. Rate coefficient and product yield measured by Wine *et al*. (1984, private communication). The $O(^3P)$ yield is less than 4%.

A9. $O(^1D) + HBr$. Rate coefficient and products measured by Wine et al. (1986). Product yields: $HBr + O(^3P)$ (20±7)%, $H + BrO$ <4.5%, and $OH + Br$ (80±12)%.

A10. $O(^1D) + Cl_2$. Rate coefficient and $O(^3P)$ product measured by Wine et al. (1985). Product yields: $Cl_2 + O(^3P)$ (25±10)%. The balance is probably $ClO + Cl$. An earlier indirect study by Freudenstein and Biedenkapp (1976) is in reasonable agreement on the yield of ClO.

A11. $O(^1D)$ + 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 CCl_4: quenching = (14±6)% and reaction = (86±6)%, (Force and Wiesenfeld, 1981a); for $CFCl_3$: quenching = (25±10)%, ClO formation = (60±15)% (Donovan, private communication, 1980); for CF_2Cl_2: quenching = (14±7)% and reaction = (86±14)% (Force and Wiesenfeld, 1981a), quenching = (10±10)%, ClO formation = (55±15)% (Donovan, private communication, 1980); for CF_4: quenching = 100% (Force and Wiesenfeld, 1981a).

A12. $O(^1D) + CCl_2O$, CFClO and CF_2O. For the reactions of $O(^1D)$ with CCl_2O and CFClO 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).

A13. $O(^1D) + NH_3$. Sanders et al. (1980a) have detected the products $NH(a^1\Delta)$ and OH formed in the reaction. They report the yield of $NH(a^1\Delta)$ is in the range 3-15% of the amount of OH detected.

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%; Finlayson-Pitts et al., 1981: <2%); and Dodonov et al., 1985: <0.3%). 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 five recent studies of this reaction: Hack et al. (1978), Hack et al. (1979c), Thrush and Wilkinson (1981b), Sridharan et al. (1982) and Keyser (1986). Related early work and combustion studies are referenced in the Sridharan et al. paper. All five 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. and Keyser because their measurements were the most direct and required the fewest corrections. The other measurements, (5.0±1.3) x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} by Thrush and Wilkinson (1981b) and (4.65 ± 1) x 10^{-11} by Hack et al. (1979c) are in reasonable agreement with the recommended value. Three of the studies reported the product channels: (a) 2OH, (b) $H_2O + O$, and (c) $H_2 + O_2$. Hack et al. (1978) $k_a/k = 0.69$, $k_b/k \le 0.02$, and $k_c/k = 0.29$; Sridharan et al. (1982) $k_a/k = 0.87 \pm 0.04$, $k_b/k = 0.04 \pm 0.02$, $k_c/k = 0.09 \pm .045$; and Keyser (1986) $k_a/k = 0.90 \pm 0.04$, $k_b/k = 0.02 \pm 0.02$, and $k_c/k = 0.08 \pm 0.04$. Hislop and Wayne (1977) and Keyser et al. (1985) reported on the yield of $O_2(b^1\Sigma)$ being formed in channel (c) as (2.8±1.3) x 10^{-4} and <8 x 10^{-3} of the total reactions. Keyser found the rate coefficient and product yields to be independent of temperature for 300 <T <245 K.

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), 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 five studies at room temperature (Keyser, 1982, Sridharan et al., 1982, Ravishankara et al., 1983b, Brune et al., 1983 and Nicovich and Wine, 1987) fitted to the temperature dependence given by Keyser (1982) and Nicovich and Wine (1987). 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. Sridharan et al. (1985) showed that the reaction products correspond to abstraction of an oxygen atom from HO_2 by the O reactant. Keyser et al. (1985) reported <1% O_2 $(b^1\Sigma)$ yield.

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. $OH + HO_2$. A new study by Keyser (1987) appears to resolve a discrepancy between low pressure discharge flow experiments which all gave rate coefficients near 7 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}: Keyser (1981), Thrush and Wilkinson (1981a), Sridharan et al. (1981, 1984), Temps and Wagner (1982), and Rozenshtein et al. (1984), and atmospheric pressure studies which gave rate coefficients near 11 x 10^{-11}: Lii et al. (1980a), Hochanadel et al. (1980), DeMore (1982), Cox et al. (1981), Burrows et al. (1981) and Kurylo et al. (1981). Laboratory measurements using a discharge flow experiment and a chemical model analysis of the results by Keyser (1987) demonstrate that the previous discharge flow measurements were probably subject to interference from small amounts of O and H. In the presence of excess HO_2 these atoms generate OH and result in a rate coefficient measurement which falls below the true value. The temperature dependence is from Keyser (1987) who covered the range 254 to 382 K. An additional study of this reaction including the temperature dependence is needed.

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), Ravishankara et al. (1979b) and Smith et al. (1984). 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 = 6.2 x 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 and 2.3) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The temperature dependence is from Wagner and Zellner, who reported rate constants for the range T = 250-580 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 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).

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), Takacs and Howard (1984, 1986), Sander (1984) and Kurylo *et al.* (1986). Data of Rozenshtein *et al.* (1984) are consistent with the low pressure recommendation but they report no change in k with pressure up to 1 atm. Earlier results of Thrush and Wilkinson (1979) are inconsistent with the recommendation. The termolecular expression is obtained from data of Sander *et al.* (1982), Simonaitis and Heicklen (1982) and Kurylo *et al.* (1986) 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 ~1 atm): (a) the HO_2 uv absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel *et al.* (1980), Sander *et al.* (1982), and Kurylo *et al.* (1987a); (b) the rate constant at 300 K: Paukert and Johnston (1972), Hamilton and Lii (1977), Cox and Burrows (1979), Lii *et al.* (1979), Tsuchiya and Nakamura (1979), Sander *et al.* (1982), Simonaitis and Heicklen (1982), and Kurylo *et al.* (1986) (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). Sahetchian *et al.* (1982, 1987) give evidence for the formation of a small amount of H_2 (~10%) at temperatures near 500 K but Baldwin *et al.* (1984) give evidence that the yield must be much less. Glinski and Birks (1985) report an upper limit of 1% H_2 yield at a total pressure of about 50 torr and 298 K but their experiment may have interference from wall reactions. For systems containing water vapor, the factors given by Lii *et al.* (1981) and Kircher and Sander (1984) can be incorporated: 1 + 1.4 x 10^{-21} $[H_2O]$ exp(2200/T).

B12. HO_2 + O_3. ~~The recommendation is based on three direct studies using discharge flow experiments:~~ Zahniser and Howard (1980) at 245 to 365 K, Manzanares et al. (1986) at 298 K, and Sinha et al. (1987) at 243 to 413 K. Indirect studies by Simonaitis and Heicklen (1973), DeMore and Tschuikow-Roux (1974), and DeMore (1979), are consistent with the direct measurements. The most extensive temperature dependence study (Sinha et al., 1987) indicates a curvature in the Arrhenius plot. A similar but less obvious curvature is found in the data of Zahniser and Howard (1980) and DeMore (1979). The recommendation incorporates only direct measurement data at temperatures less than 300 K and is not valid for temperatures greater than 300 K. The validity of the recommended expression is questionable at temperatures less than 240 K, where there are no data. High quality low temperature measurements are needed for this reaction.

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). A recent study by Iwata et al. (1986) suggested an upper limit of 3.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for the corresponding reaction involving $N(^2D)$ and $N(^2P)$ atoms (sum of all reaction channels).

C5. O + NO_2. Changed from JPL 85-37. k(298 K) is based on the results of Davis et al. (1973a), Slanger et al. (1973), Bemand et al. (1974), Ongstad and Birks (1986) and Geers-Muller and Stuhl (1987). The recommendation for E/R is from Davis et al., Ongstad and Birks, and Geers-Muller and Stuhl with the A-factor adjusted to give the recommended k(298 K) value.

C6. O + NO_3. Based on the study of Graham and Johnston (1978) at 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 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) 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 (1979b), 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, Burrows *et al*. (1979), has been dropped because of an error in the reference rate constant, k(OH + H_2O_2). The room temperature study of Rozenshtein *et al*. (1984) has also been disregarded due to an inadequate discussion of possible secondary reactions. The temperature dependence is from Howard (1980) and is in reasonable agreement with that given by Leu (1979b). A high pressure study is needed in view of the many unusual effects seen in other HO_2 reactions.

C12. NO + NO_3. Changed from JPL 85-37. The 298 K recommendation is based on the studies of Torabi and Ravishankara (1984), Hammer *et al*. (1986) and Sander and Kircher (1986), which are in excellent agreement. The T dependence is based on an average of the results from Sander and Kircher, and the data of Hammer *et al*. below 300 K.

C13. OH + HNO_3. 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; Jolly *et al*., 1985 (298 K), Stachnik *et al*., 1986); and (c) recent discharge low studies yielding the lower value for k(298 K) 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) 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*. (1986) at pressures of 10, 60 and 730 torr at 298 K. The two studies are in excellent agreement. Their "low pressure limit" agrees well with the average k(298 K) = 1.0×10^{-13} cm^3 s^{-1} derived from the four 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:

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

The coefficients 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. Jolly et al., also could not detect a pressure dependence between 1 torr (M = HNO_3) and 600 torr (M = SF_6) at 298 K. 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), C. A. Smith et al. (1984) and Barnes et al. (1986b). Trevor et al. studied this reaction over the temperature range 246-324 K and reported a temperature invariant value of 4.0×10^{-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. The early Barnes et al. study (1981) was carried out only at room temperature and 1 torr total pressure while their most recent study was performed in the pressure range 1-300 torr N_2 and temperature range 268-295 K with no rate constant variation being observed. In addition, k_{298} derived in Barnes et al. (1981) was revised upward in the later study from 4.1×10^{-12} to 5.0×10^{-12} due to a change in the rate constant for the reference reaction. The values of k at 298 K from the four studies are in excellent agreement. An unweighted least squares fit to the data from the above-mentioned studies 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 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. $N_2O_5 + H_2O$. Upper limit based on Tuazon et al. (1983) and Hjorth et al. (1987), who suggest that this limit may be close to the true homogeneous rate constant.

C18. $OH + NH_3$. 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 Pagsberg et al. (1979) and Cox et al. (1975) were not considered because these studies involved the analysis of a complex mechanism and the results are well outside the error limits implied by the above five direct studies. The results of Kurylo (1973) and Hack et al. (1974) were not considered because of their large discrepancies with the other direct studies (factors of 3.9 and 1.6 at room temperature, respectively). 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 a 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. $NH_2 + NO$. 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), Hall et al. (1986) and Dolson (1986) who observed room temperature OH yields of <22%, 13±2% and <15%, respectively. In addition, Andresen et al. set a lower limit of ≥29% for the channel $N_2 + H_2O$.

C21. $NH_2 + NO_2$. There have been four studies of this reaction (Hack et al. (1979b), Kurasawa and Lesclaux (1979), Whyte and Phillips (1983) and Xiang et al. (1985)). There is very poor agreement among these studies both for k at 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 four 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. $NH_2 + O_2$. The recommendation is based on the reported upper limits of 3×10^{-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), 1×10^{-17} (Patrick and Golden, 1984b) and 7.7×10^{-18} (Michael et al., 1985b) 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. Hack and Kurzke (1985) have observed a reaction between NH_2 and $O_2(^1\Delta)$, obtaining a rate constant of $(1 \pm 0.3) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} between 295 and 353 K.

C23. $NH_2 + O_3$. Changed from JPL-83-62. There is poor agreement between the recent studies 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. 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, 1987)). 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), Biermann 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, 1987), Hynes et al. (1986), Stachnik and Molina (private communication, 1987) and Wahner and Zetzsch (private communication, 1987). 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 298 K 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 Hynes et al. (1986)) as well as those in air (Fritz and Zellner (private communication, 1987), Niki et al. (1984), Hynes et al. (1986), Stachnik and Molina (private communication, 1987), Wahner and Zetzsch (private communication, 1987) 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 (Biermann 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 re-evaluated 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. Currently, there are no indications to suggest that the presence of O_2 has any effect on the rate coefficient other than as a third body. The E/R value in the pressure range 50-760 torr has been shown to be essentially zero between 220 and 298 K by Hynes et al. (1986), and Stachnik and Molina (private communications, 1987). Further substantiation of the temperature independence of k at 1 atm. may be worthwhile. 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. (1985) 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), DeMore (1984), and Hynes et al. (1986).

D2. OH + CH_4. This is an extremely well characterized reaction. All temperature dependence studies are in good agreement (Greiner (1970b), 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 + $^{13}CH_4$ (k_{13}). This reaction has been studied relative to the OH + CH_4 (k_{12}) reaction, since the ratio of the rate coefficients k_{13}/k_{12} is the quantity needed for identifying methane sources. Rust and Stevens (1980) obtained a value of 1.003 for $k_{13/12}$ at 298 K while the recent measurement of Davidson et al. (1987) yields 1.010±0.007 at the same temperature. No data on the temperature dependence of k_{13}/k_{12} is available. We have recommended the value measured by Davidson et al. since they present some reasons as to why Rust and Stevens' value could be low. The error bar is 1.010±0.007 and it overlaps with the measured value of Rust and Stevens.

D4. OH + C_2H_6. There is good agreement among nine studies of this reaction at 298 K, i.e., Greiner (1970a), Howard and Evenson (1976b), Overend et al. (1975), Lee and Tang (1982), Leu (1979b), Tully et al. (1983), Jeong et al. (1984), Tully et al. (1986), and Nielsen et al. (1986). All these studies were not carried out at exactly 298 K. Therefore, we have recalculated the 298 K value, by assuming an E/R of 1100 K, for those studies where the room temperature was not 298 K. The average of these nine measurements is k(298 K). 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), and Tully et al. (1986) are in agreement with the recommended value. Recent measurements by Wallington et al. (1987b) over the temperature range 234-438 K are in good agreement with the recommended values.

