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Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 6

NASA Panel for Data Evaluation:

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ABSTRACT

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

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

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

W. B. DeMore, Chairman (Chapman chemistry)

D. M. Golden (three-body reactions)

R. F. Hampson (halogen chemistry)

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

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 of 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 of 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 the Panel has provided estimates of rate constant parameters, based on analogy to similar reactions for which data are available.

DISCUSSION

General State of Laboratory Kinetics

There have been no major changes in stratospheric chemistry since the publication of our previous evaluation, JPL 82-57. There are approximately twenty changes in the rate constant recommendations in the present evaluation, but these are for the most part minor. Seventeen new reactions have been added, representing processes which play small but possibly significant roles in the stratosphere. Some important refinements have been made in certain key rate constants, such as those for $O + O_3$ and $OH + HCl$. These examples are typical of the set of critical reactions which were carefully measured about five or ten years ago, during the early stages of the stratospheric chemistry program. While these measurements have generally stood the test of time, it is appropriate to re-examine them to verify that the kinetic data being used in the models are as accurate as possible. Such refinements will go hand-in-hand with the improved reliability of field measurement methods for the in-situ measurement of trace species, permitting more exacting comparisons of the model with observation.

One important question which has been resolved during the past year is that of possible isomer formation in the $ClO + NO_2$ reaction. Recent experiments, discussed in more detail in the section on three-body reactions, indicate that chlorine nitrate is the sole product of the reaction.

O_x Reactions

The kinetics of the O, O_2, and O_3 system appear to be well established, although in the present evaluation a small change has been made in the rate parameters of the O + O_3 reaction. There remains some concern about possible roles of excited states of O_2, especially $O_2(^1\Delta)$, but at present there is no evidence that these states have any important effects on the overall chemistry of the stratosphere.

$O(^1D)$ Reactions

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

HO_x Reactions

Our knowledge of the kinetics of HO_x radicals has continued to improve. For example, several new studies have been reported on the HO_2 + HO_2 reaction. Although the reaction mechanism is complex and demonstrates both bimolecular and termolecular behavior, independent studies using different experimental techniques are in excellent agreement. Data on the temperature dependence are also consistent. More serious problems remain with the OH + HO_2 reaction, where there are indications of a pressure effect but there are few data on this and the temperature dependence. The reaction H + HO_2, which is important in the upper stratosphere, has been added to the evaluation (Table 1).

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.

Kinetic data for NH_2 reactions has been added to this evaluation. The status for this class of reactions is not so good as that for the other NO_x reactions. For nearly all NH_2 reactions the value of k at 298 K is uncertain by a factor of 2-3, the temperature dependences are not well defined, and the reaction mechanisms are complex and not well understood.

Halogen Chemistry

The recommendations for the important ClO_x reactions have not changed significantly since the previous evaluation (JPL 82-57). This reflects the fact that from the standpoint of the CFM-O_3 question many of the important rate constants have been measured reliably and recommendations can be made confidently. There may be minor changes in the rate constant recommendation for the reaction OH + HCl, since preliminary results from several new studies are slightly higher than the current recommended value. The table includes a new entry for the reaction of chlorine atoms with CH_3CCl_3. 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 released at the surface of the earth, and their degradation in the troposphere is initiated by reaction with OH (and with ozone in the case of olefins). Depending on their reactivity with OH, only a fraction of the surface flux of hydrocarbons is transported into the stratosphere where their oxidation serves as a source of water vapor. In addition, reaction of Cl atoms with these hydrocarbons (mainly CH_4) constitutes one of the major sink mechansims for active chlorine. Even though CH_4 is the predominant hydrocarbon in the stratosphere, we have included in this evaluation certain reactions of a few heavier hydrocarbon species.

In the stratosphere, CH_4 oxidation is initiated by its reaction with either OH or Cl (and to a limited extent $O(^1D)$), leading to formation of CH_3 and subsequently CH_3O_2. Several details of the subsequent chemistry are unclear, primarily because four key reactions are not well characterized. These reactions are: (1) $CH_3O_2 + HO_2$, which exhibits an unusual temperature dependence analogous to that for the $HO_2 + HO_2$ reaction; (2) $CH_3O + O_2$, which has not been directly studied at or below room temperature; (3) $CH_3OOH + OH$, which has been recently studied in a competitive system and found to be extremely rapid; and (4) OH + CO, whose pressure, O_2, and temperature dependence of the high pressure rate coefficient are uncertain. Even though the rate constants for the four 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 reasonably well known.

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

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

SO_x Reactions

There have been a number of changes and additions to this section on homogeneous sulfur chemistry. In particular, we now have more detailed information on the rates of oxidation of SO by O_2 and O_3. Nevertheless 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 still needed to fully assess the importance of SO reactions with species such as OH, HO_2, ClO, BrO, etc.

Several reactions which have been suggested as candidates for coupling the stratospheric chlorine and sulfur cycles have also been added. While the limited data base does not support a coupling hypothesis, in the absence of more detailed information we cannot presently rule it out (particularly for atmospheric regions perturbed by volcanic emissions).

More detailed evidence has been presented on the effect of molecular oxygen on the reactions of certain sulfur containing compounds. The role of the reaction of O_2 with electronically excited CS_2 has been documented as an important tropospheric loss mechanism of CS_2 and source of OCS. Quantitative information has now become available regarding the appreciable acceleration of the OH + CS_2 reaction as a function of total pressure, O_2 partial pressure, and temperature in a mixed N_2/O_2 environment. The results are strongly suggestive of the reaction of a CS_2-OH adduct intermediate 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. However, our understanding of atmospheric SH reactions, involved in the oxidation of

H_2S, is not well defined and suffers from the absence of relevant rate constant measurements. For example, the only loss mechanism for SH currently included in Table 1 is the reaction with O_2. Other reactions with HO_2 or O_3 may be important.

Another area of significant uncertainty is the oxidation of SO_2 into sulfuric acid and its potential depletion of HO_x radical concentrations. Three possible mechanistic pathways exist for this oxidation resulting in the loss of 0, 1, or 2 HO_x radicals for each H_2SO_4 formed. For example, in the scheme

$$OH + SO_2 \rightarrow HSO_3$$
$$OH + HSO_3 \rightarrow H_2O + SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

two OH radicals are lost for each H_2SO_4 formed. While the final reaction in this sequence is probably heterogeneous in nature, the initiation steps are most certainly homogeneous. If the second reaction is replaced by

$$HSO_3 + O_2 \rightarrow HO_2 + SO_3$$

the cycle leads to no net change in HO_x per H_2SO_4 formed. Another model involving HSO_5 as an intermediate species results in a net loss of one HO_x per H_2SO_4 formed. Clearly additional information is needed to fully understand aerosol formation via SO_2 oxidation.

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.

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

The chemistry of the upper stratosphere, i.e. 30-50 km, is thought to be reasonably well defined, although there appear to be some significant differences between the predicted and observed chemical 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. Historically, a major area of concern in the chemistry of the upper stratosphere has involved the reaction between HO and HO_2 radicals, which, as previously discussed in this section, has had considerable uncertainty in the rate constant. This HO_x termination reaction plays an important role in determining the absolute concentrations of HO and HO_2, and since HO plays a central role in controlling the catalytic efficiencies of both NO_x and ClO_x, it is a reaction of considerable importance. Recently the uncertainty in the rate coefficient for the reaction has decreased, now being thought to be about a factor of 1.5 over the entire range of atmospheric conditions. It should be noted that the $HO + H_2O_2$, $HO + HNO_3$ and $HO + HO_2NO_2$ reactions have little effect on controlling the HO_x concentrations above 30 km. For reactions such as $O + HO$ and $O + HO_2$, which control the HO_x radical partitioning above 40 km, the data base can only be considered to be quite good.

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

The chemistry of the lower stratosphere is quite complex, with significant coupling between the HO_x, NO_x and ClO_x families. 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. It is 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 (30-200 torr). The question of possible pressure and temperature dependences of HO and HO_2 reactions is highly pertinent here.

Our view of the chemistry of the lower stratosphere has changed in recent years, due to changes in rate constants which have in turn led to changes in the relative importance of reactions which control the HO_x budget in this region of the atmosphere. Prior to the appearance of improved kinetics data for the $HO + H_2O_2$, $HO + HNO_3$, and $HO + HO_2NO_2$ reactions, the major termination reaction for odd hydrogen species in models of the lower stratosphere was the $HO + HO_2 \rightarrow H_2O + O_2$ reaction. However, the $HO + HNO_3$ and $HO + NO_2NO_2$ reactions are now thought to play a vital role in controlling the HO_x radical concentration in the lower stratosphere. The species HNO_3, HO_2NO_2, $ClNO_3$ 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.

Heterogeneous Effects

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

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

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

In NASA Reference Publications 1010 and 1049, processes 1 and 2 above were discussed in general terms. It was shown that, with a few possibly significant exceptions, surface catalysis of chemical reactions is not expected to compete with the rates of homogeneous gas phase reactions. The essential reason was that the frequency of collision of a gas phase molecule with the aerosol surface is typically of the order of 10^4 to 10^5 sec^{-1}, whereas most of the key gas phase reactions, for example, conversion of atomic oxygen to O_2 by the $O + O_3$ reaction, occur with much greater frequency. Thus, even in the unlikely case of unit reaction efficiency on the aerosol surface the heterogeneous process cannot be significant. Possible exceptions occur for reactions which are extremely slow in the gas phase, such as hydrolysis of an anhydride, as in the reaction $N_2O_5 + H_2O \rightarrow 2HNO_3$. There remains some uncertainty with regard to the role of these latter processes.

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

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

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

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

RATE CONSTANT DATA

Format

In Table 1 (Rate Constants for Second Order Reactions) the reactions are 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 follows the same sequence.

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:

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

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

The rate constant tabulation for second-order reactions (Table 1) 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, $k_0(300)$, n, $k_\infty(300)$, and m. These can be found in Table 2. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources.

Low-Pressure Limiting Rate Constant [$k_x^o(T)$]

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

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

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:

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

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)]. A recent compilation (Patrick and Golden, 1983) gives details for reactions considered here.

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

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

Temperature Dependence of Low-Pressure Limiting Rate Constants n

The value of n recommended here comes from a calculation of $<\Delta E>_N$ from the data at 300 K, and a computation of β_{N_2} (200 K) assuming that $<\Delta E>_{N_2}$ is independent of temperature in this range. This β_{N_2}(200 K) value is combined with the computed value of k_0^{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_0(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 $k_0(T) = A_{exp}^{(-E/RT)}$ or the form $k_0(T) = A' T^{-n}$ 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 $\underline{n}$ and $\underline{m}$.

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.

Table 1. Rate Constants for Second Order Reactions.

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
		O_x Reactions			
✓ $O + O_2 \xrightarrow{M} O_3$	(See Table 2)				
* $O + O_3 \rightarrow O_2 + O_2$	8.0×10^{-12}	2060±250	8.0×10^{-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 82-57).

#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	7.4×10^{-11}	0±100	7.4×10^{-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±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
#H + $HO_2 \rightarrow$ products	7.4×10^{-11}	0±400	7.4×10^{-11}	1.6	13
$O + OH \rightarrow O_2 + H$	2.2×10^{-11}	-(117±100)	3.3×10^{-11}	1.2	14
$O + HO_2 \rightarrow OH + O_2$	3.0×10^{-11}	-(200±200)	5.9×10^{-11}	1.4	15
*$O + H_2O_2 \rightarrow OH + HO_2$	1.4×10^{-12}	2000±1000	1.7×10^{-15}	2.0	16
✓*$OH + HO_2 \rightarrow H_2O + O_2$	$(7+4P_{atm}) \times 10^{-11}$	0±500	$(7+4P_{atm}) \times 10^{-11}$	1.6	17
✓$OH + O_3 \rightarrow HO_2 + O_2$	1.6×10^{-12}	940±300	6.8×10^{-14}	1.3	18
✓$OH + OH \rightarrow H_2O + O$	4.2×10^{-12}	242±242	1.9×10^{-12}	1.4	19
$\xrightarrow{M} H_2O_2$	(See Table 2)				
✓*$OH + H_2O_2 \rightarrow H_2O + HO_2$	3.1×10^{-12}	187±200	1.7×10^{-12}	1.3	20
✓$OH + H_2 \rightarrow H_2O + H$	6.1×10^{-12}	2030±400	6.7×10^{-15}	1.2	21

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
✓*$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.3×10^{-13}	-(590±200)	1.7×10^{-12}	1.3	22
$\xrightarrow{M} H_2O_2 + O_2$	1.7×10^{-33}[M]	-(1000±400)	5×10^{-32}[M]	1.3	22
✓$HO_2 + O_3 \rightarrow OH + 2O_2$	1.4×10^{-14}	580^{+500}_{-100}	2.0×10^{-15}	1.5	23
		NO_x Reactions			
$N + O_2 \rightarrow NO + O$	4.4×10^{-12}	3220±340	8.9×10^{-17}	1.25	24
$N + O_3 \rightarrow NO + O_2$	-		$<1.0\times10^{-15}$	-	25
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}	0±100	3.4×10^{-11}	1.3	26
$N + NO_2 \rightarrow N_2O + O$	-	-	3.0×10^{-12}	3	27
$O + NO \xrightarrow{M} NO_2$	(See Table 2)				
$O + NO_2 \rightarrow NO + O_2$	9.3×10^{-12}	0^{+0}_{-150}	9.3×10^{-12}	1.1	28
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2)				
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0±150	1.0×10^{-11}	1.5	29
$O + N_2O_5 \rightarrow$ products	-	-	$<3.0\times10^{-16}$	-	30
✓$O + HNO_3 \rightarrow OH + NO_3$	-	-	$<3.0\times10^{-17}$	-	31
✓$O + HO_2NO_2 \rightarrow$ products	7.0×10^{-11}	3370±750	8.6×10^{-16}	3.0	32
✓*$O_3 + NO \rightarrow NO_2 + O_2$	1.8×10^{-12}	1370±200	1.8×10^{-14}	1.2	33
✓$NO + HO_2 \rightarrow NO_2 + OH$	3.7×10^{-12}	-(240±80)	8.3×10^{-12}	1.2	34
✓$NO + NO_3 \rightarrow 2NO_2$	-	-	2.0×10^{-11}	3.0	35
✓$OH + NO \xrightarrow{M} HONO$	(See Table 2)				

