JPL PUBLICATION 82-57

(NASA-CR-169262) CHEMICAL KINETICS AND
PHOTOCHEMICAL DATA FOR USE IN STRATOSPHERIC
MODELING: EVALUATION NUMBER 5 (Jet
Propulsion Lab.) 193 p HC A09/MF A01
CSCL 13B G3/45

N82-31824

Unclas
28804

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This publication was prepared by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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ABSTRACT

This is the fifth 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.

CHEMICAL KINETICS AND PHOTOCHEMICAL DATA FOR USE IN STRATOSPHERIC MODELING

INTRODUCTION

The present compilation of kinetic and photochemical data represents the fifth 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)

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

W. B. DeMore, Chairman (Chapman chemistry)

F. Kaufman, Advisor

D. M. Golden (three-body reactions)

R. F. Hampson (halogen chemistry)

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

M. J. Kurylo (SO_x chemistry)

M. J. Molina (photochemical cross sections)

A. R. Ravishankara (hydrocarbon oxidation)

R. T. Watson (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 evaluation by the entire Panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case.

BASIS OF THE RECOMMENDATIONS

The recommended rate constants and cross sections are based on laboratory measurements, and in general only published data are considered. Occasional exceptions are made when preprints or articles submitted for publication are available to the Panel. In no cases are rate constants adjusted to fit observations of stratospheric concentrations. The Panel does consider the question of consistency of data with expectations based on kinetics theories, and in cases where a discrepancy appears to exist, this fact is pointed out in the accompanying note. The major use of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure or temperature dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of a few important rate constants for which no experimental data are available (for example, $OH + HOCl \rightarrow H_2O + ClO$), the Panel has provided estimates of rate constant parameters, based on analogy to similar reactions for which data are available.

DISCUSSION

In this section we review the general state of laboratory kinetics and photochemistry. Specific discussions of individual reaction categories are also included.

While there have been no major upheavals in stratospheric chemistry since the last panel evaluation, the recommendations for certain key reactions (for example, $O + HO_2$, $OH + HO_2$, and $OH + HNO_4$) have changed significantly, and the implications for atmospheric models have been important. Fortunately, the resulting changes seem for the most part to bring the model predictions into closer agreement with measured stratospheric properties such as the ClO profile.

The improvements in precision, reliability, and completeness of the kinetics data have not been accompanied by a corresponding increase in theoretical understanding of the reactions in question, however. It is still unknown, for example, why the OH + CO reaction exhibits a pressure dependence, insofar as the detailed mechanism is concerned. A similar situation holds for the reactions OH + HO_2, HO_2 + HO_2, and (to some extent) OH + HNO_3. Thus, there is an element of empiricism in some of the important rate recommendations.

In our previous evaluation (JPL 81-3) we identified, as one problem, the relative paucity of advanced techniques for the identification of reaction intermediates and products. This is an area which has not progressed as rapidly in recent years as has the capability for measurement of absolute reaction rates. In some cases such information is required to fully elucidate the reaction mechanism. Several groups are now developing new apparatus for these purposes, and it may be hoped that progress will be rapidly forthcoming.

In the area of product identification, the question of isomer formation in several key reactions continues to be unresolved. Although the ClO + NO_2 reaction, giving possible isomeric forms of chlorine nitrate, is the classic example, there may conceivably be a role of isomers in at least a transient form in other important reactions, such as OH + NO_2 and HO_2 + NO_2. These questions require further clarification.

We have also pointed out previously that there are some disagreements of rate parameters, particularly pre-exponential factors, with expectations based on transition state theory. Such discrepancies are disconcerting. The principal example in this connection is the HO_2 + O_3 reaction, which exhibits an abnormally low A-factor for a reaction which presumably involves a simple hydrogen transfer in the rate-determining step.

O_x Reactions

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

$O(^1D)$ Reactions

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

HO_x Reactions

This family of reactions continues to be a major source of uncertainty in stratospheric chemistry. The principal reasons are that the HO_2 radical is relatively difficult to produce and to monitor over the wide range of temperature and pressure conditions that exist in the stratosphere and that key HO_2 reactions show an unusual dependence on these reaction conditions. Specifically the temperature, pressure, and water vapor dependencies observed for the $HO_2 + HO_2$ reaction and the pressure dependence observed for the $HO_2 + OH$ reaction are unexpected. New results on both of these reactions have led to new recommendations which attempt to incorporate some of the observed behavior. Although significant progress has been made, the data base on both reactions is still relatively weak and incomplete. The recommendations for the $O + HO_2$ and OH + OH reactions have been changed to incorporate new studies that include the temperature dependence of these important reactions.

NO_x Reactions

The kinetics data for this class of reactions are considered reliable, particularly following the recent improvements in the $OH + HNO_3$ and $OH + HNO_4$ rate constants. Furthermore, there are now measurements of the temperature and pressure dependences of the $HO_2 + NO_2$ reaction, thus providing a more reliable assessment of the role of HNO_4 in the stratosphere. It must be mentioned, however, that the NO_x class of compounds is not one in which there is particularly good agreement between field measurements and model predictions. The HNO_3 profile is an example, and there also appear to be difficulties in accounting for the observations of NO_3. It is not clear at the present time whether the discrepancies are due to incorrect chemistry or measurement problems.

Halogen Chemistry

The recommendations for the important ClO_x reactions have not changed significantly since the previous evaluation (JPL 81-3). This reflects the fact that from the standpoint of the CFM-O_3 question many of the important rate constants, such as those for Cl + O_3, NO + ClO, O + ClO and OH + HCl, have been measured reliably and recommendations can be made confidently. One rate constant recommendation which has changed substantially is that of the Cl + $ClNO_3$ reaction, which is now known to be almost two orders of magnitude faster than previously believed. This change has little impact on stratospheric models, but does have significance with regard to laboratory experiments on the photolysis of chlorine nitrate. (See discussion of chlorine nitrate cross sections.) The table now includes new entries for reactions of chlorine atoms with more organic species (C_3H_8, C_2H_2, CH_3OH) and with HOCl. In the reaction of Cl with HO_2 the channel to produce ClO + OH is now known to be much more significant (20% at 298 K) than thought previously.

Recent kinetic studies of the HO + ClO and HO_2 + ClO reactions suggest that formation of HCl is negligible, thus diminishing their potential importance in the stratosphere as chain terminators. The strong negative T-dependence of the HO_2 + ClO reaction does, however, enhance the possible role of HOCl as a chlorine reservoir in stratospheric chemistry. However, such effects are probably minor since the role as a sink is counter-balanced by the possible action of HOCl in a catalytic O_3 destruction cycle arising through photolysis.

Other than a few minor refinements, there have been no changes in the data base for BrO_x and FO_x reactions.

Hydrocarbon Oxidation

Our understanding of hydrocarbon oxidation in the atmosphere has improved considerably in the past few years. All hydrocarbons are produced in the biosphere 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, 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, reaction of Cl atoms with these hydrocarbons (mainly CH_4) constitutes one of the major sink mechanisms for active chlorine. Even though CH_4 is the predominant hydrocarbon in the stratosphere, we have included in this evaluation certain reactions of a few heavier hydrocarbon species.

In the stratosphere, CH_4 oxidation is initiated by its reaction with either OH or Cl (and to a limited extent $O(^1D)$), leading to formation of CH_3 and subsequently CH_3O_2. Several details of the subsequent chemistry are unclear, however. Three reactions which are not well characterized are: $CH_3O_2 + HO_2$, which exhibits an unusually large negative temperature dependence; $CH_3O + O_2$, which has not been well studied at or below room temperature; and the $CH_3OCH + OH$ reaction, for which the rate constant has not been measured at all. The $CH_3O_2 + HO_2$ reaction is the main source of CH_3OOH in the stratosphere, and an unusual temperature dependence has been measured for this reaction, suggesting a complex mechanism analogous to that for the $HO_2 + HO_2$ reaction. Further studies on the temperature and pressure dependence of this reaction are needed. The $CH_3O + O_2$ reaction rate constant has recently been measured directly at high temperatures, but measurements at lower temperatures are also needed. Nevertheless, it is quite clear that the main pathway for CH_3O in the stratosphere is reaction with O_2. Even though the rate constants for the three reactions mentioned above are not very well known, the effects of these uncertainties on stratospheric O_3 perturbation calculations are negligible.

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

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

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

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

SO_x Reactions

Oxidation of SO_2 is considered to be a principal source of the sulfuric acid and ammonium sulfate aerosol particles which make up the Junge layer in the lower stratosphere. This layer, originally thought to be the result of volcanic activity, has persisted during extended periods of volcanic inactivity. It is now believed that sulfur containing species such as OCS (of either biogenic or anthropogenic origin) can serve as photolytic or reactive sources of reduced sulfur which can ultimately be oxidized into SO, SO_2, and thence to sulfuric acid.

There is increasing evidence of a molecular oxygen effect on the reactions of such sulfur containing compounds. The reaction of electronically excited CS_2 with O_2 has been suggested as an important tropospheric loss mechanism of CS_2 and source of OCS. Similarly, the reaction of OH with CS_2 is appreciably accelerated in the presence of O_2, suggesting the reaction of a CS_2-OH adduct with O_2. While further such O_2 reactions have not yet been quantitatively appraised, their occurrence may be very important to a complete understanding of SO_x chemistry.

Among the simple bimolecular reactions, those involving sulfur atoms are reasonably well defined for stratospheric purposes. Our understanding of atmospheric SH reactions, on the other hand, suffers from the absence of relevant rate constant measurements. As the body of information on SH radical activity is increased, further entries describing its atmospheric behavior will be added.

The tables have been expanded to include several reactions describing the formation and subsequent oxidation of SO. A complete description of SO oxidation by both radical and molecular species cannot be presented at this time. Many SO reactions appear to occur with rate constants greatly exceeding the NO reaction analogues. Further work is needed to fully assess the importance of SO reactions with species such as OH, HO_2, ClO, BrO, etc.

Photochemical Cross Sections

The absorption cross sections of O_2 in the 185-210 nm range--i.e., in the Schumann-Runge bands and at the onset of the Herzberg continuum--require further study; estimates of the penetration of UV radiation in the stratosphere depend critically on these cross sections. Also, the absorption cross sections of O_3 and their temperature dependence should be accurately remeasured in view of their importance for atmospheric modeling and for interpreting Dobson and BUV data.

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

New results on the rate constant for the Cl + $ClNO_3$ reaction have resolved previous discrepancies on the identity of the primary photodissociation products of $ClNO_3$ (see discussion under $ClNO_3$ cross sections).

Status of Atmospheric Chemistry

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 is dependent on a detailed understanding of chemical reactions which form, remove and interconvert the catalytic species. A model calculation of stratospheric composition may include some 150 chemical reactions and photochemical processes, which vary greatly in their importance in controlling the density of ozone. Laboratory measurements of the rates of these reactions have progressed rapidly in recent years, and have given us a basic understanding of the processes involved, particularly in the upper stratosphere. Despite the basically sound understanding of overall stratospheric chemistry which presently exists, much remains to be done to quantify errors, to identify reaction channels positively, and to measure reaction rates both under conditions corresponding to the lower stratosphere (~210 K, ~75 torr) as well as the top of the stratosphere (~270 K, ~ 1 torr).

The chemistry of the upper stratosphere, i.e. 30-50 km, is thought to be reasonably well defined, although there appear to be some significant differences between the predicted and observed chemical composition of this region of the atmosphere which may be due to inaccurate rate data or missing chemistry. In this region the chemical composition of the atmosphere is predominantly photochemically controlled and the photolytic lifetimes of temporary reservoir species such as 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 on these reactions have been carried out under the conditions of pressure and temperature which are encountered in the upper stratosphere, and their overall status appears to be good. No significant changes in rate coefficients for the key reactions such as $Cl + O_3$, $O + ClO$, $NO + ClO$, $O + NO_2$, $NO + O_3$, etc., have occurred in the last few years. On the other hand, there have recently been rate and mechanistic studies on reactions such as $HO + ClO$ and $HO_2 + ClO$, which could play important roles throughout the stratosphere if they were to have product channels which generate significant amounts of HCl. However, the results to date suggest minor HCl pathways. A major area of concern in the chemistry of the upper stratosphere involves the reaction between HO and HO_2 radicals which, as previously discussed in this section, has had considerable uncertainty in

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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. Within the past few months the uncertainty in the rate coefficient for the reaction has decreased, now being thought to be less than a factor of two over the entire range of atmospheric conditions. It should be noted that the new rate coefficients for the HO + H_2O_2, HO + HNO_3 and HO + HO_2NO_2 reactions have had little effect on the model predictions of odd 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 only be considered to be fair, and some improvements need to be made before comparing theoretical predictions with certain field measurement data, e.g., the HO/HO_2 ratio.

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^*, 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. It is within this region of the atmosphere (15-30 km) where both dynamics and photochemistry play key roles in controlling the trace gas distributions. Here the model calculations predict large changes in ozone concentration (absolute number density, not percentage) from chlorofluoromethanes. It is also within this region of the stratosphere that the question of the pressure and temperature dependences of the rate coefficients is most critical, due to the low temperatures (210-255 K) and the high total pressures (40-270 mbar). The previously discussed question of possible pressure and temperature dependences of HO and HO_2 reactions is highly pertinent here.

Our view of the chemistry of the lower stratosphere has changed in recent years, due to changes in rate constants which have in turn led to changes in the relative importance of reactions which control the HO_x budget in this region of the atmosphere. Prior to the appearance of improved kinetics data for the HO + H_2C_2, HO + HNO_3, and HO + HO_2NO_2 reactions, the major termination reaction for odd hydrogen species in models of the lower stratosphere was the $HO + HO_2 \rightarrow H_2O + O_2$ reaction. Recent work on the HO + H_2O_2 and HO + HNO_3 rate constants has suggested that the previously accepted values (prior to JPL 81-3) were in error, especially at stratospheric temperatures, and that the previously undetermined rate coefficient for the HO + HO_2NO_2 reaction was significantly faster than had been estimated. The major effect occurred due to the change in rate constant for the OH + HNO_3 reaction (a factor of 3 faster at 200 K). The change in the rate constant for HO + H_2O_2 (a factor of 5 at 220 K) had relatively less effect. There are several other processes which need to be restudied in order to understand HO_x radical budgets in the lower stratosphere, and the HO_2 + HO_2 reaction is an example. The species HNO_3, HO_2NO_2, $ClNO_3$ and HOCl illustrate the strong coupling that exists between the HO_x, NO_x and ClO_x families. One disturbing problem is that while these species are currently thought to play an important role in stratospheric photochemistry, only HNO_3 has yet been positively observed by any field measurement study.

RATE CONSTANT DATA

Format

The order of data presentation has been extensively revised in the present evaluation. In Table 1 (Rate Constants for Second Order Reactions) the reactions are now grouped into the classes O_x, $O(^1D)$, HO_x, NO_x, ClO_x, BrO_x, FO_x, Hydrocarbon Reactions, 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 now follows the same sequence. It is expected that these revisions will greatly facilitate the location of data in the tables.

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 A + B 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 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:

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

The intermediate $[AB]^{*}$ is different from the transition state $[AB]^{\neq}$, in that it is a bound molecule which has a finite lifetime and which can, in principle, be isolated. (Of course, transition states are involved in all of the above reactions, both forward and backward, but are not explicitly shown.) An example of this reaction type is 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 unimolecularly to the ultimate products, $Cl + NO_2$. Reactions of the non-concerted type can have a more complex temperature dependence than those of the concerted type, and, in particular, 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 actions of this type, the distinction between the bimolecular and termolecular classification becomes less meaningful, and it is particularly necessary to study such reactions under the temperature and pressure conditions in which they are to be used in model calculations.

The rate constant tabulation for second-order reactions (Table 1) gives the following information:

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

Third-order reactions (Table 2) are given in the form

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

(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:

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

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 (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 [$k_x^o(T)$]

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

$$k_x^o(T) \equiv \beta_x k_s^{o,sc}(T)$$

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 $k_x^{o,sc}(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value [Troe (1977)].

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 via equation (5).

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 $\langle \Delta E \rangle_N$ 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. This β_{N_2}(200 K) value is combined with the computed value of k_o^{sc}(200 K) to give the expected value of the actual rate constant at 200 K. This latter in combination with the value of 300 K yields the value of n.

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

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

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

Temperature Dependence of High-Pressure Limiting Rate Constants; m

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

Error 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 $\Delta E/R$ are, respectively, the uncertainty in the rate constant at 298K and in the Arrhenius temperature coefficient, as listed in Table 1.

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

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.

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Table 1. Rate Constants for Second Order Reactions.