D5. OH + C_3H_8. There are many measurements of the rate coefficient at 298 K. In this evaluation we have considered only the direct measurements that are reported in the literature. These are measurements by Greiner (1970a), Tully et al. (1983), Droege and Tully (1986), Schmidt et al. (1985), Baulch et al. (1985), and Bradley et al. (1973). The 298 K value is the average of these six studies. Greiner (1970a), Tully et al. (1983), and Droege and Tully (1986) have measured the temperature dependence of this reaction, and the recommended E/R was obtained from a linear least squares analysis of the data from these studies at T 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 is exhibited over a wide temperature range, as shown by Tully et al., and Droege and Tully. The branching ratios were estimated from the latter:

$$k_{primary} = 6.3 \times 10^{-12} \exp(-1050/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{secondary} = 6.3 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These numbers are in reasonable agreement with the older data of Greiner.

D6. 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 activation energy (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).

D7. OH + CH_3CHO. There are six measurements of this rate coefficient at 298 K, Morris et al. (1971), Niki et al. (1978b), Atkinson and Pitts (1978), Kerr and Sheppard (1981), Semmes et al. (1985), and Michael et al. (1985a). The recommended value of k(298 K) is the average of these measurements. Atkinson and Pitts, Semmes et al., and Michael et al. measured the temperature dependence of this rate coefficient and found it to exhibit a negative temperature dependence. The recommended value of E/R is the average E/R of these studies. The A-factor has been adjusted to yield the recommended value of k(298 K).

D8. 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.

D9. 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 Phillip'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.

D10. OH + CH_3CN. 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 K, and Rhasa and Zellner (private communication, 1987) between 295 and 520 K. In addition, the 298 K value has been measured by Zetzsch (private communication, 1987) 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) Zetzsch 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.

D11. HO_2 + CH_2O. It is believed 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 the lifetime of the adduct towards decomposition to CH_2O and HO_2 is ~1 sec at 298 K.

D12. O + HCN. This reaction has been studied at high temperatures, i.e., T >1000 K, because of its importance in combustion systems, Roth et al. (1980), Szekely et al. (1984), and Louge and Hanson (1984). Davies and Thrush (1968) studied this reaction between 469 and 574 K while Perry and Melius (1984) studied it between 540 and 900 K. Results of Perry and Melius are in agreement with those of Davies and Thrush. Our recommendation is based on these two studies. This reaction has two reaction pathways: O + HCN $\rightarrow$ H + NCO, ΔH = -6 kcal/mol (ka); and O + HCN $\rightarrow$ CO + NH (kb), ΔH = -36 kcal/mol. The branching ration k_a/k_b for these two channels has been measured to be ~2 at T = 860 K. The branching ratio at lower temperatures is unknown.

D13. O + C_2H_2. The value at 298 K is an average of ten measurements; Arrington et al. (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al. (1967, 1969), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), Westenberg and deHaas (1977), and 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 known to be erroneous by Westenberg and deHaas (1969b). Westenberg and deHaas (1969b), Hoyermann et al. (1969), and Aleksandrov et al. (1981) are the only authors who have measured the temperature dependence below 500 K. Westenberg and deHaas observed a curved Arrhenius plot at higher temperature. In the range

195-450 K, Arrhenius behavior provides an adequate description and the E/R obtained by a fit of the data from these three groups 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. The study by Aleksandrov et al. using a discharge flow-resonance fluorescence method (under undefined pressure conditions) indicates that the C_2HO + H channel contributes no more than 7% to the net reaction at 298 K, while a similar study by Vinickier et al. (1985) suggests that both CH_2 and CH_2O are formed.

D14. 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 → H + CO_2 and O + HCO → OH + CO apparently do not occur. This interesting suggestion needs independent confirmation.

D15. O + CH_3CHO. The recommended k(298 K) is the average of three measurements by Cadle and Powers (1967), Mack and Thrush (1974), and Singleton et al. (1977), which are in good agreement. Cadle and Powers and Singleton et al. studied this reaction as a function of temperature between 298 K and 475 K and obtained very similar Arrhenius parameters. The recommended E/R value was obtained by considering both sets of data. This reaction is known to proceed via H-atom abstraction (Mack and Thrush, 1974; Avery and Cvetanovic, 1965; and Singleton et al., 1977).

D16. 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 temperature between 259 and 341 K.

D17. 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 x 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 → CH_2O + OH) at 368 K and placed an upper limit of 3 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} for this rate coefficient. Bhaskaran et al. (1979) measured k = 1 x 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 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} based on their inability to find HCHO in their experiments.

D18. CH_2OH + O_2. The rate coefficient was first measured directly by Radford (1980) by detecting the HO_2 product in a laser magnetic resonance spectrometer. The 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. Wang et al. (1984) measured a value of 1.4 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} by detecting the HO_2 product. Recently, Dobe et al. (1985), Grotheer et al. (1985), and Payne et al. (1987) have measured k(298 K) to be close to 1.0 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} under conditions where wall losses are small. The recommended value is the average of these three studies. Since this reaction is quite fast the E/R is expected to be close to zero. Very recently, Stief (private communications) has obtained a positive activation energy for this reaction.

D19. $CH_3O + O_2$. The recommended value for k(298 K) is the average of those reported by Lorenz *et al*. (1985) and Wantuck *et al*. (1987). The recommended A-factor and E/R are those obtained using the results of Gutman *et al*. (1982), Lorenz *et al*. (1985), and Wantuck *et al*. (1987) in the temperature range 298 to 500 K. 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*.), 298 to 450 K (by Lorenz *et al*.), and 298 to 973 K (by Wantuck *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. 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 appears to be too low for a hydrogen atom transfer reaction. The Arrhenius plot is curved at higher temperature (Wantuck *et al*.). 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), which is consistent with a reported CH_2O yield of 0.85±0.15 (Zellner, private communication, 1987).

D20. $HCO + O_2$. 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 absorption 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 concentration 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 ($k = 5.5 \times 10^{-11} T^{-(0.4\pm0.3)}$ cm^3 $molecule^{-1}$ s^{-1}).

D21. $CH_3 + O_3$. 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.

D22. $CH_3O_2 + O_3$. There are no direct studies of this reaction. The quoted upper limit is based on indirect evidence obtained by Simonaitis and Heicklen (1975).

D23. $CH_3O_2 + CH_3O_2$. The recommended value for k(298 K) was derived from the studies by Hochanadel *et al*. (1977), Parkes (1977), Anastasi *et al*. (1978), Kan *et al*. (1979), Sanhueza *et al*. (1979), Sander and Watson (1981c), McAdam *et al*. (1987), and Kurylo and Wallington (1987). 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. Therefore, the derived value of k critically depends on the value of σ used. Currently, there are large discrepancies (approximately a factor of 2) between the values of σ measured by Hochanadel *et al*., Parkes, Sander and Watson, Adachi *et al*. (1980), McAdam *et al*. (1987), and Kurylo *et al*. (1987a). To obtain the value at 298 K, an average value of σ at 250 nm was obtained. Using this value of σ and the weighted average value of k/σ at 250 nm the value of k(298 K) was derived. The recommended temperature dependence is that measured by Sander and Watson (1981c) and Kurylo and Wallington (1987) using a value of σ independent of T. It is not clear whether the above procedure of recalculating k using an average value of σ is valid. Therefore, the error limits have been increased to encompass the values of k calculated by various authors. This reaction has three possible sets of products, i.e.,

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

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 ~0.35, k_b/k ~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.

D24. $CH_3O_2 + NO$. 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 *et al*. (1986). 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 *et al*. (1986) have measured the yield of CH_3O to be 1.0±0.2. 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.

D25. $CH_3O_2 + HO_2$. The room temperature value is that of Cox and Tyndall (1979, 1980). Cox and Tyndall also report 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 $HO_2 + HO_2$). There are large discrepancies in the value of σ CH_3O_2 (see D24). Therefore, the uncertainty has been increased. There are various other recent measurements by Kurylo *et al*. (1987b), Dagaut *et al*. (1987), McAdam *et al*. (1987), Cox (private communication) that yield contradictory results. Therefore, it is cautioned that the recommended value may be incorrect. In the absence of consistent data, we have decided not to change the previous recommendation. The rate coefficient needs independent verification at one atmosphere, and further measurements of pressure, water vapor, and temperature dependences. It is also necessary to measure the yields of products in this reaction to check for the presence of multiple pathways.

D26. $NO_3 + CO$. The upper limit is based on the results of Ridley and McFarland (private communication, 1984) and Hjorth *et al*. (1986). Ridley and McFarland estimated an upper limit of 1×10^{-20} cm^3 $molecule^{-1}$ s^{-1} based on their measurements of NO_3 loss in excess CO. Hjorth *et al*. obtained an upper limit of 4×10^{-19} cm^3 $molecule^{-1}$ s^{-1} based on an FTIR analysis of isotopically labeled CO loss in the presence of NO_3. Burrows *et al*. (1985b) obtained an upper limit of 4×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, which is consistent with the other two studies. Products are expected to be $NO_2 + CO_2$.

D27. $NO_3 + CH_2O$. 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±0.26) x 10^{-16} cm^3 $molecule^{-1}$ s^{-1}, is corrected to 5.8 x 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 x 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.

D28. $NO_3 + CH_3CHO$. New entry. There are four measurements of this rate constant, Morris and Niki (1974), Atkinson _et al_. (1984), Cantrell _et al_. (1986), Dlugokencky and Howard (private communication, 1987). The value reported by Atkinson _et al_. (1984), k = (1.34±0.28) x 10^{-15} cm^3 $molecule^{-1}$ s^{1}, is corrected to 2.4 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1} as discussed for the $NO_3 + H_2CO$ reaction above and as suggested by Tuazon _et al_. (1984). The recommended value is the average of the values obtained by Atkinson _et al_. (2.4 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}), Cantrell _et al_. (2.1 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}), and Dlugokencky and Howard (2.74 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}). The results of Morris and Niki agree with the recommended value when their original data is re-analyzed using the currently recommended value for the equilibrium constant for the reaction $NO_2 + NO_3 \rightleftarrows N_2O_5$ as shown by Dlugokencky and Howard. Dlugokencky and Howard have studied the temperature dependence of this reaction. Their measured value of E/R is recommended. The A-factor has been calculated to yield k(298) recommended here. Morris and Niki, and Cantrell _et al_. observed the formation of HNO_3 and PAN in their studies, which strongly suggests that HNO_3 and CH_3CO are the products of this reaction.

E1. $Cl + O_3$. 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 consistently (~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 agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal/mol). 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±1.0) x 10^{-11} exp(-310±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 Cl_2 photosensitized decomposition of ozone. However Choo and Leu (1985) were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the $Cl + O_3$ system and set upper limits to the branching ratios for their production of 5 x 10^{-4} and 2.5 x 10^{-2}, respectively. Thus the mechanism for production of oxygen atoms in this system is unclear.

E2. $Cl + H_2$. This Arrhenius expression is based on the data below 300 K reported by Watson _et al_. (1975), Lee _et al_. (1977), Miller and Gordon (1981), and Kita and Stedman (1982). The results of these studies are in excellent agreement below 300 K; the data at higher temperatures are in somewhat poorer agreement. The results of Watson _et al_., Miller and Gordon, and Kita and Stedman 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 and Kita and Stedman also measured the rate of the reverse reaction, and found the ratio to be in good agreement with equilibrium constant data.

E3. Cl + CH_4. The values reported from the thirteen absolute rate coefficient studies for k at 298 K fall in the range (0.99 to 1.48) x 10^{-13}, with a mean value of 1.15 x 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 1.0 x 10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weight 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 (0.85-1.13) x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value of 1.0 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 $(2.11\text{-}2.54) \times 10^{-14}$ with a mean value of 2.27×10^{-14}. It can be seen from the above discussion that the average values at 230 K are: 3.19×10^{-14} (flash photolysis), 2.67×10^{-14} (discharge flow) and 2.27×10^{-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 1.04×10^{-13}, and at 230 K is 2.71×10^{-14} (this is a simple mean of the three average values). The preferred Arrhenius 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 6.4×10^{-12} (exp(-1200/T)) can be obtained (k(298 K) = 1.07×102^{-13} and k(230 K) = 3.19×10^{-14}).

A 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 7.7×10^{-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 those obtained in the competitive chlorination studies of Pritchard _et al_. (1955) and Knox and Nelson (1959).

E6. Cl + CH_3OH. This recommendation is based on the 200-500 K results of Michael _et al_. (1979b) by the flash photolysis-resonance technique and the 298 K results of Payne _et al_. (1987) by the discharge flow-mass spectrometry technique. Product analysis and isotopic substitution have established that the reaction mechanism consists of abstraction of a hydrogen atom from the methyl group rather than from the hydroxyl group. See Radford (1980), Radford _et al_. (1981), Meier _et al_. (1984), and Payne _et al_. (1987). 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.

E7. Cl + CH_3Cl. The results reported by 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}).

E8. Cl + CH_3CN. 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 x 10^{-11} exp(-2785/T) over the temperature range 478-723 K. They also reported a room temperature value of 9 x 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.

E9. Cl + CH_3CCl_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 Cl 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. Cl + 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 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(Cl + H_2CO)/k(Cl + 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 x 10^{-11} for k(Cl + 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. Cl + 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 (3.6-6.2) x 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. Heneghan and Benson (1983), using mass spectrometry, confirmed that this reaction proceeds only by the abstraction mechanism giving HCl 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 rate, Cook et al. (1981a). Ennis and Birks (1985) have measured the product distribution in a discharge flow-mass spectrometric system and found that the major reaction channel is that to give the products Cl_2 + OH with a yield of 91±6%.

E13. $Cl + HNO_3$. There are two 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 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 $(4.2\pm0.7) \times 10^{-11}$ 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 results of 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). Cattell and Cox (1986) using a molecular modulation-UV absorption technique over the pressure range 50-760 torr report results in good agreement with those of Lee and Howard both for the overall rate constant and for the relative contribution of the two reaction channels. The rate constant for the channel producing ClO + OH can be combined with that for the reaction $ClO + OH > Cl + HO_2$ to give an equilibrium constant from which a value of the heat of formation of HO_2 at 298 K of 3.0 kcal/mol can be derived.

E15. $Cl + Cl_2O$. The preferred value 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. $Cl + ClONO_2$. Flash photolysis/resonance fluorescence studies by Margitan (1983a) and by Kurylo *et al.* (1983a), which are in good agreement, 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. $Cl + NO_3$. The recommended room temperature value is the average of the results reported by Cox *et al.* (1984a), Burrows *et al.* (1985b), and Cox *et al.* (1987). In all studies the kinetic behavior of NO_3 in the modulated photolysis of $Cl_2 - ClONO_2$ mixtures was monitored in absorption. In the latest study Cox *et al.* also monitored ClO in absorption. The lack of temperature dependence is from this latest study.