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
✓ $OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2)				---
✓ $OH + HNO_3 \rightarrow$ products	9.4×10^{-15}	$-(778\pm100)$	1.3×10^{-13}	1.3	36
✓ *$OH + HO_2NO_2 \rightarrow$ products	1.3×10^{-12}	$-(380^{+270}_{-500})$	4.6×10^{-12}	1.5	37
✓ $HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(See Table 2)				---
✓ $O_3 + NO_2 \rightarrow NO_3 + O_2$	1.2×10^{-13}	2450 ± 140	3.2×10^{-17}	1.15	38
✓ $O_3 + HNO_2 \rightarrow O_2 + HNO_3$	-	-	$<5.0\times10^{-19}$	-	39
✓ $NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(See Table 2)				
✓ #$OH + NH_3 \rightarrow H_2O + NH_2$	3.3×10^{-12}	900 ± 200	1.6×10^{-13}	1.4	40
✓ #$NH_2 + OH \rightarrow$ products	-	-	1.0×10^{-13}	10	41
#$NH_2 + HO_2 \rightarrow$ products	-	-	3.4×10^{-11}	2	42
✓ #$NH_2 + NO \rightarrow$ products	3.6×10^{-12}	$-(450\pm150)$	1.6×10^{-11}	2	43
#$NH_2 + NO_2 \rightarrow$ products	1.9×10^{-12}	$-(650\pm250)$	1.7×10^{-11}	3	44
#$NH_2 + O_2 \rightarrow$ products	-	-	$<3\times10^{-18}$	-	45
#$NH_2 + O_3 \rightarrow$ products	3.4×10^{-12}	1000 ± 500	1.2×10^{-13}	3	46
		ClO_x Reactions			
✓ $Cl + O_3 \rightarrow ClO + O_2$	2.8×10^{-11}	257 ± 100	1.2×10^{-11}	1.15	47
✓ $Cl + H_2 \rightarrow HCl + H$	3.7×10^{-11}	2300 ± 200	1.6×10^{-14}	1.25	48
✓ $Cl + CH_4 \rightarrow HCl + CH_3$	9.6×10^{-12}	1350 ± 150	1.0×10^{-13}	1.1	49
$Cl + C_2H_6 \rightarrow HCl + C_2H_5$	7.7×10^{-11}	90 ± 90	5.7×10^{-11}	1.1	50
$Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}	$-(40\pm250)$	1.6×10^{-10}	1.5	51

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$Cl + C_2H_2 \rightarrow$ products	-	-	1×10^{-12}	10	52
$Cl + CH_3OH \rightarrow CH_2OH + HCl$	6.3×10^{-11}	0±250	6.3×10^{-11}	2.0	53
✓ $Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	3.4×10^{-11}	1260±200	4.9×10^{-13}	1.2	54
#$Cl + CH_3CCl_3 \rightarrow CH_2CCl_3 + HCl$	-	-	$<4\times10^{-14}$	-	55
✓ $Cl + H_2CO \rightarrow HCl + HCO$	8.2×10^{-11}	34±100	7.3×10^{-11}	1.15	56
✓ $Cl + H_2O_2 \rightarrow HCl + HO_2$	1.1×10^{-11}	980±500	4.1×10^{-13}	1.5	57
$Cl + HOCl \rightarrow$ products	3.0×10^{-12}	130±250	1.9×10^{-12}	2.0	58
✓ *$Cl + HNO_3 \rightarrow$ products	-	-	$<1.7\times10^{-14}$	-	59
✓ $Cl + HO_2 \rightarrow HCl + O_2$	1.8×10^{-11}	-(170±200)	3.2×10^{-11}	1.5	60
$\rightarrow OH + ClO$	4.1×10^{-11}	450±200	9.1×10^{-12}	2.0	60
✓ $Cl + Cl_2O \rightarrow Cl_2 + ClO$	9.8×10^{-11}	0±250	9.8×10^{-11}	1.2	61
✓ $Cl + OClO \rightarrow ClO + ClO$	5.9×10^{-11}	0±250	5.9×10^{-11}	1.25	62
✓ *$Cl + ClONO_2 \rightarrow$ products	6.8×10^{-12}	-(160±200)	1.2×10^{-11}	1.3	63
✓ $Cl + NO \xrightarrow{M} NOCl$	(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	64
✓ $Cl + O_2 \xrightarrow{M} ClOO$	(See Table 2)				
✓ $Cl + ClOO \rightarrow Cl_2 + O_2$	1.4×10^{-10}	0±250	1.4×10^{-10}	3.0	65
✓ $\rightarrow ClO + ClO$	8.0×10^{-12}	0±250	8.0×10^{-12}	3.0	65
✓ $ClO + O \rightarrow Cl + O_2$	7.7×10^{-11}	130±130	5.0×10^{-11}	1.4	66

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
$ClO + NO \rightarrow NO_2 + Cl$	6.2×10^{-12}	$-(294\pm100)$	1.7×10^{-11}	1.15	67
$ClO + NO_2 \xrightarrow{M} ClONO_2$	(See Table 2)				
$ClO + HO_2 \rightarrow HOCl + O_2$	4.6×10^{-13}	$-(710^{+250}_{-700})$	5.0×10^{-12}	1.4	68
$ClO + H_2CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>2060	$<1.0\times10^{-15}$	-	69
*$ClO + OH \rightarrow$ products	9.2×10^{-12}	$-(66\pm200)$	1.2×10^{-11}	2	70
$ClO + CH_4 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	71
$ClO + H_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>4800	$<1.0\times10^{-19}$	-	71
$ClO + CO \rightarrow$ products	$\sim1.0\times10^{-12}$	>3700	$<4.0\times10^{-18}$	-	71
$ClO + N_2O \rightarrow$ products	$\sim1.0\times10^{-12}$	>4260	$<6.0\times10^{-19}$	-	71
$ClO + ClO \rightarrow$ products	-	-	-	-	72
$ClO + O_3 \rightarrow ClOO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	73
$\rightarrow OClO + O_2$	1.0×10^{-12}	>4000	$<1.0\times10^{-18}$	-	73
$OH + HCl \rightarrow H_2O + Cl$	2.8×10^{-12}	425 ± 100	6.6×10^{-13}	1.2	74
$OH + HOCl \rightarrow H_2O + ClO$	3.0×10^{-12}	150^{+850}_{-150}	1.8×10^{-12}	10	75
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	1.8×10^{-12}	1112 ± 200	4.3×10^{-14}	1.2	76
$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	4.5×10^{-12}	1032 ± 200	1.4×10^{-13}	1.2	76
$OH + CHCl_3 \rightarrow CCl_3 + H_2O$	3.3×10^{-12}	1034 ± 200	1.0×10^{-13}	1.2	76
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	8.9×10^{-13}	1013 ± 200	3.0×10^{-14}	1.3	76
$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	7.8×10^{-13}	1530 ± 200	4.6×10^{-15}	1.2	76
$OH + CH_2ClF \rightarrow CHClF + H_2O$	2.0×10^{-12}	1134 ± 150	4.4×10^{-14}	1.2	76

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued).

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
✓ $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$	5.4×10^{-12}	1820±200	1.2×10^{-14}	1.3	77
✓ $OH + C_2Cl_4 \rightarrow$ products	9.4×10^{-12}	1200±200	1.7×10^{-13}	1.25	78
$OH + C_2HCl_3 \rightarrow$ products	5.0×10^{-13}	-(445±200)	2.2×10^{-12}	1.25	79
$OH + CFCl_3 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3650	$<5.0\times10^{-18}$	-	80
$OH + CF_2Cl_2 \rightarrow$ products	$\sim1.0\times10^{-12}$	>3560	$<6.5\times10^{-18}$	-	80
✓ $OH + ClONO_2 \rightarrow$ products	1.2×10^{-12}	333±200	3.9×10^{-13}	1.5	81
✓ $O + HCl \rightarrow OH + Cl$	1.0×10^{-11}	3340±350	1.4×10^{-16}	2.0	82
✓ $O + HOCl \rightarrow OH + ClO$	1.0×10^{-11}	2200±1000	6.0×10^{-15}	10	83
✓ $O + ClONO_2 \rightarrow$ products	3.0×10^{-12}	808±200	2.0×10^{-13}	1.5	84
✓ $O + Cl_2O \rightarrow ClO + ClO$	2.9×10^{-11}	630±200	3.5×10^{-12}	1.4	85
✓ $O + OClO \rightarrow ClO + O_2$	2.5×10^{-11}	1160±300	5.0×10^{-13}	1.5	86
✓ $NO + OClO \rightarrow NO_2 + ClO$	2.5×10^{-12}	600±300	3.4×10^{-13}	1.5	87
		BrO_x Reactions			
✓ $Br + O_3 \rightarrow BrO + O_2$	1.4×10^{-11}	755±200	1.1×10^{-12}	1.2	88
✓ $Br + H_2O_2 \rightarrow HBr + HO_2$	$\sim1.0\times10^{-11}$	>2500	$<2.0\times10^{-15}$	-	89
✓ $Br + H_2CO \rightarrow HBr + HCO$	1.7×10^{-11}	800±200	1.1×10^{-12}	1.3	90
$Br + HO_2 \rightarrow HBr + O_2$	-	-	$>1\times10^{-13}$	-	91
✓ $BrO + O \rightarrow Br + O_2$	3.0×10^{-11}	0±250	3.0×10^{-11}	3.0	92
✓ $BrO + ClO \rightarrow Br + OClO$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	93
✓ $\rightarrow Br + Cl + O_2$	6.7×10^{-12}	0±250	6.7×10^{-12}	2.0	93

*Indicates a change from the previous Panel evaluation (JPL 82-57).

#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
✓ $BrO + NO \rightarrow NO_2 + Br$	8.7×10^{-12}	$-(265 \pm 130)$	2.1×10^{-11}	1.15	94
✓ $BrO + NO_2 \overset{M}{\rightarrow} BrONO_2$	(See Table 2)				
✓ $BrO + BrO \rightarrow 2\ Br + O_2$	1.4×10^{-12}	$-(150 \pm 150)$	2.3×10^{-12}	1.25	95
✓ $\rightarrow Br_2 + O_2$	6.0×10^{-14}	$-(600 \pm 600)$	4.4×10^{-13}	1.25	95
✓ $BrO + O_3 \rightarrow Br + 2\ O_2$	$\sim 1 \times 10^{-12}$	>1600	$<5.0 \times 10^{-15}$	-	96
✓ *$BrO + HO_2 \rightarrow$ products	-	-	5.0×10^{-12}	3.0	97
✓ *$BrO + OH \rightarrow$ products	-	-	1.2×10^{-11}	5.0	98
✓ $OH + HBr \rightarrow H_2O + Br$	8.0×10^{-12}	0 ± 250	8.0×10^{-12}	1.5	99
✓ $OH + CH_3Br \rightarrow CH_2Br + H_2O$	6.1×10^{-13}	825 ± 200	3.8×10^{-14}	1.25	100
✓ *$O + HBr \rightarrow OH + Br$	6.6×10^{-12}	1540 ± 200	3.7×10^{-14}	1.3	101
		FO_x Reactions			
$F + O_3 \rightarrow FO + O_2$	2.8×10^{-11}	226 ± 200	1.3×10^{-11}	2.0	102
$F + H_2 \rightarrow HF + H$	1.9×10^{-10}	570 ± 250	2.8×10^{-11}	1.3	103
$F + CH_4 \rightarrow HF + CH_3$	3.0×10^{-10}	400 ± 300	8.0×10^{-11}	1.5	104
$F + H_2O \rightarrow HF + OH$	2.2×10^{-11}	200 ± 200	1.1×10^{-11}	5.0	105
$F + O_2 \overset{M}{\rightarrow} FO_2$	(See Table 2)				
$F + NO \overset{M}{\rightarrow} FNO$	(See Table 2)				
$F + NO_2 \overset{M}{\rightarrow} FNO_2(FONO)$	(See Table 2)				
$NO + FO \rightarrow NO_2 + F$	2.6×10^{-11}	0 ± 250	2.6×10^{-11}	2.0	106
$FO + FO \rightarrow 2\ F + O_2$	1.5×10^{-11}	0 ± 250	1.5×10^{-11}	3.0	107

