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Chemical Kinetic and Photochemical Data for Use in Stratospheric Modelling

Evaluation Number 2

NASA Panel for Data Evaluation

April 15, 1979

National Aeronautics and
Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

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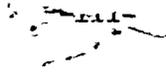
NASA Panel for Data Evaluation

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National Aeronautics and
Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California



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ABSTRACT

An evaluated set of rate constants and photochemical cross sections has been compiled for use in modelling stratospheric processes. The data are primarily relevant to the ozone layer, and its possible perturbation by anthropogenic activities. The evaluation is current to approximately January, 1979.

PREFACE

This is Evaluation Number 2 of rate constants and cross sections relevant to stratospheric chemistry, prepared by the NASA Panel for Data Evaluation:

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CHEMICAL KINETICS AND PHOTOCHEMICAL DATA
FOR USE IN STRATOSPHERIC MODELLING

Introduction

In September, 1977, the National Aeronautics and Space Administration published an assessment of the effect of chlorofluorocarbons on stratospheric ozone (Hudson, 1977; hereafter referred to as NASA RP 1010). In connection with that report a working group was formed to provide a critical evaluation and tabulation of the latest kinetic and photochemical data to be used by modellers in computer simulations of stratospheric chemistry. The report of that working group was published as Chapter I of NASA RP 1010.

Recognizing the need for a continuing assessment of data from laboratories throughout the world, the Upper Atmospheric Physics Office of NASA requested the working group to form an on-going panel and to produce an updated evaluation every nine months. The present composition of the panel and the major responsibilities of each member are listed below.

W. B. DeMore, Chairman (Chapman chemistry)
L. J. Stief, Vice-Chairman (methane oxidation, sulfur chemistry)
F. Kaufman, Advisor
D. M. Golden (three-body reactions)
R. F. Hampson (NO_x chemistry, $\text{O}(^1\text{D})$ reactions)
M. J. Kurylo (NO_x chemistry, $\text{O}(^1\text{D})$ reactions)
J. J. Margitan (HO_x chemistry)
M. J. Molina (photochemical cross sections)
R. T. Watson (halogen chemistry).

As shown above, each panel member concentrates his effort on a given area or type of data; nevertheless, the final recommendations of the panel represent a consensus evaluation by the entire panel. Each member reviews the basis for all recommendations, and is cognizant of the final decision in every case.

The present publication represents the first re-evaluation since the NASA RP 1010 report, and is designated as Evaluation Number 2. The third evaluation is expected to coincide with the forthcoming NASA report on the state of knowledge of the stratosphere, to be presented to the Environmental Protection Agency and Congress at the end of 1979.

Basis of the Recommendations

As in the NASA RP 1010 report, the recommended rate constants and cross sections are based wherever possible 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.) However, the panel does consider the question of consistency of data with expectations based on theory, and in cases where a discrepancy appears to exist, this fact is pointed out in the accompanying notations for each entry. The major usage of theoretical extrapolation of data is in connection with three-body reactions, in which the required pressure dependence is sometimes unavailable from laboratory measurements, and can be estimated by use of appropriate theoretical treatment. In the case of a few important rate constants for which no experimental data are available (for example, $\text{OH} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{ClO}$), the panel has provided estimates of rate constant parameters, based on analogy to similar reactions for which data are available.

Format

Some changes in format have been made since the NASA RP 1010 report, and further changes may be made in succeeding editions of the evaluation. In the present case the rate constant tabulations for second-order reactions (Table 1) give 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 298 K.
5. Uncertainty factor at 298 K.
6. Note giving basis of recommendation and any other pertinent information.

Recommendations which have been changed since the NASA RP 1010 report (38% of the total) are designated by an asterisk, and new entries to the table which were not in the NASA RP 1010 report (20% of the total) are designated by a dagger.

Rate constant parameters for third-order reactions are listed in Table 2. Where necessary for atmospheric applications, pressure fall-off parameters are given and may be used as discussed. (See Third-Order Reactions under Discussion Section; also see Appendix.)

Photochemical cross sections of species of stratospheric interest are also presented in tabular form. Of the approximately thirty recommendations given, about half are revised from the NASA RP 1010 recommendations, and three are new entries. For completeness, those entries which are unchanged since NASA RP 1010 are reproduced in the present report. Table 3 lists those species for which information is given. Table 4 gives recommended reliability factors for some of the more important reactions. Except as noted, these factors refer to total dissociation rate regardless of product identity.

Error Estimates

In the previous evaluation, rate constant uncertainties were expressed in the form of $\Delta \log k(230 \text{ K})$; i.e., upper and lower bounds (corresponding

approximately to one standard deviation) of the rate constant at 230 K could be obtained by multiplying or dividing the central value by the factor

$$f = 10^{(\Delta \log k)}.$$

However, that approach had drawbacks in certain cases, particularly where the rate constant was measured only at room temperature, or was known with much greater accuracy at room temperature than at other temperatures. Also, that approach gave no information on the uncertainty at other temperatures.

In the present report a somewhat different method of error estimation is used. Uncertainty factors are given for the rate constant at 298 K, and these are analogous to the previous factors given at 230 K. A satisfactory estimate of the uncertainty at temperatures below 298 K may be obtained from the following expression,

$$f_T = 10^{(\Delta \log k)_T},$$

where

$$(\Delta \log k)_T = (\Delta \log k)_{298} + \left(\frac{1}{T} - \frac{1}{298} \right) \frac{\Delta E/R}{2.3}$$

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} , $cm^3 \text{ molecule}^{-1} s^{-1}$, and $cm^6 \text{ molecule}^{-2} s^{-1}$, respectively.

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

$$I = I_0 \exp(-\sigma cl),$$

where

I_0, I = incident and transmitted light intensity

σ = absorption cross section, $\text{cm}^2 \text{ molecule}^{-1}$

c = concentration, molecule cm^{-3}

l = pathlength, cm.

Discussion

Although considerable progress has been made in the laboratory measurement of rate constants and cross sections for use in stratospheric modelling, a number of problems remain. These range from small but not insignificant differences in results from different studies (for example, different approaches to the measurement of the rate constant for the $\text{Cl} + \text{CH}_4$ reaction yield results differing by about 40% at stratospheric temperatures--see detailed Note for this reaction), to the possibility that major reaction categories have not been properly considered (e.g., the complexing of species such as ClO with O_2).

Indeed, there are discrepancies in the comparison of measurement with theory that suggest at least the possibility that the models are not completely accurate. Among these discrepancies are the somewhat higher than expected ClO measurements by Anderson and others, the fact that ClONO_2 does not seem to be present at predicted concentrations, and the apparent failure of certain

species (such as the NO_x group) to obtain the predicted ratios for photochemical steady state.