E19. $Cl + N_2O$. New Entry. This rate coefficent has been determined in a study of the halogen-catalyzed decomposition of nitrous oxide at about 1000 K by Kaufman *et al.* (1956). The largest value reported was 10^{-17} cm^3 $molecule^{-1}$ s^{-1}, with an activation energy of 34 kcal/mol. Extrapolation of these results to low temperature shows that this reaction cannot be of any significance in atmospheric chemistry.

E20. Cl + ClNO. Reported values of this rate constant differ by more than an order of magnitude. The most recent studies, which are by Nesbitt *et al.* (1987) using discharge flow-mass spectrometry, and Kita and Stedman (1982) using discharge flow-resonance fluorescence, report values substantially higher than values reported earlier. The earlier results were obtained by Nelson and Johnston (1981) using laser flash photolysis-resonance fluorescence, Grimely and Houston (1980) by pulsed laser photolysis in a static system with chemiluminescence detection, and Clyne and Cruse (1972) by discharge flow-resonance fluorescence. In all but the study by Nesbitt *et al.*, ClNO was the excess species; thus, knowledge of its absolute concentration was required. It is possible that the low value of Grimely and Houston may be due to adsorption and decomposition of ClNO on the walls of their static system. Results from the studies of Nesbitt *et al.*, Kita and Stedman, and Clyne and Cruse form the basis for the new recommendation. There are no reliable data on the temperature dependence.

E21. Cl + ClOO. Values of 1.56×10^{-10}, 9.8×10^{-11}, and 1.67×10^{-10} have been reported for $k_a(Cl + ClOO \rightarrow Cl_2 + O_2)$ 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 $k_a(Cl + ClOO \rightarrow Cl_2 + O_2)/k(Cl + ClOO \rightarrow 2\ ClO)$ 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^o (ClOO) (the values of ΔH_f^o (ClOO) 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 $k_a(Cl + ClOO \rightarrow Cl_2 + O_2)$ 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 $k_b(Cl + ClOO \rightarrow 2\ ClO)$ 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.

E22. O + ClO. Recently there have been five studies of this rate constant over an extended temperature range using a variety of techniques: Leu (1984b); Margitan (1984b); Schwab *et al.* (1984); Ongstad and Birks (1986); and Nicovich *et al.* (1987). The recommended value is based on a least squares fit to the data reported in these studies and in the earlier studies of Zahniser and Kaufman (1977) and Ongstad and Birks (1984). Values reported in the early studies of Bemand et al. (1973) and Clyne and Nip (1976b) are significantly higher and were not used in deriving the recommended value.

E23. ClO + 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 *et al.* 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 Cl + 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 *et al.*

E24. ClO + NO_3. The recommended value is based on results reported by Cox *et al.* (1984a) and by Cox *et al.* (1987) in the only reported studies of this reaction. Both studies used the modulated photolysis of Cl_2 + $ClONO_2$ mixtures. In the new study a small temperature dependence is reported, but because of uncertainties in the data a temperature-independent value is recommended in this evaluation.

E25. $ClO + HO_2$. There have now been five studies of this rate constant. Three were low pressure discharge flow studies, each using a different experimental detection technique (Reimann and Kaufman, 1978; Stimpfle et al., 1979; Leck et al., 1980), and two were molecular modulation studies; at one atmosphere (Burrows and Cox, 1981), and over the pressure range 50-760 torr (Cattell and Cox, 1986). The 298 K values reported, in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, are: 3.8±0.5 (Reimann and Kaufman), 6.3±1.3 (Stimpfle et al.), 4.5±0.9 (Leck et al.), 5.4 (Burrows and Cox), and 6.2±1.5 (Cattell and Cox). The recommended value is the mean of these values. The study of Cattell and Cox over an extended pressure range when combined with results of the low pressure discharge flow studies seem to indicate that this reaction exhibits no pressure dependence at room temperature. The only temperature dependence study (Stimpfle et al.) 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 et al. 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 et al., 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). The latter form is preferred. The two most probable pairs of reaction products are, (1) $HOCl + O_2$ and (2) $HCl + O_3$. Leu (1980b) and Leck et al. used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K) and 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.

E26. $ClO + H_2CO$. Poulet et al. (1980) have reported an upper limit of 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K using the discharge flow-EPR technique.

E27. $ClO + OH$. The recommended value is based on a fit to the 219-373 K data of Hills and Howard (1984), the 243-298 K data of Burrows et al. (1984a), and the 298 K data of Poulet et al. (1986a). Data reported in the studies of Ravishankara et al. (1983a), and Leu and Lin (1979) were not used in deriving the recommended value because in these studies the concentration of ClO was not determined directly. The results of Burrows et al. are temperature-independent while those of Hills and Howard show a slight negative temperature dependence. The fraction of total reaction yielding $HO_2 + Cl$ as products has been determined by Leu and Lin (>0.65); Burrows et al. (0.85±0.2); Hills and Howard (0.86±0.14); and Poulet et al. (0.98±0.12). The latest study gives an upper limit of 0.14 for the branching ratio to give $HCl + O_2$ as products. The uncertainties in all studies allow for the possibility that the HCl yield is indeed zero.

E28. 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.

E29. $ClO + ClO$. There are three possible bimolecular channels for this reaction: $ClO + ClO \rightarrow OClO + Cl$ (k_1); $ClO + ClO \rightarrow Cl + ClOO$ (k_2); and $ClO + ClO \rightarrow Cl_2 + O_2$ (k_3). The recommended values given here are for the total rate coefficient at low pressures. They are based largely on results obtained in the discharge flow studies of Clyne and co-workers as discussed in the reviews by Watson (1977, 1980). Note that the rate constant is here defined as $-d(ClO)/dt = 2k(ClO)^2$. Molecular modulation studies such as those of Cox and co-workers (see Hayman et al., 1986) have given a similar temperature dependence but somewhat lower rate constant values. The product branching ratios and their dependence on temperature and pressure are not well established. The low pressure results indicate that k_2 and k_3 are both important, while k_1 represents only about 10 percent of the total reaction. The reaction exhibits both bimolecular and termolecular reaction channels (see entry for this reaction in Table 2). The termolecular reaction, presumably to give the dimer, dominates at pressures higher than about 10 torr; however, the role of the dimer in the overall reaction is unclear - whether it is merely in equilibrium with ClO or decomposes to give the same products given in the bimolecular reaction channels. Some product branching ratio data have been derived from studies of the chlorine-photosensitized decomposition of ozone. In these systems there are uncertainties concerning the need for some reaction of the Cl_2O_2 complex in order to account for the strong temperature dependence of the ozone quantum yield and also concerning the possible role of ClO complex formation with O_2 and subsequent reactions of the $ClO\text{-}O_2$ complex. The equilibrium constant for formation of the Cl_2O_2 dimer is given in Table 3.

E30. $ClO + O_3$. The branching ratio between the two possible channels is not known, but, for the present discussion, is assumed to be unity. There is no evidence that either reaction actually occurs. 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).

E31. $OH + Cl_2$. The recommended room temperature value is the average of the results reported by Boodaghians et al. (1987), Loewenstein and Anderson (1984), Ravishankara et al. (1983a), and Leu and Lin (1979). The temperature dependence is from Boodaghians et al. Loewenstein and Anderson determined that the exclusive products are Cl + HOCl.

E32. OH + HCl. The recommended value is based on a least squares fit to the data reported in the recent studies by Molina et al. (1984), Keyser (1984), and Ravishankara et al. (1985b). In these studies particular attention was paid to the determination of the absolute concentration of HCl by UV and IR spectrophotometry. Earlier studies by Takacs and Glass (1973c), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), Hack et al. (1977), Husain et al. (1981), Cannon et al. (1984), Husain et al. (1984), and Smith and Williams (1986) had reported somewhat lower room temperature values.

E33. OH + HOCl. In the only reported study of this system Ennis and Birks (1987) reported the value of this rate constant at room temperature to lie in the range $(1.7 - 9.5) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. A temperature dependent expression has been estimated by choosing a pre-exponential factor by analogy with the $OH + H_2O_2$ reaction and selecting the midpoint of the experimental range for the room temperature rate constant. The large uncertainty factor is needed to encompass the entire range.

E34. 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. For example, 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 results of Jeong and Kaufman (1982) have shown a nonlinear 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 Arrhenius expressions centered at 265 K, 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 Arrhenius expressions are entered in the table of preferred values. Obviously, 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_3Cl. 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 4.3×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.7 \times 10^{-12}\exp(-1100/T)$.

OH + CH_2Cl_2. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the OH + CH_4/OH + CH_2Cl_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 1.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $4.7 \times 10^{-12}\exp(-1050/T)$.

OH + $CHCl_3$. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the OH + CH_4/OH + $CHCl_3$ 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 $6.3 \times 10^{-18}\ T^2\exp(-504/T)$ over the temperature range 245-487 K. This results in a preferred value of 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $3.4 \times 10^{-12}\exp(-1050/T)$.

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 $1.71 \times 10^{-18}\ T^2\exp(-483/T)$ 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 $0.86 \times 10^{-12}\exp(-1000/T)$.

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 $1.51 \times 10^{-18}\ T^2\exp(-1000/T)$ over the temperature range 250-482 K. This results in a preferred value of 4.5×10^{-15} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $0.83 \times 10^{-12}\exp(-1550/T)$.

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 4.4×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $2.1 \times 10^{-12}\exp(-1150/T)$.

E35. $OH + CH_3CCl_3$. This evaluation is based on the 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 newer results. The earlier results showed higher values of the rate constant, and lower E/R values. This may indicate that the CH_3CCl_3 used in the early studies was contaminated with small amounts of a reactive olefinic impurity.

E36. $OH + CH_3CF_2Cl$. New Entry. There have been three temperature dependent studies of this rate constant: Watson et al. (1977) over the temperature range 273-375 K; Handwerk and Zellner (1978) at 293 and 373 K; and Clyne and Holt (1979b) from 293 to 417 K. All studies are in agreement on the magnitude of the temperature dependence (E/R = 1800 K). The rate constant was also measured at room temperature by Howard and Evenson (1976b) and by Paraskevopoulos et al. (1981). The value recommended at room temperature is the mean of all the reported values except that of Clyne and Holt, which is significantly higher. The pre-exponential factor was fitted to the recommended value at room temperature.

E37. $OH + CH_3CHF_2$. New Entry. There has been only one study of this rate constant as a function of temperature, that by Clyne and Holt (1979b) over the temperature range 293-417 K. In addition there have been room temperature measurements by Howard and Evenson (1976b), Handwerk and Zellner (1978), and Nip et al. (1979). These three latter measurements are in good agreement, while the value of Clyne and Holt lies 50% higher. The value recommended at room temperature is the mean of all the values except that of Clyne and Holt. The temperature dependence is taken from Clyne and Holt, but with increased error limits. The pre-exponential factor was fitted to the recommended value at room temperature.

E38. $OH + CHCl_2CF_3$. New Entry. The recommended value at room temperature is the average of the values reported by Watson et al. (1979b) and by Howard and Evenson (1976b). The temperature dependence is from the 245-375 K data of Watson et al. The 293-429 K data of Clyne and Holt (1979b) were not used in deriving the recommended value.

E39. $OH + CHClFCF_3$. New Entry. The recommended value at room temperature is the average of the values reported by Watson et al. (1979b) and by Howard and Evenson (1976b). The temperature dependence is from the 250-375 K of Watson et al.

E40. $OH + CH_2ClCClF_2$. New Entry. The recommended expression is derived from a least squares fit to the corrected 250-350 K data reported by Watson et al. (1979b). The measured rate constants were corrected for the presence of alkene impurities. The 249-473 K data of Jeong, et al. (1984) are a factor of two higher at the lowest temperature and were not used in deriving the recommended value.

E41. $OH + CH_2FCF_3$. New Entry. The recommended expression is derived from a least squares fit to the 249-473 K data reported by Jeong et al. (1984) and the 298 K data of Martin and Paraskevopoulos (1983). The 294-429 K data of Clyne and Holt (1979b) were not used in deriving the recommended value.

E42. $OH + CH_3CCl_2F$. New Entry. There are no reported data on the rate of this reaction. The recommended value is estimated by analogy with similar reactions.

E43. $OH + C_2Cl_4$. 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.

E44. OH + C_2HCl_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 ~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).

E45. OH + $CFCl_3$ and OH + CF_2Cl_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.

E46. 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.

E47. 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.

E48. O + HOCl. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

E49. 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 room temperature result of Adler-Golden and Wiesenfeld (1981) is in good agreement with the recommended value.

E50. 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 (1971c) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in both studies.

E51. O + OClO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E52. OH + OClO. New Entry. The recommended value is that reported by Poulet et al. (1986b), the only reported study of this rate constant, using a discharge flow system in which OH decay was measured by LIF or EPR over the temperature range 293-473 K. Product HOCl was detected by modulated molecular beam mass spectrometry. The branching ratio for the channel to produce HOCl + O_2 was determined to be close to unity, but experimental uncertainty would allow it to be as low as 0.80.

E53. NO + OClO. The Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

E54. HCl + $ClONO_2$. Recently, results of four studies of the kinetics of this system have been published, in which the following upper limits to the homogeneous bimolecular rate constant were reported: 1×10^{-19} cm^3 $molecule^{-1}$ s^{-1} by a static wall-less long-path UV absorption technique and a steady-state flow FTIR technique (Molina et al., 1985); 5×10^{-18} using a flow reactor with FTIR analysis (Friedl et al., 1986); and 8.4×10^{-21} using a static photolysis system with FTIR analysis (Hatakeyama and Leu, 1986), and 1.5×10^{-19} by FTIR analysis of the decay of $ClONO_2$ in the presence of HCl in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers (Atkinson et al. 1987). Earlier, Birks et al. (1977) had reported a higher upper limit. All studies found this reaction to be catalyzed by surfaces. The differences in the reported upper limits can be accounted for in terms of the very different reactor characteristics and detection sensitivities of the various studies. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

E55. HCl + HO_2NO_2. This upper limit is based on results of static photolysis-FTIR experiments (M. T. Leu, private communication, 1985).