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
FO + O_3 → F + 2 O_2	-	-	-	-	108
→ FO_2 + O_2	-	-	-	-	108
FO + NO_2 $\xrightarrow{M}$ $FONO_2$	(See Table 2)				
O + FO → F + O_2	5.0×10^{-11}	0±250	5.0×10^{-11}	3.0	109
O + FO_2 → FO + O_2	5.0×10^{-11}	0±250	5.0×10^{-11}	5.0	110
		Hydrocarbon Reactions			
✓*OH + CO → CO_2 + H		See Note	$1.5\times10^{-13}(1+0.6P_{atm})$	1.4	111
✓OH + CH_4 → CH_3 + H_2O	2.4×10^{-12}	1710±200	7.7×10^{-15}	1.2	112
OH + C_2H_6 → H_2O + C_2H_5	1.9×10^{-11}	1260±250	2.7×10^{-13}	1.25	113
OH + C_3H_8 → H_2O + C_3H_7	1.6×10^{-11}	800±250	1.1×10^{-12}	1.5	114
OH + C_2H_4 → products	(See Table 2)				
OH + C_2H_2 → products	(See Table 2)				
✓OH + H_2CO → H_2O + HCO	1.0×10^{-11}	0±200	1.0×10^{-11}	1.25	115
✓*OH + CH_3OOH → products	1.0×10^{-11}	0±200	1.0×10^{-11}	2.0	116
✓#OH + HCN → products	1.2×10^{-13}	400±150	3.1×10^{-14}	3.0	117
#OH + CH_3CN → products	4.5×10^{-13}	750±300	3.7×10^{-14}	3.0	118
#HO_2 + CH_2O → adduct	-	-	4.5×10^{-14}	10.0	119
O + C_2H_2 → products	2.9×10^{-11}	1600±300	1.4×10^{-13}	1.3	120
O + H_2CO → products	3.0×10^{-11}	1550±250	1.6×10^{-13}	1.25	121
*O + CH_3 → products	1.1×10^{-10}	0±250	1.1×10^{-10}	1.3	122

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

$\xrightarrow{a}$ $CH_2OOH + H_2O \rightarrow HCHO + OH + H_2O$ $k_a = 4.35E-12$

$\xrightarrow{b}$ $CH_3O_2 + H_2O$ $k_b = 5.41E-12$

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
*$CH_3 + O_2 \rightarrow$ products	-	-	$<3\times10^{-16}$	-	123
$CH_3 + O_2 \overset{M}{\rightarrow} CH_3O_2$	(See Table 2)				
#$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	-	-	2×10^{-12}	10	124
✓*$CH_3O + O_2 \rightarrow CH_2O + HO_2$	1.2×10^{-13}	1350±500	1.3×10^{-15}	10	125
✓*$HCO + O_2 \rightarrow CO + HO_2$	3.5×10^{-12}	-(140±140)	5.5×10^{-12}	1.3	126
*$CH_3 + O_3 \rightarrow$ products	5.4×10^{-12}	220±150	2.6×10^{-12}	2	127
#$CH_3O_2 + O_3 \rightarrow$ products	-	-	$<1\times10^{-17}$		128
✓*$CH_3O_2 + CH_3O_2 \rightarrow$ products	1.6×10^{-13}	-(220±220)	3.4×10^{-13}	1.25	129
✓*$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	4.2×10^{-12}	-(180±180)	7.6×10^{-12}	1.2	130
$CH_3O_2 + NO_2 \overset{M}{\rightarrow} CH_3O_2NO_2$	(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	131
		SO_x Reactions			
✓$OH + H_2S \rightarrow SH + H_2O$	5.9×10^{-12}	65±65	4.7×10^{-12}	1.2	132
✓$OH + OCS \rightarrow$ products	1.3×10^{-12}	2300±500	6.0×10^{-16}	10	133
✓*$OH + CS_2 \rightarrow$ products	(See Note)	-	-	-	134
✓$OH + SO_2 \overset{M}{\rightarrow} HOSO_2$	(See Table 2)				
✓$O + H_2S \rightarrow OH + SH$	1.0×10^{-11}	1810±550	2.2×10^{-14}	1.7	135
✓$O + OCS \rightarrow CO + SO$	2.1×10^{-11}	2200±150	1.3×10^{-14}	1.2	136
✓$O + CS_2 \rightarrow CS + SO$	3.2×10^{-11}	650±150	3.6×10^{-12}	1.2	137
✓$O + SH \rightarrow H + SO$	-	-	1.6×10^{-10}	5.0	138

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

Table 1. (Continued)

Reaction	A-Factor	E/R±Δ(E/R)	k(298K)	Uncertainty Factor/298K	Notes
✓ $S + O_2 \rightarrow SO + O$	2.3×10^{-12}	0±200	2.3×10^{-12}	1.2	139
$S + O_3 \rightarrow SO + O_2$	-	-	1.2×10^{-11}	2.0	140
$S + OH \rightarrow SO + H$	-	-	6.6×10^{-11}	3.0	141
✓ *$SO + O_2 \rightarrow SO_2 + O$	2.4×10^{-13}	2370±500	8.4×10^{-17}	2	142
✓ *$SO + O_3 \rightarrow SO_2 + O_2$	3.6×10^{-12}	1100±200	9.0×10^{-14}	1.2	143
$SO + OH \rightarrow SO_2 + H$	-	-	8.6×10^{-11}	2.0	144
✓ $SO + NO_2 \rightarrow SO_2 + NO$	-	-	1.4×10^{-11}	1.3	145
$SO + ClO \rightarrow SO_2 + Cl$	-	-	2.3×10^{-11}	3.0	146
$SO + OClO \rightarrow SO_2 + ClO$	-	-	1.9×10^{-12}	3.0	146
$SO + BrO \rightarrow SO_2 + Br$	-	-	$>4.0 \times 10^{-11}$	-	146
✓ $SO_2 + HO_2 \rightarrow$ products	-	-	$<1.0 \times 10^{-18}$	-	147
✓ $CH_3O_2 + SO_2 \rightarrow$ products	-	-	$<5.0 \times 10^{-17}$	-	148
✓ $SH + O_2 \rightarrow OH + SO$	-	-	$<3.2 \times 10^{-15}$	-	149
#$Cl + H_2S \rightarrow HCl + SH$	-	-	7.3×10^{-11}	1.4	150
#$Cl + OCS \rightarrow SCl + CO$	-	-	$<1.1 \times 10^{-16}$	-	151
#$ClO + OCS \rightarrow$ products	-	-	$<2.4 \times 10^{-16}$	-	151
#$ClO + SO_2 \rightarrow Cl + SO_3$	-	-	$<4.0 \times 10^{-18}$	-	151

*Indicates a change from the previous Panel evaluation (JPL 82-57).

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

NOTES TO TABLE 1

1. $O + O_3$. Changed from JPL 82-57 to include the new results of Wine et al., (1983). The recommended rate expression is from Wine et al. and is a linear least squares fit of all data (unweighted) from Davis et al. (1973), McCrumb and Kaufman (1972), West et al. (1978), Arnold and Comes (1979), and Wine et el. (1983). Compared to the previous recommendation, the new rate is 9% lower at 298 K and 9% higher at 220 K.

2. $O(^1D)$ Reactions. These recommendations are based on averages of the absolute rate constant measurements reported by Streit et al. (1976), Davidson et al. (1977) and Davidson et al. (1978) for N_2O, H_2O, CH_4, H_2, N_2, O_2, O_3, HCl, CCl_4, $CFCl_3$, CF_2Cl_2, NH_3, and CO_2; by Amimoto et al. (1978), Amimoto et al. (1979), and Force and Wiesenfeld (1981a,b) for N_2O, H_2O, CH_4, N_2, H_2, O_2, O_3, CO_2, CCl_4, $CFCl_3$, CF_2Cl_2, and CF_4; by Wine and Ravishankara (1981) and (1982) for N_2O, H_2O, N_2, H_2, O_3, CO_2, and CF_2O; by Brock and Watson (1980c) 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. Wine and Ravishankara (1982) have determined the yields of $O(^3P)$ from $O(^1D)$ collisions: H_2O (4.9 ± 3.2%), N_2O (<4.0%), CH_4 (<4.3%), and H_2 (<4.9%).

3. $O(^1D) + N_2O$. The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or NO + NO is an average of the values reported by Davidson et al. (1979); Volltrauer et al. (1979); Marx et al.

(1979) and Lam et al. (1981). 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 1966b). $O(^1D)$ translational energy and temperature dependence effects are not clearly resolved.

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

5. $O(^1D) + CH_4$. 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. $O(^1D) + O_3$. The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al. (1972). This is supported by measurements of Amimoto et al. (1978) who reported that on average one ground state O is produced per $O(^1D)$ reaction with O_3. It seems unlikely that this could result from 100% quenching of the $O(^1D)$ by O_3.

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

8. $O(^1D)$ + halocarbons. 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, 1981a); for $CFCl_3$: quenching = (13±4)% and reaction = (87±4)% (Force and Wiesenfeld, 1981a), 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, 1981a).

9. $O(^1D) + CCl_2O$, CFClO and CF_2O. For the reactions of $O(^1D)$ with CCl_2O and CFClO the recommended rate constants are derived from data of Fletcher and Husain (1978). For consistency, the recommended values for these rate constants were derived using a scaling factor (0.5) which corrects for the difference between rate constants from the Husain Laboratory and the recommendations for other $O(^1D)$ rate constants in this table. The recommendation for CF_2O is from data of Wine and Ravishankara (1983). Their result is preferred over the value of Fletcher and Husain (1978) because it appears to follow the pattern of decreased reactivity with increased fluorine substitution observed for other halocarbons. These reactions have been studied only at 298 K. Based on consideration of similar $O(^1D)$ reactions, it is assumed that E/R equals zero, and therefore the value shown for the A-factor has been set equal to k(298 K).

10. $O(^1D) + NH_3$. Sanders et al. (1980a) 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. $O(^1D)$ + HF. 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. $H + O_3$. The recommendation is an average of the recent results of Lee et al. (1978b) and Keyser (1979), which are in excellent agreement over the 200-400 K range. An earlier study by Clyne and Monkhouse (1977) is in very good agreement on the T dependence in the range 300-650 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. $H + HO_2$. New entry. There are four recent studies of this reaction: Hack et al. (1978b), Hack et al. (1979c), Thrush and Wilkinson (1981b), and Sridharan et al. (1982). Related early work and combustion studies are referenced in the latter paper. All four studies used discharge flow systems. It is difficult to obtain a direct measurement of the rate constant for this reaction because both reactants are radicals and the products OH and O are very reactive toward the HO_2 reactant. The recommendation is based on the data of Sridharan et al. because their measurement was the most direct and required the fewest corrections. The other measurements, $(5.0 \pm 1.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} by Thrush and Wilkinson (1981b) and $(4.65 \pm 1) \times 10^{-11}$ by Hack et al. (1979c) are in reasonable agreement with the recommended value. Hack et al. (1978b) and Sridharan et al. (1982) reported 3 product channels: (a) 2OH, (b) $H_2O + O$, and (c) $H_2 + O_2$. The former gave $k_a/k = 0.69$, $k_b/k \lesssim 0.02$, and $k_c/k = 0.29$ and the latter gave $k_a/k = 0.87 \pm$

0.04, $k_b/k = 0.04 \pm 0.02$, and $k_c/k = 0.09 \pm .045$. Hislop and Wayne (1977) reported on the possibility of $O_2(b^1\Sigma)$ being formed in channel (c) in $(2.8 \pm 1.3) \times 10^{-4}$ of the total reactions. There are no studies of the temperature dependence of the rate constant or the product ratios in the range of atmospheric interest. It is likely that the dominant channel at room temperature, (a), which occurs on a radical-radical recombination surface will increase with decreasing temperature and that the others which involve insertion or abstraction will decrease with increasing temperature. Further high quality studies are needed.

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

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

16. $O + H_2O_2$. There are two direct studies of the $O + H_2O_2$ reaction:

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

17. $OH + HO_2$. Three measurements of the rate constant at low pressure (1-3 torr) in discharge-flow systems all give values near 7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}: Keyser (1981), Sridharan et al. (1981), and Temps and Wagner (1982). The latter two studies supersede earlier work which reported lower values from the same laboratories, Chang and Kaufman (1978) and Hack et al. (1978a). Separate studies at pressures near one atmosphere obtain consistently a larger rate constant, about 1.1×10^{-10}: Lii et al. (1980a), Hochanadel et al. (1980), DeMore (1982), Cox et al. (1981) and Braun et al. (1982). DeMore (1982) reports rate constants that increase from about 7×10^{-11} at 75 torr to about 1.2×10^{-10} at 730 torr. The present recommendation is for a rate constant that increases linearly with pressure from 7×10^{-11} at low pressure to 1.1×10^{-10} at one atmosphere. Other studies by Burrows et al. (1981), Kurylo et al. (1981), and Thrush and Wilkinson (1981a) 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. Preliminary low pressure results from Sridharan et al. (1983) indicate $E/R \simeq -400$. Further direct studies of the temperature and pressure dependences and products of this reaction are required.

18. $OH + O_3$. The recommendation for the $OH + O_3$ rate constant is based on the room temperature measurements of Kurylo (1973) and Zahniser and Howard (1980) and the temperature dependence studies of

Anderson and Kaufman (1973) and Ravishankara _et al_. (1979b). Kurylo's value was adjusted (-8%) to correct for an error in the ozone concentration measurement (Hampson and Garvin, 1977). The Anderson and Kaufman rate constants were normalized to $k = 6.3 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 295K as suggested by Chang and Kaufman (1978).

19. OH + OH. 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) $\times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The temperature dependence is from Wagner and Zellner, who reported rate constants for the range T = 250-580K.

20. OH + H_2O_2. 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_. (1981c) and Kurylo _et al_. (1982b). The first two references contain a discussion of some possible reasons for the discrepancies with earlier work and an assessment of the impact of the new value on other kinetic studies. A measurement at 298 K by Marinelli and Johnston (1982a) agrees with the recommendation. There is some evidence that the E/R decreases with temperature, therefore the recommendation incorporates a large error limit on the temperature dependence.