In the following paragraphs recent developments are discussed, and several specific problem areas are outlined for the different reaction categories. These should not necessarily be taken as a statement of priorities for further study because the definition of importance depends somewhat on the objective in mind. For example, some reactions may be relatively unimportant (as determined by a sensitivity analysis) for the overall effect on the total ozone column density, but may be rate-determining in setting the ratios of certain species in the atmosphere. Since such ratio measurements are important for testing the accuracy of the photochemical models, the corresponding rate constants need to be known reliably.

In some cases possible need for further study is suggested merely because only one study has been made of the given reaction, or because the experimental data seem to yield rate constant parameters which are unexpected from the point of view of theory or previous experience. Thus these latter research needs tend to be somewhat academic in nature, but nevertheless it must continually be stressed that anomalies in rate constants frequently suggest the presence of error.

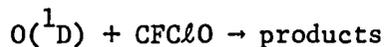
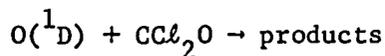
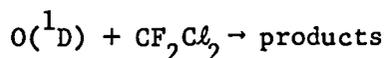
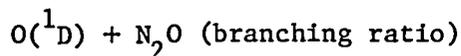
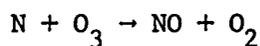
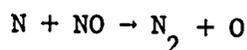
The need for studying reactions under conditions similar to those under which the results are to be applied must also be emphasized. It has long been realized that rate constants to be used at stratospheric temperatures should be measured at those same temperatures, due to the uncertainties attached to long extrapolations of rate data. It is similarly becoming apparent that other conditions, such as partial pressures of other gases (O_2 , H_2O , etc.) must be taken into account. The strange behavior of the $\text{OH} + \text{CO}$ reaction

is one of the best examples in this regard. It is further becoming evident that other reactions, such as $\text{HO}_2 + \text{HO}_2$, may show previously unrealized dependences on pressure and other conditions.

Discussions of the individual reaction categories follow.

NO_x and $\text{O}({}^1\text{D})$

Significant changes in recommendations appear for the following reactions:



These changes are based on new experimental measurements which either contradict the data upon which the earlier recommendations were formulated or fill voids in the data base where only estimated values were given. More complete details of these changes are given in the Notes for the individual reactions.

There are still reactions in this category for which the data base is weak and for which difficult decisions have necessarily been made. These reactions are listed below; the problems are discussed in the Notes that accompany Table 1.

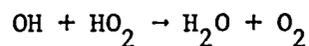
- $O_3 + NO \rightarrow NO_2 + O_2$ Independent confirmation of the temperature dependence is needed.
- $N + O_2 \rightarrow NO + O$ Independent confirmation of the temperature dependence is needed.
- $N + NO \rightarrow N_2 + O$ Independent confirmation of the new results recommended here is needed.
- $OH + HNO_3 \rightarrow H_2O + NO_3$ Direct mechanistic information is desirable.
- $N + NO_2 \rightarrow N_2O + O$ Determination of the temperature dependence and mechanism, and confirmation of the 298 K value, are necessary.
- $N + O_3 \rightarrow NO + O_2$ Confirmation of the new upper limit for k recommended herein is necessary.
- $O + NO_3 \rightarrow O_2 + NO_2$ A more precise rate constant measurement and confirmation of its temperature independence are deemed necessary.

The reaction-rate data for $O(^1D)$ are reasonably reliable but still have some unresolved problems. Measurements using two different analytical techniques (in two laboratories) differ systematically by more than the known uncertainty of either. It has been decided to base the recommendations on one of these sets. Experiments to resolve this incompatibility would improve the reliability of the recommendations. In addition, the reactions of $O(^1D)$ with chlorocarbons and halogenated derivatives of formaldehyde require more study. The products of the chemical reactions have not been determined, and it is not known whether the observed rate constants contain an appreciable contribution from physical quenching.

HO_x

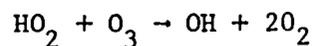
At the time of the earlier evaluation (NASA RP 1010), HO_x reactions were, as a group, the least understood and the most confusing. There has been a great deal of study in the intervening time; however, they still bear that distinction. Of the six HO_x reactions listed in RP 1010 as "top priority" candidates for further study, only the reaction $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ is in substantially better shape now than then.

The key HO_x reaction is still

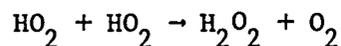


There have been no recent studies on that reaction, and there remains a discrepancy between the low pressure direct and high pressure indirect studies.

There are new data for two of the other key reactions, but they serve to emphasize our lack of understanding as much as anything. A direct study of



has resulted in an even lower A-factor than before, and a correspondingly weaker T dependence. Even more unsettling, however, have been additional studies on



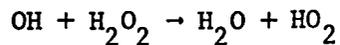
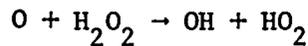
which report (a) a strong negative T dependence and (b) a positive pressure dependence. As these latter works are still preliminary, we have not changed our recommended value, but have considered these effects in assigning our uncertainties. A word of caution is needed here. The assigned lower bound

on E/R (-1245) results in values of k that are much higher than the combined pressure and temperature effects would warrant. Thus, use of this T dependence in an uncertainty analysis without the possible P effect could result in misleading values.

In addition to those three reactions, other HO_x reactions which should be given high priority in future studies are



and the two H₂O₂ reactions



which, at present, have unusual Arrhenius parameters, both absolutely and relative to each other.

With few exceptions, the remaining HO_x reactions also need additional study since most of them are still uncertain by > 25% at room temperature. Emphasis should also be placed on studying all these reactions under a variety of conditions to ensure that unanticipated effects are not present (i.e., pressure dependencies for apparently bimolecular reactions). Needless to say, improved theoretical understanding of HO_x radical reactions is sorely needed.

ClO_x, BrO_x, and FO_x

Since the RP 1010 evaluation there have been numerous changes in the recommended values for halogen rate coefficients. However, most of the modifications in the important ClO_x rate coefficients have been relatively minor (< 10% change in k at stratospheric temperatures) and as such will not significantly affect the output of the photochemical modelling calculations. The most

important changes in the ClO_x data base are that experimental data have become available for $k(ClO + HO_2)$ at 298 K, thus replacing the earlier estimate, which was significantly lower, and the value of $k(Cl + HO_2)$ has been revised upwards by 50%. However, there are still several areas which require additional study. For example, it has been postulated that the $ClO + NO_2 + M$ reaction has two primary reaction channels, producing both $ClONO_2$ and $OClNO_2$. Consequently, identification of the primary products (as a function of T and P) is required in addition to further studies of the temperature and pressure dependence of this reaction. Studies of the temperature dependence of the $ClO + HO_2$ and $ClO + BrO$ (both channels) reactions are needed. More information is required on the detailed degradation mechanisms of species such as CH_3CCl_3 and C_2Cl_4 , to determine if stable chlorinated compounds other than HCl are formed in the degradation process. The $ClO + OH$ reaction needs to be studied to determine if it acts as a significant formation pathway for HCl .