E56. H_2O + $ClONO_2$. New Entry. This recommendation is based on the upper limits to the homogeneous bimolecular rate constant reported by Atkinson et al. (1986), and by Hatakeyama and Leu (1986). Atkinson et al. observed by FTIR analysis the decay of $ClONO_2$ in the presence of H_2O in large-volume (2500 and 5800 liters) Teflon or Teflon-coated chambers. Their observed decay rate gives an upper limit to the homogeneous gas phase rate constant, and they conclude that the decay observed is due to heterogeneous processes. Hatakeyama and Leu, using a static photolysis system with FTIR analysis, derive a similar upper limit. Rowland et al. (1986) concluded that the decay they observed resulted from rapid heterogeneous processes. The homogeneous reaction is too slow to have any significant effect on atmospheric chemistry.

F1. Br + O_3. The results reported for k(298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978), Michael and Payne (1979), and Toohey et al. (1987b) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these five values. The temperature dependences reported for k by Leu and DeMore and by Toohey et al. are in good agreement, but they can only be considered to be in fair agreement with those reported by Michael et al. and Michael and Payne. The preferred value was synthesized to best fit all the data reported from these five studies.

F2. Br + H_2O_2. The recommended upper limit to the value of the rate constant at room temperature is based on results reported in the recent study by Toohey et al. (1987a) using a discharge flow-laser magnetic resonance technique. Their upper limit determined over the temperature range 298-378 K is consistent with less sensitive upper limits determined by Leu (1980a) and Posey et al. (1981) using the discharge flow-mass spectrometric technique. The much higher value reported by Heneghan and Benson (1983) may result from the presence of excited Br atoms in the very low pressure reactor. The pre-exponential factor was chosen to be consistent with that for the Cl + H_2O_2 rate constant, and the E/R value was fitted to the upper limit at 298 K.

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. This recommendation is based on results obtained over the 260-390 K temperature range in the recent study by Toohey et al. (1987a), using a discharge flow system with LMR detection of HO_2 decay in excess Br. The room temperature value reported in this study is a factor of three higher than that reported by Poulet et al. (1984b) using LIF and MS techniques and is an order of magnitude larger than the value of Posey et al. (1981). The uncertainty in E/R is set to encompass the value E/R = 0, as for other radical-radical reactions. 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. Br + Cl_2O. New Entry. The recommended value is a preliminary value by Sander and Friedl (private communication, 1987). It was derived by observing the formation of ClO using long path UV absorption following the flash photolysis of a Br_2 - Cl_2O mixture.

F6. 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 k is expected to be small for an atom-radical process, e.g., O + ClO.

F7. BrO + ClO. The recommended room temperature value is based on the DF/MS results of Clyne and Watson (1977), the recent DF/RF/LMR results of Toohey et al. (private communication, 1987), and the recent FP/UV ABS and DF/MS results of Friedl and Sander (private communication, 1987), all of which are in good agreement on the value of the total rate coefficient. The lower value reported by Hills et al. (1987), although not used in the derivation of the recommended value, is encompassed within the stated uncertainty limits. The much lower value of Basco and Dogra (1971b), derived using a different interpretation of the reaction mechanism, is not used here. It has been shown by Clyne and Watson, Toohey et al., and Hills et al. that the reaction proceeds approximately equally by the two channels indicated. In the atmosphere the ClOO peroxy radical formed in the second reaction channel will rapidly dissociate into Cl + O_2. The lack of temperature dependence reported by Hills et al. is consistent with the present estimation of E/R = 0; however, further work in other laboratories currently in progress suggests an appreciable negative temperature dependence.

F8. BrO + NO. The results of the three low pressure mass spectrometric studies (Clyne and Watson, 1975; Ray and Watson, 1981a; Leu, 1979a) and the high pressure uv absorption study (Watson et al., 1979a), 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 ClO and HO_2 reactions are also negative, and are similar in magnitude.

F9. BrO + BrO. There are two possible bimolecular channels for this reaction: BrO + BrO → 2Br + O_2 (k_1) and BrO + BrO → 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 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 latest absorption study). There was no observable pressure dependence from 50 to 475 torr in the latter 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_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 $k=(k_1 + k_2)$.

F10. $BrO + O_3$. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) 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}.

F11. $BrO + HO_2$. The preferred value is 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 $HOBr + O_2$.

F12. $BrO + OH$. Value chosen to be consistent with $k(ClO + OH)$, due to the absence of any experimental data.

F13. $OH + Br_2$. The recommended room temperature value is the average of the values reported by Boodaghians et al. (1987), Loewenstein and Anderson (1984), and Poulet et al. (1983). The temperature independence is from Boodaghians et al. Loewenstein and Anderson determined that the exclusive products are $Br + HOBr$.

F14. $OH + HBr$. The preferred value at room temperature is the average of 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, and by Ravishankara et al. (1985a) using LFP-RF and LFP-LIF techniques. In this latest study the HBr concentration was directly measured in-situ in the slow flow system by UV absorption. The rate constant determined in this reinvestigation is identical to the value recommended here. 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.

F15. $OH + CH_3Br$. 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 3.8×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for k at 298 K. The derived Arrhenius expression centered at 265 K is $6.0 \times 10^{-13}\exp(-820/T)$.

F16. O + HBr. Results of the 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 discharge flow results of Brown and Smith (1975) for 267-430 K and of Takacs and Glass (1973b) 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.

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. $F + H_2$. 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 chosen to fit the recommended room temperature value.

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.* Fasano and Nogar (1982) determined the absolute room temperature rate coefficient, and the rate coefficient relative to that of the reaction $F + D_2$. The preferred value 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 been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). The A-factor may be too high.

G4. $F + H_2O$. The recommended expression is based on the 243-369 K results of Walther and Wagner (1983) and the recent 298 K result of Frost *et al.* (1986). The pre-exponential factor has been adjusted to give the recommended room temperature value, which is the mean of the only two reported values.

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 (Table 1) are small and negative.

G6. FO + FO. 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. The value 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 this 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 $FO + FO \rightarrow 2F + O_2$ (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 x 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 analogous ClO + O_3 reactions are extremely slow ($<10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}) (DeMore et al., 1976), and upper limits of 8 x 10^{-14} (Clyne and Cruse, 1970a) and 5 x 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 ClO and BrO. The temperature dependence of the rate constant is expected to be small, as for the analogous ClO reaction.

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. 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), Michael et al. (1982), Lin (1982), Lin et al. (1985), and Barnes et al. (1986a). The value of E/R is taken from a composite unweighted least squares fit to the individual data points from the first seven studies. The studies of Leu and Smith (1982a), Lin et al. (1985), and to a lesser extent Lin (1982) show a slight parabolic temperature dependence of k with a minimum occurring near room temperature. However, within the error limits stated in this evaluation, all data are fit reasonably well by an

Arrhenius expression. 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).

H2. OH + OCS. The value of k(298 K) is an average of the determinations by Wahner and Ravishankara (1987) and Cheng and Lee (1986). The values determined by these authors lie a factor of three higher than the earlier room temperature measurements of Leu and Smith (1981). As discussed in the recent studies, this difference may be due to an overcorrection of the data by Leu and Smith to account for OH reaction with H_2S impurities and also to possible regeneration of OH. Nevertheless, the uncertainty factor at 298 K has been set to encompass the earlier study within 2σ. The work by Wahner and Ravishankara (1987) supersedes the study of Ravishankara et al. (1980b) which minimized complications due to secondary and/or excited state reactions interfering with the experiments 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 room temperature measurements Wahner and Ravishankara demonstrate the lack of an effect of total pressure (or O_2 partial pressure) on the rate constant and are supported by the more limited pressure and O_2 studies of Cheng and Lee. The E/R value recommended is that of Cheng and Lee, which is considerably lower than reported by Leu and Smith, although this difference may be due in part to the earlier-mentioned overcorrection of the data by these latter authors.

Product observations by Leu and Smith indicate that SH is a primary product of this reaction and tentatively confirm the suggestion of Kurylo and Laufer (1979) that the reaction produces predominantly SH + CO_2 through a complex (adduct) mechanism (similar to the adduct formation seen in the OH + CO_2 reactions). However, the absence of an O_2/pressure effect for OH + OCS is markedly different from observations in the OH + CS_2 reaction system (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} cm^3 $molecule^{-1}$ s^{-1}. A consistent upper limit is also reported by Iyer and Rowland (1980) for the rate of direct production of OCS in this reaction system, suggesting that OCS and SH are primary products of a bimolecular process. This mechanistic interpretation is further supported by the studies of Leu and Smith (1982b) and Biermann et al. (1982), which set somewhat higher upper limits on k(298 K). 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) as well as by the accelerating effect of O_2 on the OH + CS_2 reaction which has been observed by other workers and is summarized below. The importance of the electronically excited CS_2 reaction in the tropospheric oxidation of CS_2 to OCS has been discussed by Wine et al. (1981d).

An accelerating effect of O_2 on the OH + CS_2 reaction rate has been observed by Jones et al. (1982), Barnes et al. (1983), and Ravishankara et al. (1986), along with a near unity product yield for SO_2 and OCS. In the latter two studies, the effective bimolecular rate constant 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 adduct as postulated by Kurylo (1978) and Kurylo and Laufer (1979), followed by its reaction with O_2:

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

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

Ravishankara *et al.* (1986) have, in fact, directly observed the approach to equilibrium in this reversible adduct formation. In their study, the equilibrium constant was measured as a function of temperature and the heat of formation of $HOCS_2$ calculated (-12.4 kcal/mole). A rearrangement of this adduct followed by dissociation into OCS and SH corresponds to the low k (bimolecular) channel referred to earlier. Ravishankara *et al.* (1986) measure a rate constant for this process in the absence of O_2 (at approximately one atmosphere of N_2) equal to 5×10^{-16} cm^3 $molecule^{-1}$ s^{-1}. The effective second-order rate constant for CS_2 or OH removal in the above reaction scheme can be expressed as

$$1/k_{eff} = (k_b/k_a k_c)(1/P_{O2}) + (1/k_a)(1/P_M)$$

where P_{O2} is the partial pressure of O_2 and P_M equals $P_{O2} + P_{N2}$. The validity of this expression requires that k_a and k_b are invariant with the P_{O2}/P_{N2} ratio. A 1/k vs $1/P_{O2}$ plot of the data of Jones *et al.* (taken at atmospheric pressure) exhibits marked curvature, suggesting a more complex mechanistic involvement of O_2, whereas the data of Barnes *et al.* and Ravishankara *et al.* are more satisfactorily represented by this analysis. Nevertheless, while the qualitative features of the data from all three laboratories agree, there are some quantitative inconsistancies. First, under similar conditions of O_2 and N_2 pressures, the Barnes *et al.* rate constants lie approximately 60% higher than those of Jones *et al.* and up to a factor of 2 higher than the measurements by Ravishankara *et al.* Secondly, two fits each of both the Barnes and Ravishankara data can be made: one at fixed P_M and varying P_{O2}, and the other at fixed P_{O2} and varying P_M (i.e., varying added N_2). Within each data set, rate constants calculated from both fits agree reasonably well for mole fractions of O_2 near 0.2 (equivalent to air), but disagree by more than a factor of 2 for measurements in a pure O_2 system. Finally, the temperature dependence (from 264-293 K) of the k_{eff} values from Barnes *et al.* varies systematically from an E/R of -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. An Arrhenius fit of the Ravishankara *et al.* data (from 251-348 K) recorded in synthetic air at 690 torr yields an E/R = -3250 K. These observations suggest that k_a and k_b are not independent of the identity of M. For this reason, we limit our recommendation to air mixtures (i.e., $P_{O2}/P_{N2} = 0.25$).

The present recommendation accepts the measurements of Ravishankara *et al.* (1986) which appear to be the most sensitive of the three investigations. Thus, k(298 K) is based on an average of the two (above-mentioned) fits of the Ravishankara data yielding (in unites of cm^3 $molecule^{-1}$ s^{-1})

$$k(298\ K) = (1.8 \times 10^{-15})\ P$$

where P (the total pressure) is expressed in torr. The uncertainty factor ($f_{298} = 1.5$) encompasses the results of Barnes *et al.* (1983) within 2σ. To compute values of k below 298 K we have taken the E/R value from the Ravishankara data and adjusted the pre-exponential factor to give exact agreement with k(298 K). The resulting expression is

$$k(T) = \{(3.3 \times 10^{-20})\exp[(3250 + 500)/T]\}\ P$$

Again, this recommendation is valid only for oxygen-nitrogen mixtures at a total pressure P (in torr) having an oxygen mole fraction of 0.2. The ΔE/R has been set to encompass (within 2σ) the average E/R value from the study of Barnes et al. It is interesting to note that measurements by Ravishankara et al. (1986) at approximately 250 K result in k_{eff} values which are independent of the presence (or amount) of O_2. This suggests that the adduct is quite stable with respect to dissociation into the reactants ($OH + CS_2$) at this low temperature and the effective rate constant for reactant removal is equal to the elementary rate constant for the adduct formation. Clearly additional work may be needed before the full details of this complex reaction are understood.

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, ΔE/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 kinetics studies 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), Homann 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). ΔE/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. $S + O_2$. 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). The study by Clyne and Whitefield (1979), which indicates a slightly negative E/R between 300 and 400 K, is encompassed by the present recommendation.

H8. $S + O_3$. This recommendation accepts the only available experimental data; that from 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.

H9. S + OH. This recommendation is based on the single study by Jourdain et al. (1979). Their measured value for k(298 K) compares favorably with the recommended value of k(O + OH) when one considers the slightly greater exothermicity of the present reaction.

H10. $SO + O_2$. This recommendation is based on the 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). A room temperature upper limit on k set by Breckenridge and Miller (1972) is in good agreement with the Black et al. data.

H11. $SO + O_3$. The value of k(298 K) 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 K).

H12. SO + OH. The value recommended for k(298 K) 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.

H13. $SO + NO_2$. The value of k(298 K) is an average of the measurements by Clyne and MacRobert (1980), Black et al. (1982a), and Brunning and Stief (1986a), which agree quite well with the rate constant calculated from the relative rate measurements of Clyne et al. (1966). The Arrhenius parameters are taken from Brunning and Stief (1986a).