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

22. $HO_2 + HO_2$. Two separate expressions are given for the rate constant for the $HO_2 + HO_2$ reaction. The effective rate constant is given by the sum of these two equations. This reaction has been shown to have a pressure independent bimolecular component and a pressure dependent termolecular component. Both components have negative temperature coefficients. The bimolecular expression is obtained from data of Cox and Burrows (1979), Thrush and Tyndall (1982a,b), Kircher and Sander (1983), and Takacs and Howard (1983). Earlier results of Thrush and Wilkinson (1979) are inconsistent with these data. The termolecular expression is obtained from data of Sander et al. (1982), Simonaitis and Heicklen (1982) at room temperature and Kircher and Sander (1983) for the temperature dependence. This equation applies to M = air. On this reaction system there is general agreement among investigators on the following aspects of the reaction at high pressure ($P \sim 1$ atm): (a) the HO_2 uv absorption cross section: Paukert and Johnston (1972), Cox and Burrows (1979), Hochanadel et al. (1980), and Sander et al. (1982); (b) the rate constant at 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 $(2.5 \text{ to } 4.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}); (c) the rate constant temperature dependence: Cox and Burrows (1979), Lii et al. (1979), and Kircher and Sander (1983); (d) the rate constant water vapor dependence: Hamilton (1975), Hochanadel et al. (1972), Hamilton and Lii (1977), Cox and Burrows (1979), DeMore (1979), Lii et al. (1981), and Sander et al. (1982); (e) the H/D isotope effect: Hamilton and Lii (1977) and Sander et al. (1982); and (f)

the formation of $H_2O_2 + O_2$ as the major products at 300K: Su et al. (1979), Niki et al. (1980), Sander et al. (1982), and Simonaitis and Heicklen (1982). Recent measurements by Sahetchian et al. (1982) give evidence for the formation of a small amount of H_2 in this system. For systems containing water vapor, the factors given by Lii et al. (1981) and Sander et al. (1982) can be incorporated.

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

24. $N + O_2$. Unchanged from JPL 82-57. 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.

25. $N + O_3$. Unchanged from JPL 82-57. 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).

26. N + NO. Unchanged from JPL 82-57. 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.

27. $N + NO_2$. Changed from JPL 82-57. Accepts the results of Clyne and Ono (1982) for the value of the rate constant at 298 K. This is a factor of 2 higher than that reported by Clyne and McDermid (1975). However, Clyne and Ono consider that the more recent study

is probably more reliable. Husain and Slater (1980) reported a room temperature rate constant of 3.8×10^{-11} cm^3 $molecule^{-1}$ s^{-1} which is a factor of 12 greater than the value reported by Clyne and Ono. This high value may indicate the presence of catalytic cycles as discussed by Clyne and McDermid, and Clyne and Ono. There are no studies of the temperature dependence of the rate constant. The reaction products are taken to be $N_2O + O$ (Clyne and McDermid).

28. $O + NO_2$. Unchanged from JPL 82-57. Based on results of Davis *et al*. (1973a), Bemand *et al*. (1974) and Slanger *et al*. (1973), there may be a slight negative temperature coefficient, but the evidence at low temperature is uncertain.

29. $O + NO_3$. Unchanged from JPL 82-57. 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.

30. $O + N_2O_5$. Unchanged from JPL 82-57. Based on Kaiser and Japar (1978).

31. $O + HNO_3$. Unchanged from JPL 82-57. Accepts the upper limit reported by Chapman and Wayne (1974).

32. $O + HO_2NO_2$. Unchanged from JPL 82-57. 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.

33. $O_3 + NO$. Unchanged from JPL 82-57. The recommended Arrhenius expression is a least squares fit to the data reported by Birks *et al*. (1976), Lippmann *et al*. (1980), Ray and Watson (1981b), Michael *et al*.

(1981) and Borders and Birks (1982) at and below room temperature, with the data at closely spaced temperatures reported in Lippmann et al. and Borders and Birks being grouped together so that these five studies are weighted equally. This expression fits all the data within the temperature range 195-304K reported in these five 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., Michael et al. and Borders and Birks). Clough and Thrush, Birks et al., Schurath et al. (1981), and Michael et al. have all reported individual Arrhenius parameters for each of the two primary reaction channels. The range of values for k at stratospheric temperatures is somewhat larger than would be expected for such an easy reaction to study. The measurements of Stedman and Niki (1973) and Bemand et al (1974) of k at 298K are in excellent agreement with the recommended value of k at 298K.

34. $NO + HO_2$. Unchanged from JPL 82-57. 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.

35. $NO + NO_3$. Unchanged since JPL 82-57. Value reported by Graham and Johnston (1978).

36. $OH + HNO_3$. Unchanged from JPL 82-57. Even though there have been several recent studies of this reaction, all of the reported data are not completely 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_. (1982b), Margitan and Watson (1982), Marinelli and Johnston (1982a), Ravishankara _et al_. (1982), Jourdain _et al_. (1982) and Smith _et al_. (1983) 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 (1983). 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_., Marinelli and Johnston and Smith _et al_.) 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 $\geq$ 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 x 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 x 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.and Smith et al., who reported linear Arrhenius behavior from 251-403K and 240-370K, respectively. 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.

37. OH + HO_2NO_2. Unchanged from JPL 82-57. Recommendation for both k at 298K and the Arrhenius expression based upon the data of Trevor et al. (1982), Barnes et al. (1981) and Smith et al. (1983). 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, Smith et al. studied the reaction over the temperature range 240-330 K and observed a negative

temperature dependence with an E/R value of -(650±30)K. Barnes et al. only studied the reaction at room temperature. The values of k at 298K from the three studies are in excellent agreement. An unweighted least squares fit to all the experimental data of Trevor et al., Barnes et al., and Smith et al. yields the recommended Arrhenius expression. The large difference in E/R values may be due to the reaction being complex and having different E/R values at low pressure, i.e., <1 torr (Trevor et al.) and high pressures (760 torr (Smith et al.)). The less precise value for k at 298 K reported by Littlejohn and Johnston (1980) is in fair agreement with the recommended value. The error limits on the recommended E/R are sufficient to encompass the results of both Trevor et al. and Smith et al. It should be noted that the values of k at 220 K deduced from the two studies differ by a factor of 2. Clearly additional studies of k as a function of temperature, and the identification of the reaction products are needed.

38. $O_3 + NO_2$. Unchanged from JPL 82-57. Based on least squares fit to data in studies of Davis et al. (1974b), Graham and Johnston (1974) and Huie and Herron (1974).

39. $O_3 + HNO_2$. Unchanged from JPL 82-57. Based on Kaiser and Japar (1977) and Streit et al. (1979).

40. $OH + NH_3$. New entry. The recommended value at 298K is the average of the values reported by Stuhl (1973b), Smith and Zellner (1975), Perry et al. (1976b), and Silver and Kolb (1980). The values reported by Kurylo (1973), Hack et al. (1974), Pagsberg et al. (1979) and Cox et al. (1975) were not included. The temperature dependence is based on the results reported by Hack et al., Smith and Zellner, Perry et al., and Silver and Kolb, and the preexponential factor has been selected to fit the recommended room temperature value.

41. NH_2 + OH. New entry. No experimental data exist. Based upon mechanistic and thermodynamic considerations, the reaction is expected to be quite rapid, probably producing NH and H_2O

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

43. NH_2 + NO. New entry. The recommended value for k at 298K is the average of the values reported by Gordon _et al_. (1971), Gehring _et al_. (1973), Lesclaux _et al_., (1975), Hancock _et al_., (1975), Sarkisov _et al_. (1978), Hack _et al_. (1979b), Stief _et al_. (1982) and Silver and Kolb (1982). The values reported in these studies for k at 298K range from 8.3 to 27.0 (x 10^{-12}) cm^3 $molecule^{-1}$ s^{-1}, which is not particularly satisfactory. The results tend to separate into two groups. The flash photolysis results average 1.9 x 10^{-11} $cm3$ $molecule^{-1}$ s^{-1}, while those obtained using the discharge flow technique average 0.9 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. The apparent discrepancy cannot simply be due to a pressure effect as the pressure ranges of the flash photolysis and discharge flow studies overlapped, and none of the studies observed a pressure dependence for k. There have been four studies of the temperature dependence of k. Each study reported k to decrease with increasing temperature, i.e. $T^{-1.25}$ (Lesclaux _et al_. from 300-500K), $T^{-1.85}$ (Hack _et al_. from 210-503K), $T^{-1.67}$ exp(-684/T) (Silver and Kolb from 294-1215K). The recommended temperature dependence is taken to be a weighted average of the data below 500K from all four studies. The expression is: k = 1.6 x 10^{-11} $(T/298)^{-1.5}$ for the temperature range 210-500K.

While there are many conceivable reaction channels, the channel yielding H_2O and N_2 appears to be the dominant channel with strong vibrational excitation of the product H_2O observed by Gehring et al., and more recently by Wolfrum et al. (1981). To date atomic hydrogen has not been observed as a reaction product, suggesting that the channel producing N_2 + H + OH is of limited importance. The hydroxyl radical has been observed by both Silver and Kolb, and Wolfrum et al. However, while Silver and Kolb reported a yield of 40% for OH production, Wolfrum et al. tentatively placed an upper limit of 15% on OH production. Stief et al. failed to observe OH production and placed an upper limit of 22% on OH production in agreement with Wolfrum et al. Clearly more work on this reaction is required.

44. $NH_2 + NO_2$. New entry. There have been two studies of this reaction (Hack et al. (1979b), and Kurasawa and Lesclaux (1979)). There is very poor agreement between these two studies both for k at 298K (factor of 2.3) and for the temperature dependence of k ($T^{-3.0}$ and $T^{-1.3}$). The recommended values of k at 298K and the temperature dependence of k are averages of the results reported in these two studies. Hack et al. have shown that the predominant reaction channel (>95%) produces $N_2O + H_2O$.

45. $NH_2 + O_2$. New entry. There have been five studies of this reaction. Upper limits have been reported by Lesclaux and Demissy (1977), Pagsberg et al. (1979), and Cheskis and Sarkisov (1979) of 2×10^{-18}, 8×10^{-15} and 1.5×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively. Jayanty et al. (1976) reported a lower limit of 4×10^{-15} cm^3 molecule^{-1} s^{-1} from a relative study. Hack et al. (1982) reported that there was an association reaction between NH_2 and O_2 from 295-353K whose rate constant could be expressed: $k = 3.6 \times 10^{-33}$ $(T/295)^{-2.0}$ cm^6 molecule^{-2} s^{-1}. Lesclaux (1982) restudied this reaction under the conditions employed by Hack et al. and reported

that there was no detectible reaction at room temperature. The upper limit recommended is based on the study of Lesclaux and Demissy.

46. $NH_2 + O_3$. New entry. There have been three studies of this reaction, by Kurasawa and Lesclaux (1980a), Bulatov et al. (1980), and Hack et al. (1981). The vaues of k at 298K vary by a factor of three and the values of E/R reported by Kurasawa and Lesclaux, and Hack et al. differ by a factor of ~2. The recommended values of k at 298K and E/R are averages of the reported data. Bulatov et al., and Hack et al. observed a deviation of first order decay kinetics at higher pressures of O_3 and in both instances interpreted the observations to indicate that the principal reaction channel leads to formation of $NH_2O + O_2$ which is followed by the reaction of NH_2O with O_3 to regenerate NH_2.

47. $Cl + O_3$. Unchanged from JPL 82-57. 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.

48. $Cl + H_2$. Unchanged from JPL 82-57. This Arrhenius expression is based on the data below 300K reported by Watson <u>et al</u>. (1975), Lee <u>et al</u>. (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 <u>et al</u>. and those of Miller and Gordon agree well (after extrapolation) with the results of Benson <u>et al</u>. (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 <u>et al</u>. (1980). Miller and Gordon also measured the rate of the reverse reaction, and the ratio was found to be in good agreement with equilibrium constant data. Results of a new study by Kita and Stedman (1982) are in excellent agreement with this recommendation. They also measured the rate of the reverse reaction and found the ratio to be in good agreement with equilibrium constant data.

49. $Cl + CH_4$. Unchanged from JPL 82-57. The values reported from the thirteen absolute rate coefficient studies for k at 298K fall in the range (0.99 to 1.48) $\times 10^{-13}$, with a mean value of 1.15×10^{-13}. However, based upon the stated confidence limits reported in each study, the range

of values far exceeds that to be expected. A preferred average value of 1.04×10^{-13} can be determined from the absolute rate coefficient studies for k at 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 $(0.95 - 1.13) \times 10^{-13}$, with an average value of 1.02×10^{-13}. The preferred value of 1.04×10^{-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 $(2.64\text{-}3.32) \times 10^{-14}$. The mean of the two discharge flow values (Zahniser et al. (1978) and Keyser (1978)) is 2.67×10^{-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.

50. Cl + C_2H_6. Unchanged from JPL 82-57. 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.

51. Cl + C_3H_8. Unchanged from JPL 82-57. 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 these obtained in the competitive chlorination studies of Pritchard et al. (1955) and Knox and Nelson (1959).

52. Cl + C_2H_2. Unchanged from JPL 82-57. Since abstraction would be endotherm 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.

53. Cl + CH_3OH. Unchanged from JPL 82-57. 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).

54. Cl + CH_3Cl. Unchanged from JPL 82-57. 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 ($> 2 \times 10^{-10}$).