Whereas most of the important ClO_x rate coefficients are quite well established, this is not the case in the BrO_x system. Although many of the BrO_x reactions have been studied since RP 1010, all reactions, except the $NO + BrO$ and $Br + O_3$ reactions, should be re-examined. The key reactions requiring further examination are: $ClO + BrO$, $Br + HO_2$, $OH + HBr$ and $BrO + NO_2 + M$. Reactions such as $Br + H_2CO$ may also be important.

Although the rate coefficient data base for FO_x reactions is rather poor, it is difficult to identify those reactions which need to be better understood in order to improve our understanding of the distribution of fluorine-containing species in the stratosphere. In addition it should be stated that it is generally assumed that the catalytic efficiency of FO_x for destroying

ozone is low due to the rapid formation of HF and the unreactivity of this species.

While all previous photochemical models have included chlorine chemistry, few have included bromine or fluorine chemistry. However, it appears that more photochemical models might in the future include a complete set of bromine reactions due to recent evidence that there is a synergistic effect between ClO_x and BrO_x , leading to an efficient catalytic destruction of ozone through the $\text{BrO} + \text{ClO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2$ reaction.

Third-Order Reactions

The present evaluation uses a somewhat different approach for the presentation of third-order rate constants than that of NASA RP 1010, which employed either curve-fitted analytical expressions (as for ClONO_2 and HNO_3 formation) or otherwise gave only the limiting low pressure rate constants in the Arrhenius form. Table 2 lists the low pressure rate constants in the form (where the value is suitable for air as the third body),

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

along with the recommended value of n . Where pressure fall-off corrections are necessary, an additional entry gives the limiting high pressure rate constant in similar form:

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

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

$$k(z) = k(M, T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)} \right) 0.8 \left\{ 1 + \left[\log_{10} \left(k_o(T)[M]/k_\infty(T) \right) \right]^2 \right\}^{-1}$$

There has not been a great deal of improvement in the experimental data base for third-order reactions since the NASA RP 1010 evaluation, with the possible exception of HO_2NO_2 . A major remaining problem is the ClONO_2 formation reaction, in which there is a discrepancy between combination and pyrolysis data. The related question of possible isomer formation in the combination reaction needs to be resolved.

Photochemical Processes

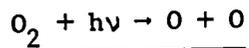
Much laboratory work has been carried out since the NASA RP 1010 evaluation on photochemical reactions of atmospheric importance, such as the production of $\text{O}(^1\text{D})$ from ozone, the quantum yields for production of H_2 and HCO from CH_2O , etc. However, more work remains to be done in several areas before the results can be considered to be sufficiently well established for atmospheric purposes.

There is a large discrepancy between the theoretical calculations of HOCl absorption cross sections (indicating negligible absorption beyond 300 nm) and some of the experimental results; the reason is not known. More experiments should be carried out, if possible, using a different approach such as monitoring directly the HOCl photodissociation fragments.

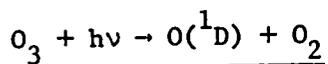
There are conflicting reports on the identity of the decomposition products in the photolysis of ClONO_2 ; further work is in order.

The quantum yields for photodissociation, and the identity of the products, in the photolysis of N_2O_5 , CF_2O , and CFC_2O remain to be determined.

Discussions of the individual photochemical reactions follow.



The absorption spectrum of O_2 in the Schumann-Runge bands has been re-examined recently by Frederick and Hudson (1979), who found some of the line widths to be smaller than those reported earlier by Ackerman and Biauume (1970). The recommended values are the new results of Frederick and Hudson, which will affect the calculations of solar flux penetration into the Earth's atmosphere in the 180-200 nm region. Due to the highly structured nature of the spectrum in question and due to the complications in the solar flux calculations, these results are not presented here; the reader is referred to the original publication of Frederick and Hudson.



The recommended values for the quantum yields as a function of wavelength and temperature are given by the mathematical expression developed by Moortgat and Kudszus (1978). The expression fits their own data (Moortgat and Warneck, 1975; Moortgat, et al., 1977; Arnold, et al., 1977), as well as the low temperature data of Lin and DeMore (1973/74). The results agree within 10% with the data recommended in the NASA 1010 publication, which is only for 235 K. Moortgat's data are reproduced in Table 5. Note that beyond 310 nm, at 298 K, the mathematical expression is fitted to the values obtained with the Xe-arc lamp, and these values are somewhat larger than the corresponding laser values. It is likely, however, that the laser results are more reliable due to the much narrower bandwidth of the laser. The mathematical expression is the following:

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

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

In the limits where $\varphi_C(\lambda, T) > 1$, the quantum yield is set $\varphi_C = 1$, and similarly for $\varphi_C(\lambda, T) < 0$, the quantum yield is set $\varphi_C = 0$.

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

$$A(\tau) = 0.369 + 2.85 \times 10^{-4} \tau + 1.28 \times 10^{-5} \tau^2 + 2.57 \times 10^{-8} \tau^3$$

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

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

$$C(\tau) = 0.518 + 9.87 \times 10^{-4} \tau - 3.94 \times 10^{-5} \tau^2 + 3.91 \times 10^{-7} \tau^3.$$

The recommended value for the quantum yield for $O(^1D)$ production at wavelengths shorter than 300 nm is unity, as in the NASA 1010 publication. The results of Fairchild, et al. (1978) indicate, however, that the quantum yield at 274 nm is ~ 0.9 ; this question requires further study.

NO + h ν \rightarrow N + O

The problem concerning the calculation of the photodissociation rate of NO in the upper stratosphere and mesosphere has been re-examined recently by Frederick and Hudson (1978). This problem is closely related to the question of penetration of solar radiation in the Schumann-Runge bands of O_2 mentioned earlier. Here again the reader is referred to the original publications of Frederick and Hudson.

NO₂ + h ν \rightarrow NO + O

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). These two earlier sets of data were the basis for the NBS and NASA 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 6, are those of Harker et al. (1977). The recommendation for the cross sections (Table 7), which are temperature dependent, is unchanged from the NASA 1010 publication. Davenport's results indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced.

NO₃ + hv → Products

Wayne et al. (1978) have new measurements of the absorption cross sections of NO₃. Their results agree reasonably well with those of Johnston and Graham (1974), but disagree with the updated results given by Graham and Johnston (1978), which were used for the NASA recommendation, and which are larger by a factor of 1.5 to 5 than the 1974 numbers. The recommended values, taken from the work of Wayne et al. (1978), are listed in Table 8.