H14. SO + ClO. The value of k(298 K) is an average of the measurements by Clyne and MacRobert (1981) and by Brunning and Stief (1986a). The temperature independence is taken from Brunning and Stief, with the A-factor calculated to fit the value of k(298 K).

H15. SO + OClO. This recommendation is based on the single room temperature study by Clyne and MacRobert (1981). The uncertainty reflects the absence of any confirming investigation.

H16. SO + BrO. This recommendation is based on the measurements of Brunning and Stief (1986b) performed under both excess BrO and excess SO conditions. The rate constant is supported by the lower limit assigned by Clyne and MacRobert (1981) from measurements of SO_2 production.

H17. $SO_2 + HO_2$. This upper limit is based on the atmospheric pressure study of Graham et al. (1979). A low pressure laser magnetic resonance study by Burrows et al. (1979) places a somewhat higher upper limit on k(298 K) 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).

H18. $SO_2 + CH_3O_2$. 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 K) values approximately 100 times larger. A later 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 $CH_2O_2SO_2$ 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. This interpretation, unfortunately, does not explain the high rate constant derived by Cocks *et al.* (1986) under conditions of low [CH_3O_2].

H19. $SO_2 + NO_2$; $SO_3 + NO_2$. The recommendations for both of these reactions are based on the 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.

H20. $SO_2 + NO_3$. This recommended upper limit on k(298 K) is the result of Daubendiek and Calvert (1975). Considerably more conservative upper limits have been derived by Burrows *et al.* (1985b) and Wallington *et al.* (1986).

H21. $SO_2 + O_3$. 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.

H22. $Cl + H_2S$. The value of k(298 K) is an average of the measurements by Nesbitt and Leone (1980), which refines the data of Braithwaite and Leone (1978), Clyne and Ono (1983), Clyne *et al.* (1984), and Nava *et al.* (1985). The zero activation energy is derived from the data of Nava *et al.* and the A-factor is calculated to agree with k(298 K). Lu *et al.* (1986) also measure a temperature independent rate constant, and their larger value of k(298 K) = 10.5×10^{-11} may be indicative of a slight pressure dependence for the reaction, since their experiments were performed at 4000 torr.

H23. Cl + OCS. This upper limit is based on the minimum detectable decrease in atomic chlorine measured by Eibling and Kaufman (1983). Based on the observation of product SCl, these authors set a lower limit on k(298 K) of 10^{-18} for the reaction as written. Considerably more conservative upper limits on k(298 K) were determined in the studies of Clyne *et al.* (1984) and Nava *et al.* (1985).

H24. ClO + OCS; $ClO + SO_2$. These recommendations are based on the discharge flow mass spectrometric data of Eibling and Kaufman (1983). The upper limit on k(298 K) for ClO + OCS was set from the minimum detectable decrease of ClO in this reaction system. No products were observed. The upper limit on k(298 K) for $ClO + SO_2$ is based on the authors' estimate of their detectability for SO_3. Their estimates of k(298 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.

H25. $SH + H_2O_2$. This recommended upper limit for k(298 K) is based on the single study of Friedl *et al.* (1985). 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 $HSO + H_2O$.

H26. SH + O. 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.~~

H27. SH + O_2. This new upper limit for k(298 K) is based on the recent study by Stachnik and Molina (1987) in experiments sensitive to the production of OH. More conservative upper limits on k(298 K) of 1.0×10^{-17} and 1.5×10^{-17} were assigned by Friedl et al. (1985) and Wang et al. (1987) respectively from detection sensitivities for OH production and SH decay, respectively. An even higher upper limit by Black (1984), based on the lack of SH decay, may have been complicated by SH regeneration. Much less sensitive upper limits had been calculated by Tiee et al. (1981), Nielsen (1979), and Cupitt and Glass (1975). Stachnik and Molina (1987) also report a more conservative upper limit ($<1.0 \times 10^{-18}$) for the rate constant for the sum of the two SH + O_2 reaction channels (producing OH + SO and H + SO_2).

H28. SH + O_3. The value for k(298 K) is an average of the determinations by Friedl et al. (1985) (laser induced fluorescence detection of SH), Schonle et al. (1987) (mass spectrometric detection of reactant SH and product HSO), and Wang and Howard (1987) (laser magnetic resonance detection of SH). The temperature dependence is from Wang and Howard, with the A-factor calculated to agree with the recommended value of k(298 K). Δ(E/R) reflects the fact that the temperature dependence comes from measurements above room temperature and thus extrapolation to lower temperatures may have additional uncertainties.

H29. SH + NO_2. This recommendation accepts the recent measurements by Wang et al. (1987). These authors suggest that the lower values of k(298 K) measured by Black (1984), Friedl et al. (1985), and Bulatov et al. (1985) are due to SH regeneration from the H_2S source compound. In the recent study by Stachnik and Molina (1987), attempts were made at minimizing such regeneration. These authors obtained a k(298 K) value significantly higher than did the earlier investigators, but still 30% lower than that measured by Wang et al., who used two independent SH source reactions. A still higher rate constant value measured by Schonle et al. (1987) has not been recommended due to the somewhat limited data base for their determination. The reaction as written represents the most exothermic channel. The absence of a primary isotope effect, as observed by Wang et al. (1987), coupled with the large magnitude of the rate constant, suggests that the (four-center intermediate) channels producing SO + HNO and OH + SNO are of minor importance. No evidence for a three-body combination reaction was found by either Black (1984) or Friedl et al. (1985). Based on a pressure-independence of the rate constant between 30 and 300 torr, Black set an upper limit of 7.0×10^{-31} for the third body rate constant. Similarly, Stachnik and Molina (1987) saw no change in decay rate between 100 and 730 torr with O_2 (although these O_2 experiments were designed primarily to limit SH regeneration).

H30. HSO + NO, HSO + NO_2, HSO + O_2. These recommendations for all three reactions are based on the measurements of Lovejoy et al. (1987), who used laser magnetic resonance detection to monitor HSO in a discharge flow reactor. Their upper limit for the NO reaction is a factor of 25 lower than the rate constant measured by Bulatov et al. (1985) using intracavity laser absorption at pressures between 10 and 100 torr. Since it is unlikely that this reaction rate undergoes a factor of 25 increase between 1 torr (the pressure of the Lovejoy et al. work) and 10 torr, the higher rate constant may be due to secondary chemistry associated with the HSO production.

The recommendation for the NO_2 reaction is a factor of two higher than the rate constant reported by Bulatov et al. (1984). Lovejoy et al. have attributed this difference to HSO regeneration under the experimental conditions used by Bulatov et al. (1984). The product assignment for the NO_2 reaction is discussed in note H32.

H31. $HSO + O_3$. This recommendation is based on the single determination by Friedl et al. (1985) in their study of the $SH + O_3$ reaction. At higher O_3 concentrations, greater quantities of HSO were produced in the flow tube and SH approached a steady state due to its regeneration via $HSO + O_3$. The rate constant for this latter reaction was thus determined relative to $SH + O_3$ from measurements of the steady state SH concentration as a function of the initial SH concentration. The lack of an isotope effect when SD was employed suggests that the products of the $HSO + O_3$ reaction are $SH + 2O_2$ (analogous to those for $HO_2 + O_3$).

H32. $HSO_2 + O_2$. This recommendation is based on the rate of HO_2 formation measured by Lovejoy et al. (1987) upon addition of O_2 to the $HSO + NO_2$ reaction system. While HSO_2 was not observed directly, a consideration of the mechanistic possibilities for $HSO + NO_2$, coupled with measurements of the HO_2 production rate at various O_2 pressures, led these authors to suggest that HSO_2 is both a major product of the $HSO + NO_2$ reaction and a precursor for HO_2 via reaction with O_2.

H33. $HOSO_2 + O_2$. This recommendation is based on the recent studies of Gleason et al. (1987) and Gleason and Howard (1987), in which the $HOSO_2$ reactant was directly monitored using a chemical ionization mass spectrometric technique. Gleason and Howard conducted their measurements over the 297-423 K temperature range, constituting the only temperature dependence investigation. Thus $\Delta E/R$ has been increased from their quoted limits to account for the potential uncertainties in extrapolating their data to subambient temperatures. The value of k(298 K) derives further support from the study of Bando and Howard (1987), who employed laser magnetic resonance detection of product HO_2, and from the studies of Margitan (1984a) and Martin et al. (1986), both of whom used modeling fits of OH radical decays in the $OH + SO_2 + M$ reaction system in the presence of O_2 and NO. In this latter analysis, the $HOSO_2$ (produced by $OH + SO_2 + M$) reacts with O_2 yielding HO_2, which subsequently regenerates OH through its reaction with NO.

H34. $H_2S + NO_3$. This recommendation is based on the measurements of Wallington et al. (1986), performed using flash photolysis kinetic absorption spectroscopy.

H35. $CS + O_2$. 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.

H36. $CS + O_3$; $CS + NO_2$. 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 and Kolb (1986a) and Ager et al. (1986). These values are not in good agreement, differing by about a factor of two. Measurements made by Husain et al. (1985) at 500 K are consistent with the recommendation but are not included because they did not recognize that secondary chemistry, $NaO + O_3 \rightarrow Na + 2O_2$, interferes with the rate coefficient measurement. Ager et al. (1986) estimate that the $NaO_2 + O$ product channel ≤ 5%.

J2. Na + N_2O. The recommendation incorporates the data of Husain and Marshall (1985), Ager et al. (1986), and Silver and Kolb (1986a). Husain and Marshall and Ager et al. measured the temperature dependence over the ranges 349 to 917 K and 240 to 429 K, respectively, and are in good agreement. Silver and Kolb measured a rate coefficient at 295 K which is about 35% lower than the other two. Earlier less direct studies are discussed by Ager et al. (1986). The NaO product does not react significantly with N_2O at room temperature (k (for Na + N_2 + O products) $\leq 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} and k (for NaO_2 + N_2) $\leq 2 \times 10^{-15}$ Ager et al).

J3. Na + Cl_2. Two measurements of the rate coefficient for this reaction are in excellent agreement: Silver (1986) and Talcott et al. (1986). The recommended value is the average of these room temperature results.

J4. NaO + O. The recommendation is based on a measurement at 573 K by Plane and Husain (1986). They reported that $\leq$ 1% of the Na product is in the 3^2P excited state.

J5. NaO + O_3. This reaction was studied by Silver and Kolb (1986a) and Ager et al. (1986), who agree on the rate coefficient and branching ratio. This agreement may be fortuitous because Silver and Kolb used an indirect method and an analysis based on their rate coefficient for the Na + O_3 reaction which is about 1/2 that reported by Ager et al. Ager et al. employed a somewhat more direct measurement but the study is complicated by a chain reaction mechanism in the Na/O_3 system.

J6. NaO + H_2. The recommendation is based on a measurement by Ager and Howard (1987a). They also reported a significant Na + H_2O product channel and that a small fraction of the Na from this channel is in the 3^2P excited state.

J7. NaO + H_2O. The recommendation is based on a measurement by Ager and Howard (1987a).

J8. NaO + NO. The recommendation is based on an indirect measurement reported by Ager et al. (1986).

J9. NaO + HCl. There is only one indirect measurement of the rate coefficient for this reaction, that from the study of Silver et al. (1984a). They indicate that the products are NaCl and OH, although some NaOH and Cl production is not ruled out.

J10. NaO_2 + NO. This reaction is endothermic. The upper limit recommended is from an experimental study by Ager et al. (1986).

J11. NaO_2 + HCl. The recommendation is based on a measurement reported by Silver and Kolb (1986b). They indicated that the products are NaCl + HO_2, but NaOOH + Cl may be possible products.

J12. NaOH + HCl. 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

	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		
Reaction	k_o^{300}	n	k_∞^{300}	m	Notes
& $O + O_2 \xrightarrow{M} O_3$	(6.0±0.5)(-34)	2.3±0.5	- -	-	1
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0)(-37)	$0.6\pm^{2.0}_{0.6}$	- -	-	2
* $H + O_2 \xrightarrow{M} HO_2$	(5.7±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)	$0.8\pm^{2.0}_{0.8}$	(1.0±0.5)(-11)	1±1	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
* $HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(1.8±0.3)(-31)	3.2±0.4	(4.7±1.0)(-12)	1.4±1.4	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
$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0)(-32)	1.6±0.5	- -	-	11
$Cl + NO_2 \xrightarrow{M} ClONO$	(1.3±0.2)(-30)	2.0±1.0	(1.0±0.5)(-10)	1±1	12
$\xrightarrow{M} ClNO_2$	(1.8±0.3)(-31)	2.0±1.0	(1.0±0.5)(-10)	1±1	12
$Cl + O_2 \xrightarrow{M} ClOO$	(2.0±1.0)(-33)	1.4±1.4	- -	-	13
# $Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	(1.0±0.2)(-29)	3.5±0.5	(5.0±1.5)(-11)	2.6±0.5	14
# $ClO + ClO \xrightarrow{M} Cl_2O_2$	(4.0±2.0)(-32)	2.0±1.0	(1.0)(-11±1)	2±2	15
& $ClO + NO_2 \xrightarrow{M} ClONO_2$	(1.8±0.3)(-31)	3.4±1.0	(1.5±0.7)(-11)	1.9±1.9	16
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.0±2.0)(-31)	2.0±2.0	(1.0±0.5)(-11)	1±1	17

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.

a Units are $cm^6/molecule^2$-sec

b Units are cm^3/molecule-sec

* Indicates a change from the previous Panel evaluation (JPL 85-37).

& Indicates a change in the note from the previous evaluation.