55. Cl + CH_3CCl_3. New reaction. There has been only one study of this rate, that by Wine et al. (1982) using a laser flash photolysis-resonance fluorescence technique. It was concluded that the presence of a reactive

impurity accounted for a significant fraction of the Cl removal, and therefore only upper limits to the rate were reported for the temperature range 259-356K. This reaction is too slow to be of any importance in atmospheric chemistry.

56. Cl + H_2CO. Unchanged from JPL 82-57. 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.

57. Cl + H_2O_2. Unchanged from JPL 82-57. 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.

58. Cl + HOCl. Unchanged from JPL 82-57. 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.

59. Cl + HNO_3. Changed from JPL 82-57. Since the previous evaluation there have been two studies of this rate, in which the decay of Cl atoms in excess HNO_3 was monitored by resonance fluorescence (Kurylo et al., 1983b) or by resonance absorption (Clark et al., (1982). Both report values higher than those obtained in earlier discharge flow-mass spectrometric studies by Leu and DeMore (1976) and by Poulet et al. (1978a) which monitored the decay of HNO_3 in excess Cl. Kurylo et al. report a value for E/R of 1700K for the temperature range 243-298K. Poulet et al. report a value for E/R of 4380K for the temperature range 439-633K. The higher temperature data of Poulet et al. are not directly applicable to stratospheric conditions, and extrapolation to room temperature may not be valid. The preferred value is based on assuming that the room temperature data of Kurylo et al. represents an upper limit. The higher value reported by Clark et al. is based on data which exhibit significant scatter and is not considered in deriving the preferred value.

60. Cl + HO_2. Unchanged from JPL 82-57. The recommendations for the two reaction channels are based upon the recent results by Lee and Howard (1982) using a discharge flow system with laser magnetic resonance detection of HO_2, OH and ClO. The total rate constant is temperature independent with a value of $(4.2\pm0.7) \times 10^{-11}$ 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.

61. Cl + Cl_2O. Unchanged from JPL 82-57. The preferred value of 9.8×10^{-11} $cm^3 molecule^{-1} s^{-1}$ was determined from two independent absolute rate coefficient studies reported by Ray _et al_. (1980), using the discharge flow-resonance fluorescence and discharge flow-mass spectrometric techniques. This value has been confirmed by Burrows and Cox (1981) who determined the ratio $k(Cl + Cl_2O)/k(Cl + H_2) = 6900$ in modulated photolysis experiments. The earlier value reported by Basco and Dogra (1971a) has been rejected. The Arrhenius parameters have not been experimentally determined; however, the high value of k at 298 K precludes a substantial positive activation energy.

62. Cl + OClO. Unchanged from JPL 82-57. Data reported by Bemand, Clyne and Watson (1973).

63. Cl + $ClONO_2$. Minor change from JPL 82-57. Recent flash photolysis/resonance fluorescence studies by Margitan (1983a) and by Kurylo _et al_. (1983a) which are in good agreement show that the rate constant for this reaction is almost two orders of magnitude faster than that indicated by the previous work of Kurylo and Manning (1977) and Ravishankara _et al_. (1977b). It is probable that the slower reaction observed by Kurylo and Manning was actually O + $ClNO_3$, not Cl + $ClNO_3$. The preferred value averages the results of

the two new studies.

64. Cl + ClNO. Unchanged from JPL 82-57. This value is based on the discharge flow-resonance fluorescence study of Clyne and Cruse (1972) and the flash photolysis-resonance fluorescence study of Nelson and Johnston (1981). Grimley and Houston (1980) reported a value which is lower than this preferred value by a factor of four. This low value may be due to adsorption of ClNO on the vessel walls in their static experiment. There are no reliable data on the temperature dependence. A new study by Kita and Stedman (1982) using the same technique as that of Clyne and Cruse (1972) report a value which is a factor of three higher than the preferred value. However, there are insufficient data reported to assess the reliability of this result, and the preferred value has therefore been left unchanged.

65. Cl + ClOO. Unchanged from JPL 82-57. Values of 1.56×10^{-10}, 9.8×10^{-11}, and 1.67×10^{-10} have been reported for $k_a(\mathrm{Cl} + \mathrm{ClOO} \rightarrow \mathrm{Cl_2} + \mathrm{O_2})$ by Johnston et al. (1969), Cox et al. (1979), and Ashford et al. (1978), respectively. Values of 108, 20.9, 17, and 15 have been reported for $k_a(\mathrm{Cl} + \mathrm{ClOO} \rightarrow \mathrm{Cl_2} + \mathrm{O_2})/k(\mathrm{Cl} + \mathrm{ClOO} \rightarrow 2\ \mathrm{ClO})$ by Johnston et al., Cox et al., Ashford et al., and Nicholas and Norrish (1968). Obviously the value of 108 by Johnston et al. is not consistent with the others, and the preferred value of 17.6 was obtained by averaging the other three values (this is in agreement with a value that can be derived from a study by Porter and Wright (1953)). The absolute values of k_a and k_b are dependent upon the choice of ΔH°_f (ClOO) (the values of ΔH°_f (ClOO) reported by Cox et al. and Ashford et al. are in excellent agreement, i.e. 22.7 and 22.5 kcal/mol, respectively). The preferred value of $k_a(\mathrm{Cl} + \mathrm{ClOO} \rightarrow \mathrm{Cl_2} + \mathrm{O_2})$ is taken to be the average of the three reported values, i.e. 1.4×10^{-10} $\mathrm{cm^3\ molecule^{-1}s^{-1}}$. Consequently, the preferred value of $k_b(\mathrm{Cl} + \mathrm{ClOO} \rightarrow 2\ \mathrm{ClO})$ is $k_a/17.6$, i.e. 8.0×10^{-12} $\mathrm{cm^3\ molecule^{-1}s^{-1}}$. The E/R values are estimated to be zero, which is consistent with other experimentally determined E/R values for atom-

radical reactions.

66. O + ClO. Unchanged from JPL 82-57. The recommended rate constant is base on the experimental data of Bemand _et al_. (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.

67. ClO + NO. Unchanged from JPL 82-57. The absolute rate coefficients determined in the four discharge flow mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978), Ray and Watson (1981a) and Clyne and MacRobert (1980)) and the discharge flow laser magnetic resonance study Lee _et al_. (1982) are in excellent agreement at 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_.

68. ClO + HO_2. Unchanged from JPL 82-57. 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_., 1978b), 3.8 ± 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.

69. ClO + H_2CO. Unchanged from JPL 82-57. 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.

70. ClO + OH. Changed from JPL 82-57, which recommendation was based on preliminary, uncorrected results of a discharge flow-resonance fluorescence temperature dependent study, which is now published (Ravishankara _et al._ (1983a)) and a similar study at room temperature by Leu and Lin (1979). In the published paper by Ravishankara _et al._, the preliminary values have been corrected for interference due to OH regeneration by the reaction Cl + $HO_2 \rightarrow$ OH + ClO. The same correction applied to the published results of Leu and Lin gives a room temperature value in very good agreement with Ravishankara

et al.'s corrected value (M. T. Leu, private communication). 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.

71. ClO Reactions. Unchanged from JPL 82-57. 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.

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

73. $ClO + O_3$. Unchanged from JPL 82-57. The branching ratio between the two channels is not known, but, for the present discussion, is assumed to be unity. The Arrhenius parameters were estimated, and the upper limit rate constants are based on data reported by DeMore, Lin and Jaffe (1976) and by Wongdontri-Stuper et al. (1979).

74. OH + HCl. Unchanged from JPL 82-57. There is good agreement between six groups of workers at ~298K (Takacs and Glass (1973c), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), Hack et al. (1977) and Husain et al. (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 _et al._, Ravishankara _et al._, and Smith and Zellner. There have been several very recent studies of this rate. Preliminary values by Molina, by Ravishankara, and by Keyser are all higher than the preferred value, and therefore the error limit has been increased slightly.

75. OH + HOCl. Unchanged from JPL 82-57. 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.

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

The preferred values shown in this review were obtained by first fitting all of the absolute rate data for each reaction (except Clyne and Holt (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 $AT^2exp(-B/T)$ 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 $k = AT^2exp(-B/T)$ 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 82-57. The preferred values were obtained using only absolute rate coefficient data. The data of Howard and Evenson (1976a), Davis et al. (1976), Perry et al. (1976a), Paraskevopoulos et al. (1981) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. Fitting the data to an expression of the form $AT^2exp(-B/T)$ results in the equation 3.49×10^{-18} $T^2exp(-582/T)$ over the temperature range (247-483)K. This results in a preferred value of $4.40 \times 10^{-14} cm^3$ $molecule^{-1}s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.81 \times 10^{-12}exp(-1112/T)$.

$OH + CH_2Cl_2$

Unchanged from JPL 82-57. 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 $AT^2exp(-B/T)$ 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 $1.41 \times 10^{-13} cm^3$ $molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $4.45 \times 10^{-12} \exp(-1032/T)$.

OH + $CHCl_3$

Unchanged from JPL 82-57. The preferred values were obtained using only absolute rate coefficient data. The accuracy of the OH + CH_4/ OH + $CHCl_3$ study (Cox *et al.* (1976a)) was probably no better than a factor of 2. The data of Howard and Evenson (1976a), Davis *et al.* (1976) and Jeong and Kaufman (1982) are in good agreement and were used to determine the preferred values. Fitting the data to an expression of the form $AT^2 \exp(-B/T)$ results in the equation $6.3 \times 10^{-18} \exp(-504/T)$ 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 3.27×10^{-12} $\exp(-1034/T)$.

OH + $CHFCl_2$

Unchanged from JPL 82-57. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Perry *et al.* (1976a), Watson *et al.* (1977), Chang and Kaufman (1977a), Paraskevopoulos *et al.* (1981) and Jeong and Kaufman (1982). The data of Clyne and Holt (1979b) was not considered as it is in rather poor agreement with the other data within the temperature range studied, e.g. there is a difference of ~65% at 400 K. Fitting the data to an expression of the form $AT^2 \exp(-B/T)$ results in the equation $1.71 \times 10^{-18}\, T^2 \exp(-483/T)$ over the temperature range 241-483 K. This results in a preferred value of $3.0 \times 10^{-14} cm^3 molecule^{-1} s^{-1}$ 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 82-57. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Atkinson *et al*. (1975), Watson *et al*. (1977), Chang and Kaufman (1977a), Handwerk and Zellner (1978), Paraskevopoulos *et al*. (1981) and Jeong and Kaufman (1982), which are in good agreement. The data of Clyne and Holt (1979b) was not considered as it is in rather poor agreement with the other data within the temperature range studied, except at 298 K (the reported A-factor of $\sim 1 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ is inconsistent with that expected theoretically). Fitting the data to an expression of the form $AT^2 exp(-B/T)$ results in the equation $1.51 \times 10^{-18}\ T^2 exp(-1000/T)$ over the temperature range 250-482 K. This results in a preferred value of $4.68 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $0.78 \times 10^{-12} exp(-1530/T)$.

OH + CH_2FCl

Unchanged from JPL 82-57. The preferred values were derived using the absolute rate coefficient data reported by Howard and Evenson (1976a), Watson *et al*. (1977), Handwerk and Zellner (1978), Paraskevopoulos *et al*. (1981) and Jeong and Kaufman (1982) which are in fair agreement. Fitting the data to an expression of the form $AT^2 exp(-B/T)$ results in the equation $3.77 \times 10^{-18}\ T^2 exp(-604/T)$ over the temperature range 245-486 K. This results in a preferred value of $4.41 \times 10^{-14}\ cm^3\ molecule^{-1} s^{-1}$ for k at 298 K. The derived Arrhenius expression centered at 265 K is $1.96 \times 10^{-12} exp(-1134/T)$.

77. OH + CH_3CCl_3. Unchanged from JPL 82-57. 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.

78. OH + C_2Cl_4. Unchanged from JPL 82-57. 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.

79. OH + C_2HCl_3. Unchanged from JPL 82-57. 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).

80. OH + $CFCl_3$ and OH + CH_2Cl_2. Unchanged from JPL 82-57. 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.

81. OH + $ClONO_2$. Unchanged from JPL 82-57. 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.

82. O + HCl. Unchanged from JPL 82-57. 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 those reported by Balakhnin _et al_.

83. O + HOCl. Unchanged from JPL 82-57. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.

84. O + $ClONO_2$. Unchanged from JPL 82-57. The results reported by Molina _et al_. (1977b) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara _et al_. (1977b) at 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.

85. O + Cl_2O. Minor change from JPL 82-57. Recommendation averages the reslts of Miziolek and Molina (1978) for 236-295K with the approximately 30 percent lower values of Wecker _et al_. (1982) over the same temperature range. Earlier results by Basco and Dogra (1971a) and Freeman and Phillips (1968) have not been included in the

derivation of the preferred value due to data analysis difficulties in both studies.

86. O + OClO. Unchanged from JPL 82-57. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

87. NO + OClO. Unchanged from JPL 82-57. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

88. Br + O_3. Unchanged from JPL 82-57. The results reported for k (298K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael _et al._ (1978) and Michael and Payne (1979) are in excellent agreement. The preferred value at 298 K is derived by taking a simple mean of these four values. The temperature dependences reported for k by Leu and DeMore, Michael _et al._ and Michael and Payne can only be considered to be in fair agreement. There is a spread of 25% in k at 200 K and 50% at 360 K. Although the results reported by Michael _et al._ and Michael and Payne are in good agreement, there is no reason at present to discard the results of Leu and DeMore. Therefore, until further results are reported, the preferred value was synthesized to best fit all the data reported from these four studies.