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
		O_x Reactions			
$O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
$O + O_3 \rightarrow O_2 + O_2$	1.5×10^{-11}	2218±150	8.8×10^{-15}	1.15	1
		$O(^1D)$ Reactions			
*$O(^1D) + N_2O \rightarrow N_2 + O_2$	4.9×10^{-11}	0±100	4.9×10^{-11}	1.4	2,3
$\rightarrow NO + NO$	6.7×10^{-11}	0±100	6.7×10^{-11}	1.4	2,3
$O(^1D) + H_2O \rightarrow OH + OH$	2.2×10^{-10}	0±100	2.2×10^{-10}	1.2	2,4
$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.4×10^{-10}	0±100	1.4×10^{-10}	1.2	2,5
$\rightarrow H_2 + CH_2O$	1.4×10^{-11}	0±100	1.4×10^{-11}	1.2	2,5
*$O(^1D) + H_2 \rightarrow OH + H$	1.0×10^{-10}	0±100	1.0×10^{-10}	1.2	2
$O(^1D) + N_2 \rightarrow O + N_2$	1.8×10^{-11}	-(107±100)	2.6×10^{-11}	1.2	2
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(See Table 2)				
$O(^1D) + O_2 \rightarrow O + O_2$	3.2×10^{-11}	-(67±100)	4.0×10^{-11}	1.2	2
$O(^1D) + O_3 \rightarrow O_2 + O_2$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	2,6
$\rightarrow O_2 + O + O$	1.2×10^{-10}	0±100	1.2×10^{-10}	1.3	2,6
$O(^1D) + HCl \rightarrow OH + Cl$	1.4×10^{-10}	0±100	1.4×10^{-10}	1.3	2,7
#$O(^1D) + CCl_4 \rightarrow$ products	3.3×10^{-10}	0±100	3.3×10^{-10}	1.2	2,8
*$O(^1D) + CFCl_3 \rightarrow$ products	2.3×10^{-10}	0±100	2.3×10^{-10}	1.2	2,8
$O(^1D) + CF_2Cl_2 \rightarrow$ products	1.4×10^{-10}	0±100	1.4×10^{-10}	1.3	2,8

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

Table 1. (Continued).

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
#$O(^1D) + CF_4 \rightarrow CF_4 + O$	1.8×10^{-13}	0 ± 100	1.8×10^{-13}	2.0	2,8
$O(^1D) + CCl_2O \rightarrow$ products	3.6×10^{-10}	0 ± 100	3.6×10^{-10}	2.0	2,9
$O(^1D) + CFClO \rightarrow$ products	1.9×10^{-10}	0 ± 100	1.9×10^{-10}	2.0	2,9
*$O(^1D) + CF_2O \rightarrow$ products	8.0×10^{-11}	0 ± 100	8.0×10^{-11}	2.0	2,9
$O(^1D) + NH_3 \rightarrow OH + NH_2$	2.5×10^{-10}	0 ± 100	2.5×10^{-10}	1.3	2,10
$O(^1D) + CO_2 \rightarrow O + CO_2$	7.4×10^{-11}	$-(117 \pm 100)$	1.1×10^{-10}	1.2	2
$O(^1D) + HF \rightarrow OH + F$	1.0×10^{-10}	0 ± 100	1.0×10^{-10}	5.0	11
		HO_x Reactions			
$H + O_2 \xrightarrow{M} HO_2$	(See Table 2)				
$H + O_3 \rightarrow OH + O_2$	1.4×10^{-10}	470 ± 200	2.9×10^{-11}	1.25	12
*$O + OH \rightarrow O_2 + H$	2.2×10^{-11}	$-(117 \pm 100)$	3.3×10^{-11}	1.2	13
*$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	$-(200 \pm 200)$	5.9×10^{-11}	1.4	14
*$O + H_2O_2 \rightarrow OH + HO_2$	1.0×10^{-11}	2500 ± 1000	2.3×10^{-15}	3.0	15
*$OH + HO_2 \rightarrow H_2O + O_2$	$(7+4P_{atm}) \times 10^{-11}$	0 ± 250	$(7+4P_{atm}) \times 10^{-11}$	1.6	16
$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940 ± 300	6.8×10^{-14}	1.3	17
*$OH + OH \rightarrow H_2O + O$	4.2×10^{-12}	242 ± 242	1.9×10^{-12}	1.4	18
$OH + OH \xrightarrow{M} H_2O_2$	(See Table 2)				
*$OH + H_2O_2 \rightarrow H_2O + HO_2$	3.1×10^{-12}	187 ± 100	1.7×10^{-12}	1.3	19
*$OH + H_2 \rightarrow H_2O + H$	6.1×10^{-12}	2030 ± 400	6.7×10^{-15}	1.2	20

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

Table 1. (Continued).

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
*$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$(3.4+2.5P_{atm})x10^{-14}$	$-(1150 \pm 600)$	$(1.6+1.2P_{atm})x10^{-12}$	1.5	21
*$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.4x10^{-14}$	580^{+500}_{-100}	$2.0x10^{-15}$	1.5	22
		NO_x Reactions			
$N + O_2 \rightarrow NO + O$	$4.4x10^{-12}$	3220 ± 340	$8.9x10^{-17}$	1.25	23
$N + O_3 \rightarrow NO + O_2$	-		$<1.0x10^{-15}$	-	24
$N + NO \rightarrow N_2 + O$	$3.4x10^{-11}$	0 ± 100	$3.4x10^{-11}$	1.3	25
$N + NO_2 \rightarrow N_2O + O$	-	-	$1.4x10^{-12}$	3	26
$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
$O + NO_2 \rightarrow NO + O_2$	$9.3x10^{-12}$	0^{+0}_{-150}	$9.3x10^{-12}$	1.1	27
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	$1.0x10^{-11}$	0 ± 150	$1.0x10^{-11}$	1.5	28
$O + N_2O_5 \rightarrow$ products	-	-	$<3.0x10^{-16}$	-	29
$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0x10^{-17}$	-	30
*$O + HO_2NO_2 \rightarrow$ products	$7.0x10^{-11}$	3370 ± 750	$8.6x10^{-16}$	3.0	31
*$O_3 + NO \rightarrow NO_2 + O_2$	$2.2x10^{-12}$	1430 ± 200	$1.8x10^{-14}$	1.2	32
*$NO + HO_2 \rightarrow NO_2 + OH$	$3.7x10^{-12}$	$-(240 \pm 80)$	$8.3x10^{-12}$	1.2	33
$NO + NO_3 \rightarrow 2NO_2$	-	-	$2.0x10^{-11}$	3.0	34
$OH + NO \xrightarrow{M} HONO$	(See Table 2)				
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				---
*$OH + HNO_3 \rightarrow$ products	$9.4x10^{-15}$	$-(778 \pm 100)$	$1.3x10^{-13}$	1.3	35
*$OH + HO_2NO_2 \rightarrow$ products	$1.3x10^{-12}$	$-(380^{+270}_{-580})$	$4.2x10^{-12}$	1.5	36

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$HO_2 + NO_2 \overset{M}{\rightarrow} HO_2NO_2$	(See Table 2)				---
$O_3 + NO_2 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450±140	3.2×10^{-17}	1.15	37
$O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0 \times 10^{-19}$	-	38
$NO_2 + NO_3 \overset{M}{\rightarrow} N_2O_2$	(See Table 2)				
		ClO_x Reactions			
$Cl + O_3 \rightarrow ClO + O_2$	2.8×10^{-11}	257±100	1.2×10^{-11}	1.15	39
*$Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300±200	1.6×10^{-14}	1.25	40
$Cl + CH_4 \rightarrow HCl + CH_3$	9.6×10^{-12}	1350±150	1.0×10^{-13}	1.1	41
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	7.7×10^{-11}	90±90	5.7×10^{-11}	1.1	42
#$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}	-(40±250)	1.6×10^{-10}	1.5	43
#$Cl + C_2H_2 \rightarrow$ products	-	-	1×10^{-12}	10	44
#$Cl + CH_3OH \rightarrow CH_2OH + HCl$	6.3×10^{-11}	0±250	6.3×10^{-11}	2.0	45
$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.4×10^{-11}	1260±200	4.9×10^{-13}	1.2	46
*$Cl + H_2CO \rightarrow HCl + HCO$	8.2×10^{-11}	34±100	7.3×10^{-11}	1.15	47
$Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	48
#$Cl + HOCl \rightarrow$ products	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	49
$Cl + HNO_3 \rightarrow$ products	$<1.0 \times 10^{-11}$	2170^{+2500}_{-500}	$<7.0 \times 10^{-15}$	-	50
*$Cl + HO_2 \rightarrow HCl + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	51
$\rightarrow OH + ClO$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	52
$Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	53
$Cl + OClO \rightarrow ClO + ClO$	5.9×10^{-11}	0±250	5.9×10^{-11}	1.25	54

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued).

Reaction	A-Factor	$E/R\pm\Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
•$Cl + ClONO_2 \rightarrow$ products	6.0×10^{-12}	$-(150\pm200)$	1.0×10^{-11}	1.5	55
$Cl + NO \xrightarrow{M} NOCl$	(See Table 2)				
$Cl + NO_2 \xrightarrow{M} ClONO\ (ClNO_2)$	(See Table 2)				
•$Cl + ClNO \rightarrow NO + Cl_2$	2.3×10^{-11}	0^{+500}_{-250}	2.3×10^{-11}	3.0	56
$Cl + O_2 \xrightarrow{M} ClOO$	(See Table 2)				
$Cl + ClOO \rightarrow Cl_2 + O_2$	1.4×10^{-10}	0 ± 250	1.4×10^{-10}	3.0	57
$\rightarrow ClO + ClO$	8.0×10^{-12}	0 ± 250	8.0×10^{-12}	3.0	57
$ClO + O \rightarrow Cl + O_2$	7.7×10^{-11}	130 ± 130	5.0×10^{-11}	1.2	58
$ClO + NO \rightarrow NO_2 + Cl$	6.2×10^{-12}	$-(294\pm100)$	1.7×10^{-11}	1.15	59
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(See Table 2)				
•$ClO + HO_2 \rightarrow HOCl + O_2$	4.6×10^{-13}	$-(710^{+250}_{-700})$	5.0×10^{-12}	1.4	60
$ClO + H_2CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>2060	$<1.0\times10^{-15}$	-	61
•$ClO + OH \rightarrow$ products	5.1×10^{-12}	$-(180\pm200)$	9.4×10^{-12}	2	62
$ClO + CH_4 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	63
$ClO + H_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>4800	$<1.0\times10^{-19}$	-	63
$ClO + CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	63
$ClO + N_2O \rightarrow$ products	$\sim1.0\times10^{-12}$	>4260	$<6.0\times10^{-19}$	-	63
$ClO + ClO \rightarrow$ products	-	-	-	-	64
$ClO + O_3 \rightarrow ClOO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	65
$\rightarrow OClO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	65
$OH + HCl \rightarrow H_2O + Cl$	2.8×10^{-12}	425 ± 100	6.6×10^{-13}	1.1	66

•Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	150^{+850}_{-150}	1.8×10^{-12}	10	67
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	1.8×10^{-12}	1112±200	4.3×10^{-14}	1.2	68
$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	4.5×10^{-12}	1032±200	1.4×10^{-13}	1.2	68
$OH + CHCl_3 \rightarrow CCl_3 + H_2O$	3.3×10^{-12}	1034±200	1.0×10^{-13}	1.2	68
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	8.9×10^{-13}	1013±200	3.0×10^{-14}	1.3	68
$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	7.8×10^{-13}	1530±200	4.6×10^{-15}	1.2	68
$OH + CH_2ClF \rightarrow CHClF + H_2O$	2.0×10^{-12}	1134±150	4.4×10^{-14}	1.2	68
$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$	5.4×10^{-12}	1820±200	1.2×10^{-14}	1.3	69
$OH + C_2Cl_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	70
$OH + C_2HCl_3 \rightarrow$ products	5.0×10^{-13}	-(445±200)	2.2×10^{-12}	1.25	71
$OH + CFCl_3 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3650	$<5.0\times10^{-18}$	-	72
$OH + CF_2Cl_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3560	$<6.5\times10^{-18}$	-	72
$OH + ClCNO_2 \rightarrow$ products	1.2×10^{-12}	333±200	3.9×10^{-13}	1.5	73
*$O + HCl \rightarrow OH + Cl$	1.0×10^{-11}	3340±350	1.4×10^{-16}	2.0	74
$O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10	75
$O + ClONO_2 \rightarrow$ products	3.0×10^{-12}	808±200	2.0×10^{-13}	1.5	76
*$O + Cl_2O \rightarrow ClO + ClO$	2.7×10^{-11}	560±200	4.1×10^{-12}	1.5	77
$O + OClO \rightarrow ClO + O_2$	2.5×10^{-11}	1166±300	5.0×10^{-13}	1.5	78
$NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600±300	3.4×10^{-13}	1.5	79
		BrO_x Reactions			
$Br + O_3 \rightarrow BrO + O_2$	1.4×10^{-11}	755±200	1.1×10^{-12}	1.2	80

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued).

Reaction	A-Factor	$E/R \pm \Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
*$Br + H_2O_2 \rightarrow HBr + HO_2$	-1.0×10^{-11}	>2500	$<2.0\times10^{-15}$	-	31
*$Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	82
*$Br + HO_2 \rightarrow HBr + O_2$	-	-	$>1\times10^{-13}$	-	83
$BrO + O \rightarrow Br + O_2$	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	84
$BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	85
$\rightarrow Br + Cl + O_2$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	85
$BrO + NO \rightarrow NO_2 + Br$	8.7×10^{-12}	-(265±130)	2.1×10^{-11}	1.15	86
$BrO + NO_2 \xrightarrow{M} BrONO_2$	(See Table 2)				
*$BrO + BrO \rightarrow 2\ Br + O_2$	1.4×10^{-12}	-(150±150)	2.3×10^{-12}	1.25	87
$\rightarrow Br_2 + O_2$	6.0×10^{-14}	-(600±600)	4.4×10^{-13}	1.25	87
$BrO + O_3 \rightarrow Br + 2\ O_2$	-1×10^{-12}	>1600	$<5.0\times10^{-15}$	-	88
$BrO + HO_2 \rightarrow HOBr + O_2$	-	-	5.0×10^{-12}	5.0	89
$BrO + OH \rightarrow$ products	-	-	9.0×10^{-12}	5.0	90
*$OH + HBr \rightarrow H_2O + Br$	8.0×10^{-12}	0±250	8.0×10^{-12}	1.5	91
$OH + CH_3Br \rightarrow CH_2Br + H_2O$	6.1×10^{-13}	825±200	3.8×10^{-14}	1.25	92
$O + HBr \rightarrow OH + Br$	7.6×10^{-12}	1570±300	3.9×10^{-14}	1.5	93
		FO_x Reactions			
$F + O_3 \rightarrow FO + O_2$	2.8×10^{-11}	226±200	1.3×10^{-11}	2.0	94
*$F + H_2 \rightarrow HF + H$	1.9×10^{-10}	570±250	2.8×10^{-11}	1.3	95
$F + CH_4 \rightarrow HF + CH_3$	3.0×10^{-10}	400±300	8.0×10^{-11}	2.0	96

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$F + H_2O \rightarrow HF + OH$	2.2×10^{-11}	200±200	1.1×10^{-11}	5.0	97
$F + O_2 \xrightarrow{M} FO_2$	(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	98
$FO + FO \rightarrow 2\ F + O_2$	1.5×10^{-11}	0±250	1.5×10^{-11}	3.0	99
$FO + O_3 \rightarrow F + 2\ O_2$	-	-	-	-	100
$\rightarrow FO_2 + O_2$	-	-	-	-	100
$FO + NO_2 \xrightarrow{M} FONO_2$	(See Table 2)				
$O + FO \rightarrow F + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	3.0	101
$O + FO_2 \rightarrow FO + O_2$	5.0×10^{-11}	0±250	5.0×10^{-11}	5.0	102
		Hydrocarbon Reactions			
$OH + CO \rightarrow CO_2 + H$	$1.35\times10^{-13}(1+P_{atm})$	0±200	$1.35\times10^{-13}(1+P_{atm})$	1.25	103
$OH + CH_4 \rightarrow CH_3 + H_2O$	2.4×10^{-12}	1710±200	7.7×10^{-15}	1.2	104
#$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	1.9×10^{-11}	1260±250	2.7×10^{-13}	1.25	105
#$OH + C_3H_8 \rightarrow H_2O + C_3H_7$	1.6×10^{-11}	800±250	1.1×10^{-12}	1.5	106
#$OH + C_2H_4 \rightarrow$ products	2.1×10^{-12}	-(400±150)	8.0×10^{-12}	1.7	107
#$OH + C_2H_2 \rightarrow$ products	6.5×10^{-12}	650±100	7.3×10^{-13}	2	108
$OH + H_2CO \rightarrow H_2O + HCO$	1.0×10^{-11}	0±200	1.0×10^{-11}	1.25	109
*$OH + CH_3OOH \rightarrow$ products	2.6×10^{-12}	190±100	1.4×10^{-12}	5.0	110
#$O + C_2H_2 \rightarrow$ products	2.9×10^{-11}	1600±300	1.4×10^{-13}	1.3	111

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued)