N₂O + hv → N₂ + 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 this data, shown in Table 9, with the following expression:

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

where

| | |
|----------------------------------|----------------------------------|
| $A_1 = 68.21023$ | $B_1 = 123.4014$ |
| $A_2 = -4.071805$ | $B_2 = -2.116255$ |
| $A_3 = 4.301146 \times 10^{-2}$ | $B_3 = 1.111572 \times 10^{-2}$ |
| $A_4 = -1.777846 \times 10^{-4}$ | $B_4 = -1.881058 \times 10^{-5}$ |
| $A_5 = 2.520672 \times 10^{-7}$ | |

$N_2O_5 + h\nu \rightarrow$ Products

Table 10 lists data for N_2O_5 taken from Graham (1975), which supersedes the results from the review article by Johnston and Graham (1974). The quantum yields for photodissociation are unknown; possible products are $NO_2 + NO_3$ and $N_2O_4 + O$.

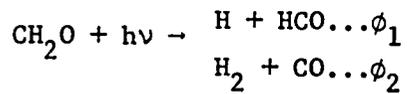
$H_2O_2 + h\nu \rightarrow OH + OH$

There are now two measurements of the absorption cross sections of H_2O_2 vapor in the 300 nm region (Molina et al. (1977b) and Lin et al. (1978b)). The data are listed in Table 11. The recommended values are the mean of the two sets of data.

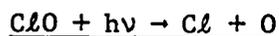
$HONO + h\nu \rightarrow HO + NO$

The ultraviolet spectrum of HONO between 300 and 400 nm has been studied recently 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 12. No recommendation is given for the 200-300 nm range.



The quantum yields and cross sections have been reviewed recently by Lloyd (1978) and by Cox (1978b). The recommended values, taken from the review by Cox, are listed in Table 13. There are indications that the temperature dependence of the cross sections is significant (Jesson et al., 1978).



The absorption cross sections of chlorine monoxide, ClO, have been reviewed by Watson (1974). Two recent calculations (Langhoff et al., 1977; and Coxon et al., 1976) indicate that photodecomposition (predissociation of the $A^2\Pi_{3/2}$ state) 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.

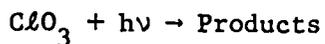


Table 14 lists absorption cross sections of chlorine trioxide, ClO₃, for the 200-350 nm range obtained by graphical interpolation between the data points of Goodeve and Richardson (1937). Although the quantum yield for decomposition has not been measured, the continuous nature of the spectrum indicates that it is likely to be unity.

HOCl + hv → OH + Cl

There are now two theoretical calculations of the absorption cross sections (Jaffe and Langhoff, 1978; Hirsch, et al., 1977), and various new sets of measurements (Molina and Molina, 1978a; Timmons, quoted by Jaffe and Langhoff, 1978). The calculations of Jaffe and Langhoff as well as the measurements of Timmons suggest negligible absorption cross sections in the 300 nm region, whereas the measurements of Molina and Molina yield cross section values in that wavelength region of the order of 10^{-19} cm^2 , in qualitative agreement with the earlier values of DeMore reported in the NASA 1010 publication. The recommended values are taken from the data of Molina and Molina, and are listed in Table 15.

ClNO + hv → Cl + NO

Nitrosyl chloride--a green gas--has a continuous absorption extending beyond 650 nm. There is good agreement between the work of Martin and Gareis (1956) for the 240-420 nm wavelength region, of Ballash and Armstrong (1974) for the 185-540 nm region, and of Illies and Takacs (1976) for the 190-400 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 results of Ballash and Armstrong (1974) and of Illies and Takacs (1976) are listed in Table 16. 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 recommended cross sections (also listed in Table 16) were obtained by taking the mean of the two studies.

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

$\text{ClNO}_2 + h\nu \rightarrow \text{Products}$

The absorption cross sections of nitryl chloride, ClNO_2 , have been measured between 230 and 330 nm by Martin and Gareis (1956) and between 185 and 400 nm by Illies and Takacs (1976). The results are in good agreement. Table 17 lists the recommended cross sections, taken from Illies and Takacs (1976).

The photochemistry of ClNO_2 has not yet been studied. Likely photolysis products are Cl and NO_2 , and the quantum yield for decomposition is probably unity, due to the characteristics of the spectrum.

$\text{ClONO} + h\nu \rightarrow \text{Products}$

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 18. 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.

$\text{ClONO}_2 + h\nu \rightarrow \text{Products}$

The cross sections recommended in the NASA 1010 publication were based on measurements by Rowland, Spencer and Molina (1976). Molina and Molina (1978b) carried out new measurements using essentially the same technique but under conditions of higher sensitivity (a longer absorption path), and as a function of temperature. Their room temperature values are $\sim 15\%$ lower than

the earlier measurements. The recommended values, taken from the work of Molina and Molina (1978b) are listed in Table 19.

The identity of the primary photolytic fragments has been investigated by two groups: Smith et al. (1977) report $O + ClONO$ as the most likely products, using end product analysis and steady-state photolysis, whereas the results of Chang et al. (1978), who employed the "Very Low Pressure Photolysis" (VLPPh) technique, indicate that the products are $Cl + NO_3$. In view of the more direct nature of the VLPPh technique these later results are preferred.

$CFCl_3 + h\nu \rightarrow$ Products

The ultraviolet spectrum of the $CFCl_3$ has been examined by several groups. The results are in excellent agreement, as shown in Table 20, which includes the room-temperature data for Chou et al. (1976), Robbins et al. (1975), and Bass (private communication, 1976). The preferred value is the mean, listed in the last column of the table. The low-temperature data of Chou et al. (1976) and Bass (private communication, 1976) are shown in Table 21; the agreement is also very good.

Although no such simple expression is available for $CFCl_3$, the temperature effect at stratospherically important wavelengths (near the 200 nm "window") is much smaller than for CF_2Cl_2 .

$CF_2Cl_2 + h\nu \rightarrow$ Products

Vanlaethem-Meuree et al. (1978) measured the absorption cross sections as a function of temperature. At the lower temperatures their results are up to a factor of two smaller than those of Bass and Ledford (1976) and Chou et al. (1977b); they are, however, in agreement with the values reported by

Rebbert and Ausloos (1975). Their results for CFCl_3 are in quite good agreement with those of earlier measurements. The recommendations remain unchanged from the NASA 1010 publication (Tables 22 and 23); note, however, that the uncertainty factor listed in Table 4 for CF_2Cl_2 is 0.06, reflecting the low temperature discrepancy.

$\text{CF}_3\text{Cl} + h\nu \rightarrow \text{Products}$ and $\text{CCl}_2\text{FCClF}_2 + h\nu \rightarrow \text{Products}$

The absorption cross sections of CF_3Cl (fluorocarbon 13) and $\text{CCl}_2\text{FCClF}_2$ (fluorocarbon 113) have been measured at room temperature by Chou et al. (1978); the results are listed in Table 24.