89. Br + H_2O_2. Unchanged from JPL 82-57. Using the discharge flow-mass spectrometric technique Leu (1980a), and Posey _et al._ (1981) determined an upper limit for k of $\sim 2 \times 10^{-15}$ at ~298 K. Leu also reported an upper limit for k of 3×10^{-15} at 417 K. An estimate of the Arrhenius expression would be $<1 \times 10^{-11}\exp(-2500/T)$. The A-factor was chosen to be consistent with that determined for the Cl + H_2O_2 reaction, and the E/R value was calculated to yield the upper limit at 298 K.

90. Br + H_2CO. Unchanged from JPL 82-57. 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.).

91. Br + HO_2. Unchanged from JPL 82-57. 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.

92. BrO + O. Unchanged from JPL 82-57. 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.

93. BrO + ClO. Unchanged from JPL 82-57. 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).

94. BrO + NO. Unchanged from JPL 82-57. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1981a) and Leu (1979) and the high pressure uv absorption study

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

95. BrO + BrO. Unchanged from JPL 82-57. There are two possible bimolecular channels for this reaction: $BrO + BrO \rightarrow 2Br + O_2$ (k_1) and $BrO + BrO \rightarrow Br_2 + O_2$ (k_2). The total rate constant for disappearance of BrO ($k = k_1 + k_2$) has been studied by a variety of techniques, including discharge flow-ultraviolet absorption (Clyne and Cruse, 1970a), discharge flow-mass spectrometry (Clyne and Watson, 1975) and flash photolysis-ultraviolet absorption (Basco and Dogra, 1971b; Sander and Watson, 1981b). Since this reaction is second order in [BrO], those studies monitoring [BrO] by ultraviolet absorption required the value of the cross section σ to determine k. There is substantial disagreement in the reported values of σ. Although the magnitude of σ is dependent upon the particular spectral transition selected and instrumental parameters such as spectral bandwidth, the most likely explanation for the large differences in the reported values of σ is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies were used incorrectly (see discussion by Clyne and Watson). The recent study of Sander and Watson used totally independent methods to determine the values of σ and (σ/k). The recommendations for k_1 and k_2 are consistent with a recommendation of $k = 1.14 \times 10^{-12}$

exp(+255/T) cm^3 $molecule^{-1}$ s^{-1}. This temperature dependence is the corrected value from Sander and Watson, and the pre-exponential has been chosen to fit the value of k(298K) = 2.7 x 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 $k(=k_1 + k_2)$.

96. $BrO + O_3$. Unchanged from JPL 82-57. Based on a study reported by Sander and Watson (1981b). Clyne and Cruse (1970a) also reported an upper limit of 8 x $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 $<10^{-18}$ $cm^3 molecule^{-1} s^{-1}$.

97. $BrO + HO_2$. Unchanged from JPL 82-57 in which the preferred value was based on value of $k(ClO + HO_2)$. Cox and Sheppard (1982) have studied the rate of this reaction in an investigation of the photolysis of O_3 in the presence of Br_2, H_2, and O_2 using the molecular modulation - ultraviolet absorption technique. Although the reported value is not very precise, it does show that this reaction occurs and at a rate comparable to that for $ClO + HO_2$. By analogy with the $ClO + HO_2$ system, the products may be expected to be $HOBr + O_2$.

98. $BrO + OH$. Changed from JPL 82-57. Value chosen to be consistent with $k(ClO + OH)$, due to the absence of any experimental data.

99. $OH + HBr$. Unchanged from JPL 82-57. 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.

100. $OH + CH_3Br$. Unchanged from JPL 82-57. 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 1.17×10^{-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).

101. O + HBr. Changed from JPL 82-57. Results of the recent flash photolysis-resonance fluorescence study of Nava et al. (1983) for 221-455K provide the only data at stratospheric temperatures. The previous recommendation was based on results reported by Singleton and Cvetanovic (1978) for 298-554K by a phase-shift technique, and on discharge flow results of Brown and Smith (1975) for 267-430K and of Takacs and Glass at 298K. The preferred value is based on the results of Nava et al. and those of Singleton and Cvetanovic over the same temperature range, since these results are less subject to complications due to secondary chemistry than are the results using discharge flow techniques. The uncertainty at 298K has been set to encompass these latter results.

102. F + O_3. Unchanged from JPL 82-57. 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.

103. F + H_2. Unchanged from JPL 82-57. 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}.

104. F + CH_4. Unchanged from JPL 82-57. 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. Since the previous evaluation there has been one study of this reaction, by Fasano and Nogar (1982). The reported value at 298K is 30% lower than the preferred value, well within the stated uncertainty limits. The preferred value is based on results of five studies and inclusion of this new result does not change the preferred value.

105. F + H_2O. Unchanged from JPL 82-57. 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).

106. NO + FO. Unchanged from JPL 82-57. This is the value reported by Ray and Watson (1981a) for k at 298K using the discharge flow-mass spectro-

metric 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.

107. FO + FO. Unchanged from JPL 82-57. 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.

108. $FO + O_3$. Unchanged from JPL 82-57. 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 $FO + FO \rightarrow 2 F + O_2$ (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 $F + 2 O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts

with ozone rather than with either FO or itself). Wagner _et al_ utilized a low pressure discharge flow-mass spectrometric system to study the F + O_3 and FO + FO reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the FO + O_3 reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$, or 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.

109. O + FO. Unchanged from JPL 82-57. 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)).

110. O + FO_2. Unchanged from JPL 82-57. 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.

111. OH + CO. The recommendation allows for an increase in k with pressure. The zero pressure value was derived by averaging all direct low pressure determinations (those listed in Baulch *et al.* (1980) and the values reported by Dreier and Wolfrum (1980), Husain *et al.* (1981), and Ravishankara and Thompson (1983)). An increase in k with pressure has been observed by a large number of investigators (Overend and Paraskevopoul (1977a), Perry *et al.* (1977), Chen *et al.* (1977), Bierman *et al.* (1978), Cox *et al.* (1976b), and Butler *et al.* (1978)). There are a large number of inconsistencies in these data, however. Bierman *et al.* (1978) found the rate coefficient to be dependent on both pressure and presence of O_2 (or other impurities). Recent measurements by Paraskevopoulos and Irwin (1982a indicate that the pressure effects are seen in the absence of O_2. DeMore (1983) reported a similar lack of dependence on O_2 when N_2 was the pressurizing gas, and found less than a 10% increase in k when pressure of Argon diluent was changed from ~50 torr to ~760 torr, both in the presence and absence of O_2.

Refinements in the rate coefficient data for the OH + HO_2 and OH + H_2O_2 reactions require reinterpretation of many of the above mentioned studies. For example, the possibility of the OH + HO_2 reaction causing interference in the studies of Bierman *et al.* needs to be considered. The study of Butler *et al.* can be reevaluated by using the value of k(OH + H_2O_2) recommended here to yield the rate coefficients for OH + CO of 1.5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 100 torr increasing to 3.7×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 600 torr of synthetic air.

The weight of the present evidence suggests that there is no O_2 effect, but there is a pressure effect. The exact value of the high pressure limit and the pressure at which it is reached remain undefined. In the absence of such data, the recommended value is quite uncertain (~40%). Until proven otherwise, the E/R value is assumed to be zero.

112. OH + CH_4. This is an extremely well characterized reaction. All

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

113. OH + C_2H_6. There is excellent agreement between five studies of this reaction at 298K, i.e., Greiner (1970a), Howard and Evenson (1976b), Overend et al. (1975), Lee and Tang (1982) and Tully et al. (1983). k(298K) is the average of these five measurements. The temperature dependence was computed by using the data of Greiner (1970a) and Tully et al. (1983).

114. OH + C_3H_8. There are five measurements of the rate coefficient at 298K; Greiner (1970a), Gorse and Volman (1974), Bradley et al. (1973), Overend et al. (1975), and Tully et al. (1983). Gorse and Volman measured k(OH + C_3H_8) relative to k(OH + CO) in the presence of O_2 and calculated k(OH + C_3H_8) assuming that k(OH + CO) = 1.5×10^{-13} cm^3 molecule^{-1} s^{-1}. If the current recommended value for k(OH + CO) at high pressure is used, k(OH + C_3H_8) will be approximately 4×10^{-12} cm^3 molecule^{-1} s^{-1}. Therefore the results of Overend et al. (1975) ($k = 2 \times 10^{-12}$ cm^3 s^{-1}) and Gorse and Volman are in disagreement with the other values. The most probable cause for the discrepancy is the presence of secondary reactions in their system. The 298K value is the average of the three studies. Only Greiner (1970a) and Tully et al. (1983) have measured the temperature dependence of this reaction, and the recommended E/R was obtained from a linear least squares analysis of the data below 500 K. The A factor was adjusted to reproduce k(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:

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

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

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

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

117. OH + HCN. New entry. This reaction is pressure dependent. The recommended value is the high pressure limit measured by Lorenz *et al.* (1983) using a laser photolysis-resonance fluorescence apparatus. Phillips (1978) studied this reaction using a discharge flow apparatus at low pressures and found the rate coefficient to have reached the high pressure limit at ~10 torr at 298K. Lorenz *et al.*'s results contradict this finding. They agree with Phillips' measured value, within a factor of two, at 7 torr but they find k to increase further with pressure. The products of

the reaction are unknown. The measured A factor appears to be low.

118. OH + CH_3CN. New entry. This rate coefficient has been measured in the temperature range 298-424K by Harris et al. (1981) using flash photolysis-resonance fluorescence method. Zellner (1983) has measured (k_{298}), using flash photolysis-resonance fluorescence method, to be approximately a factor of two lower than that determined by Harris et al. The recommended E/R is that of Harris et al. k(298K) is the average of Harris et al.'s and Zellner's values. The A factor has been adjusted to reproduce k(298K). The products of the reaction are unknown. The measured A factor appears to be low.

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

120. O + C_2H_2. The value at 298K is an average of nine measurements; Arrington et al. (1965), Sullivan and Warneck (1965), Brown and Thrush (1967), Hoyermann et al. (1967), Westenberg and deHaas (1969b), James and Glass (1970), Stuhl and Niki (1971), Westenberg and deHaas (1977) and Aleksandrov et al. (1981). 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. Under molecular beam conditions C_2HO has been shown to be the major product. However, a recent study by Aleksandrov _et al_. using a discharge flow-resonance fluorescence method (under undefined pressure conditions) indicates that the CH_2O + H channel contributes no more than 7% to the net reaction at 298K.

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

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

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

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

125. $CH_3O + O_2$. 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 413 to 608K. Cox _et al_. (1980) used an end product analysis technique to measure k down to 298K. The previous high temperature measurements (Barker _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_. (1980b). 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).

126. $HCO + O_2$. The value of k(298K) is the average of the determinations by Washida _et al_. (1974), Shibuya _et al_. (1977), Veyret and Lesclaux

126. HCO + O_2. 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 (1983). There are three measurements of k where HCO was monitored via the intracavity dye laser technique (Reilly _et al_. (1978), Nadtochenko _et al_. (1979), and Gill _et al_ (1981)). Even though there is excellent agreement between these three studies, they yield consistently lower values than those obtained by other techniques. There are several possible reasons for this discrepancy. (a) The relationship between [HCO] and laser attenuation might not be linear, (b) there could have been depletion of O_2 in the static systems that were used (as suggested by Veyret and Lesclaux), and (c) these experiments were designed more for the study of photochemistry than kinetics. Therefore, these values are not included in obtaining the recommended value. The recommended temperature dependence is essentially identical to that measured by Veyret and Lesclaux. We have expressed the temperature dependence in an Arrhenius form even though the authors preferred a T^n form ($k = 5.5 \times 10^{-11}\ T^{-(0.4\pm0.3)}$ cm^3 $molecule^{-1}$ s^{-1}).

127. CH_3 + O_3. The recommended A factor and E/R are those obtained from the results of Ogryzlo _et al_. (1981). The results of Simonaitis and Heicklen (1975) based on an analysis of a complex system have been neglected. Washida _et al_. (1980b) used O + C_2H_4 as the source of CH_3. Recent results (Buss _et al_. (1981), Kleinermanns and Luntz (1981), Hunziker _et al_. (1981), and Inoue and Akimoto (1981)) have shown the O + C_2H_4 reaction to be a poor source of CH_3. Therefore, the results of Washida _et al_. are also neglected.

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

129. CH_3O_2 + CH_3O_2. 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

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.,

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

FTIR studies by Kan *et al.* (1980) and Niki *et al.* (1981) are in reasonable agreement on branching ratios at 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.

130. CH_3O_2 + NO. The value of k(298K) is the average of those determined by Sander and Watson (1980), Ravishankara *et al.* (1981a), 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.* (1981a) and Simonaitis and Heicklen (1981) have measured the temperature dependence of k over limited temperature ranges. The recommended A factor and E/R were obtained by a least squares analysis of the data from the two studies. The value of k(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. (1981a) 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.

131. $CH_3O_2 + HO_2$. The room temperature value is that of Cox and Tyndall (1979, 1980). This study also reports a large negative E/R value over a temperature range 274 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.

132. $OH + H_2S$. The value of k(298) is an average of the rate constants reported by Perry et al. (1976b), Cox and Sheppard (1980), Wine et al. (1981a), Leu and Smith (1982a), and Michael et al. (1982). The value of E/R is taken from a composite unweighted least squares fit to the individual data points from these same five studies. The study 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 data from the very recent study by Lin (1982) are in excellent agreement with the present recommendation They also show a slight non-Arrhenius behavior. The weight of evidence from these recent measurements suggests that the earlier study by Westenberg and deHaas (1973b) was in error (quite possibly due to secondary reactions). The room temperature value of Stuhl (1974) lies just outside the 2σ error limit set for k(298).