Reaction	A-Factor	$E/R\pm\Delta(E/R)$	k(298K)	Uncertainty Factor/298K	Notes
$O + H_2CO \rightarrow$ products	3.0×10^{-11}	1550 ± 250	1.6×10^{-13}	1.25	112
*$O + CH_3 \rightarrow$ products	1.4×10^{-10}	0 ± 250	1.4×10^{-10}	1.5	113
$CH_3 + O_2 \rightarrow$ products	-	-	$<1\times10^{-16}$	-	114
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(See Table 2)				
#$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	-	-	2×10^{-12}	10	115
*$CH_3O + O_2 \rightarrow CH_2O + HO_2$	1.2×10^{-13}	1350 ± 500	1.3×10^{-15}	10	116
*$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	$-(140\pm140)$	5.5×10^{-12}	1.3	117
#$CH_3 + O_3 \rightarrow$ products	-	-	7.0×10^{-13}	6	118
#$CH_3O_2 + O_3 \rightarrow$ products	-	-	$<1\times10^{-17}$		119
*$CH_3O_2 + CH_3O_2 \rightarrow$ products	1.6×10^{-13}	$-(220\pm220)$	3.4×10^{-13}	1.25	120
*$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	$-(180\pm180)$	7.6×10^{-12}	1.2	121
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(See Table 2)				
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	7.7×10^{-14}	$-(1300^{+500}_{-1300})$	6.0×10^{-12}	3.0	122
		SO_x Reactions			
*$OH + H_2S \rightarrow SH + H_2O$	5.9×10^{-12}	65 ± 65	4.7×10^{-12}	1.2	123
*$OH + OCS \rightarrow$ products	1.3×10^{-12}	2300 ± 500	6.0×10^{-16}	10	124
$OH + CS_2 \rightarrow$ products	-	-	$<1.5\times10^{-15}$	-	125
$OH + SO_2 \xrightarrow{M} HOSO_2$	(See Table 2)				
*$O + H_2S \rightarrow OH + SH$	1.0×10^{-11}	1810 ± 550	2.2×10^{-14}	1.7	126
$O + OCS \rightarrow CO + SO$	2.1×10^{-11}	2200 ± 150	1.3×10^{-14}	1.2	127
$O + CS_2 \rightarrow CS + SO$	3.2×10^{-11}	650 ± 150	3.6×10^{-12}	1.2	128

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

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Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$O + SH \rightarrow H + SO$	-	-	1.6×10^{-10}	5.0	129
#$S + O_2 \rightarrow SO + O$	2.3×10^{-12}	0±200	2.3×10^{-12}	1.2	130
#$S + O_3 \rightarrow SO + O_2$	-	-	1.2×10^{-11}	2.0	131
#$S + OH \rightarrow SO + H$	-	-	6.6×10^{-11}	3.0	132
#$SO + O_2 \rightarrow SO_2 + O$	-	-	9.0×10^{-18}	10	133
#$SO + O_3 \rightarrow SO_2 + O_2$	3.2×10^{-12}	1100±400	7.9×10^{-14}	1.5	134
#$SO + OH \rightarrow SO_2 + H$	-	-	8.6×10^{-11}	2.0	135
#$SO + NO_2 \rightarrow SO_2 + NO$	-	-	1.4×10^{-11}	1.5	136
#$SO + ClO \rightarrow SO_2 + Cl$	-	-	2.3×10^{-11}	3.0	137
#$SO + OClO \rightarrow SO_2 + ClO$	-	-	1.9×10^{-12}	3.0	137
#$SO + BrO \rightarrow SO_2 + Br$	-	-	$>4.0\times10^{-11}$	-	137
#$SO_2 + HO_2 \rightarrow$ products	-	-	$<1.0\times10^{-18}$	-	138
$CH_3O_2 + SO_2 \rightarrow$ products	-	-	$<5.0\times10^{-17}$	-	139
#$SH + O_2 \rightarrow OH + SO$	-	-	$<3.2\times10^{-15}$	-	140

*Indicates a change from the previous Panel evaluation (JPL 81-3).

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

NOTES TO TABLE 1

1. This recommendation is based on the measurements of McCrumb and Kaufman (1972) and Davis et al. (1973).

2. 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) and (1982) for N_2O, H_2O, N_2, H_2, O_3, CO_2, and CF_2O; by Brock and Watson (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_2O. 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.

3. 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). This result, $\Phi(N_2) = 1.42$, agrees well with earlier measurements of the N_2 quantum yield from N_2O photolysis: $\Phi(N_2) = 1.44$ (Calvert and Pitts 1966). $O(^1D)$ translational energy and temperature dependence effects are not clearly resolved.

4. Measurements by Zellner et al. (1980) indicate 1(+0.5 or −1)% of the $O(^1D) + H_2O$ reaction products are $H_2 + O_2$.

5. The branching ratio for 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.

6. 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.

7. The reaction $O(^1D)$ + HCl may give a small amount of H + ClO products (Davidson et al., 1977).

8. The halocarbon rate constants are for 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, 1981); for $CFCl_3$: quenching = (13±4)% and reaction = (87±4)% (Force and Wiesenfeld, 1981), quenching = (25±10)%, ClO formation = (60±15)% (Donovan, 1980); for CF_2Cl_2: quenching = (14±7)% and reaction = (86±14)% (Force and Wiesenfeld, 1981), quenching = (20±10)%, ClO formation = (55±15)%

(Donovan, 1980); for CF_4: quenching = 100% (Force and Wiesenfeld, 1981).

9. 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 data of Wine and Ravishankara (1982). 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).

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

11. No experimental data are known for $O(^1D)$ + HF. k is estimated to be large and not strongly temperature dependent, based on comparison with other $O(^1D)$ reactions. The products OH + F are exothermic but quenching may also occur.

12. The recommendation is an average of the recent results of Lee <u>et al</u>. (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 300-650 K but lies about 60% below the recommended values. Although we have no reason not to believe the Clyne and Monkhouse values, we prefer the two studies that are in excellent agreement, especially since

they were carried out over the T range of interest. Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendations. Reports of a channel forming HO_2 + O (Finlayson-Pitts and Kleindienst, 1979: ~25%, and Force and Wiesenfeld, 1981b: ~40%) have been contradicted by other studies (Howard and Finlayson-Pitts, 1980: < 3%; Washida et al., 1980a: < 6%; and Finlayson-Pitts et al., 1981: < 2%). Secondary chemistry is believed to be responsible for the observed O atoms in this system. Washida et al. (1980c) measured a low limit (< 0.1%) for the production of singlet molecular oxygen in the reaction H + O_3.

13. The rate constant for O + OH is a fit to three temperature dependence studies: Westenberg et al. (1970a), Lewis and Watson (1980), and Howard and Smith (1981). This recommendation is consistent with earlier work near room temperature as reviewed by Lewis and Watson (1980).

14. The recommendation for the O + HO_2 reaction rate constant is the average of two studies at room temperature (Keyser, 1982, and Sridharan and Kaufman, 1982) fitted to the temperature dependence given by Keyser (1982). Earlier studies by Hack et al. (1979) 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.

15. Only one study of the O + H_2O_2 reaction has been published (Davis et al., 1974c). The recommendation is based on their data, but the A factor has been increased (x3.6) because the experimental value is low in comparison to similar atom-molecule reactions. The temperature coefficient has been adjusted to fit their rate constant at 298K.

16. The recommendation for the OH + HO_2 rate constant has been changed. Three new measurements at low pressure (1-3 torr) in discharge-flow systems all give values near 7 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}: Keyser (1981), Sridharan et al. (1981), and Temps and Wagner (1982). The latter two studies supersede earlier work which reported lower values from the same laboratories, Chang and Kaufman (1978) and Hack et al. (1978). Separate studies at pressures near one atmosphere obtain consistently a larger rate constant, about 1.1 x 10^{-10}: Lii et al. (1980a), Hochanadel et al. (1980), DeMore (1982), and Cox et al. (1981). DeMore (1982) reports rate constants that increase from about 7 x 10^{-11} at 75 torr to about 1.2 x 10^{-10} at 730 torr. The present recommendation is for a rate constant that increases linearly with pressure from 7 x 10^{-11} at low pressure to 1.1 x 10^{-10} at one atmosphere. Other studies by Burrows et al. (1981) Kurylo et al. (1981), and Thrush and Wilkinson (1981) agree with these values. Although this recommendation incorporates the most reliable and thorough studies, it has not been reconciled in terms of the current models of reaction rate theory. The observed pressure dependence implies the formation of an H_2O_3 intermediate. Further direct studies of the temperature and pressure dependences and products of this reaction are required.

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

18. The recommendation for the OH + OH reaction is the average of six measurements near 298K: 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 = 250-580K.

19. There are extensive new 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. (1981) and Kurylo et al. (1982). 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.

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

21. The kinetics of the HO_2 + HO_2 reaction are very complex and a comprehensive picture of the reaction mechanism from either an experimental or a theoretical point of view has not developed. The reaction rate constant has been shown to have unusual pressure, temperature and water vapor dependences. There is general

agreement between investigators on the following aspects of the reaction at high pressures (P ~1 atm): (a) the HO_2 uv absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel et al. (1980), and Sander et al. (1982); (b) the rate constant at 300K: Paukert and Johnston (1972), Hamilton (1975), Hamilton and Lii (1977), Cox and Burrows (1979), Lii et al. (1979), Tsuchiya and Nakamura (1979), Sander et al. (1982), and Simonaitis and Heicklen (1982) (all values fall in the range (2.5 to 4.7) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}); (c) the rate constant temperature dependence: Cox and Burrows (1979), and Lii et al. (1979); (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); and (e) the formation of $H_2O_2 + O_2$ as the major products at 300K: Su et al. (1979), Niki et al. (1980), Sander et al. (1982), and Simonaitis and Hiecklen (1982); and (f) the H/D isotope effect: Hamilton and Lii (1977) and Sander et al. (1982). At low pressures there are fewer results and less agreement between investigators. Thrush and Wilkinson (1979) report low rate constants at pressures between 2 and 4 torr that extrapolate to k ~ 0 at P = 0. Cox and Burrows (1979), and Lii et al. (1980b) observe no pressure dependence of the reaction between 25 and 760 torr and 400 and 1500 torr, respectively, while Sander et al. (1982) and Simonaitis and Heicklen (1982) see pressure dependence over a broader range and suggest k ~ 1.6 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, when extrapolated to P = 0. The present recommendation is derived from the 298K data for the pressure dependence in N_2 given by Sander et al. (1982) and Simonaitis and Heicklen (1982) and the temperature dependence given by Cox and Burrows (1979) and Lii et al. (1979). For systems containing water vapor, the factors given by Lii et al. (1981) and Sander et al. (1982) can be incorporated. Our recommendation must be used with caution because of major uncertainties in the behavior at low pressure and at low temperature and the products at low temperature.

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

23. Activation energy based on Becker et al. (1969). Value and uncertainty at 298K assigned from 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.

24. Recommendation 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).

25. Recommendation is based on the results of Lee et al. (1978c). A recent study by Husain and Slater (1980) reports a room temperature rate constant 30 percent higher than the recommended value.

26. Accepts the 298K results of Clyne and McDermid (1975) for both the value of the rate constant and the identity of the products. A recent study (Husain and Slater, 1980) reports a room temperature rate constant value of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the overall reaction of N with NO_2. This high value may indicate the presence of catalytic cycles as discussed in Clyne and McDermid (1975). Clearly, temperature dependent studies are needed.

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

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

29. Based on Kaiser and Japar (1978).

30. Accepts the upper limit reported by Chapman and Wayne (1974).

31. Changed from JPL 81-3. Recommended value is based on the study of Chang et al. (1981). The previous recommendation was based upon the unpublished results of the same group. The large uncertainties in E/R and k at 298K are due to the fact that this is a single study.

32. Changed from JPL 81-3. 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 (1981), and Michael et al. (1981) at and below room temperature, with the data at closely spaced temperatures reported in Lippmann et al. being grouped together so that these four studies are weighted equally. This expression fits all the data within the temperature range 195-304K reported in these four studies to within 20 percent. Only the data between 195 and 304K 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., and Michael et al.). Clough and Thrush, Birks et al., Schurath et al. (1981), and Michael et al. have all reported individual Arrhenius parameters for each of the two primary reaction channels. The range of values for k at stratospheric temperatures is somewhat larger than would be expected for such an easy reaction to study. The measurements of Stedman and Niki (1973) and Bemand et al (1974)

of k at 298K are in excellent agreement with the recommended value of k at 298K.

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

34. Value reported by Graham and Johnston (1978).

35. Changed from JPL 81-3. Even though there have been several recent studies of this reaction, all of the reported data are not consistent. However, the data which are relevant for stratospheric conditions of temperature and pressure are in reasonable agreement. The recommended Arrhenius expression is based on a least squares fit to the data reported by Wine et al. (1981b), Kurylo et al. (1982), Margitan and Watson (1982), Marinelli and Johnston (1982), Ravishankara et al. (1982), and Jourdain et al. (1982) at and below room temperature, i.e. ~300K, but did not utilize the data of Smith and Zellner (1975), Margitan et al. (1975), Nelson et al. (1981) and Connell and Howard (1982). While the data of Margitan and Watson appear to be in good agreement with data reported in the other recent flash photolysis studies (Wine et al., Kurylo et al., Ravishankara et al. and Marinelli and Johnston) it exhibits one rather significant difference, i.e., a small but measurable pressure dependence which is greatest at low temperatures (a factor of 1.1 increase in k from 20-100 torr He at 298 K, and a factor of 1.4

increase in k from 20-100 torr He at ~235K). Consequently it is difficult to reconcile the data of Margitan and Watson with that of the other flash photolysis studies where no pressure dependence was observed. Although the low pressure discharge flow results of Jourdain et al. are in excellent agreement with the results from the higher pressure studies (at least below 300K), this agreement does not preclude a pressure dependence as the magnitude of the effect at temperatures ≥ 250 K is small in the range 1-40 torr (1 torr is a typical discharge flow tube pressure, and 40 torr is the typical flash photolysis pressure). The data of Margitan and Watson at 40 torr (He and Ar) at each temperature were used in deriving the recommended Arrhenius expression (data relevant to the mid-stratosphere and typical of the pressure conditions used in other flash photolysis studies). Under these conditions the data are in excellent agreement with the data from the other preferred studies. It should be noted that the 40 torr data is the average of all the data; consequently, the preferred value is not dependent upon which subset of Margitan and Watson data is used. The recent work of Nelson et al. should be disregarded as it has been superseded by the more careful and comprehensive Marinelli and Johnston study. However, it is not presently possible to explain the difference between the data from the preferred studies and that from the discharge flow study of Connell and Howard, who determined a value for k at 301K of 8.4×10^{-14} cm^3 molecule s^{-1} (consistent with the earlier values of Smith and Zellner, and Margitan et al.), in contrast to the recommended value of 12.5×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. In addition Connell and Howard reported a value for E/R of -430K, in contrast to the recommended value of -778K and the earlier values of zero.

The recommended Arrhenius expression was derived using only data from ~220-300K due to the non-linear Arrhenius behavior noted above 300K in all the recent studies except Jourdain et al., who reported linear Arrhenius behavior from 251-403K. Marinelli and Johnston fit all their data (218-363K) to an Arrhenius expression, but curvature is noticeable and hence their value of -644K for E/R would be greater over the temperature range 218-298K. This non-linear Arrhenius behavior can easily be rationalized in terms of an addition channel (dominating at low temperatures), and an H atom abstraction channel (dominating at high temperatures). Nelson et al., Jourdain et al., and Ravishankara et al. (1982) have all shown that within experimental evidence the yield of NO_3 per HO removed is unity at 298 K. In addition Ravishankara et al. obtained similar product distribution results at 250 K. There is no evidence for the production of H_2O_2.

36. Changed from JPL 81-3. Recommendation based upon the data of Trevor et al. (1981), Barnes et al. (1981) and Molina et al. (1982). Trevor et al., studied this reaction over the temperature range 246-324 K and reported a temperature invariant value of 4.2 x 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 Molina et al., studied the reaction over the temperature range 242-295 K and observed a negative temperature dependence with an E/R value of -(650±50)K. An unweighted least squares fit to all the experimental data of Trevor et al., Barnes et al., and Molina et al. yields the recommended value. The large difference in E/R values may be due to the reaction being complex and having different E/R vaues at low pressure, i.e., <1 torr (Trevor et al.) and high pressures (750 torr (Molina et al.)). The less precise value reported by Littlejohn and Johnston (1980) is in fair agreement with the recommended value. The error limits on the recommended E/R are sufficient to encompass the results of both Trevor et al. and Molina et al.

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

38. Based on Kaiser and Japar (1977) and Streit et al. (1979).

39. Unchanged from JPL 81-3. The results reported for k(298K) 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 205-300K. 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 studies agree so well at 298K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal mole^{-1}). However, there is no reason to prefer any one set of data to any other; therefore, the preferred Arrhenius expression shown above was obtained by computing the mean of the four results between 205 and 298K. Inclusion of higher temperature (≤466K) experimental data would yield the following Arrhenius expression: $k = (3.4 \pm 1.0) \times 10^{-11} \exp(-310 \pm 76)/T)$.