$\text{CClF}_2\text{CClF}_2 + h\nu \rightarrow \text{Products}$ and $\text{CClF}_2\text{CF}_3 + h\nu \rightarrow \text{Products}$

Two groups (Chou et al., 1978; and Robbins, private communication, 1976) have examined the spectra of $\text{CClF}_2\text{CClF}_2$ (fluorocarbon 114) and CClF_2CF_3 (fluorocarbon 115). Table 25 lists the results; the recommended value is the mean, which is also listed in Table 25.

$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{Products}$

The absorption cross sections of trichloroethane, CH_3CCl_3 , are listed in Table 26. The data are taken from Rowland (private communication, 1976). Christiansen et al. (1972) have studied the photochemical decomposition of this molecule in air. By analysis of the reaction products, the quantum yield for phosgene formation was determined to be 1.3, and the quantum yield for the primary process was assumed to be unity. An absorption spectrum from 190 to 220 nm was also reported in graphical form, but it is not suited for quantitative purposes. No information pertinent to this spectrum was provided, and the results are in poor agreement with those listed in Table 26.

CCl₂O + hν → Products, CClFO + hν → Products, and CF₂O + hν → Products

Table 27 shows the absorption cross sections of CCl₂O (phosgene), CClFO, and CF₂O taken from the work of Chou et al. (1977a). The spectrum of CF₂O shows considerable structure. The values listed in Table 27 are averages over each 50-wave number interval. Preliminary photochemical studies (Chou et al., 1977a) indicate unit quantum yield for photodissociation at 184 nm. The spectrum of CClFO shows less structure, and the CCl₂O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1967).

CH₃OOH + hν → Products

The absorption cross sections of CH₃OOH in the atmospherically important wavelength region beyond 290 nm have not been measured yet. The recommendation is to assume the same cross sections as for H₂O₂. The uncertainty is, of course, large (see Table 4).

COS + hν

The recommended cross section values, listed in Table 28 are those measured as a function of temperature by Chou et al. (1979). Their room temperature results agree within 8% with the values reported earlier by Breckenridge and Taube (1970). The photodissociation quantum yields have not been measured yet in the atmospherically important wavelength region around 200 nm, although they are likely to be unity.

SO₂ + hν → Products

The photodissociation of SO₂ in the atmosphere as well as the potential role of excited states of SO₂ in atmospheric chemistry has been reviewed recently by Calvert (1978) and will not be repeated here.

BrONO₂ + hν → Products

The bromine nitrate cross sections have been measured at room temperature by Spencer and Rowland (1978) in the wavelength region 186-390 nm. The recommended values are given in Table 29. By analogy with ClONO₂, some temperature dependence may be expected. The photolysis products are not known.