133. OH + OCS. 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).

134. OH + CS_2. There appears to be a consensus of experimental evidence indicating that this reaction proceeds very slowly as a direct bimolecular process. Based on the study by Wine et al. (1980), an upper limit on k(298) of 1.5×10^{-15} can be set. This determination is consistent with the upper limit reported by Iyer and Rowland (1980) for the rate of direct production of OCS in an OH + CS_2 reaction system suggesting that OCS and SH are the primary products of the bimolecular process. This mechanistic interpretation is further supported by the studies of Leu and Smith (1982b) and Biermann et al. (1982) which set upper limits on k(298) somewhat higher than Wine et al. (1980). The more rapid reaction rates observed by Atkinson et al. (1978), Kurylo (1978), and Cox and Sheppard (1980) may be attributed to severe complications arising from excited state and secondary chemistry in their photolytic systems. The Cox and Sheppard study in particular may have been affected by the reaction of electronically excited CS_2 (produced via the 350 nm photolysis) with O_2 (in the 1 atmosphere synthetic air mix). The

importance of this reaction in the tropospheric photooxidation of CS_2 to OCS has been suggested by Wine _et al_. (1981d).

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

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

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

The effective second order rate constant of CS_2 or OH removal in such a scheme can be written as

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

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

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

$$k(298) = 3.2 \times 10^{-15}\ P\ \mathrm{cm^3\ molec^{-1}\ s^{-1}}$$

for air mixtures (i.e. $P_{O_2}/P_{N_2} = 0.25$) where P (the total pressure) is expressed in torr. The uncertainty factor at 298K has been set to encompass the synthetic air data of Jones *et al.*

$$f_{298} = 1.5$$

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

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

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

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

135. O + H_2S. This recommendation is derived from an unweighted least squares fit of the data of Singleton et al. (1979) and Whytock et al. (1976). The results of Slagle et al. (1978) show very good agreement for E/R in the temperature region of overlap (300-500K) 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, $\Delta E/R$ 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 additional channel (resulting in H atom displacement) has been proposed for this reaction by Slagle et al. (1978), Singleton et al. (1979), and Singleton et al. (1982). In the two Singleton studies an upper limit of 20% is placed on the displacement channel. Direct observation of product HSO was made in the recent reactive scattering experiments of Clemo et al. (1981) and Davidson et al. (1982). A threshold energy of 3.3 Kcal/mole was observed (similar to the activation energy measured in earlier studies) suggesting the importance of this direct displacement channel. Addition products from this reaction have been seen in a matrix by Smardzewski and Lin (1977). Further kinetic study in the 200 to 300K range as well as quantitative direct mechanistic information could clarify these issues. This reaction is thought to be of limited stratospheric importance, however.

136. O + OCS. The value for k (298 K) is the average of five different studies

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

137. O + CS_2. The value of k (298 K) is the average of seven determinations: Wei and Timmons (1975), Westenberg and de Haas (1969a), Slagle _et al_. (1974a), Callear and Smith (1967), Callear and Hedges (1970), Homann _et al_. (1968), and Graham and Gutman (1977). The E/R value is an average of those determined by Wei and Timmons (1975) and Graham and Gutman (1977). 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.

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

139. S + O_2. 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.

140. S + O_3. This recommendation accepts the only available experimental

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

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

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

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

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

145. SO + NO_2. The value of k(298) is an average of the measurements by Clyne and MacRobert (1980) and Black et al. (1982a) which agree quite

well with the rate constant calculated from the relative rate measurements of Clyne _et al_. (1966).

146. SO + OClO. 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.

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

148. CH_3O_2 + SO_2. This recommendation accepts results from the study of Sander and Watson (1981a), which is believed to be the most appropriate study for stratospheric modeling purposes among those which have been conducted. Their experiments were conducted using much lower CH_3O_2 radical concentrations than in the earlier studies of Sanhueza _et al_. (1979) and Kan _et al_. (1979), both of which resulted in k(298) values approximately 100 times larger. A more recent report by Kan _et al_. (1981) postulates that these differences are due to 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.

149. $SH + O_2$. 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. A pulse radiolysis study by Nielsen (1979) sets an upper limit for k(298) approximately 2.5 times greater than that found by Tiee *et al.* (1981).

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

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

Similarly, the upper limit on k(298) for the ClO + OCS reaction was set from the minimum detectible decrease of ClO in this reaction system. No products were observed.

The recommended upper limit on k(298) for the $ClO + SO_2$ reaction is based on the authors' estimate of their detectibility for SO_3. Other estimates of k at 298K and 220K, based on the minimum detectible decrease in ClO, have not been used because of the potential problem of ClO reformation from the Cl + O_3 source reaction.

Table 2. Rate Constants for Three-Body Reactions

Reaction	Low Pressure Limit $k_o(T) = k_o^{300}(T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		Notes
	k_o^{300}	n	k_∞^{300}	m	
✓$O + O_2 \overset{M}{\rightarrow} O_3$	(6.0±0.5)(-34)	2.3±0.5	-	-	1
$^{+}O(^1D) + N_2 \overset{M}{\rightarrow} N_2O$	(3.5±3.0)(-37)	$0.6^{+2}_{-.6}$	- -	-	2
✓$^{+}H + O_2 \overset{M}{\rightarrow} HO_2$	(5.5±0.5)(-32)	1.6±0.5	- -	-	3
$^{+}OH + OH \overset{M}{\rightarrow} H_2O_2$	(6.9±3.0)(-31)	$0.8^{+2.0}_{-0.8}$	(1.0±0.5)(-11)	1.0±1.0	4
$O + NO \overset{M}{\rightarrow} NO_2$	(1.2±0.3)(-31)	1.8±0.5	(3.0±1.0)(-11)	0±1	5
$O + NO_2 \overset{M}{\rightarrow} NO_3$	(9.0±1.0)(-32)	2.0±1.0	(2.2±0.3)(-11)	0±1	6
✓$^{*}OH + NO \overset{M}{\rightarrow} HONO$	(7.0±2.0)(-31)	2.6±1.0	(1.5±1.0)(-11)	0.5±0.5	7
✓$^{+}OH + NO_2 \overset{M}{\rightarrow} HNO_3$	(2.6±0.3)(-30)	3.2±0.7	(2.4±1.2)(-11)	1.3±1.3	8
✓$HO_2 + NO_2 \overset{M}{\rightarrow} HO_2NO_2$	(2.3±0.2)(-31)	4.6±1.0	(4.2±1.0)(-12)	0±2.0	9
✓$NO_2 + NO_3 \overset{M}{\rightarrow} N_2O_5$	(2.2±1.1)(-30)	2.8±1.0	(1.0±0.8)(-12)	0±1.0	10
✓$^{+}Cl + NO \overset{M}{\rightarrow} ClNO$	(9.0±2.0)(-32)	1.6±0.5	- -	-	11
$^{+}Cl + NO_2 \overset{M}{\rightarrow} ClONO$	(1.6±0.6)(-30)	2.0±1.0	(1.0±0.5)(-10)	1.0±1.0	12
$+ \quad \overset{M}{\rightarrow} ClNO_2$	(2.2±1.2)(-31)	2.0±1.0	(1.0±0.5)(-10)	1.0±1.0	12
✓$^{+}Cl + O_2 \overset{M}{\rightarrow} ClOO$	(2.0±1.0)(-33)	1.4±1.4	- -	-	13
✓$ClO + NO_2 \overset{M}{\rightarrow} ClONO_2$	(1.8±0.3)(-31)	3.4±1.0	(1.5±0.7)(-11)	1.9±1.9	14
✓$BrO + NO_2 \overset{M}{\rightarrow} BrONO_2$	(5.0±2.0)(-31)	2.0±2.0	(1.0±0.5)(-11)	1.0±1.0	15

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

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

+Minor changes from JPL 82-57 for consistency with calculations of Patrick and Golden (1983).

*Changed from JPL 82-57.

Table 2. (Continued).

	Low Pressure Limit $k_o(T) = k_o^{300}\ (T/300)^{-n}$		High Pressure Limit $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$		
Reaction	k_o^{300}	n	k_∞^{300}	m	Notes
+$F + O_2 \xrightarrow{M} FO_2$	(1.6±0.8)(-32)	1.4±1.0	- -	-	16
$F + NO \xrightarrow{M} FNO$	(5.9±3.0)(-32)	1.7±1.7	- -	-	17
$F + NO_2 \xrightarrow{M}$ Products	(3.3±1.7)(-30)	2.0±2.0	(2.0±1.0)(-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
✓ $CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(6.0±3.0)(-31)	2.0±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)	3.4±1.5	(2.0±1.5)(-12)	0±1.0	22
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(3.7±2)(-28)	3.1±2.0	(8.8±0.9)(-12)	0^{+0}_{-2}	23
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(3.5±2)(-29)	3.5±2.0	(8.0±1.0)(-13)	$-2.6^{+2.6}_{-1.5}$	24

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.

+Minor changes from JPL 82-57 for consistency with calculations of Patrick and Golden (1983).

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 previous 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 $\langle\Delta E\rangle_N \sim .05$ kcal mole^{-1}. This very low number reflects rotational effects.

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

5. 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 Evenson (1974), Harris and Wayne (1975), Atkinson et al. (1975), Overend et al. (1976), Anastasi and Smith (1978), and Burrows et al. (1983). The general agreement is good, and the recommended value is a weighted average, with heavy weighting to the work of Anastasi and Smith. The reported high pressure limit rate constant is generally obtained from extrapolation. The recommended value is a weighted average of the reports in Anastasi and Smith (1978) and Anderson et al. (1974). [Both cis and trans - HONO are formed.]

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 $n = 3.2$ comes from $\langle\Delta E\rangle_{N_2} = 0.55$ kcal mole^{-1}. (This value is consistent with the experiments.) Burrows et al. (1983) confirm the value of 295 K. The high-pressure limit and T-dependence come from RRKM model of Smith and Golden (1978), although the error limits have been expanded to encompass $m = 0$.

   Robertshaw and Smith (1982) have measured k up to 8.6 atmospheres of CF_4. Their work suggests that k_∞ might be higher than suggested here (~50%). This might also be due to other causes (i.e., isomer formation or involvement of excited electronic states). The recommendation 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 (1978b), who used 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, and $\Delta H_{f,298} = -14.1$ 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 $k_o{}^{300}$ = 3.7×10^{-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. A recent study in O_2 (Fowles _et_ _al_. 1982) is in rough agreement for the high pressure limit.

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_. (1966).

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_. (1978c) saw two products with ClONO dominating. $\beta = 0.28$ was arrived at by dividing the sum of k_{sc} for both paths

into measured rate constant for overall reaction of Cl + NO_2. [Both cis and trans - ClONO are formed.] 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 $<\Delta E>$.

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).

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

The high-pressure limit rate constants and their temperature dependence are from the model of Smith and Golden (1978). The rate constants above fit measured rate data for the disappearance of reactants (Cox and Lewis, 1979; Dasch *et al.*, 1981). Data from 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.

    Even though isomer formation seems to have been ruled out for the $ClO + NO_2$ reaction (i.e. the isomer stability is too low to make a significant contribution to the measured rate constant), this does not eliminate the possibility that $BrO + NO_2$ leads to more than one stable compound. In fact, if the measured value of k_o is accepted, it can only be theoretically reconciled with a single isomer, $BrONO_2$, which would have a 6-7 kcal mole^{-1} stronger bond than $ClONO_2$! This would fix the heat of formation of $BrONO_2$ to be the same as $ClONO_2$, an unlikely possibility.

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

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

17. Parameters estimated from strong collision calculations with $\langle \Delta E \rangle$ set at .42 kcal/mole^{-1}, yielding $\beta = .30$ at 300K and $\beta = .38$ at 200K. T-dependence as per text.

18. Low-pressure limit rate constant from strong collision calculation and $\beta = 0.30$. T-dependence from constant $\langle \Delta E \rangle = 0.42$ kcal mole^{-1}. High-pressure limit and T-dependence are estimated by analogy to $Cl + NO_2$, assuming the same relative stability of the analogous isomers (i.e. FONO is formed more rapidly than FNO_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.

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

20. Low pressure limit from recent reports of Plumb and Ryan (1982) and Selzer and Bayes (1983) who each report $k_o \sim 3 \times 10^{-31}$ cm^{-6} sec^{-1} in He. 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._ (1980a).

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

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

    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
$F_c = e^{-T/320} + e^{-1280/T}$; $F_c = .41$ 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 from Baulch et al. (1980). Temperature dependence from $\beta = .07$ ($E = .24$ kcal mole^{-1}) as forced by the data. They suggest a value of $F_c = 0.7$. In a supplementary review, Baulch et al. (1982) suggest that $F_c = 0.55$ at 300K and is temperature dependent, such that $F_c = 0.67$ at 200K, and they raise $k_\infty 300$ 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. Recent work of Leu (1982) and Ravishankara (1983) are in excellent agreement with the recommended values.

23. Experimental data of Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970a), Morris et al. (1971) and Overend and Paraskevopolous (1977b) in helium, Atkinson et al. (1977) in argon and Lloyd et al. (1976) and Cox (1975) in nitrogen/oxygen mixtures, have been considered in the evaluation. All data are for $T > 290$ K.

The low-pressure limiting rate constant and its temperature dependence are from calculations of the type discussed earlier and in Patrick and Golden (1983). Most of the data is close to the high pressure limit and relatively insensitive to k_o.