Vanderzanden and Birks (1982) have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1-0.5%) of O_2 ($^1\Sigma_g^+$) in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore (1981), in connection with the Cl_2 photosensitized decomposition of ozone.

40. Minor change from JPL 81-3. This Arrhenius expression is based on the data below 300K reported by Watson *et al.* (1975), Lee *et al.* (1977) and Miller and Gordon (1981). The results of these three

studies are in excellent agreement below 300K; the data at higher temperatures are in somewhat poorer agreement. The results of Watson et al. and those of Miller and Gordon agree well (after extrapolation) with the results of Benson et al. (1969) and Steiner and Rideal (1939) at higher temperatures. For a discussion of the large body of rate data at high temperatures see the review by Baulch et al. (1980). Miller and Gordon also measured the rate of the reverse reaction, and the ratio was found to be in good agreement with equilibrium constant data.

4'. Unchanged from JPL 81-3. The values reported from the thirteen absolute rate coefficient studies for k at 298K 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 1.04 x 10^{-13} can be determined from the absolute rate coefficient studies for k at 298K by giving equal weighting to the values reported in Lin et al. (1978a), Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), Zahniser et al. (1978), Michael and Lee (1977), Keyser (1978), and Ravishankara and Wine (1980). The values derived for k at 298K from the competitive chlorination studies of Pritchard et al. (1954), Knox (1955), Pritchard et al. (1955), Knox and Nelson (1959), and Lin et al. (1978a) range from (0.95 - 1.13) x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value of 1.04 x 10^{-13} was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

There have been nine absolute studies of the temperature dependence of k. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported studies it is best to discuss them in terms of two distinct temperature regions, (a) below 300 K, and (b) above 300 K. Three resonance fluorescence studies have been performed over the temperature range ~200-500 K (Whytock et al. (1977), Zahniser et al. (1978) and Keyser (1978)) and in each case a strong nonlinear Arrhenius behavior was observed. Ravishankara and Wine (1980) also noted nonlinear Arrhenius behavior over a more limited temperature range. This behavior tends to explain partially the large variance in the values of E/R reported between those other investigators who predominantly studied this reaction below 300 K (Watson et al. (1976) and Manning and Kurylo (1977)) and those who only studied it above 300 K (Clyne and Walker (1973), Poulet et al. (1974), and Lin et al. (1978a)). The agreement between all studies below 300 K is good, with values of (a) E/R ranging from 1229-1320 K, and (b) k(230 K) ranging from (2.64-3.32) x 10^{-14}. The mean of the two discharge flow values (Zahniser et al. (1978) and Keyser (1978)) is 2.67 x 10^{-14}, while the mean of the four flash photolysis values (Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), and Ravishankara and Wine (1980) is 3.22 x 10^{-14} at 230 K. There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. Ravishankara and Wine (1980) have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures (<240 K) due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ states of atomic chlorine. Ravishankara and Wine observed that at temperatures below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture; i.e., if the mixture did not contain an efficient spin equilibrator, e.g. Ar or CCl_4, the bimolecular rate constant decreased at high CH_4 concentrations. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the hypothesis of Ravishankara and Wine is proven it is assumed that the discharge flow and competitive chlorination results are reliable. Above 300 K the three resonance fluorescence studies reported (a) "averaged" values of E/R ranging from 1530-1623 K, and (b) values for k (500 K) ranging from (7.74-8.76) x 10^{-13}. These mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409-1790 K. The data of Poulet et al. (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k(298 K) is ~20% higher than the preferred value at 298 K, while that of Lin et al. (1978a) is in fair agreement with the resonance fluorescence results. In conclusion, it should be stated that the best values of k from the absolute studies, both above and below 300 K, are obtained from the resonance fluorescence studies. The competitive chlorination results differ from those obtained from the absolute studies in that linear Arrhenius behavior is observed. This difference is the major discrepancy between the two types of experiments. The values of E/R range from 1503 to 1530 K, and k (230 K) from (2.11-2.54) x 10^{-14} with a mean value of 2.27 x 10^{-14}. It can be seen from the above discussion that the average values at 230 K are: 3.19 x 10^{-14} (flash photolysis), 2.67 x 10^{-14} (discharge flow) and 2.27 x 10^{-14} (competitive chlorination). These differences increase at lower temperatures. Until the hypothesis of Ravishankara and Wine (1980) is re-examined, the preferred Arrhenius expression attempts to best fit the results obtained between 200 and 300 K from all sources. The average value of k at 298 K is 1.04 x 10^{-13}, and at 230 K is 2.71 x 10^{-14} (this is a simple mean of the three average values). The preferred Arrhenius expression is 9.6 x 10^{-12} exp(-1350/T). This expression yields values similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used then an alternate expression of 6.4 x 10^{-12} (exp (-1220/T) can be obtained (k(298 K) = 1.07 x 10^{-13}, and k(230 K) = 3.19 x 10^{-14}).

A recent study (Heneghan et al. (1981)) using very low pressure reactor techniques reports results from 233 to 338K 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 298K of 35.1±0.1 kcal/mol.

42. Unchanged from JPL 81-3. The absolute rate coefficients reported in all four studies (Davis et al. (1970), Manning and Kurylo (1977), Lewis et al. (1980), and Ray et al. (1980) are in good agreement at 298 K. The value reported by Davis et al. was probably overestimated by ~10% (the authors assumed that I_f was proportional to $[Cl]^{0.9}$, whereas a linear relationship between I_f and [Cl] probably held under their experimental conditions). The preferred value at 298 K was taken to be a simple mean of the four values (the value reported by Davis et al. was reduced by 10%), i.e., 5.7×10^{-11}. The two values reported for E/R are in good agreement; E/R = 61 K (Manning and Kurylo) and E/R = 130 K (Lewis et al.). A simple least squares fit to all the data would unfairly weight the data of Lewis et al. due to the larger temperature range covered. Therefore, the preferred value of $7.7 \times 10^{-11} \exp(-90/T)$ is an expression which best fits the data of Lewis et al. and Manning and Kurylo between 220 and 350 K.

43. New entry. This recommendation is based on results over the temperature range 220-607K 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).

44. New entry. Since abstraction would be endothermic by 9 kcal/mol, the initial step must be addition to give an excited C_2H_2Cl radical which either will be stabilized or will decompose to give the original

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

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

46. Unchanged from JPL 81-3. The results reported by both groups (Clyne and Walker (1973), and Manning and Kurylo (1977)) are in good agreement at 298 K. However, the value of the activation energy measured by Manning and Kurylo is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the Cl + CH_4 and, similarly, the activation energy measured by Manning and Kurylo was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique was in this case subject to a systematic error, and it is recommended that the flash photolysis results be used for stratospheric calculations in the 200-300 K temperature range (see

discussion of the Cl + CH_4 studies). In the discussion of the Cl + CH_4 reaction it was suggested that some of the apparent discrepancy between the results of Clyne and Walker and the flash photolysis studies can be explained by nonlinear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A-factor (as measured in the flash photolysis studies) is already $\sim 3.5 \times 10^{-11}$ 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 ($> 2 \times 10^{-10}$).

47. Changed from JPL 81-3. 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 ~298K, but ~50% greater than the value reported by Foon et al. (1979). The preferred value at 298K (7.3×10^{-11}) was obtained by combining the absolute values reported by Michael et al., Anderson and Kurylo, and Fasano and Nogar, with the values obtained by combining the ratio of k(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 5.7×10^{-11} for k(Cl + C_2H_6) at 298K. 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 298K.

48. Unchanged from JPL 81-3. 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 $(3.6-6.2) \times 10^{-13}$. The studies of Michael et al., Keyser, and Poulet et al. are presently considered to be the most reliable. The preferred value for the Arrhenius expression is taken to be that reported by Keyser. The A-factor reported by Michael et al. is considerably lower than that expected from theoretical considerations and may possibly be attributed to

decomposition of H_2O_2 at temperatures above 300 K. The data of Michael et al. at and below 300 K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well established.

49. New entry. This recommendation is based on results over the temperature range 243-365K using the discharge flow-mass spectrometric technique in the only reported study of this reaction, Cook et al. (1981a). In a subsequent paper, Cook et al. (1981b) argue that Cl_2 + OH are the major products of this reaction, even though the reaction channel giving HCl + ClO is more exothermic.

50. Unchanged from JPL 81-3. Neither study (Leu and DeMore (1976), and Poulet et al. (1978a)) can be considered to be definitive. Poulet et al. postulated that Leu and DeMore were observing removal of HNO_3 via a heterogeneous process. While this hypothesis is possibly correct, the value of E/R reported by Poulet et al. is much higher than would be expected (resulting in a surprisingly low value for k at 298 K). Although this reaction is not important in atmospheric chemistry, additional studies are required to provide accurate Arrhenius parameters. Until further data becomes available, the preferred value is based on assuming that the data of Leu and DeMore represents an upper limit.

51. Changed from JPL 81-3. The recommendations for the two reaction channels are based upon the recent results by Lee and Howard (1981) 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 $(4.2 \pm 0.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 250-420K. This value for the total rate constant is in agreement with the value recommended in JPL 81-3, which was based on indirect studies relative to Cl + H_2O_2 (Leu and DeMore (1976), Poulet et al.

(1978a), Burrows et al. (1979) or to Cl + H_2 (Cox (1980)). The contribution of the reaction channel producing OH + ClO (21% at room temperature) is much higher than the upper limit reported by Burrows et al. (1% of total reaction). The value of the rate constant for this channel, when combined with the rate constant for the reaction ClO + OH (assuming the products are Cl + HO_2), yields an equilibrium constant of 1.0. This gives a value for the heat of formation of HO_2 at 298K of 3.3 kcal/mol, in reasonably good agreement with the Howard (1980) value of 2.5±0.6 kcal/mole. Weissman et al. (1981) propose that the reaction proceeds by radical combination to give an excited HOOCl intermediate whose stabilization may become important at stratospheric temperatures.

52. See note 51.

53. Unchanged from JPL 81-3. The preferred value of 9.8 x 10^{-11} $cm^3 molecule^{-1} s^{-1}$ was determined from two independent absolute rate coefficient studies reported by Ray et al. (1980), using the discharge flow-resonance fluorescence and discharge flow-mass spectrometric techniques. This value has been confirmed by Burrows and Cox (1981) who determined the ratio k(Cl + Cl_2O)/k(Cl + H_2) = 6900 in modulated photolysis experiments. The earlier value reported by Basco and Dogra (1971) 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.

54. Unchanged from JPL 81-3. Data reported by Bemand, Clyne and Watson (1973).

55. Changed from JPL 81-3. Recent flash photolysis/resonance fluorescence studies by Margitan (1982) 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 $Cl + ClNO_3$.

56. Changed from JPL 81-3. This value is based on the discharge flow-resonance fluorescence study of Clyne and Cruse (1972) and the flash photolysis-resonance fluorescence study of Nelson and Johnston (1981). Grimley and Houston (1980) reported a value which is lower than this preferred value by a factor of four. This low value may be due to adsorption of ClNO on the vessel walls in their static experiment. There are no reliable data on the temperature dependence.

57. Unchanged from JPL 81-3. 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 <u>et</u> <u>al</u>. (1969), Cox <u>et</u> <u>al</u>. (1979), and Ashford <u>et</u> <u>al</u>. (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 <u>et</u> <u>al</u>., Cox <u>et</u> <u>al</u>., Ashford <u>et</u> <u>al</u>., and Nicholas and Norrish (1968). Obviously the value of 108 by Johnston <u>et</u> <u>al</u>. 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 <u>et</u> <u>al</u>. and Ashford <u>et</u> <u>al</u>. 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.

58. Unchanged from JPL 81-3. The recommended rate constant is based on the experimental data of Bemand <u>et</u> <u>al</u>. (1973), Clyne and Nip (1976b),

and Zahniser and Kaufman (1977). The E/R values reported by Clyne and Nip and Zahniser and Kaufman are in poor agreement. Before this rate constant can be considered to be well established, additional data are required.

59. Minor change from JPL 81-3. The absolute rate coefficients determined in the four discharge flow mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978), Ray and Watson (1981) and Clyne and MacRobert (1980)) and the discharge flow laser magnetic resonance study Lee et al. (1982) are in excellent agreement at 298K, 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.

60. Unchanged from JPL 81-3. There have been four low pressure discharge flow studies, each using a different experimental detection technique, and one high pressure molecular modulation study (Burrows and Cox, 1981) at 298 K. The values reported at 298 K, in units of 10^{-12} cm^3 $molecule^{-1}s^{-1}$, are 0.85±0.19 (Poulet et al., 1978), 3.3±0.5 (Reimann and Kaufman, 1978), 4.5±0.9 (Leck et al., 1980), 6.3±1.3 (Stimpfle et al., 1979), and 5.4^{+4}_{-2} (Burrows and Cox, 1981). The value of Poulet et al. was disregarded and the preferred value taken to be the mean of the other four values, i.e. k = $5.0 \times 10^{-12} cm^3$ $molecule^{-1}s^{-1}$. The agreement between the low pressure values and the one atmosphere value suggests the absence of a third order complex forming process. The only temperature dependence study

(Stimpfle 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), i.e., $4.6 \times 10^{-13} \exp(710/T)$. The latter expression is preferred. The two most probable pairs of reaction products are, (1) $HOCl + O_2$ and (2) $HCl + O_3$. Both Leu (1980b) and Leck et al. used mass spectrometric detection of ozone to place upper limits of 1.5% (298 K), 3.0% (248 K) and 2.0% (298 K), respectively, on k_2/k. Burrows and Cox report an upper limit of 0.3% for k_2/k at 300 K.

61. Unchanged from JPL 81-3. Poulet et al. (1980) have determined an upper limit of $10^{-15} cm^3 molecule^{-1} s^{-1}$ for k at 298 K using the discharge flow-EPR technique.

62. Changed from JPL 81-3. This recommendation is based on the recent discharge flow-resonance fluorescence, temperature dependent, study of Ravishankara and Eisele (1982), and a similar study at room temperature by Leu and Lin (1979). The preferred value at 298 K is the mean of the values reported in these two studies. The A-factor was adjusted to give the preferred value at 298 K. Leu and Lin determined a lower limit of 0.65 for $k_1(OH + ClO \rightarrow HO_2 + Cl)/k\ (OH + ClO \rightarrow \text{products})$ at 298K. The approach was somewhat indirect and the actual value of k_1/k may be unity. If in fact it is unity, then the value of this rate constant and that for the reverse reaction ($Cl + HO_2 \rightarrow OH + ClO$) are consistent with the Howard (1980) value of 2.5±0.6 kcal/mol for the heat of formation of HO_2. See note on $Cl + HO_2$ reaction. Additional studies of the rate and mechanism as a function of

pressure and temperature are needed.

63. Unchanged from JPL 81-3. 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 K or 670 K. The Arrhenius expressions were estimated based on this ~600 K data.

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

65. Unchanged from JPL 81-3. The branching ratio between the two channels is not known, but, for the present discussion, is assumed to be unity. The Arrhenius parameters were estimated, and the upper limit rate constants are based on data reported by DeMore, Lin and Jaffe (1976) and by Wongdontri-Stuper <u>et al</u>. (1979).

66. Unchanged from JPL 81-3. There is good agreement between six groups of workers at ~298K (Takacs and Glass (1973c), Zahniser <u>et al</u>. (1974), Smith and Zellner (1974), Ravishankara <u>et al</u>. (1977a), Hack <u>et al</u>. (1977) and Husain <u>et al</u>. (1981)) and the preferred value at this temperature is the average of the six. The Arrhenius expression was derived by giving an equal weighting to data reported by Zahniser <u>et al</u>., Ravishankara <u>et al</u>., and Smith and Zellner.

67. Unchanged from JPL 81-3. There are no experimental data for this reaction. This is an estimated value based on the OH + H_2O_2 reaction, which should have roughly similar E/R and A values.

68. There have been several studies of each of the OH + $CH_xF_yX_{(4-x-y)}$ (X = Cl or Br) reactions, i.e. OH + CH_3Cl, CH_2Cl_2, $CHCl_3$, $CHFCl_2$, CHF_2Cl, CH_2ClF, and CH_3Br. In each case there has been quite good agreement between the reported results (except for Clyne and Holt,

(1979b)), both at ~298 K and as a function of temperature. However, in certain cases it can be noted that the E/R values obtained from studies performed predominantly above 298 K were greater than the E/R values obtained from studies performed over a lower temperature range, e.g. the E/R value for OH + CH_3Cl reported by Perry *et al.* (1976a) is significantly higher than that reported by Davis *et al.* (1976). These small but significant differences could be attributed to either experimental error or non-linear Arrhenius behavior. The recent results of Jeong and Kaufman (1982) have shown a non-linear Arrhenius behavior for each reaction studied. They found that their data could best be represented by a three parameter equation of the form $AT^2\exp(-B/T)$. The experimental $AT^2\exp(-B/T)$ fit is stated by the authors to be in agreement with that expected from transition state theory.