Table 1

Summary of Recommended Rate Constants

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|--|--------------------------------|--------------------------|--------------------------------|-------------------------------|------|
| * O + O ₂ \xrightarrow{M} O ₃ | (See Table 2) | | | | 1 |
| * O + O ₃ \rightarrow O ₂ + O ₂ | 1.5 \times 10 ⁻¹¹ | 2218 \pm 150 | 8.8 \times 10 ⁻¹⁵ | 1.15 | 2 |
| * O ₃ + NO \rightarrow NO ₂ + O ₂ | 2.3 \times 10 ⁻¹² | 1450 \pm 200 | 1.8 \times 10 ⁻¹⁴ | 1.2 | 3 |
| * OH + NO ₂ \xrightarrow{M} HNO ₃ | (See Table 2) | | | | |
| * O + NO ₂ \rightarrow NO + O ₂ | 9.3 \times 10 ⁻¹² | 0 + 0 - 150 | 9.3 \times 10 ⁻¹² | 1.1 | 4 |
| * N + O ₂ \rightarrow NO + O | 4.4 \times 10 ⁻¹² | 3220 \pm 340 | 8.9 \times 10 ⁻¹⁷ | 1.25 | 5 |
| * N + NO \rightarrow N ₂ + O | 3.4 \times 10 ⁻¹¹ | 0 \pm 100 | 3.4 \times 10 ⁻¹¹ | 1.4 | 6 |
| * OH + HNO ₃ \rightarrow prod. ^{NO₂ + H₂O} | 8.5 \times 10 ⁻¹⁴ | 0 \pm 100 | 8.5 \times 10 ⁻¹⁴ | 1.25 | 7 |
| N + NO ₂ \rightarrow N ₂ O + O | 2.1 \times 10 ⁻¹¹ | 800 \pm 350 | 1.4 \times 10 ⁻¹² | 1.25 | 8 |
| * N + O ₃ \rightarrow NO + O ₂ | - | - | < 1 \times 10 ⁻¹⁵ | - | 9 |
| NO ₂ + O ₃ \rightarrow NO ₃ + O ₂ | 1.2 \times 10 ⁻¹³ | 2450 \pm 140 | 3.2 \times 10 ⁻¹⁷ | 1.15 | 10 |
| * HO ₂ + NO ₂ \xrightarrow{M} HO ₂ NO ₂ | (See Table 2) | | | | |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|---|-------------------------|--------------------------|-------------------------|-------------------------------|------|
| * O(¹ D) + N ₂ O → N ₂ + O ₂ | 5.1 × 10 ⁻¹¹ | 0 ± 50 | 5.1 × 10 ⁻¹¹ | 1.3 | 11 |
| * O(¹ D) + N ₂ O → NO + NO | 5.9 × 10 ⁻¹¹ | 0 ± 50 | 5.9 × 10 ⁻¹¹ | 1.3 | 11 |
| O(¹ D) + H ₂ O → OH + OH | 2.3 × 10 ⁻¹⁰ | 0 ± 50 | 2.3 × 10 ⁻¹⁰ | 1.3 | 11 |
| O(¹ D)+CH ₄ → OH + CH ₃ | 1.3 × 10 ⁻¹⁰ | 0 ± 50 | 1.3 × 10 ⁻¹⁰ | 1.3 | 11 |
| O(¹ D) + CH ₄ → H ₂ + CH ₂ O | 1.4 × 10 ⁻¹¹ | 0 ± 50 | 1.4 × 10 ⁻¹¹ | 1.3 | 11 |
| O(¹ D) + H ₂ → OH + H | 9.9 × 10 ⁻¹¹ | 0 ± 50 | 9.9 × 10 ⁻¹¹ | 1.3 | 11 |
| O(¹ D) + N ₂ → O + N ₂ | 2.0 × 10 ⁻¹¹ | -(107 ± 50) | 2.9 × 10 ⁻¹¹ | 1.3 | 11 |
| * O(¹ D) + N ₂ \xrightarrow{M} N ₂ O | (See Table 2) | | | | - |
| O(¹ D) + O ₂ → O + O ₂ | 2.9 × 10 ⁻¹¹ | -(67 ± 50) | 3.6 × 10 ⁻¹¹ | 1.3 | 11 |
| O(¹ D) + O ₃ → O ₂ + O ₂ | 1.2 × 10 ⁻¹⁰ | 0 ± 50 | 1.2 × 10 ⁻¹⁰ | 1.3 | 11 |
| O(¹ D) + O ₃ → O ₂ + O + O | 1.2 × 10 ⁻¹⁰ | 0 ± 50 | 1.2 × 10 ⁻¹⁰ | 1.3 | 11 |
| O(¹ D) + HCl → OH + Cl | 1.4 × 10 ⁻¹⁰ | 0 ± 50 | 1.4 × 10 ⁻¹⁰ | 1.3 | 11 |
| O(¹ D) + CFCl ₃ → prod. | 2.2 × 10 ⁻¹⁰ | 0 ± 50 | 2.2 × 10 ⁻¹⁰ | 1.3 | 11 |
| * O(¹ D) + CF ₂ Cl ₂ → prod. | 1.4 × 10 ⁻¹⁰ | 0 ± 50 | 1.4 × 10 ⁻¹⁰ | 1.3 | 11 |
| * O(¹ D) + CCl ₂ O → prod. | 3.6 × 10 ⁻¹⁰ | 0 ± 50 | 3.6 × 10 ⁻¹⁰ | 1.4 | 11 |
| * O(¹ D) + CFClO → prod. | 1.9 × 10 ⁻¹⁰ | 0 ± 50 | 1.9 × 10 ⁻¹⁰ | 1.4 | 11 |
| * O(¹ D) + CF ₂ O → prod. | 2.3 × 10 ⁻¹⁰ | 0 ± 50 | 2.3 × 10 ⁻¹⁰ | 1.4 | 11 |
| † O(¹ D) + NH ₃ → OH + NH ₂ | 2.5 × 10 ⁻¹⁰ | 0 ± 50 | 2.5 × 10 ⁻¹⁰ | 1.3 | 11 |
| † O(¹ D) + CO ₂ → O + CO ₂ | 6.8 × 10 ⁻¹¹ | -(117 ± 50) | 1.0 × 10 ⁻¹⁰ | 1.3 | 11 |
| † O + NO ₃ → O ₂ + NO ₂ | 1 × 10 ⁻¹¹ | 0 ± 150 | 1 × 10 ⁻¹¹ | 1.6 | 12 |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|---|---|--|---|----------------------------|------|
| $\dagger \text{O} + \text{N}_2\text{O}_5 \rightarrow \text{prod.}$ | - | - | $< 3 \times 10^{-16}$ | - | 13 |
| $\dagger \text{O}_3 + \text{HNO}_2 \rightarrow \text{O}_2 + \text{HNO}_3$ | - | - | $< 5 \times 10^{-19}$ | - | 14 |
| * $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ | 4×10^{-11} | 0 ± 250 | 4×10^{-11} | 2 | 15 |
| $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ | 2.5×10^{-12} | $0 \begin{smallmatrix} + 0 \\ - 1245 \end{smallmatrix}$ | 2.5×10^{-12} | 1.2 | 16 |
| * $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ | 3.4×10^{-12} | $-(250 \pm 250)$ | 7.9×10^{-12} | 1.2 | 17 |
| * $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2$ | 1.1×10^{-14} | $580 \begin{smallmatrix} + 500 \\ - 100 \end{smallmatrix}$ | 1.6×10^{-15} | 1.4 | 18 |
| * $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ | 1.6×10^{-12} | 940 ± 300 | 6.8×10^{-14} | 1.25 | 19 |
| $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ | 4×10^{-11} | 0 ± 300 | 4.0×10^{-11} | 1.5 | 20 |
| $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$ | 3.5×10^{-11} | 0 ± 350 | 3.5×10^{-11} | 1.5 | 21 |
| $\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$ | 2.8×10^{-12} | 2125 ± 400 | 2.2×10^{-15} | 1.4 | 22 |
| * $\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$ | (See Table 2) | | | | - |
| * $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ | 1.4×10^{-10} | 470 ± 200 | 2.9×10^{-11} | 1.25 | 23 |
| * $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ | 1×10^{-11} | 500 ± 400 | 1.9×10^{-12} | 1.25 | 24 |
| * $\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$ | (See Table 2) | | | | - |
| $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$ | 1×10^{-11} | 750 ± 350 | 8.1×10^{-13} | 1.4 | 25 |
| * $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ | $1.35 \times 10^{-13} (1 + P_{\text{atm}})$ | 0 ± 200 | $1.35 \times 10^{-13} (1 + P_{\text{atm}})$ | 1.25 | 26 |
| $\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ | 2.4×10^{-12} | 1710 ± 200 | 7.7×10^{-15} | 1.2 | 27 |
| $\dagger \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ | 1.2×10^{-11} | 2200 ± 200 | 7.5×10^{-15} | 1.2 | 28 |
| $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ | 2.8×10^{-11} | 257 ± 100 | 1.2×10^{-11} | 1.15 | 29 |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|--|--------------------------|--|--------------------------|--|------|
| $O + ClO \rightarrow Cl + O_2$ | 7.7×10^{-11} | 130 ± 130 | 5.0×10^{-11} | 1.2 | 30 |
| * $NO + ClO \rightarrow NO_2 + Cl$ | 7.8×10^{-12} | $-(250 \pm 100)$ | 1.8×10^{-11} | 1.25 | 31 |
| $OH + HCl \rightarrow H_2O + Cl$ | 2.8×10^{-12} | 425 ± 100 | 6.6×10^{-13} | 1.15 | 32 |
| † $OH + HOCl \rightarrow H_2O + ClO$ | 3×10^{-12} | 800 ± 500 | 2×10^{-13} | 10 | 33 |
| * $Cl + CH_4 \rightarrow HCl + CH_3$ | 9.9×10^{-12} | 1359 ± 150 | 1.0×10^{-13} | 1.15 | 34 |
| * $Cl + HO_2 \rightarrow HCl + O_2$ | 4.5×10^{-11} | 0 ± 250 | 4.5×10^{-11} | 1.6 | 35 |
| * $ClO + NO_2 \xrightarrow{M} ClONO_2$ | (See Table 2) | | | | - |
| $O + ClONO_2 \rightarrow \text{prod.}$ | 3.0×10^{-12} | 808 ± 200 | 1.9×10^{-12} | 1.5 | 36 |
| $OH + ClONO_2 \rightarrow \text{prod.}$ | 1.2×10^{-12} | 333 ± 200 | 3.9×10^{-13} | 1.5 | 37 |
| $Cl + ClONO_2 \rightarrow \text{prod.}$ | 1.7×10^{-12} | 607 ± 388 | 2.2×10^{-13} | 2 | 38 |
| $O + HCl \rightarrow OH + Cl$ | 1.14×10^{-11} | 3370 ± 350 | 1.4×10^{-16} | 2 | 39 |
| † $O + HOCl \rightarrow OH + ClO$ | 1×10^{-11} | 2200 ± 800 | 6×10^{-15} | 10 | 40 |
| $Cl + H_2 \rightarrow HCl + H$ | 3.5×10^{-11} | 2290 ± 200 | 1.8×10^{-14} | 1.5 | 41 |
| $Cl + H_2O_2 \rightarrow HCl + HO_2$ | 1.7×10^{-12} | 384 ± 400 | 4.7×10^{-13} | 1.5 | 42 |
| $Cl + HNO_3 \rightarrow HCl + NO_3$ | $\leq 1 \times 10^{-11}$ | $2170 \begin{matrix} + 2500 \\ - 500 \end{matrix}$ | $\leq 7 \times 10^{-15}$ | $\begin{matrix} + 2 \\ - 300 \end{matrix}$ | 43 |
| † $Cl + H_2CO \rightarrow HCl + HCO$ | 9.2×10^{-11} | 68 ± 100 | 7.3×10^{-11} | 1.15 | 44 |
| † $Cl + CH_3Cl \rightarrow CH_2Cl + HCl$ | 3.4×10^{-11} | 1256 ± 200 | 4.9×10^{-13} | 1.2 | 45 |
| * $Cl + NO \xrightarrow{M} NOCl$ | (See Table 2) | | | | - |
| $Cl + ClNO \rightarrow NO + Cl_2$ | 3.0×10^{-11} | $0 \begin{matrix} + 500 \\ - 250 \end{matrix}$ | 3×10^{-11} | 2 | 46 |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|---|------------------------------|-----------------------------|------------------------------|-------------------------------|------|
| * Cl + O ₂ \xrightarrow{M} ClOO | (See Table 2) | | | | - |
| * ClOO \xrightarrow{M} Cl + O ₂ | 2.7 x 10 ⁻⁹ | 2650 \pm 800 | 3.7 x 10 ⁻¹³ | 7 | 47 |
| * Cl + ClOO \rightarrow Cl ₂ + O ₂ | 1 x 10 ⁻¹¹ | 0 \pm 250 | 1 x 10 ⁻¹¹ | 3 | 48 |
| * Cl + ClOO \rightarrow ClO + ClO | 5 x 10 ⁻¹² | 0 \pm 250 | 5 x 10 ⁻¹² | 3 | 48 |
| * ClO + HO ₂ \rightarrow HOCl + O ₂ | 3.8 x 10 ⁻¹² | 0 ^{+ 200} - 500 | 3.8 x 10 ⁻¹² | 1.5 | 49 |
| ClO + CH ₄ \rightarrow prod. | \leq 1 x 10 ⁻¹² | \geq 3700 | \leq 4 x 10 ⁻¹⁸ | - | 50 |
| ClO + H ₂ \rightarrow prod. | \leq 1 x 10 ⁻¹² | \geq 4800 | \leq 1 x 10 ⁻¹⁹ | - | 50 |
| ClO + CO \rightarrow prod. | \leq 1 x 10 ⁻¹² | \geq 3700 | \leq 4 x 10 ⁻¹⁸ | - | 50 |
| ClO + N ₂ O \rightarrow prod. | \leq 1 x 10 ⁻¹² | \geq 4260 | \leq 6 x 10 ⁻¹⁹ | - | 50 |
| ClO + BrO \rightarrow Br + OClO | 6.7 x 10 ⁻¹² | 0 \pm 250 | 6.7 x 10 ⁻¹² | 1.5 | 51 |
| ClO + BrO \rightarrow Br + Cl + O ₂ | 6.7 x 10 ⁻¹² | 0 \pm 250 | 6.7 x 10 ⁻¹² | 1.5 | 51 |
| ClO + ClO \rightarrow Cl + ClOO | - | - | - | - | 52 |
| ClO + ClO \rightarrow Cl ₂ + O ₂ | - | - | - | - | 52 |
| ClO + ClO \xrightarrow{M} Cl ₂ + O ₂ | - | - | - | - | 52 |
| ClO + O ₃ \rightarrow ClOO + O ₂ | 1 x 10 ⁻¹² | \geq 4000 | $<$ 1 x 10 ⁻¹⁸ | - | 53 |
| ClO + O ₃ \rightarrow OClO + O ₂ | 1 x 10 ⁻¹² | \geq 4000 | $<$ 1 x 10 ⁻¹⁸ | - | 53 |
| Cl + OClO \rightarrow ClO + ClO | 5.9 x 10 ⁻¹¹ | 0 \pm 250 | 5.9 x 10 ⁻¹¹ | 1.25 | 54 |
| NO + OClO \rightarrow NO ₂ + ClO | 2.5 x 10 ⁻¹² | 600 \pm 300 | 3.4 x 10 ⁻¹³ | 1.5 | 55 |
| * O + OClO \rightarrow ClO + O ₂ | 2.5 x 10 ⁻¹¹ | 1166 \pm 300 | 5 x 10 ⁻¹³ | 1.5 | 56 |
| OH + CH ₃ Cl \rightarrow CH ₂ Cl + H ₂ O | 2.2 x 10 ⁻¹² | 1142 \pm 200 | 4.8 x 10 ⁻¹⁴ | 1.25 | 57 |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|---|-------------------------|--------------------------|---------------------------|-------------------------------|------|
| OH + CH ₂ Cl ₂ → CHCl ₂ + H ₂ O | 5.5 × 10 ⁻¹² | 1094 ± 200 | 1.4 × 10 ⁻¹³ | 1.25 | 58 |
| OH + CHCl ₃ → CCl ₃ + H ₂ O | 4.7 × 10 ⁻¹² | 1134 ± 200 | 1.0 × 10 ⁻¹³ | 1.25 | 59 |
| * OH + CHFCl ₂ → CFCl ₂ + H ₂ O | 1.5 × 10 ⁻¹² | 1184 ± 200 | 2.8 × 10 ⁻¹⁴ | 1.3 | 60 |
| * OH + CHF ₂ Cl → CF ₂ Cl + H ₂ O | 1.2 × 10 ⁻¹² | 1666 ± 200 | 4.5 × 10 ⁻¹⁵ | 1.25 | 61 |
| * OH + CH ₂ ClF → CHClF + H ₂ O | 3.5 × 10 ⁻¹² | 1322 ± 150 | 4.0 × 10 ⁻¹⁴ | 1.25 | 62 |
| * OH + CH ₃ CCl ₃ → CH ₂ CCl ₃ + H ₂ O | 2.5 × 10 ⁻¹² | 1450 ± 150 | 1.9 × 10 ⁻¹⁴ | 1.25 | 63 |
| OH + C ₂ Cl ₄ → prod. | 9.4 × 10 ⁻¹² | 1199 ± 200 | 1.7 × 10 ⁻¹³ | 1.25 | 64 |
| * OH + C ₂ HCl ₃ → prod. | 5.0 × 10 ⁻¹³ | -(445 ± 200) | 2.2 × 10 ⁻¹² | 1.25 | 65 |
| OH + CFCl ₃ → prod. | 1.0 × 10 ⁻¹² | > 3650 | < 5 × 10 ⁻¹⁸ | - | 66 |
| OH + CF ₂ Cl ₂ → prod. | 1.0 × 10 ⁻¹² | > 3560 | < 6.5 × 10 ⁻¹⁸ | - | 66 |
| * Br + O ₃ → BrO + O ₂ | 1.4 × 10 ⁻¹¹ | 755 ± 200 | 1.12 × 10 ⁻¹² | 1.2 | 67 |
| O + BrO → Br + O ₂ | 3.0 × 10 ⁻¹¹ | 0 ± 250 | 3.0 × 10 ⁻¹¹ | 3 | 68 |
| * BrO + NO → NO ₂ + Br | 8.7 × 10 ⁻¹² | -(265 ± 130) | 2.1 × 10 ⁻¹¹ | 1.15 | 69 |
| * BrO + NO ₂ \xrightarrow{M} BrONO ₂ | (See Table 2) | | | | |
| * BrO + BrO → 2 Br + O ₂ | 2.1 × 10 ⁻¹² | -(244 ± 150) | 4.8 × 10 ⁻¹² | 1.25 | 70 |
| * BrO + BrO → Br ₂ + O ₂ | 3.5 × 10 ⁻¹³ | -(244 ± 150) | 8.0 × 10 ⁻¹³ | 1.25 | 70 |
| * BrO + O ₃ → Br + 2 O ₂ | 1.0 × 10 ⁻¹² | > 1600 | < 5 × 10 ⁻¹⁵ | +3;-? | 71 |
| * Br + H ₂ O ₂ → HBr + HO ₂ | 2.0 × 10 ⁻¹² | > 1400 | < 2 × 10 ⁻¹⁴ | +2;-50 | 72 |
| * Br + HO ₂ → HBr + O ₂ | 2.0 × 10 ⁻¹¹ | 0 ± 250 | 2.0 × 10 ⁻¹¹ | 3 | 73 |
| * OH + HBr → H ₂ O + Br | 8.5 × 10 ⁻¹² | 0 ± 250 | 8.5 × 10 ⁻¹² | 2 | 74 |