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

Table 2. (Continued)

	Low Pressure Limit[a] $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit[b] $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		
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	- -	-	18
$F + NO \xrightarrow{M} FNO$	(5.9±3.0)(-32)	1.7±1.7	- -	-	19
$F + NO_2 \xrightarrow{M}$ Products	(1.1±0.6)(-30)	2.0±2.0	(3.0±2.0)(-11)	1±1	20
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0)(-31)	1.3±1.3	(2.0±1.0)(-11)	1.5±1.5	21
& $CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5)(-31)	2.0±1.0	(1.8±0.2,(-12)	1.7±1.7	22
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8)(-30)	4.0±2.0	(6.5±3.2)(-12)	2±2	23
& $OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.0)(-31)	3.3±1.5	(1.5±0.5)(-12)	$0\pm^{0}_{2}$	24
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.5±0.6)(-28)	0.8±2.0	(8.8±0.9)(-12)	$0\pm^{0}_{2}$	25
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0)(-30)	0.0±0.2	(8.3±1.0)(-13)	$-2\pm^{2}_{1}$	25
* $CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(1.5±0.3)(-29)	4±2	(8.5±1.0)(-12)	1±1	27
$CFCl_2 + O_2 \xrightarrow{M} CFCl_2O_2$	(5.0±0.8)(-30)	2±2	(6.0±1.0)(-12)	1±1	28
$CCl_3 + O_2 \xrightarrow{M} CCl_3O_2$	(1.0±0.7)(-30)	2±2	(2.5±2)(-12)	1±1	29
$CFCl_2O_2 + NO_2 \xrightarrow{M} CFCl_2O_2NO_2$	(3.5±0.5)(-29)	4±2	(6.0±1.0)(-12)	2±2	30
$HS + NO \xrightarrow{M} HSNO$	(2.4±0.4)(-31)	3±1	(2.7±0.5)(-11)	$0\pm^{0}_{2}$	31
$Na + O_2 \xrightarrow{M} NaO_2$	(1.9±1)(-30)	1.1±0.5	(2.0±1.8)(-10)	0±1	32
# $NaO + O_2 \xrightarrow{M} NaO_3$	(3.5±0.7)(-30)	2±2	(5.7±3)(-10)	0±1	33
# $NaO + CO_2 \xrightarrow{M} NaCO_3$	(8.7±2.6)(-28)	2±2	(6.5±3)(-10)	0±1	34
# $NaOH + CO_2 \xrightarrow{M} NaHCO_3$	(1.3±0.3)(-28)	2±2	(6.8±4)(-10)	0±1	35

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.

a Units are $cm^5/molecule^2$-sec

b Units are cm^3/molecule-sec

* Indicates a change from the previous Panel evaluation (JPL 85-37).

& Indicates a change in the note from the previous evaluation.

# 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). Kaye (1986) has calculated isotope effects for this reaction, using methods similar to those discussed in the Introduction; Troe (1977), Patrick and Golden (1983).

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

3. $H + O_2$. Kurylo (1972), Wong and Davis (1974) and Hsu *et al.* (1987) are averaged to obtain the low pressure limiting value at 300 K. The first two studies include T-dependence, as does a recent study by Hsu *et al.* (1987b). The recommended value is chosen with constant $\langle\Delta E\rangle_{N_2} \sim .05$ 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. $O + NO$. Low-pressure limit and n from direct measurements of Schieferstein *et al.* (1983) and their re-analysis 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). Burkholder *et al.* (1987) have shown that $HONO_2$ is the only isomer formed (yield = $.75\pm^{.25}_{.10}$). The recommendation here fits all data over the range of atmospheric interest.

9. $HO_2 + NO_2$. Changed from JPL 85-37. Recently Kurylo and Ouellette (1986) have remeasured the 300 K range constants. Kurylo and Ouellette (1987) have also remeasured the temperature dependence. The recommended values are taken from this latter reference wherein their data were combined with that of Sander and Peterson (1984). The recommended k_o(300 K) is consistent with Howard (1977). Other studies by Simonaitis and Heicklen (1978) and Cox and Patrick (1979) are in reasonable agreement with the recommendations.

10. $NO_2 + NO_3$. 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 can be found in Malko and Troe (1982). Recent studies by Kircher et al. (1984), Croce de Cobos et al. (1984), Smith et al. (1985), Burrows et al. (1985a), and Wallington et al. (1987a) confirm the current recommendation.

The values in Table 2 yield a curve that 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±0.5 is from Kircher et al. The study of Fowles et al. (1982) is noted but not used in the analysis. Johnston et al. (1986) have reviewed this reaction.

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). (Assuming similar T-dependence in 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). 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. The recommended value is based on $k(N_2)/k(Ar)$ = 1.8., and the T-dependence is based on the assumption of constant $\langle\Delta E\rangle$.

14. $Cl + C_2H_2$. Taken from Brunning and Stief (1985), who measured k from 210 to 361 K in Ar between approximately 10 torr and 300 torr. Experiments in N_2 at 296 K were used to scale the low-pressure limiting rate constant. Error limits were increased to account for the fact that only one temperature-dependent study exists.

As pointed out in Brunning and Stief (1985), these values are reasonably compatible with earlier studies of Poulet et al. (1973), Atkinson and Aschmann (1985), Lee and Rowland (1977), and Iyer et al. (1983).

15. ClO + ClO. For the termolecular reaction (with N_2 and O_2 as third bodies), Hayman et al. (1986) report

$$k = (6.0\pm0.4) \times 10^{-32} \times (T/300)^{-2.1\pm0.7}\ cm^6/s$$

This result is in good agreement with the earlier molecular modulation result of Johnston et al. (1969), which gave $k = 5 \times 10^{-32}\ cm^6/s$ with O_2 as third body. Other previous measurements, such as Cox and Derwent (1979), Basco and Hunt (1979), and Walker (1972), gave somewhat lower results (approximately a factor of two) for similar third bodies. The reasons for these differences are not known. The recommendation encompasses these values.

16. $ClO + NO_2$. The available kinetics data for this reaction have fallen 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 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. (1985a) indicate that there are no isomers of $ClONO_2$ formed. Thus, either explanation (1) and/or (2) above must be invoked. Wallington and Cox (1986) confirm current values, but are unable to explain the effect of OClO observed by both Molina et al. (1980a) and themselves.

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_∞.

17. $BrO + NO_2$. Data at 300 K are from Sander et al. (1981). They suggest $k_o = (5.0 \pm 1.0)(-31)$ $k_\infty = (2.0 \pm^{0.5}_{1.9})(-11)$ and $F_c = 0.4 \pm^{0.1}_{0.05}$. The temperature dependences are simple estimates.

Even though isomer formation seems to have been ruled out for the $ClO + NO_2$ reaction (i.e. the isomer stability is too low to make a significant contribution to the measured rate constant), this does not eliminate the possibility that $BrO + NO_2$ leads to more than one stable compound. In fact, if the measured 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 $ClONO_2$! This would fix the heat of formation of $BrONO_2$ to be the same as $ClONO_2$, an unlikely possibility.

18. $F + O_2$. 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 Kotov (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).

19. $F + NO$. Parameters estimated from strong collision calculations with $\langle \Delta E \rangle$ set at .42 $kcal/mole^{-1}$, yielding $\beta = 0.30$ at 300 K and $\beta = 0.38$ at 200 K.

20. $F + NO_2$. 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 $ClNO_2$ isomers. Thus, they concluded that $k^o_{300}(FNO_2) = 8.9 \times 10^{-31}$ and $k^o_{300}(FONO) = 2.4 \times 10^{-30}$, 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 $k^o_{300}(FONO) = 1.06 \times 10^{-29}$, and thus an overwhelming amount of FONO. The measured value is $k \sim 1.06 \times 10^{-30}$, 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.

21. $FO + NO_2$. 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 16) 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.

22. $CH_3 + O_2$. 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. Pilling and Smith (1985) have measured this process in Ar (32-490 torr). Their low pressure limiting rate constant is consistent with this evaluation, but their high pressure value is a little low. Cobos et al. (1985) have made measurements in Ar and N_2 from 0.25 to 150 atmospheres. They report parameters somewhat different than recommended here, but their data are reproduced well by the recommended values. 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 β, ~.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 fits the data of Cobos et al. (1985). The temperature dependence is an estimate. (Data of van 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.)

23. $CH_3O_2 + NO_2$. 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:

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

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 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.

24. $OH + SO_2$. Values of the rate constant as a function of pressure at 298 K from Leu (1982), Paraskevopoulos *et al.* (1983), and Wine *et al.* (1984). 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 (1984). 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. Recent work of Martin *et al.* (1986) and Barnes *et al.* (1986a) confirm the current evaluation.

25. $OH + C_2H_4$. 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 energies, 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 constant is too high for this possibility. If there is a product channel that proceeds with 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.

26. $OH + C_2H_2$. 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.*

27. $CF_3 + O_2$. Changed from JPL 85-37. Caralp *et al.* (1986) have measured the rate constant in N_2 between 1 and 10 torr. This supplants the value from Caralp and Lesclaux (1983). They recommend different parameters, but the data are well represented by the currently recommended values. Data of Ryan and Plumb (1982) are in agreement.

28. $CFCl_2 + O_2$. 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.

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

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

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

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

The recommended value of $k_o^{300}(N_2)$ is 2.5 times the value in He.

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).

30. $CFCl_2O_2 + NO_2$. 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.

31. HS + NO. Data and analysis are from the recent work of Black _et al_. (1984). The temperature dependence of k_∞ has been estimated.

32. $Na + O_2$. 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 $\beta_N^{300} = 0.3$. The high-pressure limiting rate constant is an estimate by Silver _et al_. (1984b).^{2} The error limits and temperature dependence are estimated.

33. $NaO + O_2$. New Entry. Ager and Howard (1986) have measured the low-pressure limit at room temperature in several bath gases. Their value in N_2 is used in the recommendation. They performed a Troe calculation as per Patrick and Golden (1983) to obtain collision efficiency and temperature dependence. They obtained a high-pressure limit rate constant by use of a simple model. The temperature dependence is estimated.

34. $NaO + CO_2$. New Entry. Ager and Howard (1986) have measured the rate constant for this process in the "fall-off" regime. Their lowest pressures are very close to the low-pressure limit. The temperature dependence is an estimate. Ager and Howard calculate the high-pressure rate constant from a simple model. The temperature dependence is an estimate.

35. $NaOH + CO_2$. New Entry. Ager and Howard (1987b) have measured the low-pressure limiting rate constant. The temperature dependence is an estimate. Ager and Howard have calculated the high-pressure limit using a simple model. The temperature dependence is an estimate.

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 298 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:

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

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:

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

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

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

C-2

Table 3. Equilibrium Constants

Reaction	A/cm^3 molecule^{-1}	B±ΔB/°K	K_{eq}(298 K)	f(298 K)^a	Note
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.1×10^{-27}	10,900±1,000	1.6×10^{-11}	5	1
# $NO + NO_2 \rightarrow N_2O_3$	3.0×10^{-27}	4,700±100	2.1×10^{-20}	2	2
* $NO_2 + NO_3 \rightarrow N_2O_5$	1.1×10^{-27}	11,200±500	2.3×10^{-11}	2	3
$Cl + O_2 \rightarrow ClOO$	2.3×10^{-25}	3,000±750	5.4×10^{-21}	20	4
$ClO + O_2 \rightarrow ClO \cdot O_2$	$<2.9 \times 10^{-26}$	<5,000±1,500	$<5.6 \times 10^{-19}$	500	5
# $ClO + ClO \rightarrow Cl_2O_2$	7.9×10^{-27}	8,600±2,500	2.7×10^{-14}	100	6
& $F + O_2 \rightarrow FOO$	5.3×10^{-25}	7,600 -	6.3×10^{-14}	-	7a
	1.1×10^{-25}	3,600 -	1.9×10^{-20}	-	7b
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.3×10^{-28}	11,200±1,000	2.7×10^{-12}	10	8

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

[a] f(298 K) is the uncertainty at 298 K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298\ K) \exp(\Delta B \left| \frac{1}{T} - \frac{1}{298} \right|)$.

* Indicates a change from the previous Panel evaluation (JPL 85-37).

& Indicates a change in the note from the previous evaluation.

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

NOTES TO TABLE 3

1. $HO_2 + NO_2$. 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. $NO + NO_2$. The data are from JANAF. This process is included because a recent measurement of the rate constant by Smith and Yarwood (1986) shows that it is too slow to be an important rate process, but there will be some equilibrium concentration present.

3. $NO_2 + NO_3$. Note changed from JPL 85-37. Recent measurements and a re-evaluation of the entropy of NO_3 lead to a slightly altered value. Burrows et al. (1985c), taking their data and those of Graham and Johnston (1978) and the room temperature data of Perner et al. (1985), have performed a "3rd law" fitting that yields the recommended parameters. These values are well within the range of measurements of Kircher et al. (1984), Tuazon et al. (1983) and Smith et al. (1985).

4. $Cl + O_2$. Cox et al. (1979) measured K at 298 K. Their reported value of K, (5.4 ± 2.6 x 10^{-21} cm^3 $molecule^{-1}$, when combined with JANAF values for the entropy change, gives $\Delta H_f(298)(ClO_2) = 22.5$ $kcal/mol^{-1}$. This is in excellent agreement with Ashford et al. (1978), who suggest $\Delta H_f(298)\ (ClO_2) = 22.5 \pm .5$ $kcal/mol^{-1}$. The expression of Cox et al. is:

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

5. $ClO + O_2$. Zellner (private communication, 1982) suggests $K < 12\ atm^{-1}$ and $\Delta H \geq -11$ kcal/mol. The corresponding value of A leads to $S^o 300(ClO{\cdot}O_2)$ ~73 cal mol^{-1} K^{-1}. A higher value of K has been proposed by Prasad (1980), but it requires $S^o(ClO{\cdot}O_2)$ to be about 83 cal mol^{-1} K^{-1}, which seems unreasonably high. Carter and Andrews (1981) found no experimental evidence for $ClO{\cdot}O_2$ in matrix experiments.

6. $ClO + ClO$. This equilibrium constant is not well established. The quoted value is based primarily on the work of Cox and co-workers (Cox and Derwent, 1979 and Hayman et al., 1986). The corresponding entropy of the dimer is 76 cal mol^{-1} K^{-1} and ΔH is -17.6 kcal mol^{-1}.

7. $F + O_2$. (a) From JANAF thermochemical values. (This value favored by k_o calculation, see Note 18, Table 2.) (b) From Benson's (1976) thermochemical values. Wallington et al. favor the Benson value for FO_2, based on the independence of NO_3 on diluent gas (i.e. N_2, O_2) when making NO_3 by $F + HNO_3$. The conclusion is that $F + O_2 = FO_2$ is a fast equilibrium; they conclude that the Benson value is correct. However, the value of the low-pressure rate constant favors the JANAF value (Patrick and Golden, 1983).