The preferred values shown in this review were obtained by first fitting all of the absolute rate data for each reaction (except Clyne and Holt (1976b)) to the three parameter equation $AT^2\exp(-B/T)$, and then simplifying these equations to a set of "derived Arrhenius expressions" centered at 265 K. The derived Arrhenius expressions were centered at 265 K as a temperature representative of the mid-troposphere. The $AT^2\exp(-B/T)$ expressions are given for each reaction in the individual notes, while the "derived Arrhenius expressions" are entered in the table of preferred values. Obviously "derived" Arrhenius expressions can be centered at any temperature from the three parameter equations (these should be restricted to within the temperature range studied). Transforming $k = AT^2\exp(-B/T)$ to the form $k = A'\exp(-E/T)$: $E' = B + 2T$ and $A' = A \times e^2 \times T^2$.

OH + CH_3Cl

Unchanged from JPL 81-3. 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. (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 $3.49 \times 10^{-18}\ T^2\exp(-582/T)$ over the temperature range (247-483)K. This results in a preferred value of $4.40 \times 10^{-14}\mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.81 \times 10^{-12}\exp(-1112/T)$.

$OH + CH_2Cl_2$

Unchanged from JPL 81-3. 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 $1.41 \times 10^{-13}\mathrm{cm}^3\ \mathrm{molecule}^{-1}\mathrm{s}^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $4.45 \times 10^{-12}\exp(-1032/T)$.

$OH + CHCl_3$

Unchanged from JPL 81-3. 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 x

$10^{-18}\exp(-504/T)$ over the temperature range 245-487 K. This results in a preferred value of $1.03 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $3.27 \times 10^{-12} \exp(-1034/T)$.

OH + $CHFCl_2$

Unchanged from JPL 81-3. 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), 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 $3.0 \times 10^{-14} cm^3 molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $0.89 \times 10^{-12}\exp(-1013/T)$.

OH + CHF_2Cl

Unchanged from JPL 81-3. 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), 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 ~1 x $10^{-11} cm^3 molecule^{-1} s^{-1}$ 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 $4.68 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$

for k at 298 K. The derived Arrhenius expression centered at 265 K is 0.78 x 10^{-12}exp(-1530/T).

OH + CH_2FCl

Unchanged from JPL 81-3. 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), and Jeong and Kaufman (1982) which are in fair agreement. Fitting the data to an expression of the form AT^2exp(-B/T) results in the equation 3.77 x 10^{-18} T^2exp(-604/T) over the temperature range 245-486 K. This results in a preferred value of 4.41 x 10^{-14} cm^3 $molecule^{-1}s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is 1.96 x 10^{-12}exp(-1134/T).

69. Unchanged from JPL 81-3. This evaluation is based on the recent data of Jeong and Kaufman (1979) and Kurylo *et al* (1979). Their results are in excellent agreement over the temperature range 250-460 K. The earlier results of Howard and Evenson (1976b), Watson *et al*. (1977), Chang and Kaufman (1977a) and Clyne and Holt (1979a) were discounted in favor of the recent results. The earlier results showed higher values of the rate constant, and lower E/R values. This may be indicative of the CH_3CCl_3 used in the early studies being contaminated with small amounts of a reactive olefinic impurity.

70. Unchanged from JPL 81-3. 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.

71. Unchanged from JPL 81-3. The preferred value at 298K is a mean of the values reported by Howard (1976) and Chang and Kaufman (1977a).

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

72. Unchanged from JPL 81-3. 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.

73. Unchanged from JPL 81-3. The results reported by Zahniser et al. (1977) and Ravishankara et al. (1977b) are in good agreement at ~245K (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.

74. Minor change from JPL 81-3. 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 300K (some of the values for k (300K) 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 2260-3755K. 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 these reported by Balakhnin et al.

75. Unchanged from JPL 81-3. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

76. Unchanged from JPL 81-3. The results reported by Molina <u>et al</u>. (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 <u>et al</u>. (1977b) at 245K is a factor of 2 greater than those from the other studies, and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in the $ClONO_2$, or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products. The recent room temperature result of Adler-Golden and Wiesenfeld (1981) is in good agreement with the recommended value.

77. This recommendation is based on results obtained by Miziolek and Molina (1978) over the temperature range 236-295K in a discharge flow system under pseudo first order conditions for O atom decay. The values reported by Basco and Dogra (1971a) and Freeman and Phillips (1968) have not been included in the derivation of the preferred value due to data analysis difficulties in each of these studies.

78. Unchanged from JPL 81-3. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

79. Unchanged from JPL 81-3. Arrhenius expression was estimated based on 298K data reported by Bemand, Clyne and Watson (1973).

80. Unchanged from JPL 81-3. The results reported for k (298K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael <u>et al</u> (1978) and Michael and Payne (1979) are in excellent agreement. The preferred value at 298K is derived by taking a simple mean of these four values. The temperature dependences reported for k by

Leu and DeMore, Michael _et al_. and Michael and Payne can only be considered to be in fair agreement. There is a spread of 25% in k at 220K and 50% at 360K. Although the results reported by Michael _et al_. and Michael and Payne are in good agreement, there is no reason at present to discard the results of Leu and DeMore. Therefore, until further results are reported, the preferred value was synthesized to best fit all the data reported from these four studies.

81. Minor change from JPL 81-3. Using the discharge flow-mass spectrometric technique Leu (1980a), and Posey _et al_. (1981) determined an upper limit for k of ~2 x 10^{-15} at ~298 K. Leu also reported an upper limit for k of 3 x 10^{-15} at 417 K. An estimate of the Arrhenius expression would be <1 x 10^{-11}exp(-2500/T). The A-factor was chosen to be consistent with that determined for the Cl + H_2O_2 reaction, and the E/R value was calculated to yield the upper limit at 298 K.

82. Changed from JPL 81-3. 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_.).

83. Posey _et al_. (1981) used the discharge flow-mass spectrometric technique to determine a value of 2 x 10^{-13} (±factor of 2) for k at 298K. This value seems low for an atom-radical reaction; for example, it is two orders of magnitude lower than the corresponding reaction of HO_2 with Cl. Therefore, until there is additional data, it is suggested that this be used as a lower limit.

84. Unchanged from JPL 81-3. The preferred value is based on the value reported by Clyne _et al_. (1976). This value appears to be quite reasonable in light of the known reactivity of ClO radicals with atomic oxygen. The temperature dependence of k is expected to be small for an atom-radical process, e.g., O + ClO.

85. Unchanged from JPL 81-3. The results reported by Clyne and Watson (1977) and Basco and Dogra (1971b) differ not only in the magnitude of the rate constants, but also in the interpretation of the reaction mechanism. The preferred value is that reported by Clyne and Watson. The temperature dependence for such processes is expected to be small, as for BrO + BrO. Although the second reaction channel is shown proceeding directly to Br + Cl + O_2, it may proceed through Br + ClOO (ΔH^o = -6.6 kcal/mol^{-1}) or Cl + BrOO (ΔH^o unknown).

86. Unchanged from JPL 81-3. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1981) and Leu (1979) and the high pressure uv absorption study (Watson _et al_. (1979)), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure uv absorption study (Clyne and Cruse (1970b)). The results of the two temperature dependence studies are in good agreement and both show a small negative temperature dependence. The preferred Arrhenius expression was derived from a least squares fit to all the data reported in the four recent studies. By combining the data reported by Watson _et al_. with that from the three mass spectrometric studies, it can be shown that this reaction does not exhibit any observable pressure dependence between 1 and 700 torr total pressure. The temperature dependences of k for the analogous ClO and HO_2 reactions are also negative, and are similar in magnitude.

87. Changed from JPL 81-3. 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, 1970), discharge flow-mass spectrometry (Clyne and Watson, 1975) and flash photolysis-ultraviolet absorption (Basco and Dogra, 1971; Sander and Watson, 1981b). Since this reaction is second order in [BrO], those studies monitoring [BrO] by ultraviolet absorption required the value of the cross section σ to determine k. There is substantial disagreement in the reported values of σ. Although the magnitude of σ is dependent upon the particular spectral transition selected and instrumental parameters such as spectral bandwidth, the most likely explanation for the large differences in the reported values of σ is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies were used incorrectly (see discussion by Clyne and Watson). The recent study of Sander and Watson used totally independent methods to determine the values of σ and (σ/k). The recommendations for k_1 and k_2 are consistent with a recommendation of $k = 1.14 \times 10^{-12}$ exp(+255/T) cm^3 $molecule^{-1}$ s^{-1}. This temperature dependence is the corrected value from Sander and Watson, and the pre-exponential has been chosen to fit the value of $k(298K) = 2.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, which is the average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required) and by Sander and Watson (the recent absorption study). There was no observable pressure dependence from 50 to 475 torr in the latter study. In a recent study, Cox et al. (1982) used the molecular modulation technique with ultraviolet absorption to derive a temperature independent value of k_2 which is 50 percent greater than the 298K 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 298K, by Jaffe and Mainquist (1980) from 258 to 333K, and by Cox et al. (1982) from 278 to 348K. All are in agreement that k_1/k = 0.84±0.03 at 298K. 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 298K on [Br_2], and their results were obtained at much higher [Br_2] values than were those of Cox et al. This makes a comparison of results difficult. From an analysis of both sets of temperature dependent data, the following expressions for k_1/k were derived: 0.98 exp(-44/T) (Jaffe and Mainquist); 1.42 exp(-163/T) (Cox et al); and 1.18 exp(-104/T) (mean value). This mean value has been combined with the expression for k given above to yield the expression for k_1 shown in the table. The expression for k_2 results from the numerical values of k_2 at 200K and 300K derived from the evaluation of these expressions for k_1 and for $k(=k_1 + k_2)$.

88. Unchanged from JPL 81-3. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) also reported an upper limit of $8 \times 10^{-14} cm^3 molecule^{-1} s^{-1}$ for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $<10^{-18} cm^3 molecule^{-1} s^{-1}$.

89. Unchanged from JPL 81-3. Value chosen to be comparable with the value of k(ClO + HO_2) at 298 K, as there are no experimental data. The uncertainty factor in k at 298 K precludes the need to estimate the temperature dependence in k, as it would have a smaller magnitude than the uncertainty over the temperature range of the stratosphere.

90. Unchanged from JPL 81-3. Value chosen to be consistent with k(ClO + OH), due to the absence of any experimental data.

91. Changed from JPL 81-3. Takacs and Glass (1973a) and Jourdain et al. (1981) used the discharge flow - EPR technique and reported k (298K) to be 5.1 and 9.2 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. Ravishankara et al. (1979a) and Husain et al. (1981) used the flash photolysis-resonance fluorescence technique and reported values of 11.9 and 6.0 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. The preferred value of k (298K) is taken to be a simple mean of these four values. The data reported by Ravishankara et al. show that the rate constant exhibits no temperature dependence between 249-416K.

92. Unchanged from JPL 81-3. 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 x 10^{-18} $T^2\exp(-295/T)$ over the temperature range 244-350 K. This results in a preferred value of 3.86 x $10^{-14} cm^3 molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is 6.09 x 10^{-13} exp(-825/T).

93. Unchanged from JPL 81-3. As the values reported for k at 298 K (Takacs and Glass (1973b), Brown and Smith (1975) and Singleton and Cvetanovic (1978)) are in fair agreement, the mean is taken to be the preferred value. The agreement between the values deduced from the reported Arrhenius expressions (Brown and Smith (1975) and Singleton and Cvetanovic (1978)) at stratospheric temperatures is rather poor; e.g., the values differ by ~70% at 250 K. The preferred value has been synthesized to best fit both sets of data between 250 and 400 K. The A-factor derived for the preferred expression and that reported by Brown and Smith appear to be lower than would be expected. This, combined with the absence of data at stratospheric temperatures, leads to considerable uncertainty in

the values of k between 200 and 260 K.

94. Unchanged from JPL 81-3. The only experimental data is that reported by Wagner et al. (1972). Value appears to be quite reasonable in view of the well known reactivity of atomic chlorine with O_3.

95. Minor change from JPL 81-3. The value of k at 298K seems to be well established with the results reported by Homann et al. (1970), Warnatz et al. (1972), 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 2.3-3.3 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}). The preferred value at 298K is taken to be the mean of the values reported in these references. The magnitude of the temperature dependence is not quite as well established with values of E/R ranging from 433-755K (Homann et al., Warnatz et al., Heidner et al., Wurzburg and Houston, Igoshin et al.). The preferred value of E/R is taken to be the mean of the results from all of the studies. The A-factor was calculated by taking E/R to be 570K, and k at 298K to be 2.8 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

96. Unchanged from JPL 81-3. The three absolute rate coefficients determined by Wagner et al. (1971), Clyne et al. (1973) and Kompa and Wanner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0 x 10^{-11} for k (298) is a weighted mean of all the results. The magnitude of the temperature

dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al., and Foon and Reid, and the preferred Arrhenius parameters of the F + H_2 reaction. This reaction has recently been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). A-factor may be too high.

97. Unchanged from JPL 81-3. This is the value of Zetzsch (1971) which was reported in the review of Jones and Skolnik (1976). The reactivity appears to be somewhat lower than might be expected for such a hydrogen abstraction reaction (see review of Foon and Kaufman (1975).

98. Unchanged from JPL 81-3. This is the value reported by Ray and Watson (1981) for k at 298K using the discharge flow-mass spectrometric technique. The temperature dependence of k is expected to be small for such a radical-radical reaction. The temperature dependences of k for the analogous ClO and BrO reactions have been reported to be negative, with E/R preferred values of -294K and -265K, respectively.

99. Unchanged from JPL 81-3. Although the value of k (FO + FO) reported by Clyne and Watson (1974b) was obtained in a more direct manner than that of Wagner et al. (1972), and as such is less susceptible to error due to the presence of complicating secondary reactions and thus would normally be preferred, the value to be recommended in this assessment is a weighted average of the two studies. From the data of Wagner et al. it can be seen that the dominant reaction channel is that producing 2F + O_2. However, their data base is not adequate to conclude that it is the only process.

100. Unchanged from JPL 81-3. 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 inferred 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 $FO + O_3 \rightarrow F + O_2$ 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)), but 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 FL + O_3 reaction producing either $F + 2O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or that the $FO + O_3$ reactions were 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 that 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 8×10^{-14} (Clyne and Cruse (1970a)) and $5 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$ (Sander and Watson (1981b)) have been reported for $BrO + O_3$.

101. Unchanged from JPL 81-3. 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 experimentally determined rate constants for ClO and BrO at ~298 K are 5.0×10^{-11} and 3.0×10^{-11}, respectively (NASA preferred values). The temperature dependence of the rate constant is expected to be small. The temperature dependence of the analogous ClO reaction has been studied twice with somewhat different results. The values reported for E/R are -76 K (Zahniser and Kaufman (1977) and +224 K Clyne and Nip (1976b)).

102. Unchanged from JPL 81-3. 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.

103. The recommended expression allows for a factor of two increase in k with pressure. This increase has been seen in many high pressure studies (Overend and Paraskevopoulos (1977a), Perry _et al_. (1977), Biermann _et al_. (1978), Cox _et al_ (1976b), and Butler _et al_ (1978)). The most detailed study was carried out by Biermann _et al_. (1978) who found the rate coefficient to depend on both pressure and presence of O_2 (or other impurities). There is still some uncertainty as to exactly what conditions (impurities?) are required to produce the pressure effects.

The enhanced reaction rate is thought to go through an addition complex which yields HO_2 and CO_2 in the presence of O_2. Therefore, in the atmosphere, it is appropriate to write the products to be H + CO_2 since H atoms are quickly converted to HO_2. Further studies of the combined pressure, $[O_2]$, and temperature effects are needed.

104. This is an extremely well characterized reaction. All temperature dependence studies are in good agreement (Greiner (1970a), Davis et al. (1974), Margitan et al. (1974), Zellner and Steinert (1976), Tully and Ravishankara (1980)). 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 $240 < T < 373K$ is recommended.

105. There is excellent agreement between four studies of this reaction at 298K, i.e., Greiner (1970a), Howard and Evenson (1976), Overend et al. (1975), and Tully et al. (1982). k(298K) is the average of these four measurements. The temperature dependence was computed by using the data of Greiner (1970a) and Tully et al. (1982).