| Reaction | A-Factor | E/R \pm $\Delta(E/R)$ | k(298) | Uncertainty Factor at 298K | Note |
|--|-----------------------|--|-----------------------|-------------------------------|------|
| $O + HBr \rightarrow OH + Br$ | 7.6×10^{-12} | 1571 ± 300 | 3.9×10^{-14} | 1.5 | 75 |
| $\dagger BrO + HO_2 \rightarrow HOBr + O_2$ | 4.0×10^{-12} | $0 \begin{smallmatrix} + 200 \\ - 500 \end{smallmatrix}$ | 4.0×10^{-12} | 3 | 76 |
| $OH + CH_3Br \rightarrow CH_2Br + H_2O$ | 7.9×10^{-13} | 889 ± 200 | 3.8×10^{-14} | 1.25 | 77 |
| $\dagger F + O_3 \rightarrow FO + O_2$ | 2.8×10^{-11} | 226 ± 200 | 1.3×10^{-11} | 2 | 78 |
| $\dagger F + O_2 \xrightarrow{M} FO_2$ | (See Table 2) | | | | - |
| $\dagger F + H_2 \rightarrow HF + H$ | 2.0×10^{-10} | 620 ± 250 | 2.5×10^{-11} | 1.5 | 79 |
| $\dagger F + CH_4 \rightarrow HF + CH_3$ | 3.0×10^{-10} | 400 ± 300 | 8.0×10^{-11} | 2 | 80 |
| $\dagger F + H_2O \rightarrow HF + OH$ | 2.2×10^{-11} | 200 ± 200 | 1.1×10^{-11} | 5 | 81 |
| $\dagger O + FO \rightarrow F + O_2$ | 5×10^{-11} | 0 ± 250 | 5×10^{-11} | 3 | 82 |
| $\dagger NO + FO \rightarrow NO_2 + F$ | 2×10^{-11} | 0 ± 250 | 2×10^{-11} | 3 | 83 |
| $\dagger FO + FO \rightarrow 2 F + O_2$ | 1.5×10^{-11} | 0 ± 250 | 1.5×10^{-11} | 3 | 84 |
| $\dagger FO + O_3 \rightarrow F + 2 O_2$ | - | - | - | | 85 |
| $\dagger FO + O_3 \rightarrow FO_2 + O_2$ | - | - | - | | 85 |
| $\dagger O + FO_2 \rightarrow FO + O_2$ | 5×10^{-11} | 0 ± 250 | 5×10^{-11} | 5 | 86 |
| $\dagger O(^1D) + HF \rightarrow OH + F$ | 1×10^{-10} | 0 ± 100 | 1×10^{-10} | 3 | 87 |
| $* CH_3 + O_2 \xrightarrow{M} CH_3O_2$ | (See Table 2) | | | | |
| $* CH_3O_2 + NO \rightarrow CH_3O + NO_2$ | 8×10^{-12} | 0 ± 500 | 8×10^{-12} | 3 | 88 |
| $* CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$ | (See Table 2) | | | | |
| $\dagger CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$ | 1×10^{-12} | 0 ± 500 | 1×10^{-12} | 10 | 89 |