8. $CH_3O_2 + NO_2$. 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 ± 0.26) x 10^{-10} cm^3. Our values predict 3.94 x 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 only a sample of the data are 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 and SO_2, some comments are given in the text, but the photochemical data are not presented. The species CH_2O, NO_2, NO_3 and OClO 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).

Table 4. Photochemical Reactions of Stratospheric Interest

& $O_2 + h\nu \rightarrow O + O$		$CCl_4 + h\nu \rightarrow$ products	
* $O_3 + h\nu \rightarrow O_2 + O$		$CCl_3F + h\nu \rightarrow$ products	
$O_3 + h\nu \rightarrow O_2 + O(^1D)$		$CCl_2F_2 + h\nu \rightarrow$ products	
* $HO_2 + h\nu \rightarrow$ products		$CHClF_2 + h\nu \rightarrow$ products	
$H_2O + h\nu \rightarrow H + OH$	(1)	$CH_3Cl + h\nu \rightarrow$ products	
$H_2O_2 + h\nu \rightarrow OH + OH$		$CCl_2O + h\nu \rightarrow$ products	
$NO + h\nu \rightarrow N + O$		$CClFO + h\nu \rightarrow$ products	
* $NO_2 + h\nu \rightarrow NO + O$		$CF_2O + h\nu \rightarrow$ products	
* $NO_3 + h\nu \rightarrow$ products		$CH_3CCl_3 + h\nu \rightarrow$ products	
$N_2O + h\nu \rightarrow N_2 + O(^1D)$		# $CBrClF_2 + h\nu \rightarrow$ products	
$N_2O_5 + h\nu \rightarrow$ products		# $CBrF_3 + h\nu \rightarrow$ products	
$NH_3 + h\nu \rightarrow NH_2 + H$	(1)	$BrO + h\nu \rightarrow Br + O$	
$HNO_2 + h\nu \rightarrow OH + NO$		$BrONO_2 + h\nu \rightarrow$ products	
$HNO_3 + h\nu \rightarrow OH + NO_2$		$HF + h\nu \rightarrow H + F$	
$HNO_4 + h\nu \rightarrow$ products		$CO + h\nu \rightarrow C + O$	(1)
$Cl_2 + h\nu \rightarrow Cl + Cl$		$CO_2 + h\nu \rightarrow CO + O$	(1)
$ClO + h\nu \rightarrow Cl + O$		$CH_4 + h\nu \rightarrow$ products	(2)
$ClOO + h\nu \rightarrow$ products		$CH_2O \rightarrow$ products	
* $OClO + h\nu \rightarrow O + ClO$		$CH_3OOH + h\nu \rightarrow$ products	
$ClO_3 + h\nu \rightarrow$ products		$HCN + h\nu \rightarrow$ products	
# $Cl_2O_2 + h\nu \rightarrow$ products		$CH_3CN + h\nu \rightarrow$ products	
$HCl + h\nu \rightarrow H + Cl$		$SO_2 + h\nu \rightarrow SO + O$	
$HOCl \rightarrow OH + Cl$		$OCS + h\nu \rightarrow CO + S$	
* $ClNO + h\nu \rightarrow Cl + NO$		$H_2S + h\nu \rightarrow HS + H$	(2)
$ClNO_2 + h\nu \rightarrow$ products		$CS_2 + h\nu \rightarrow$ products	
$ClONO + h\nu \rightarrow$ products		# $NaCl + h\nu \rightarrow Na + Cl$	
$ClONO_2 + h\nu \rightarrow$ products		$NaOH + h\nu \rightarrow Na + OH$	

(1) Hudson and Kieffer (1975)
(2) Turco (1975)
New entry
* Indicates a change in the recommendation from the previous evaluation.
& Indicates a change in the note.

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

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

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

where I_0 and 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.

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

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 are three recent laboratory studies (Johnston et al., 1984; Chueng et al., 1984; Jenouvrier et al., 1986) which confirm the lower values obtained from solar irradiance measurements. There is also, however, a 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 dependence 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, except for the wavelength range 185 to 225 nm, where the present recommendation incorporates the averaged values from the recent work of Molina and Molina (1986); the older values were based on the work of Inn and Tanaka (1953). The temperature effect is negligible for wavelengths shorter than ~260 nm. Recent work by Mauersberger <u>et al</u>. (1986, 1987) yields a value of 1137 x 10^{-20} cm^2 for the cross section at 253.7 nm, the mercury line wavelength; it is about 1% smaller than the commonly accepted value of 1147 x 10^{-20} cm^2 reported by Hearn (1961), and about 2% smaller than the value obtained by Molina and Molina (1986), 1157 x 10^{-20} cm^2. The reason for the small discrepancy, which appears to be beyond experimental precision, is unclear.

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 <u>et al</u>. (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is, $\Phi(O^3P)$ ~0.1, at 274 nm; Sparks <u>et al</u>. (1980) also report $\Phi(O^3P)$ ~0.1, at 266 nm; according to Brock and Watson (1980b) $\Phi(O^1D)$ - 0.88 at 266 nm; Amimoto <u>et al</u>. (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, 1980a,b).

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	62.2	256.410-259.740	1120
186.916-188.679	57.6	259.740-265.158	1060
188.679-190.476	52.6	263.158-266.667	965
190.476-192.308	47.6	266.667-270.270	834
192.308-194.175	42.8	270.270-273.973	692
194.175-196.078	38.3	273.973-277.778	542
196.078-198.020	34.7	277.778-281.690	402
198.020-200.000	32.3	281.690-285.714	277
200.000-202.020	31.4	285.714-289.855	179
202.020-204.082	32.6	289.855-294.118	109
204.082-206.186	36.4	294.118-298.507	62.4
206.186-208.333	43.4	298.507-303.030	34.3
208.333-210.526	54.2	303.030-307.692	18.5
210.526-212.766	69.9	307.692-312.5	9.80
212.766-215.054	92.1	312.5-317.5	5.01
215.054-217.391	119	317.5-322.5	2.49
217.391-219.780	155	322.5-327.5	1.20
219.780-222.222	199	327.5-332.5	0.617
222.222-224.719	256	332.5-337.5	0.274
224.719-227.273	323	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

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 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 the wavelength in nm, and arctan is expressed in radians.

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

$$A(\tau) = 0.332 + 2.565\text{x}10^{-4}\tau + 1.152\text{x}10^{-5}\tau^2 + 2.313\text{x}10^{-8}\tau^3$$

$$B(\tau) = -0.575 + 5.59\text{x}10^{-3}\tau - 1.439\text{x}10^{-5}\tau^2 - 3.27\text{x}10^{-8}\tau^3$$

$$\lambda_o(\tau) = 308.20 + 4.4871\text{x}10^{-2}\tau + 6.9380\text{x}10^{-5}\tau^2 - 2.5452\text{x}10^{-6}\tau^3$$

$$C(\tau) = 0.466 + 8.883\text{x}10^{-4}\tau - 3.546\text{x}10^{-5}\tau^2 + 3.519\text{x}10^{-7}\tau^3.$$

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; 1980), Cox and Burrows (1979), McAdam et al. (1987), and Kurylo et al. (1987a); and by Sander et al. (1982) at 227.5 nm.

There are significant discrepancies in the shape of the spectrum as well as in the absolute cross section values; at 227.5 nm, the value ranges from 250 to 309 x 10^{-20} cm^2/molecule, the average of all measurements being 269 x 10^{-20} cm^2/molecule.

Table 8 lists the recommended cross sections, which are computed from the mean of the five sets of reported values. This recommendation is given here merely to indicate that photolysis of HO_2 in the stratosphere and troposphere is not an important process and can be neglected. However, for chemical kinetics studies the simple average presented here need not be the best choice and the most suitable cross section values to be used should be considered on a case-by-case basis.

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)	$10^{20}\sigma(cm^2)$
200	430
210	430
220	360
230	240
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 10 lists the values only at the indicated wavelengths.

Recent cross section measurements by Schneider et al. (1987) 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. Furthermore, measurements by Calvert et al. (private communication) indicate that the temperature effect on the cross sections is significantly smaller than reported by Bass et al. (1978). The discrepancies are probably due to inaccuracies in the correction required to account for the presence of N_2O_4 in the absorption cells.

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 well with those of Harker et al., and they indicate that the quantum yields themselves are temperature dependent. Direct measurements of the solar photodissociation rate of NO_2 in the troposphere by Parrish et al. (1983) agree better with theoretical

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

λ (nm)	$10^{20}\sigma(cm^2)$ 235 K	298 K	λ (nm)	$10^{20}\sigma(cm^2)$ 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

calculations that incorporate the quantum yield values of Jones and Bayes (1973) rather than those of Harker et al. (1977).

The previous recommendation for quantum yields was based on the work of Harker et al. (1977) and of Davenport (1978) for the atmospherically-important 375-470 nm region. Recent work by Gardner et al. (1987) yields values which are in much better agreement with the values reported earlier by Jones and Bayes (1973). The recommended quantum yield values, listed in Table 11, are in agreement with the recommendation of Gardner et al. (1987); they are based on a smooth fit to the data of Gardner et al. (1987) for the wavelength range from 334 to 404 nm; Harker et al. (1977) for 397-420 nm (corrected for cross sections); Davenport (1978) for 400-420 nm; and Jones and Bayes (1973) for 297-412 nm.

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

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

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); (5) Ravishankara and Wine (1983); (6) Burrows et al. (1985b); (7) Ravishankara and Mauldin (1986); (8) Sander (1986); and (9) Cantrell et al. (1987). The 1st and 4th studies required calculation of the NO_3 concentration by modeling a complex kinetic system. The other studies are more direct and the results in terms of integrated absorption coefficients are in good agreement. The recommended values at 298 K are the averages of the results of Ravishankara and Wine (1983) and Sander (1986). Table 12 lists a sample of these values; the original literature should be consulted for a more extended wavelength range, and for values at other temperatures. The effects of secondary

Table 11. Quantum Yields for NO_2 Photolysis

λ, nm	Φ	λ, nm	Φ
< 285	1.00	393	0.953
290	0.999	394	0.950
295	0.998	395	0.942
300	0.997	396	0.922
305	0.996	397	0.870
310	0.995	398	0.820
315	0.994	399	0.760
320	0.993	400	0.695
325	0.992	401	0.635
330	0.991	402	0.560
335	0.990	403	0.485
340	0.989	404	0.425
345	0.988	405	0.350
350	0.987	406	0.290
355	0.986	407	0.225
360	0.984	408	0.185
365	0.983	409	0.153
370	0.981	410	0.130
375	0.979	411	0.110
380	0.975	412	0.094
381	0.974	413	0.083
382	0.973	414	0.070
383	0.972	415	0.059
384	0.971	416	0.048
385	0.969	417	0.039
386	0.967	418	0.030
387	0.966	419	0.023
388	0.964	420	0.018
389	0.962	421	0.012
390	0.960	422	0.008
391	0.959	423	0.004
392	0.957	424	0.000

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)
600	261	625	804	648	61
601	266	626	710	649	52
602	305	627	722	650	50
603	354	628	709	651	53
604	417	629	679	652	56
605	419	630	644	653	62
606	325	631	475	654	77
607	227	632	348	655	94
608	172	633	196	656	133
609	155	634	144	657	174
610	194	635	129	658	224
611	173	636	161	659	360
612	204	637	193	660	665
613	244	638	195	661	1320
614	245	639	164	662	2020
615	212	640	122	663	1760
616	192	641	100	664	1120
617	191	642	92	665	760
618	210	643	94	666	468
619	231	644	93	667	257
620	295	645	86	668	165
621	455	646	73	669	114
622	950	647	70	670	86
623	1420				
624	1150				

chemistry were minimized in these two studies by working with short time scales and direct titration of the radicals, but some unexplained discrepancy of up to 20% remains. The recommended peak cross section value around 662 nm is 2.1 x 10^{-17} cm^2 at 298 K, and 2.7 x 10^{-17} at 220 K, as computed from the average of the studies by Ravishankara and Mauldin (1986) and Sander (1986); within experimental error, the variation is linear with temperature. Note, however, that Cantrell et al. (1987) find no measurable temperature effect on the peak cross section; the reason is not clear.

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 λ <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:

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

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

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

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

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

where T: temperature, Kelvin; λ : nm

$A_1 = 68.21023$ $B_1 = 123.4014$

$A_2 = -4.071805$ $B_2 = -2.116255$

$A_3 = 4.301146 \times 10^{-2}$ $B_3 = 1.111572 \times 10^{-2}$

$A_4 = -1.777846 \times 10^{-4}$ $B_3 = -1.881058 \times 10^{-5}$

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

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 380 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 et al. (1986) report values of 0.72, 0.38, 0.21 and 0.15 at 248, 266, 287 and 289 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 < λ < 380 nm; 300 K > T > 225 K:
$10^{20}\sigma = \exp[2.735 + ((4728.5 - 17.127\ \lambda)/T)]$
where σ is in cm^2/molecule; λ in nm; and T in Kelvin.

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

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.

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

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

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

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.

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. Jolly _et al_. (1986) measured a quantum yield for OH production of 0.89 ± 0.08 at 222 nm.

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 remains to be determined. MacLeod et al. (1987) report that photolysis at 248 nm yields one third OH and NO_3 and two thirds $HO_2 + NO_2$.

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), Fergusson et al. (1936), and Burkholder and Bair (1983).

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

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

The absorption cross sections of chlorine monoxide, ClO, 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 ClO accounts for at most 2 to 3 percent of the total destruction rate of ClO 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

OClO + hν → O + ClO

The spectrum of OClO 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 OClO of a few seconds.

The recommended absorption cross section values are those reported by Wahner et al. (1987), who measured the spectra with a resolution of 0.25 nm at 204, 296 and 378 K, in the wavelength range 240 to 480 nm. Table 21 lists the cross section values at the peak of the bands [a(0) to a(26)].