106. There are five measurements of the rate coefficient at 298K; Greiner (1970a), Gorse and Volman (1974), Bradley et al. (1973), Overend et al. (1975), and Tully et al. (1982). Gorse and Volman measured $k(OH + C_3H_8)$ relative to $k(OH + CO)$ in the presence of O_2 and calculated $k(OH + C_3H_8)$ assuming that $k(OH + CO) = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. If the current recommended value for $k(OH + CO)$ in the presence of O_2 is used, $k(OH + C_3H_8)$ will be approximately 1×10^{-12} cm^3 molecule^{-1} s^{-1}. Only the results of Overend et al. (1975) ($k = 2 \times 10^{-12}$ cm^3 s^{-1}) are in disagreement with the other values. The most probable cause for this discrepancy is the presence of secondary reactions in their system. The 298K value is the average of the four studies. Only Greiner (1970a) and Tully et al. (1982) have measured the temperature dependence of this reaction, and the recommended E/R was obtained from a linear least squares analysis of the data below 500 K. The A factor was adjusted to reproduce k(298K). This reaction has two possible channels, i.e., abstraction of the primary or the secondary H atom. Therefore, non-Arrhenius behavior may be exhibited over a wide temperature range, as seen by Tully et al. The branching ratios can be estimated from Greiner's (1970a) formula:

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

$k_{secondary} = 4.6 \times 10^{-12} \exp(-430/T)$ cm^3 molecule^{-1} s^{-1}
Only the high pressure limiting rate constant is considered here.

107. This reaction is pressure dependent, and there is reasonable agreement (factor of 2) between various studies on the high pressure limiting rate coefficient (Greiner (1970b), Smith and Zellner (1973), Stuhl (1973), Davis *et al.* (1975), Gordon and Mulac (1975), Atkinson *et al.* (1977), and Overend and Paraskevopoulos (1977b)). The preferred value is essentially that of Atkinson *et al.* (1977); the error bounds are such that most measurements fall within the limits.

108. The rate coefficient for this reaction has been measured in discharge flow tubes by three groups of investigators; Wilson and Westenberg (1967), Breen and Glass (1970), and Pastrana and Carr (1974). There is poor agreement between these three studies. There have also been flash photolysis studies of this reaction. Smith and Zellner (1973) measured k(298K) = 8×10^{-13} cm^3 molecule^{-1} s^{-1}. Davis *et al.* (1975) found the rate coefficient to be independent of pressure, which is contradicted by Perry *et al.* (1977) and Michael *et al.* (1980), who found k(298K) to increase up to a pressure of ~200 torr of argon and then reach a pressure-independent value.

The recommended value of k(298K) is the average of those obtained by Perry *et al.* (1977) and Michael *et al.* (1980) and represents k_{∞}. The temperature dependence, E/R, is that measured by Michael *et al.* since the 200 torr values measured by Perry *et al.* at 350K and 422k were unlikely to have been at the high pressure limit. The A factor has been adjusted to reproduce k(298K). In the troposphere and lower stratosphere, the high pressure limited rate coefficient should apply.

This reaction has five possible reaction channels: $C_2H + H_2O$, $CH_3 + CO$, $CH_2CO + H$, CH_2CHO, and $CHCO + H_2$. A low pressure study has shown

CH_2CO + H to be a major product (Kanofsky et al. (1974)). However, under high pressure conditions, other channels might be more important.

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

110. There are no direct measurements of this rate constant. The estimate given is based on an assumed similarity to OH + H_2O_2 and OH + CH_3OH. The k(298K) values for these two reactions are reported to be similar: k(OH + H_2O_2) = 1.7 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (this evaluation) and k(Oh + CH_3CH) = 1.0 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (average of three measurements, i.e., Campbell et al. (1976), Overend and Paraskevopoulos (1978) and Ravishankara and Davis (1978)). Since the temperature dependence of the OH + CH_3OH reaction has not been measured, the E/R value for OH + CH_3OOH reaction is assumed to be same as that for OH + H_2O_2. The reaction products are not specified since abstraction of H from either end of the molecule is possible.

1. The value at 298K is an average of eight measurements; Arrington et al. (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al. (1967), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), and Westenberg and deHaas (1977). There is reasonably good agreement between these studies. Arrington et al. (1965) did not observe a temperature dependence, an observation which was later shown to be erroneous by Westenberg and deHaas (1969). Westenberg and deHaas are the only ones who have measured the temperature dependence, and they observed a curved Arrhenius plot. In the range of 195-450K, Arrhenius behavior provides an adequate description and the E/R obtained by them in this temperature range is recommended. The A factor was calculated to reproduce k(298K). This reaction can have two sets of products, i.e., C_2HO + H or CH_2 + CO. Even though under molecular beam conditions C_2HO is shown to be the major product, it is not clear what the branching ratio would be under high pressure conditions.

2. 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.

113. The recommended k(298K) is the average of three measurements - Washida and Bayes (1976), Slagle *et al.* (1974) and Washida (1980). 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 341K. All three studies employed the O + C_2H_4 reaction as the CH_3 source, and CH_3 was assumed to be the major product. Recently, however, it has been shown (Buss *et al.*, 1981, Kleinermanns and Luntz, 1981 and Hunziker *et al.* 1981) that C_2H_3O is also a significant product of the O + C_2H_4 reaction. It is not clear how this finding will affect the measured rate coefficient for the O + CH_3 reaction.

114. 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 1200K. Klais *et al.* (1979) failed to detect OH (via $CH_3 + O_2 \rightarrow CH_2O + OH$) at 368K and placed an upper limit of 3 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} for this rate coefficient. Basharan, Frank and Just (1980) measured k = 1 x 10^{-11} exp(-12,900/T) cm^3 $molecule^{-1}$ s^{-1} for 1800 < T < 2200K. The latter two studies, thus, support the results of Baldwin and Golden. However, both Washida and Bayes (1976) and Washida (1980) detected a bimolecular reaction and obtained k(298K) to be ~1.5 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1}, thereby directly contradicting the above three studies. In this evaluation the results of Washida and Bayes (1976) and Washida (1980) have not been included.

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

116. The recommended A factor and E/R are those obtained from the results of Gutman *et al.* (1982). These investigators have measured k directly under pseudo-first order conditions by following CH_3O

via laser induced fluorescence. The temperature interval was 423 to 628K. Cox et al. (1980) used an end product analysis technique to measure k down to 298K. The previous high temperature measurements (Baker et al. (1977) and Batt and Robinson (1979)), are in reasonable agreement with the derived expression. k(298K) is calculated from the recommended expression. This value is consistent with the 298K results of Cox et al. (1980) and with the upper limit measured by Sanders et al. (1980). The A factor, shown above, appears to be too low for a hydrogen atom transfer reaction. The products of this reaction are HO_2 and CH_2O, as shown by Niki et al. (1981).

117. The value of k(298K) is the average of the determinations by Washida et al. (1974), Shibuya et al. (1977), Veyret and Lesclaux (1981), and Langford and Moore (1981). There are three measurements of k where HCO was monitored via the intercavity dye laser technique (Reilly et al. (1978), Nadtochenko et al. (1979), and Gill et al (1981)). Even though there is excellent agreement between these three studies, they yield consistently lower values than those obtained by other techniques. There are several possible reasons for this discrepancy. (a) The relationship between [HCO] and laser attenuation might not be linear, (b) there could have been depletion of O_2 in the static systems that were used (as suggested by Veyret and Lesclaux), and (c) these experiments were designed more for the study of photochemistry than kinetics. Therefore, these values are not included in obtaining the recommended value. The recommended temperature dependence is essentially identical to that measured by Veyret and Lesclaux. We have expressed the temperature dependence in an Arrhenius form even though the authors preferred a T^n form ($k = 5.5 \times 10^{-11}\ T^{-(0.4\pm0.3)}$ cm^3 $molecule^{-1}$ s^{-1}).

118. The rate coefficient for this reaction has been measured by Washida et al. (1980) and Simonaitis and Heicklen (1975). The value reported by Simonaitis and Heicklen is 9.1×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298K and thus seems to be in agreement with the results

of Washida *et al*. (7.0×10^{-13} cm^3 molecule^{-1} s^{-1}). However, the rate coefficient derived by Simonaitis and Heicklen is based on the assumption that the high pressure limit rate coefficient for the $CH_3 + O_2 + M$ reaction, k_∞, equals 4×10^{-13} cm^3 molecule^{-1} s^{-1}, independent of temperature, a value which disagrees with the current recommendation of 2×10^{-12} cm^3 s^{-1}. If the current recommendation is used, a value of 4.4×10^{-12} cm^3 molecule^{-1} s^{-1} is calculated for k(298K). In view of this discrepancy, the results of the only direct study, i.e., Washida *et al*. (1980), are recommended. In the absence of direct measurements, no temperature dependence is recommended. This reaction has at least four possible sets of products; $HCOOH + OH$, $CH_2O + HO_2$, $CH_3O + O_2$, and $CH_2O_2 + H$. The branching ratios are unknown.

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

120. The recommended value for k(298K) is the average of those reported by Hochanadel *et al*. (1977), Parkes (1977), Anastasi *et al*. (1978), Kan *et al*. (1979), Sanhueza *et al*. (1979), and Sander and Watson (1980). All the above determinations used ultraviolet absorption techniques to monitor CH_3O_2 and hence measured k/σ, where σ is the absorption cross section for CH_3O_2 at the monitored wavelength. To obtain a set of numbers that can be compared, the values of k have been recalculated using the absorption cross sections measured by Hochanadel *et al*. (1977). k(298K) is the average of these numbers. The recommended temperature dependence is that measured by Sander and Watson (1981c).

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

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

$\rightarrow CH_3OOCH_3 + O_2$ k_c

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

121. The value of k(298K) is the average of those determined by Sander and Watson (1980), Ravishankara et al. (1981), Cox and Tyndall (1980), Plumb et al. (1981), and Simonaitis and Heicklen (1981). 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. (1981) 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(218K) obtained by Simonaitis and Heicklen (1981) has been neglected; however, the large error bounds allow the calculated value of k at 218K to overlap that measured by Simonaitis and Heicklen. Ravishankara et al. (1981) find that the reaction channel leading to NO_2 accounts for at least 80% of the reaction. This result, in conjunction with the indirect evidence obtained by Pate et al. (1974), confirms that NO_2 formation is the major, if not the only, reaction path.

122. The room temperature value is that of Cox and Tyndall (1979, 1980). This study also reports a large negative E/R value over a temperature range 274 to 338K, which is similar to that found for the $HO_2 + HO_2$ reaction by many groups (see note on $HO_2 + HO_2$). This measurement

has been carried out only at 1 atmosphere pressure. The above results are not inconsistent with the suggested value for the $HO_2 + HO_2$ reaction. The rate coefficient needs independent verification at one atmosphere, and measurements as functions of pressure, water vapor concentration, and temperature.

123. The value of k(298) is an average of the rate constants reported by Perry *et al*. (1976b), Cox and Sheppard (1980), Wine *et al*. (1981a), Leu and Smith (1982a), and Michael *et al*. (1982). The value of E/R is taken from a composite unweighted least squares fit to the individual data points from these same five studies. The study by Leu and Smith (1982a) shows a slight parabolic temperature dependence of k with a minimum occurring near room temperature. Within the error limits stated in this evaluation, all data are fit reasonably well with an Arrhenius expression. The weight of evidence from the 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 2 error limits set for k(298).

124. This recommendation accepts with broad uncertainties the work of Leu and Smith (1981) who report rate constants between 300 and 500K approximately an order of magnitude lower than Ravishankara *et al*. (1980b), who had been thought to have minimized the complications due to secondary chemistry and/or excited state reactions present in the studies of Atkinson *et al*. (1978) and Kurylo (1978). The upper limit of k(298) reported by Cox and Sheppard (1980) is too insensitive to permit valid comparison with the newer results. The Ravishankara *et al*. (1980b) data can be used to calculate an E/R value of ~2000K. The similarity between this value and the 230K value of Leu and Smith (1981) suggests a temperature invariant removal of OH in the Ravishankara experiment possibly due to impurities in the OCS. Product observations by Leu and Smith (1981) tentatively confirm the suggestion of Kurylo and Laufer (1979) that

the reaction produces predominantly HS + CO_2. Until these lower measurements are independently confirmed, the error limits on k(298) and E/R will encompass the results of Ravishankara et al. (1980b).

125. This upper limit is based on the study by Wine et al. (1980a). These authors dealt with severe complications due to excited state and secondary chemistry. The extremes in experimental variation which were necessary to minimize these effects indicate remaining complications in the studies of Atkinson et al. (1978), Kurylo (1978) and Cox and Sheppard (1980). The Cox and Sheppard (1980) study in particular may have been affected by the reaction of electronically excited CS_2 (produced via the 350 nm photolysis) with O_2 (in the 1 atmosphere synthetic air mix). The importance of this reaction in the tropospheric photooxidation of CS_2 into OCS has been suggested by Wine et al. (1980b). In addition, Ravishankara (1982) has observed an acceleration of the OH + CS_2 reaction in the presence of O_2, thereby suggesting a reaction between O_2 and an OH-CS_2 adduct. The Wine et al. (1980a) determination is consistent with an upper limit for the rate of production of OCS in the OH + CS_2 reaction system reported by Iyer and Rowland (1980), suggesting that OCS and SH are the primary reaction products. This mechanistic interpretation is further supported by the recent study of Leu and Smith (1982b), which also sets an upper limit on k(298) somewhat higher than recommended here.

126. 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 (300-500K) but lie systematically higher at every temperature. The uncertainty factor at 298K has been chosen to encompass the values of k(298K) determined by Slagle et al. (1978) and Hollinden et al. (1970). Other than the 263K data point of Whytock et al. (1976) and the 281K point of Slagle et al. (1978) the main body of rate constant data below 298K comes from the study of Hollinden et al. (1970), which indicates a dramatic change in E/R in

this temperature region. Thus, E/R was set to account for these observations. Such a non-linearity in the Arrhenius plot might indicate a change in reaction mechanism from abstraction (as written) to addition. An addition channel has been proposed for this reaction by Slagle et al. (1978) as well as by Singleton et al. (1979), and addition products from this reaction have been seen in a matrix by Smardzewski and Lin (1977). Further kinetic study in the 200 to 300K range as well as direct mechanistic information could clarify these issues. This reaction is thought to be of limited stratospheric importance, however.

127. 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.

128. The value of k (298 K) is the average of seven determinations: Wei and Timmons (1975), Westenberg and de Haas (1969a), Slagle et al. (1974), 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). E/R has been set to encompass the limited temperature data of Westenberg and de Haas (1969a). The principal reaction products are thought to be CS + SO. However, Hsu et al. (1979) report that 1.4% of the reaction at 298K 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.

129. 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.

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

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

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

133. The value of k(298) is based on an extrapolation of the data of Homann et al. (1968) obtained over the temperature range 580-1145K. Their results are consistent with an E/R value of 3300K. Other high temperature measurements of the reaction give widely varying Arrhenius parameters (cf. Baulch et al. (1980)). The large uncertainty in k(298) reflects the possible unreliability of this extrapolation.

134. The value of k(298) is an average of the determinations by Halstead and Thrush (1966) and Robertshaw and Smith (1980) using widely differing techniques. The value of E/R is from Halstead and

Thrush (1966) with the A-factor calculated to fit the value recommended for k(298).

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

136. The value of k(298) is based on the recent measurement of Clyne and MacRobert (1980), which agrees quite well with the rate constant calculated from the relative rate measurements of Clyne et al. (1966).

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

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

139. 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 then in the earlier studies of Sanhueza

et al. (1979) and Kan et al. (1979), both of which resulted in k(298) values approximately 100 times larger. A more recent study by Kan et al. (1981) postulates that these differences are due to reactive removal of the $CH_3O_2SO_2$ adduct at high CH_3O_2 radical concentrations, prior to its reversible decomposition into CH_3O_2 + SO_2. They suggest that such behavior of $CH_3O_2SO_2$ or its equilibrated adduct with O_2 ($CH_3O_2SO_2O_2$) would be expected in the studies yielding high k values, while decomposition of $CH_3O_2SO_2$ into reactions 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 compete with the adduct decomposition.

140. The basis of this recommendation is the recent work of Tiee et al. (1981) employing laser induced fluorescence detection of HS. Their preliminary measurement is lower than the upper limit for this rate constant estimated by Cupitt and Glass (1975) by nearly two orders of magnitude.

Table 2. Rate Constants for Three-Body Reactions

Reaction	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
$^*O + O_2 \xrightarrow{M} O_3$	(6.0±0.5)(-34)	2.3±0.5	-	-	1
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0)(-37)	$0.5^{+2}_{-.5}$	- -	-	2
$H + O_2 \xrightarrow{M} HO_2$	(5.5±0.5)(-32)	1.4±0.5	- -	-	3
$^*OH + OH \xrightarrow{M} H_2O_2$	(6.9±3.0)(-31)	$1.0^{+2.0}_{-1.0}$	(1.0±0.5)(-11)	1.0±1.0	4
$O + NO \xrightarrow{M} NO_2$	(1.2±0.3)(-31)	1.8±0.5	(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
$^*OH + NO \xrightarrow{M} HONO$	(6.7±1.2)(-31)	2.5±1.0	(1.5±1.0)(-11)	0.5±0.5	7
$OH + NO_2 \xrightarrow{M} HNO_3$	(2.6±0.3)(-30)	2.9±0.7	(2.4±1.2)(-11)	1.3±1.3	8
$^*HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(2.3±0.2)(-31)	4.6±1.0	(4.2±1.0)(-12)	0±2.0	9
$^*NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.2±1.1)(-30)	2.8±1.0	(1.0±0.8)(-12)	0±1.0	10
$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0)(-32)	1.8±0.5	- -	-	11
$^*Cl + NO_2 \xrightarrow{M} ClONO$	(1.5±0.6)(-30)	1.9±1.0	(1.0±0.5)(-10)	1.0±1.0	12
$\xrightarrow{M} ClNO_2$	(3.1±1.2)(-31)	1.9±1.0	(1.0±0.5)(-10)	1.0±1.0	12
$Cl + O_2 \xrightarrow{M} ClOO$	(2.0±1.0)(-33)	1.3±1.3	- -	-	13
$^*ClO + NO_2 \xrightarrow{M} ClONO_2$	(4.5±2.3)(-32)	3.8±1.0	(1.5±0.7)(-11)	1.9±1.9	14
$\xrightarrow{M}$ Isomer	(1.3±0.2)(-31)	3.8±1.0	(1.5±0.7)(-11)	1.9±1.9	14

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.