The value of the high-pressure limiting rate constant and its temperature dependence were arrived at from the same data base as above.

The consensus value of k_∞ is already so high, that is unlikely to have much temperature dependence. This is not a radical-radical reaction, such as all the previous entries in Table 2, and is unlikely to have a positive value of m. The extreme limit of m = -2 corresponds to a real activation energy of ~1 kcal $mole^{-1}$.

24. 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 (1971), and Pastrana and Carr (1974). There is poor agreement between these three studies. 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), Michael _et al_. (1980), and Perry and Williamson (1982) who found k(298K) to increase up to a pressure of ~200 torr of argon and then reach a pressure-independent value.

The recommended values fit the temperature and pressure dependence of the latter three reports, when the differences between Ar and N_2 as bath gases are considered.

The low pressure limiting rate constant and its temperature dependence are calculated as always. Thermo-chemical parameters are adjusted within reason to fit the data.

The high pressure rate constant and its temperature dependence are from Michael _et al_. (1980), extrapolated downward in temperature. The error limits on m reflect the positive activation energy requirement.

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 equations were then used to calculate the parameters A and B:

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

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

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

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^{-27}	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

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

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.

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

2. 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:

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

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. (This value favored by k_o calculation, see Note 16, Table 2.)
   (b) From Benson's (1976) thermochemical values.

6. Thermochemical values at 300 K for $CH_3O_2NO_2$ and CH_3O_2 are from

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

PHOTOCHEMICAL DATA

Discussion of Format and Error Estimates

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

For some other species having highly structured spectra, such as CS_2, SO_2 and OClO, some comments are given in the text, but the photochemical data are not presented. The species 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_o, 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.

Table 4. Photochemical Reactions of Stratospheric Interest

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

(1) Hudson and Kieffer (1975)
(2) Turco (1975)
New entry

Table 5. Combined Uncertainties for Cross Sections and Quantum Yields

Species	Uncertainty
O_2 (Schumann-Runge bands)	1.4
O_2 (Continua)	1.3
O_3	1.15
$O_3 \rightarrow O(^1D)$	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

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

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

There is considerable disagreement among the cross section values measured in the laboratory around 200 nm. Hasson and Nicholls (1971) report the largest values: $\sim 1.4 \times 10^{-23}$ cm^2 at 200 nm and $\sim 1.1 \times 10^{-23}$ cm^2 at 210 nm. Shardanand and Prasad Rao (1977) obtain the smallest cross sections, 1.0×10^{-23} cm^2 at 200 nm and 7.7×10^{-24} cm^2 at 210 nm. Other investigators (Ditchburn and Young, 1962; Ogawa, 1971) report values lying between the two extremes.

Frederick and Mentall (1982) and Herman and Mentall (1982) have estimated O_2 absorption cross sections from balloon measurements of solar irradiance in the stratosphere. The latter authors find the cross sections in the 200-210 nm range to be ~35% smaller than the smallest of the laboratory results, which are those of Shardanand and Prasad Rao. Additional laboratory studies should be carried out to resolve the discrepancies.

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

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

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

The 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; Amimoto et al. (1980) report $\Phi(O^1D) = 0.85$ at 248 nm, and Wine and Ravishankara (1982) measured directly $\Phi(O^3P) = 0.09$ at 248 nm. There are also some indications that $\Phi(O^1D)$ decreases slightly between 304 and 275 nm (see Brock and Watson, 1980 a, b).

The recommendation for the quantum yields in the fall-off region is given in Table 5, and is taken from the mathematical expression given by Moortgat and Kudzus (1978), scaled down by a factor of 0.9 to account for the absolute magnitude of $\Phi(O^1D)$ at short wavelengths. The relative values are in good agreement with those reported by Brock and Watson (1980a).

There are several reviews of the O_3 absorption cross sections; see, for example, Ackerman (1971) and Hudson and Kieffer (1975). Additional laboratory measurements are required in order to better establish the cross sections and their temperature dependency, particularly in the critical 280-320 nm range (such work is in progress; see Bass and Paur, 1981).

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

$$\Phi(\lambda,T) = A(\tau)\ \arctan[B(\tau)(\lambda-\lambda_0(\tau))] + C(\tau)$$

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

The coefficients $A(\tau)$, $B(\tau)$, $\lambda_0(\tau)$ and $C(\tau)$ are expressed as interpolation polynomials of the third order:

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

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

$\lambda_0(\tau) - 308.20 + 4.4871 \times 10^{-2}\tau + 6.9380 \times 10^{-5}\tau^2 - 2.5452 \times 10^{-6}\tau^3$

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

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 and Burrows (1979). Hochanadel *et al.* (1980) give a cross section value of $4.0 \pm 0.5 \times 10^{-18}$ cm^2 at 205 nm, and Sander *et al.* (1982) a value of $3.0 \pm 0.4 \times 10^{-18}$ cm^2 at 227.5 nm.

The shape of the spectrum reported by the first three groups cited above is in reasonable agreement. The recommended absorption cross sections, listed in Table 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.

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

Table 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 (1981). 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} σ (cm^2)	λ (nm)	10^{20} σ (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. However, in view of the importance of the NO_2 atmospheric photodissociation process additional studies of the temperature dependence of the quantum yield should be carried out.

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 11 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 (1978), listed in Table 11, are above unity for $\lambda < 610$ nm, which is, of course, impossible; hence, there is some systematic error and it is most likely in the primary quantum yield measurements. Magnotta and Johnston (1980) and Marinelli _et al_. (1982) have discussed the probable sources of this error, but the question remains to be resolved and further studies are in order. At present, the recommendation remains unchanged from the previous two, 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

$A_1 = 68.21023$

$A_2 = -4.071805$

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

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

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

$B_1 = 123.4014$

$B_2 = -2.116255$

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

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

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 (1975) between 205 and 310 nm; and for temperatures in the 223 to 300 K range by Yao _et al._ (1982), between 200 and 380 nm. The agreement is good particularly considering the difficulties in handling N_2O_5. The recommended cross section values, listed in Table 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 products appear to be NO_2 and NO_3: Swanson and Johnston (1983) have measured directly the primary quantum yield for NO_3 production obtaining a value of 0.9 ± 0.1.

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

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

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

Table 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

$HO_2NO_2 + h\nu \rightarrow$ products

There are four studies of the UV spectrum of HO_2NO_2 vapor: Cox and Patrick (1979), Morel *et al*, (1980), Graham *et al*. (1978b) and Molina and Molina (1981). The latter two studies are the only ones covering the gas phase spectrum in the critical wavelength range for atmospheric photodissociation, that is, wavelengths longer than 290 nm. The recommended values, listed in Table 16 are taken from the work of Molina and Molina (1981), which is the more direct study. The temperature dependence of the cross sections at these longer wavelengths and the identity of the photodissociation products remain to be determined.

Table 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 progressions of bands extending from ~ 280 to 480 nm. The spectroscopy of this molecule has been studied extensively, and the quantum yield for photodissociation appears to be unity throughout the above wavelength range--see, for example, the review by Watson (1977).

Birks *et al*. (1977) have estimated a half-life against atmospheric photodissociation of OClO of a few seconds.

$ClO_3 + h\nu \rightarrow$ 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 ~6 x 10^{-20}cm^2 around 310 nm, again in excellent agreement with the data of Knauth et al. (1979).

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

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

Table 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 (1976) for the 190 to 400 nm region. These results indicate that the early data of Goodeve and Katz (1939) were seriously in error between 186 and 300 nm, whereas, at longer wavelengths, they are in good agreement with the 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 (1966a) 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

$ClNO_2$ + hν → products

The absorption cross sections of nitryl chloride, $ClNO_2$, nave 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 + hν → products

Measurements in the near-ultraviolet of the cross sections of chlorine nitrite (ClONO) have been made by Molina and Molina (1977). Their results are listed in Table 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

$ClONO_2 + h\nu \rightarrow$ 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%. Marinelli and Johnston (1982b) report a quantum yield for NO_3 production at 249 nm between 0.45 and 0.85 with a most likely value of 0.55; they monitored NO_3 by tunable dye-laser absorption at 662 nm. Margitan (1983a) used atomic resonance fluorescence detection of O- and Cl-atoms and finds the quantum yield at 266 and at 355 nm to be 0.9 ± 0.1 for Cl-atom production, and ~0.1 for O-atom production, with no discernible difference at the two wavelengths.

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

Table 25. Absorption Cross Sections of $ClONO_2$

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

HALOCARBON ABSORPTION CROSS SECTIONS AND QUANTUM YIELDS

The primary process in the photodissociation of chlorinated hydrocarbons is well established: absorption of ultraviolet radiation in the lowest frequency band is interpreted as an n-σ^* transition involving excitation to a repulsive electronic state (antibonding in C-Cl), which dissociates by breaking the carbon-chlorine bond (Majer and Simons, 1964). As expected, the chlorofluoromethanes--which are just a particular type of chlorinated hydrocarbons--behave in this fashion (Sandorfy, 1976). Hence, the quantum yield for photodissociation is expected to be unity for these compounds. There are several studies which show specifically that this is the case for CF_2Cl_2, $CFCl_3$ 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).

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	64.8	244	0.414
202	62.2	246	0.314
204	60.4	248	0.240
206	56.5	250	0.183
208	52.0	255	0.0661
210	46.6	260	0.0253
212	39.7	265	0.0126
214	33.3	270	0.0061
216	27.2	275	0.0024

Table 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

$CHClF_2 + h\nu \rightarrow$ 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	0.825
186	0.476
188	0.339
190	0.235
192	0.157
194	0.100
196	0.070
198	0.039
200	0.026
202	0.022
204	0.013

$CH_3Cl + h\nu \rightarrow$ 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 (nm)	$10^{20}\sigma(cm^2)$		
	296 K	279 K	255 K
186	24.7	24.7	24.7
188	17.5	17.5	17.5
190	12.7	12.7	12.7
192	8.86	8.86	8.86
194	6.03	6.03	6.03
196	4.01	4.01	4.01
198	2.66	2.66	2.66
200	1.76	1.76	1.76
202	1.09	1.09	1.09
204	0.691	0.691	0.691
206	0.483	0.475	0.469
208	0.321	0.301	0.286
210	0.206	0.189	0.172
212	0.132	0.121	0.102
214	0.088	0.074	0.059
216	0.060	0.048	0.033

CCl_2O + hν → products, CClFO + hν → products, and CF_2O + hν → 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-wave number interval. The spectrum of CFClO shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1966a).

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

Table 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

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

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

The recommended absorption cross sections averaged over 5 nm wavelength intervals are taken from the recent work of Cox *et al*. (1982), and are listed in Table 33. These authors estimate a BrO lifetime against atmospheric photodissociation of ~20 seconds at the earth's surface, for a solar zenith angle of 30°.

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

Table 33. Absorption Cross Sections of BrO

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

$BrONO_2 + h\nu \rightarrow$ products

The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm; their results are given in Table 34. The photolysis products are not known.

Table 34. 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.

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

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

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 Moortgat et al. (1980; 1983) with a resolution of 0.5 nm in the 210-360 K temperature range; their values are ~30% larger than those of Bass et al. for wavelengths longer than 300 nm. The recommended cross section values, listed in Table 35, are the mean of the two sets of data (as computed in CODATA, 1982).

The quantum yields have been reported with good agreement by Horowitz and Calvert (1978), Clark et al. (1978a), Tang et al. (1979), Moortgat and Warneck (1979), and Moortgat et al. (1980; 1983). The recommended values listed in Table 35 are based on the results of all of these investigators. The quantum yield Φ_2 is pressure dependent for wavelengths longer than 329 nm, and is given by the expression at the bottom of Table 35, which is based on the values reported by Moortgat et al. (1980; 1983) for 300 K.

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

Table 35. Absorption Cross Sections and Quantum Yields for Photolysis of CH_2O.

λ (nm)	$10^{20}\sigma$ (cm^2)		Φ_1 (H + HCO)	Φ_2 (H_2 + CO)
	290 K	220 K		
240	0.03	0.08	0.21	0.42
250	0.13	0.08	0.24	0.46
260	0.47	0.47	0.30	0.48
270	0.86	0.85	0.40	0.46
280	1.86	1.93	0.59	0.35
290	2.51	2.47	0.71	0.26
300	2.62	2.58	0.78	0.22
310	2.45	2.40	0.77	0.23
320	1.85	1.71	0.62	0.38
330	1.76	1.54	0.31	0.80
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 36.

Table 36. 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	2.5	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 (1957) have studied the spectroscopy of hydrogen cyanide, HCN, which starts absorbing weakly at $\lambda < 190$ nm. McElcheran *et al.* (1958) have reported the spectrum of methyl cyanide, CH_3CN; the first absorption band appears at $\lambda < 216$ nm.

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

$SO_2 + h\nu \rightarrow$ products

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

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

The absorption cross sections of OCS have been measured by 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; by Leroy *et al.* (1981) at 294 K, between 210 and 260 nm, using photographic plates; and by Molina *et al.* (1981) between 180 and 300 nm, at 295 and 225 K. The results are in good agreement in the regions of overlap, except for $\lambda > 280$ 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 37, 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 37. Absorption Cross Sections of OCS

λ (nm)	$10^{20}\sigma(\mathrm{cm}^2)$		λ (nm)	$10^{20}\sigma(\mathrm{cm}^2)$	
	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.

The photooxidation of CS_2 in the atmopshere has been discussed by Wine *et al*. (1981d), who report that electronically excited CS_2 may react with O_2 to yield eventually OCS.

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