Table 21. Absorption Cross Sections of OClO at the Band Peaks

	$10^{20}\sigma$ (cm^2)		
λ(nm)	204 K	296 K	378 K
475.53	--	13	-
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
391.77	138	114	130
287.80	105	86	105
283.51	089	72	90
279.64	073	60	79
275.74	059	46	-
272.93	053	33	-

$ClO_3 + h\nu \rightarrow$ products

Table 22 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 22. 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

$Cl_2O_2 + h\nu$

The UV spectrum of Cl_2O_2 has been studied by Basco and Hunt (1979), who report cross sections at six wavelengths between 277 and 232 nm, with increasing values towards the shorter wavelengths; by Molina and Molina (1987), who observed a maximum at about 270 nm; and by Cox and Hayman (1987), who report the maximum around 245 nm. Using IR spectroscopy, Molina and Molina (1987) showed that several isomers of Cl_2O_2 exist, so that the discrepancies in the UV spectra might be due at least in part to the presence of different isomers. On the other hand, for the atmospherically-important wavelength region around 310 nm the agreement between the last two sets of data is good. Clearly, additional studies are needed. Molina and Molina (1987) suggest a quantum yield of unity for the production of Cl-atoms, but direct studies of the identity of the photodissociation products also need to be carried out.

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

The absorption cross sections of HCl, listed in Table 23, are taken from the work of Inn (1975).

Table 23. 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 24.

Molina et al. (1980b), by monitoring directly OH radicals produced by laser photolysis of HOCl, obtain an absorption cross section value of $\sim 6 \times 10^{-20}$ 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.

Recently, Mishalanie et al. (1986) reported measurements of the UV spectrum of HOCl, using a dynamic source to generate this species, instead of equilibrium mixtures with Cl_2O and H_2O. Overall, their results are in reasonable agreement with the recommended cross section values, and lead to slightly smaller atmospheric photodissociation rates below ~30 km, but yield, at higher altitudes, rates which are larger by a factor of up to ~1.7. The reason for the discrepancy is not known.

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 24. 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

$ClNO + h\nu \rightarrow Cl + NO$

Nitrosyl chloride has a continuous absorption extending beyond 650 nm. 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, and of Tyndall et al. (1987) for the 190 to 350 region except around 230 nm, where the values of Ballash and Armstrong are larger by almost a factor of two. The recommended absorption cross sections, listed in Table 25, are taken from the recent work of Tyndall et al. (1987).

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 25. ClNO Absorption Cross Sections

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
190	4320	230	266	270	12.9	310	11.5
192	5340	232	212	272	12.3	312	11.9
194	6150	234	164	274	11.8	314	12.2
196	6480	236	120	276	11.3	316	12.5
198	6310	238	101	278	10.7	318	13.0
200	5860	240	82.5	280	10.6	320	13.4
202	5250	242	67.2	282	10.2	322	13.6
204	4540	244	55.1	284	9.99	324	14.0
206	3840	246	45.2	286	9.84	326	14.3
208	3210	248	37.7	288	9.71	328	14.6
210	2630	250	31.7	290	9.64	330	14.7
212	2180	252	27.4	292	9.63	332	14.9
214	1760	254	23.7	294	9.69	334	15.1
216	1400	256	21.3	296	9.71	336	15.3
218	1110	258	19.0	298	9.89	338	15.3
220	896	260	17.5	300	10.0	340	15.2
222	707	262	16.5	302	10.3	342	15.3
224	552	264	15.3	304	10.5	344	15.1
226	436	266	14.4	306	10.8	346	15.1
228	339	268	13.6	308	11.1	348	14.9
						350	14.5

$ClNO_2 + h\nu \rightarrow$ products

The absorption cross sections of nitryl chloride, $ClNO_2$, 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 26 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% Cl_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 Cl-atoms; they also report a negligible quantum yield for the production of oxygen atoms.

Table 26. Absorption Cross Sections of $ClNO_2$

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 27. 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 27. 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 28, 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. (1979b), 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 found 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 28. Absorption Cross Sections of $ClONO_2$

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-Cl), 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_2Cl_2, $CFCl_3$ and CCl_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 CCl_4, CCl_3F, CCl_2F_2, $CHClF_2$, and CH_3Cl--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 29, 30 and 31 list the present recommendations for the cross sections of CCl_4, CCl_3F and CCl_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 CCl_4 and $CFCl_3$; for CF_2Cl_2 the temperature dependence is given by the expression at the bottom of Table 31. The species $CHClF_2$, CH_3Cl, CH_3CCl_3, $CBrF_3$ and $CBrClF_2$ are discussed individually; their absorption cross sections are listed in Tables 32, 33, 35 and 36, respectively.

Table 29. 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 30. Absorption Cross Sections of CCl_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	222	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 31. 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	1.52
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

The absorption cross sections for various other halocarbons not listed in this evaluation have also been investigated: for $CClF_3$, CCl_2FCClF_2, $CClF_2CClF_2$ and $CClF_2CF_3$ 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: $CHCl_2F$ by Hubrich et al. (1977); $CHCl_3$, CH_2Cl_2, CH_2ClF, CF_3CH_2Cl, CH_3CClF_2 and CH_3CH_2Cl by Hubrich and Stuhl (1980); $CHCl_3$, CH_3Br, $CHFCl_2$, $C_2F_4Br_2$, C_2HCl_3 and $C_2H_3Cl_3$ by Robbins (1977); CH_2Cl_2 and $CHCl_3$ by Vanlaethem-Meuree et al. (1978a); $CHCl_2F$, $CClF_2CH_2Cl$, CF_3CH_2Cl, CF_3ChCl_2 and CH_3CF_2Cl by Green and Wayne (1976-1977); and CH_3Br, CH_2Br_2, CBr_2F_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.

$CHClF_2 + h\nu \rightarrow$ products

The preferred absorption cross sections, listed in Table 32, 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 32. 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
190	0.235
192	0.157
194	0.100
196	0.070
198	0.039
200	0.026
202	0.022
204	0.013

$CH_3Cl + h\nu \rightarrow$ products

The preferred absorption cross sections, listed in Table 33, 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 33. Absorption Cross Sections of CH_3Cl

λ	$10^{20}\sigma(cm^2)$		
(nm)	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 + hν → products, CClFO + hν → products, and CF_2O + hν → products

Table 34 shows the absorption cross sections of CCl_2O (phosgene) and CFClO given by Chou et al. (1977), 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 34 are averages over each 50 wavenumber 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.

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 35 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 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
103.0	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	-

Table 35. 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	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

$CBrClF_2 + h\nu \rightarrow$ products

The absorption cross sections of $CBrClF_2$ (Halon 1211, or fluorocarbon 12B1) have been measured by Giolando <u>et al</u>. (1980), and by Molina <u>et al</u>. (1982), both at room temperature. The recommended cross sections, listed in Table 36, are taken from this latter work. These cross section values are about 20% lower than those reported by Giolando <u>et al</u>. in the atmospherically important 285-305 nm wavelength region.

$CBrF_3 + h\nu \rightarrow$ products

Table 36 shows the absorption cross sections of CF_3Br (Halon 1301, or fluorocarbon 13B), taken from the work of Molina <u>et al</u>. (1982) who report measurements at 298 K.

Table 36. Absorption Cross Sections of $CBrF_3$ and of $CBrClF_2$

λ (nm)	$10^{20}\sigma$ (cm^2)		λ (nm)	$10^{20}\sigma$ (cm^2)	
	$CBrF_3$	$CBrClF_2$		$CBrF_3$	$CBrClF_2$
190	6.71	42.4	265	0.00905	0.721
195	9.61	71.1	270	0.00348	0.392
200	11.8	96.2	275	0.00138	0.190
205	12.9	109	280	0.00055	0.0883
210	12.3	105	285	0.00022	0.0398
215	10.3	89.6	290	0.00008	0.0182
220	7.50	70.0	295	0.003	0.00821
225	4.83	51.3	300	0.001	0.00361
230	2.70	34.2	305		0.00165
235	1.48	23.3	310		0.00066
240	0.695	14.4	315		0.00026
245	0.325	8.87	320		0.000098
250	0.139	5.29	325		0.000037
255	0.0589	2.97	330		0.000025
260	0.0234	1.56			

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

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 37. 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 37. Absorption Cross Sections of BrO

λ (nm)	$10^{20}\sigma(\text{cm}^2)$ 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 38. The photolysis products are not known.

Table 38. 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 39, 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 39 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 39. 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 40.

Table 40. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm2)	λ (nm)	$10^{20}\sigma$ (cm2)
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 + hν → 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.

The absorption cross sections have been measured recently by McGee and Burris (1987) at 295 and 210 K, between 300 and 324 nm, which is the wavelength region commonly used for atmospheric monitoring of SO_2.

OCS + hν → 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; by Molina et al. (1981) between 180 and 300 nm, at 295 and 225 K, and by Locker et al. (1983) between 195 and 260 nm, in the 195 K to 403 K temperature range. 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 41, 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.

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

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.

$NaCl + h\nu \rightarrow Na + Cl$

There are several studies of the UV absorption spectra of NaCl vapor. For a review of the earlier work, which was carried out at high temperatures, see Rowland and Rogers (1982). The recommended cross sections, listed in Table 42, are taken from the work of Silver et al. (1986), who measured spectra of gas phase NaCl at room temperature in the range from ~190 to 360 nm, by directly monitoring the product Na atoms.

Table 41. Absorption Cross Sections of OCS

λ (nm)	$10^{20}\sigma(\text{cm}^2)$		λ (nm)	$10^{20}\sigma(\text{cm}^2)$	
	295 K	225 K		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 $\Phi = 0.72$

Table 42. Absorption Cross Sections of NaCl Vapor at 300 K

λ (nm)	$10^{20}\sigma$ (cm^2)
189.7	612
193.4	556
203.1	148
205.3	90.6
205.9	89.6
210.3	73.6
216.3	151
218.7	46.3
225.2	146
230.4	512
231.2	947
234.0	1300
237.6	638
241.4	674
248.4	129
251.6	251
254.8	424
260.2	433
268.3	174
277.0	40
291.8	0.8

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

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.

APPENDIX.

GAS PHASE ENTHALPY DATA

The following data are adapted mainly from CODATA (1984), although a few entries have been updated.

MOLECULE	$\Delta H_f(298)$ (Kcal/mol)	MOLECULE	$\Delta H_f(298)$ (Kcal/mol)	MOLECULE	$\Delta H_f(298)$ (Kcal/mol)	MOLECULE	$\Delta H_f(298)$ (Kcal/mol)
H	52.1	CH_3O	3.5	HSO	-1±2	CCl_3	19±1
H_2	0.00	CH_3O_2	3.8±2	HSO_3	-92±2	CCl_4	-22.9
O	59.57	CH_2OH	-6.2	CS	65	$CHCl_3$	-24.6
$O(^1D)$	104.9	CH_3OH	-48.0	CS_2	28.0	CH_2Cl	28±1
O_2	0.00	CH_3OOH	-31.3	CH_3S	33±2	CH_2Cl_2	-22.8
$O_2(^1$-DELTA)	22.5	CH_3ONO	-15.6	CH_3SCH_3	-8.9	CH_3Cl	-19.6
$O_2(^1$-SIGMA)	37.5	CH_3ONO_2	-28.6	CH_3SSCH_3	-5.8	ClCO	-4.1
O_3	34.1	$CH_3O_2NO_2$	-10.6±2	OCS	-34	$COCl_2$	-52.6
HO	9.3	C_2H	135	F	18.98	CFCl	7±6
HO_2	3±1	C_2H_2	54.35	F_2	0.00	CH_2F	-8±2
H_2O	-57.81	C_2H_3	68.1	HF	-65.34	$CHCl_2$	23.5±1
H_2O_2	-32.6	C_2H_4	12.45	HOF	-23.4±1	$CFCl_2$	-22.9
N	113.00	C_2H_5	28.4	FO	26±2	$CFCl_3$	-68.1
N_2	0.00	C_2H_6	-20.0	FO_2	12±3	CF_2Cl	-64.3
NH	82.0	CH_2CN	58.6	FONO	-15.2	CF_2Cl_2	-117.9
NH_2	45.3	CH_3CN	19.1	FNO_2	-25.4	CF_3Cl	-169.2
NH_3	-10.98	CH_2CO	-14.23	$FONO_2$	2.4	$CHFCl_2$	-68.1
NO	21.57	CH_3CO	-5.8	CF_2	-44±2	CHF_2Cl	-115.6
NO_2	7.9	CH_3CHO	-39.7	CF_3	-112±1	COFCl	-102±8
NO_3	17±1	C_2H_5O	-4.1	CF_4	-223.0	C_2Cl_4	-3.0
N_2O	19.61	CH_2CH_2OH	-13.2	FCO	-41±14	C_2HCl_3	-1.9
N_2O_3	19.8	C_2H_5OH	-56.2	COF_2	-151.7	CH_2CCl_3	11±7
N_2O_4	2.2	CH_3CO_2	-49.6	Cl	28.9	CH_3CCl_3	-34.0
N_2O_5	2.7	$C_2H_5O_2$	-1.8	Cl_2	0.00	Br	26.7
HNO	23.8	CH_3OOCH_3	-30.0	HCl	-22.07	Br_2	7.39
HNO_2	-19.0	C_3H_5	39.4	ClO	24.4	HBr	-8.70
HNO_3	-32.3	C_3H_6	4.8	ClOO	22.5±1	HOBr	-19±2
HO_2NO_2	-11±2	n-C_3H_7	22.6±2	OClO	23±2	BrO	30
CH	142.0	i-C_3H_7	18.2±2	$ClOO_2$	>13.4	BrNO	19.7
CH_2	92.3	C_3H_8	-24.84	ClO_3	37	$BrONO_2$	5±7
CH_3	35.1	C_2H_5CHO	-44.8	Cl_2O	19.5	BrCl	3.5
CH_4	-17.88	CH_3COCH_3	-51.9	Cl_2O_2	31±5	CH_2Br_2	-2.6±2
CN	104.0	CH_3CHCH_2OH	-18.0	HOCl	-18.6±3	CH_2Br	41±2
HCN	32.3	S	66.22	ClNO	12.4	CH_3Br	-9.0
NCO	38	S_2	30.72	$ClNO_2$	3.0	$CHBr_2$	45±3
CO	-26.42	HS	34±1	ClONO	19.8	I	25.52
CO_2	-94.07	H_2S	-4.93	$ClONO_2$	6.3	I_2	14.92
HCO	9.0	SO	1.2	FCl	-12.1	HI	6.30
CH_2O	-26.0	SO_2	-70.96	CCl	120±5	IO	41.1
HCOOH	-90.5	SO_3	-94.6	CCl_2	56.9±5	INO	29.0
						INO_2	14.4

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