*Changed from JPL 81-3.

Table 2. (Continued).

	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		
Reaction	k_o^{300}	n	k_∞^{300}	m	Notes
*$ClO + NO_2 \xrightarrow{M} ClONO_2$(a)	(1.8±0.3)(-31)	3.4±1.0	(1.5±0.7)(-11)	1.9±1.9	14
*$BrO + NO_2 \xrightarrow{M} BrONO_2$	(5.0±2.0)(-31)	2.0±2.0	(1.0±0.5)(-11)	1.0±1.0	15
$F + O_2 \xrightarrow{M} FO_2$	(1.6±0.8)(-32)	2.5±1.0	- -	-	16
*$F + NO \xrightarrow{M} FNO$	(8.7±4.4)(-32)	1.7±1.7	- -	-	17
*$F + NO_2 \xrightarrow{M} FNO_2$	(1.1±0.6)(-30)	2.3±2.3	(1.0±0.5)(-10)	1.0±1.0	18
*$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0)(-31)	1.3±1.3	(2.0±1.0)(-11)	1.5±1.5	19
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(2.2±1.1)(-31)	2.2±1.0	(2.0±1.0)(-12)	1.7±1.7	20
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8)(-30)	4.0±2.0	(6.5±3.2)(-12)	2.0±2.0	21
$OH + SO_2 \xrightarrow{M} HOSO_2$	(3.0±1.5)(-31)	2.9±1.0	(2.0±1.5)(-12)	0±1.0	22

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.

*Changed from JPL 81-3.

(a) This is an alternative recommendation for the $ClO + NO_2 + M$ reaction which assumes that isomer formation is unimportant. See note 14.

NOTES TO TABLE 2

1. 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 earlier work (see references therein).

2. Low-pressure limit from Kajimoto and Cvetanovic (1976). T-dependence assuming constant β. Rate constant is extremely low in this special system due to electronic curve crossing.

3. Kurylo (1972), Wong and Davis (1974) averaged. Both studies include T-dependence; the recommended value is chosen with constant $\langle\Delta E\rangle_N$ - .04 kcal mole^{-1}. This very low number reflects rotational effects.

4. Zellner et al. (1982) report 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. Values of rate constants and temperature dependences from the evaluations of Baulch et al. (1980). They suggest $F_c = 0.85 \pm .1$, compared to our fixed value of 0.6. They also suggest $m = -0.3$. These make very small differences over the range of stratospheric conditions.

   (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 $F_c = 0.89$ at 200 K.)

6. 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 298K, 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 200K.)

7. 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 Evanson (1974), Harris and Wayne (1975), Atkinson et al. (1975), Overend et al. (1976), and Anastasi and Smith (1978). 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).

8. Low-pressure limit 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 $n = 2.9$ comes from $\langle \Delta E \rangle_{N_2} = 0.31$ kcal mole^{-1}. The high-pressure limit and T-dependence come from RRKM model of Smith and Golden (1978), although the error limits have been expanded to encompass $m = 0$.

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

9. Low-pressure limit from Howard (1977) and Sander and Peterson (1982). The latter work includes a complete study of pressure and temperature dependence, and all other parameters are from this study. The previous values from Baldwin and Golden (1978), who used

C-2

RRKM theory and data on the reverse reaction from Graham, Winer, and Pitts (1977), differ slightly in the value and the temperature dependence of k_∞. The absence of negative temperature dependence for k yields an equilibrium constant that, in turn, yields values of $S^o(HO_2NO_2)$ -76 cal mole^{-1} deg^{-1} and $\Delta H_f(HO_2NO_2) = -12.7$ kcal mole^{-1}. This compares to Baldwin and Golden's values of $S^o{}_{298} =$ 71.6, or $\Delta H_{f,298} = -14.1$ kcal/mole^{-1}. This value of 71.6 e.u. should be a fairly conservative upper limit, and suggests that some negative T-dependence may be required to fit all the data. The discrepancy in the high-pressure limiting rate constants has a small effect at stratospheric pressures.

Other studies by Simonaitis and Heicklen (1978) and Cox and Patrick (1979) are in reasonable agreement with the recommendations.

10. Data on the reverse reaction from Connell and Johnston (1979) and Viggiano _et al_. (1981). A very thorough analysis of this data by Malko and Troe (1982) concludes that the data is best fit with $k_o{}^{300} = 3.7 \times 10^{-30}$, $n = 4.1$, $k_\infty{}^{300} = 1.6 \times 10^{-12}$, $m = -0.2$, and $F_c = \exp(-T/250) + \exp(-1050/T)$, $F_c = .33$ at 300K. The values recommended here fit the data just as well.

11. 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_. (1968).

12. Low-pressure limit and T-dependence from Ravishankara _et al_. (1978), Ravishankara (1982), and Chang _et al_. (1979). The latter paper shows why Niki _et al_. (1978) saw two products with ClONO dominating (see Note 14). $\beta = 0.41$ was arrived at by dividing the sum of k_{sc} for both paths into measured rate constant for overall reaction of $Cl + NO_2$. High-pressure limit and temperature dependence are fixed to match measurement at 200 torr.

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

14. The available kinetics data for this reaction fall into two sets, which are in substantial disagreement. Several independent low-pressure determinations (Zahniser et al., 1977; Birks et al., 1977; Leu et al., 1977; Lee et al., 1982) of the rate of ClO disappearance via the $ClO + NO_2 + M$ reaction are in excellent agreement and give an average $k_0(300)$ 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 $k_0(300) = 4.5 \times 10^{-32}$ cm^6 s^{-1} for the three-body reaction forming $ClONO_2$. Since the measured rate of ClO disappearance seems well established by four groups, the Knauth results can be reconciled with the higher number by three different explanations: (1) the measured thermal decomposition rate is incorrect; (2) the equilibrium constant is in error by a factor of three (requiring that the ΔH_f's are off by ~1 kcal/mole, which, while small, is outside the stated error limits); (3) all the data are correct, and the low-pressure ClO disappearance studies measured not only a reaction forming $ClONO_2$, but another channel forming an isomer, such as $OClNO_2$, ClOONO, or OClONO (Chang et al., 1979; Molina et al., 1980a).

When the isomer-forming reaction is included in models, the fate of the isomer must also be stated. While rapid photolysis back to $ClO + NO_2$ seems most reasonable, an isomer of the form ClOONO could, in fact, dissociate to ClOO + NO, and thus enhance catalytic destruction of ozone. The entire matter will remain speculative and unsettled until there is conclusive evidence for or against isomer formation.

Both of the above possibilities are represented by the two sets of recommendations. The first set, which takes into account possible isomer formation, used the Knauth rate constant for $ClONO_2$ formation and assigns the difference between this value and the rate constant for ClO disappearance to the other pathway. Temperature dependence is estimated from the value of $\langle \Delta E \rangle$, as explained in the text. The second set uses the average value for total ClO disappearance, treating the process as if only $ClONO_2$ is formed. The temperature dependence comes from assuming that $\langle \Delta E \rangle$ is constant.

The high-pressure limit rate constants and their temperature dependence are from the model of Smith and Golden (1979). Either set of the rate constants above fit measured rate data for the disappearance of reactants (Cox and Lewis, 1979; Dasch et al., 1981). Data from Zellner (1982) indicate an approximately 50% lower k_∞.

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

16. Low-pressure limit and temperature dependence from Baulch et al. (1982), who averaged the results of Zetzsch (1973), Arutyunov et al. (1976), Chen et al. (1977), and Shamonima and Ketov (1979).

17. Parameters estimated from strong collision calculations with $\langle \Delta E \rangle$ set at .52 kcal/mole^{-1}, yielding β = .33 at 300K and β = .43 at 200K. T-dependence as per text.

18. Low-pressure limit rate constant from strong collision calculation and $\beta = 0.33$. T-dependence from constant $\langle \Delta E \rangle = 0.52$ kcal mole^{-1}. High-pressure limit and T-dependence are estimated by analogy to Cl + NO_2.

Caveat: The formation of FONO might be the more important path (see Cl + NO_2).

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

Caveat: There could be multiple channels here, which would mean that the reaction between FO and NO_2 could be much faster.

20. Low-pressure limit from extrapolation of data of Washida and Bayes (1976), Basco *et al*. (1972), and Parkes (1977). [The extrapolation techniques were poor, but this (being the only reaction of methyl radicals) is not a very sensitive reaction.] Low-pressure limit T-dependence as per text. High-pressure limit from van den Bergh and Callear (1971), and Hochanadel *et al*. (1977). [Data of Basco *et al*. (1972), Washida and Bayes (1976), Laufer and Bass (1975), Washida (1980), are also considered.] High-pressure limit T-dependence estimated.

21. Parameters from a reasonable fit to the temperature and pressure-dependent data in Sander and Watson (1980) and Ravishankara *et al*. (1980), using equation (1).

The former reference reports their room-temperature data in the same form as herein, but they allow F_c to vary. They report:

$k_o = 2.33 \times 10^{-30}$, $k_\infty = 8 \times 10^{-12}$, $F_c = 0.4$

which is not a qualitatively different fit to the data at 300K. The later reference reports temperature dependence as:

$k_o = 2.2 \times 10^{-30}(T/300)^{-2.5}$, $k_\infty = 7 \times 10^{-12}(T/300)^{-3.5}$, $F_c = 0.4$

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

The most recent CODATA recommendations (Baulch *et al.*, 1982) are:

$k_o = 2.3 \times 10^{-30}(T/300)^{-4}$, $k_{\infty} = 8 \times 10^{-12}$ and
$F_c = e^{-T/32} + e^{-1280/T}$ $\therefore$ $F_c = .41$ at 300K and .54 at 200K.
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_{∞} unlike $HO_2 + NO_2$, and that the value of β at 300K is ~.2.

22. Values of rate constants and temperature dependences from Baulch *et al.* (1980). They suggest a value of $F_c = 0.7$. In a supplementary review, Baulch *et al.* (1982) suggest tht $F_c = 0.55$ at 300K and is temperature dependent, such that $F_c = 0.67$ at 200K, and they raise k_{∞}^{300} to 2.5×10^{-12} to accommodate this change. The computed rate constants are essentially the same over stratospheric conditions as when using $F_c = 0.6$ as recommended herein.

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):

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

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

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:

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

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

$$B/{}^{\circ}K = 2.303 \log \frac{K_{200}}{K_{300}} \frac{300 \cdot 200}{300 - 200}$$

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

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

Table 3. Equilibrium Constants

Reaction	A/cm^3 molecule^{-1}	B/^{o}K	log K(300)	Note
$HO_2 + NO_2 \rightarrow HO_2NO_2$	2.33×10^{-17}	10, 870	-10.90	1
$NO_2 + NO_3 \rightarrow N_2O_5$	1.77×10^{-27}	11, 001	-10.83	2
$Cl + O_2 \rightarrow ClOO$	2.43×10^{-25}	2, 979	-20.30	3
$ClO + O_2 \rightarrow ClO \cdot O_2$	$<1.3 \times 10^{-26}$	<5, 230	<-18.30	4
$F + O_2 \rightarrow FOO$	5.32×10^{-25}	7, 600	-13.27	5a
	1.15×10^{-25}	3, 582	-19.75	5b
$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	1.30×10^{-28}	11, 192	-11.68	6

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

NOTES TO TABLE 3

1. The value was obtained by combining the data of Sander and Peterson (1982) for the rate constant of the reaction as written and that of Graham *et al*. (1977) for the reverse reaction.

2. The parameters A and B were calculated from JANAF equilibrium constants at 200 and 300 K.

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

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

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.

4. Zellner (1982) suggests $K < 12$ atm^{-1} and $\Delta H \geq - 11$ kcal/mole. The corresponding value of A leads to $S^o300(ClO \cdot O_2)$ -73 cal $mole^{-1}$ 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 $mole^{-1}$ K^{-1}, which seems unreasonably high. Carter and Andrews (1981) found no experimental evidence for $ClO \cdot O_2$.

5. (a) From JANAF thermochemical values.
   (b) From Benson's (1976) thermochemical values.

6. Thermochemical values at 300 K for $CH_3O_2NO_2$ and CH_3O_2 are from Baldwin (1982). In the absence of data, ΔH^o and ΔS^o were assumed to be independent of temperature. Bahta *et al*. (1982) have measured

k(dissociation) at 263 K. Using the values of k(recombination) suggested in this evaluation, they compute $K(263) = (2.68 \pm 0.26) \times 10^{-10}$ cm^3. Our values predict 3.94×10^{-10} cm^3, in good agreement.

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

In Table 4 we present a list of photochemical reactions considered to be of stratospheric interest. In cases where the data presentation is very complex, or where the reaction is of lesser importance, only a reference to a data source is given. For example, discussions of the absorption cross sections of O_2 and O_3, which largely determine the extent of penetration of solar radiation into the stratosphere and troposphere, are found in Hudson and Kieffer (1975), NASA RP 1049 and WMO Report #11. The photodissociation of NO in the O_2 Schumann-Runge band spectral range is another important process requiring special treatment (see Frederick and Hudson (1979) and WMO Report #11). Some references are given on the photochemistry of SO_2 and CS_2, but the data are not discussed here. These molecules have highly structured spectra with photodissociation quantum yields which are not simple functions of the wavelength. Other species, such as CH_2O and NO_2, also have complicated spectra, but in view of their importance for atmospheric chemistry the data are summarized 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 total dissociation rate regardless of product identity (except in the case of $O(^1D)$ production from photolysis of O_3).

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

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

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

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Table 4. Photochemical Reactions of Stratospheric Interest

$\mathrm{O_2 + h\nu \rightarrow O + O}$	(1)	$\mathrm{ClONO + h\nu \rightarrow products}$	
$\mathrm{O_3 + h\nu \rightarrow O_2 + O}$	(1)	$\mathrm{ClONO_2 + h\nu \rightarrow products}$	
$\mathrm{O_3 + h\nu \rightarrow O_2 + O(^1D)}$		$\mathrm{CCl_4 + h\nu \rightarrow products}$	
$\mathrm{HO_2 + h\nu \rightarrow products}$		$\mathrm{CCl_3F + h\nu \rightarrow products}$	
$\mathrm{H_2O + h\nu \rightarrow H + OH}$	(1)	$\mathrm{CCl_2F_2 + h\nu \rightarrow products}$	
$\mathrm{H_2O_2 + h\nu \rightarrow OH + OH}$		$\mathrm{CHClF_2 + h\nu \rightarrow products}$	
$\mathrm{NO + h\nu \rightarrow N + O}$	(2)	$\mathrm{CH_3Cl + h\nu \rightarrow products}$	
$\mathrm{NO_2 + h\nu \rightarrow NO + O}$		$\mathrm{CCl_2O + h\nu \rightarrow products}$	
$\mathrm{NO_3 + h\nu \rightarrow products}$		$\mathrm{CClFO + h\nu \rightarrow products}$	
$\mathrm{N_2O + h\nu \rightarrow N_2 + O(^1D)}$		$\mathrm{CF_2O + h\nu \rightarrow products}$	
$\mathrm{N_2O_5 + h\nu \rightarrow products}$		$\mathrm{CH_3CCl_3 + h\nu \rightarrow products}$	
$\mathrm{NH_3 + h\nu \rightarrow NH_2 + H}$	(1)	$\mathrm{BrONO_2 + h\nu \rightarrow products}$	
$\mathrm{HNO_2 + h\nu \rightarrow OH + NO}$		$\mathrm{HF + h\nu \rightarrow H + F}$	
$\mathrm{HNO_3 + h\nu \rightarrow OH + NO_2}$		$\mathrm{CO + h\nu \rightarrow C + O}$	(1)
$\mathrm{HNO_4 + h\nu \rightarrow products}$		$\mathrm{CO_2 + h\nu \rightarrow CO + O}$	(1)
$\mathrm{Cl_2 + h\nu \rightarrow Cl + Cl}$		$\mathrm{CH_4 + h\nu \rightarrow products}$	(3)
$\mathrm{ClO + h\nu \rightarrow Cl + O}$		$\mathrm{CH_2O + h\nu \rightarrow products}$	
$\mathrm{ClOO + h\nu \rightarrow products}$		$\mathrm{CH_3OOH + h\nu \rightarrow products}$	
$\mathrm{OClO + h\nu \rightarrow O + ClO}$		$\mathrm{HCN + h\nu \rightarrow products}$	
$\mathrm{ClO_3 + h\nu \rightarrow products}$		$\mathrm{CH_3CN + h\nu \rightarrow products}$	
$\mathrm{HCl + h\nu \rightarrow H + Cl}$		$\mathrm{SO_2 + h\nu \rightarrow SO + O}$	
$\mathrm{HOCl + h\nu \rightarrow OH + Cl}$		$\mathrm{H_2S + h\nu \rightarrow HS + H}$	(3)
$\mathrm{ClNO + h\nu \rightarrow Cl + NO}$		$\mathrm{COS + h\nu \rightarrow CO + S}$	
$\mathrm{ClNO_2 + h\nu \rightarrow products}$		$\mathrm{CS_2 + h\nu \rightarrow products}$	

(1) Hudson and Kieffer (1975)
(2) Frederick and Hudson (1979)
(3) Turco (1975)

Table 5. Combined Uncertainties for Cross Sections and Quantum Yields

Species	Uncertainty
O_2 (Schumann-Runge bands)	1.4
O_2 (Continua)	1.25
O_3	1.15
O_3 $O(^1D)$	1.4
NO_2	1.25
NO_3	2.0
N_2O	1.2
N_2O_5	2.0
H_2O_2	1.4
HNO_3	1.25
HO_2NO_2	2.0
CH_2O	1.4
HCl	1.15
HOCl	1.4
$ClONO_2$	1.25
CCl_4	1.1
CCl_3F	1.1
CCl_2F_2	1.15
CH_3Cl	1.1
CF_2O	2.0
CH_3OOH	1.4
$BrONO_2$	1.4

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

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 now several studies which indicate that this assumption is not correct: Fairchild _et al_. (1978) observed approximately 10% of the primary photolysis products in the ground state channel, that is, $\Phi(O^3P) \simeq 0.1$, at 274 nm; Sparks _et al_. (1980) also report $\Phi(O^3P) \simeq 0.1$, at 266 nm; according to Brock and Watson (1980b) $\Phi(O^1D) = 0.88$ at 266 nm; and Amimoto _et al_. (1980) report $\Phi(O^1D) = 0.85$ at 248 nm. There are also some indications that (O^1D) decreases slightly between 304 and 275 nm (see Brock and Watson, 1980 a, b).

The earlier recommendation for the quantum yields in the fall-off region was to employ the mathematical expression given by Moortgat and Kudzus (1978), which gives relative values in good agreement with those reported by Brock and Watson (1980a). Our present recommendation, shown in Table 5, merely scales down these values by a factor of 0.9 to account for the absolute magnitude of $\Phi(O^1D)$ at short wavelengths.

Table 6. Mathematical Expression for $O(^1D)$ Quantum Yields, Φ, in the Photolysis of O_3

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

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

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

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

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

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

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

The shape of the spectrum reported by the first three groups cited above is in reasonable agreement. The recommended absorption cross sections, listed in Table 7, are computed from the mean of the three after normalization of each spectrum to the value at 227.5 nm reported by Sander *et al*. (1982). This latter study gives the most direct measurement of an absolute cross section value for HO_2.

Table 7. Absorption Cross Sections of HO_2

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

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

The recommended absorption cross section values, listed in Table 8, are the mean of the data of Lin et al. (1978b) and of Molina and Molina (1980). This latter work supersedes the earlier results of Molina et al. (1977a).

Table 8. 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 9 lists 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. The effect of the dimer (N_2O_4) absorption was considered in detail, and the measurements are probably correct to within ±10%.

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), whose data provided the basis for earlier recommendations. Recent measurements of the quantum yields by Davenport (1978) at six different wavelengths agree very well with those of Harker et al. The recommended values for the quantum yields, presented in Table 9, are those of Harker et al. (1977). Davenport's results indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced.

For quantum yields in the 295-365 nm region the recommendation is to use the expression given by Jones and Bayes (1973), listed at the bottom of Table 10. More accurate values should be established in this wavelength region, although their contribution to the overall atmospheric photodissociation rate is not of major importance. Direct measurements of the solar photodissociation rate in the troposphere (Stedman et al., 1975; Dickerson and Stedman, 1980) indicate that the present data base is adequate for atmospheric modeling purposes.

Table 9. NO_2 Absorption Cross Sections at 235 and 298 K

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

Table 10. Quantum Yields for NO_2 Photolysis

λ, nm	Φ	λ, nm	Φ	λ, nm	Φ
375	0.73	389	0.74	400	0.65
376	0.75	390	0.74	401	0.62
377	0.86	391	0.81	402	0.57
378	0.74	392	0.73	403	0.50
379	0.83	393	0.78	404	0.40
380	0.81	394	0.83	405	0.32
381	0.73	394.5	0.78	406	0.30
382	0.65	395	0.81	407	0.23
383	0.62	395.5	0.75	408	0.18
384	0.66	396	0.78	409	0.17
385	0.70	396.5	0.81	410	0.14
386	0.74	397	0.77	411	0.10
387	0.69	398	0.72	415	0.067
388	0.76	399	0.70	420	0.023

295-365 nm: $\Phi(\lambda) - 1.0-0.0008\,(\lambda-275)$

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

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

The absorption cross sections of the nitrate free radical, NO_3, have been studied by (1) Johnston and Graham (1974); (2) Graham and Johnston (1978); (3) Mitchell et al. (1980); and (4) Marinelli et al. (1982). The 1st and 4th studies required calculation of the NO_3 concentration by modelling a complex kinetic system. The 2nd and 3rd studies are the most direct ones and the results in terms of integrated absorption coefficients are in very good agreement; the discrepancies in peak heights can be attributed to the difference in instrumental resolution, which was higher in the 2nd study. The recommended absorption cross sections, listed in Table 10 for every 2 nm, are taken from this latter study (Graham and Johnston, 1978), which reports values every nm.

The 4th study was designed to characterize under high resolution the strong absorption band around 662 nm; for spectroscopic measurements of NO_3 in the atmosphere the preferred cross sections are those reported in this 4th study, which have been scaled to yield the same integrated absorption coefficient as in the 2nd and 3rd studies.

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 (1980), listed in Table 11, 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 from our previous one, namely, to use the following photodissociation rates estimated by Magnotta and Johnston (1980) for overhead sun at the earth's surface:

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

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

Table 11. Absorption Cross Sections of NO_3

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)
400	0	476	64	552	216	628	689
402	1	478	66	554	245	630	641
404	2	480	64	556	295	632	327
406	3	482	63	558	317	634	132
408	3	484	62	560	323	636	123
410	6	486	74	562	268	638	176
412	3	488	80	564	248	640	98
414	7	490	93	566	258	642	68
416	3	492	89	568	257	644	71
418	6	494	88	570	253	646	56
420	9	496	104	572	248	648	48
422	8	498	108	574	255	650	32
424	12	500	98	576	292	652	39
426	9	502	91	578	303	654	57
428	12	504	105	580	299	656	89
430	12	506	119	582	310	658	168
432	14	508	106	584	247	660	512
434	17	510	130	586	275	662	1708
436	21	512	161	588	448	664	1154
438	18	514	141	590	567	666	486
440	19	516	140	592	483	668	175
442	20	518	121	594	392	670	75
444	21	520	144	596	416	672	57
446	23	522	172	598	354	674	36
448	28	524	150	600	245	676	31
450	27	526	137	602	284	678	55
452	31	528	179	604	400	680	49
454	34	530	209	606	338	682	25
456	32	532	181	608	159	684	9
458	37	534	177	610	135	686	3
460	39	536	232	612	169	688	4
462	35	538	211	614	224	690	1
464	41	540	181	616	174	692	0
466	45	542	168	618	183	694	1
468	50	544	139	620	247	696	4
470	49	546	204	622	761	698	4
472	54	548	275	624	1166		
474	56	550	224	626	700		

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

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 12. Hubrich and Stuhl (1980) have recently measured the N_2O cross sections at 298K and 208K, and their results are in very good agreement with those of Selwyn *et al.*

Table 12. 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

$A_1 = 68.21023$ $B_1 = 123.4014$

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

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

$A_4 = -1.777846 \times 10^{-4}$ $B_4 = -1.881058 \times 10^{-5}$

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

Range: 173 to 240 nm; 194 to 320 K

$N_2O_5 + h\nu \rightarrow$ 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 (1979) between 205 and 310 nm; and for temperatures in the 223 to 300 K range by Yao et al. (1982), between 200 and 380 nm. The agreement is good particularly considering the difficulties in handling N_2O_5. The recommended cross section values, listed in Table 13, 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 13.

The primary quantum yield for photodissociation appears to be unity and the primary products appear to be $2NO_2 + O$ (Connell, 1979; Magnotta, 1979).

Table 13. 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/cm^2; λ/nm; T/K.

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

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 interrerences by these compounds were taken into account. The recommended cross sections, taken from this work, are listed in Table 14.

Table 14. 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	396	0.0

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

The recommended absorption cross sections, listed in Table 15, are taken from the work of Molina and Molina (1980). These data are in good agreement throughout the 190-330 nm range with the values reported by Biaume (1973). They are also in very good agreement with the data of Johnston and Graham (1973) except towards both ends of the wavelength range. Okabe (1980) has measured the cross sections in the 110-190 nm range; his results are 20-30% lower than those of Biaume and of Johnston and Graham around 185-190 nm.

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

Table 15. 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 + hν → 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 (1980). 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 16 are taken from the work of Molina and Molina (1980), which is the more direct study. The temperature dependence of the cross sections at these longer wavelengths and the identity of the photodissociation products remain to be determined.

Table 16. 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 17, are taken from the work of Seery and Britton (1964). These results are in good agreement with those reported by Gibson and Bayliss (1933), and Fergusson _et al_. (1936).

Table 17. 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 some 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 18 are taken from their work.

Table 18. 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

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

The spectrum of OClO is characterized by a series of well developed progression 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.

$ClO_3 + h\nu \rightarrow$ products

Table 19 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 19. ClO_3 Absorption Cross Sections

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

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

The absorptions cross sections of HCl, listed in Table 20, are taken from the work of Inn (1975).

Table 20. 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 21.

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.

Table 21. 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 nanometers. There is good agreement between the work of Martin and Gareis (1956) for the 240 to 420 nm wavelength region, of Ballash and Armstrong (1974) for the 185 to 540 nm region, and of Illies and Takacs 81976) for the 190 to 400 nm region. These results indicate that the early data of Goodeve and Katz (1939) were seriously in error between 186 and 300 nm, whereas, at longer wavelengths, they are in good agreement with the more recent measurements.

The recommended absorption cross sections, listed in Table 22, are obtained by taking the mean of the results of Ballash and Armstrong (1974) and of Illies and Takacs (1976). The two sets of measurements agree within 20 percent, except in the region near 240 nm, where the values of Ballash and Armstrong are about 60 percent higher.

The quantum yield for the primary photolytic process has been reviewed by Calvert and Pitts (1967); it is unity over the entire visible and near-ultraviolet bands.

Table 22. ClNO Absorption Cross Sections

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

$ClNO_2 + h\nu \rightarrow$ 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 23 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 a ~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 23. 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		

$ClONO + h\nu \rightarrow$ 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 24. 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 24. 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 25, 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. (1979), 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%. The preferred results are those of Chang et al. (1979), and it appears that the reason Adler-Golden and Wiesenfeld failed to observe Cl was that the rate constant for Cl + $ClNO_3$ is much faster (two orders of magnitude) than thought at the time of their experiments, Margitan (1982), and the Cl had disappeared on the time scale of their observations. Very recent studies by Margitan (1982) on $ClNO_3$ photolysis show a near 100% yield of atomic Cl. None of these studies have been carried out at wavelengths longer than 290 nm, which is the relevant range for atmospheric photodissociation. Further studies are required on this question.

Table 25. Absorption Cross Sections of $ClONO_2$

λ (nm)	$10^{20}\sigma$ (cm^2)			λ (nm)	$10^{20}\sigma$ (cm^2)		
	227K	243K	296K		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- * 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, $CFCl_3$ aand 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 investigated recently 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 26, 27 and 28 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 28.

The species $CHClF_2$, CH_3Cl and CH_3CCl_3 are discussed individually; their absorption cross sections are listed in Tables 29, 30 and 32, respectively.

The absorption cross sections for various other halocarbons not listed in this evaluation have been investigated recently. 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.

Absorption cross sections have also been measured recently for several other halocarbons, including 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, $CBrF_3$, CBr_2F_2, $CBrClF_2$, $CBrF_2CBrF_2$ and $CBrF_2CF_3$ by Molina *et al.* (1982).

For atmospheric modeling purposes the present recommendations for halocarbon cross section values are essentially the same as those listed in our previous evaluation. As before, the recommendation for the photodissociation quantum yield value is unity for all these species.

Table 26. 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.[illegible]	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 27. 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 28. Absorption Cross Sections of CCl_2F_2

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

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

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

λ : nm

T : temperature, Kelvin

$CHClF_2$ + hν → products

The preferred absorption cross sections, listed in Table 29, 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 29. 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	0.625
186	0.476
188	0.339
190	0.235
192	0.157
194	0.100
196	0.070
198	0.039
200	0.026
202	0.022
204	0.013

$CH_3Cl + h\nu \rightarrow$ products

The preferred absorption cross sections, listed in Table 30, 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 30. 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

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

Table 31 shows the absorption cross sections of CCl_2O (phosgene) and CFClO given by Chou *et al.* (1977a), and of CF_2O taken from the work of Molina and Molina (1982). The spectrum of CF_2O shows considerable structure; the values listed in Table 31 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, 1967).

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

Table 31. Absorption Cross Sections of CCl_2O, CClFO, and CF_2O

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

$CH_3CCl_3 + h\nu \rightarrow$ 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 32 lists the values at 210 K, 250 K and 295 K, every 5 nm; the odd wavelength values were computed by linear interpolation.

Table 32. Absorption Cross Sections of CH_3CCl_3

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

$BrONO_2 + h\nu \rightarrow$ 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 33. The photolysis products are not known.

Table 33. 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	2.8

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

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.

$CH_2O + h\nu \rightarrow H + HCO \quad (\Phi_1)$

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

Bass *et al.* (1980) have recently 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 Moor' *et al.* (1980) 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 34, are the mmean 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.* (1978), Tang *et al.* (1979), Moortgat and Warneck (1979), and Moortgat *et al.* (1981). The recommended values listed in Table 34 are taken from the latter work. 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 34, which is based on the values reported by Moortgat *et al.* (1981) for 300 K.

Table 34. Absorption Cross Sections and Quantum Yields for Photolysis of CH_2O.

λ (nm)	$10^{20}\sigma$ (cm^2) 290 K	220 K	Φ_1 (H + HCO)	Φ_2 (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	0.17	0.80
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 indicated wavelength.

* : at p = 760 torr

For $\lambda > 329$ nm, Φ_2 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 35.

Table 35. Absorption Cross Sections of CH_3OOH

λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)	λ (nm)	$10^{20}\sigma$ (cm^2)
210	37.5	260	3.8	310	0.34
220	22.0	270	2.3	320	0.19
230	13.8	280	1.5	330	0.11
240	8.8	290	0.90	340	0.06
250	5.8	300	0.58	350	0.04

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

Herzberg and Innes (1975) have studied the spectroscopy of hydrogen cyanide, HCN, which starts absorbing weakly at $\lambda < 190$ nm. McElcheran et al. (1953) have reported the spectrum of methyl cyanide, CH_3CN; the first absorption band appears at $\lambda < 216$ nm.

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

$SO_2 + h\nu \rightarrow$ products

The UV absorption spectrum of SO_2 is highly structured, with a very weak absorption in the 340-390 nm region, a weak absorption in the 260-340 nm, and a strong absorption extending from 180 to 235 nm; the threshold wavelength for photodissociation is ~220 nm. The atmospheric photochemistry of SO_2 has been reviewed by Calvert et al. (1978), the conclusion being that direct photooxidation at wavelengths longer than ~300 nm by way of the electronically excited states of SO_2 is relatively unimportant.

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

The absorption cross sections of OCS have been measured by Chou et al. (1979) between 186 and 226 nm, at 296, 251 and 232 K (the results are unpublished); 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; and by Molina et al. (1981) between 180 and 300 nm, at 295 and 225 K. The results are in good agreement in the regions of overlap, except for λ > 280 nm, where the cross section values reported by Rudolph and Inn (1981) are significantly larger than those reported by Molina et al. (1981). The latter authors concluded that solar photodissociation of OCS in the troposphere occurs only to a negligible extent.

The recommended cross sections, given in Table 36, are taken from Molina et al. (1981). (The original publication also lists a table with cross sections values averaged over 1 nm intervals, between 185 and 300 nm).

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

Table 36. Absorption Cross Sections of OCS

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

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

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.

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