| Reaction | A-Factor | E/R \pm Δ (E/R) | k(298) | Uncertainty Factor at 298K | Note |
|--|-----------------------|--------------------------|-----------------------|-------------------------------|------|
| * $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{HO}_2$ | 5.0×10^{-13} | 2000 ± 750 | 6.1×10^{-16} | 2 | 90 |
| * $\text{OH} + \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}_2\text{O}$ | 1.7×10^{-11} | 100 ± 250 | 1.2×10^{-11} | 1.5 | 91 |
| * $\text{O} + \text{H}_2\text{CO} \rightarrow \text{OH} + \text{HCO}$ | 2.8×10^{-11} | 1540 ± 350 | 1.6×10^{-13} | 1.4 | 92 |
| * $\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$ | 5×10^{-12} | 0 ± 250 | 5×10^{-12} | 1.4 | 93 |
| † $\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$ | 6.2×10^{-12} | 750 ± 250 | 5×10^{-13} | 1.4 | 94 |
| † $\text{O} + \text{H}_2\text{S} \rightarrow \text{OH} + \text{SH}$ | 2.4×10^{-12} | 1300 ± 600 | 3.1×10^{-14} | 1.4 | 95 |
| † $\text{O} + \text{OCS} \rightarrow \text{CO} + \text{SO}$ | 2.1×10^{-11} | 2200 ± 150 | 1.3×10^{-14} | 1.12 | 96 |
| † $\text{O} + \text{CS}_2 \rightarrow \text{CS} + \text{SO}$ | 3.1×10^{-11} | 640 ± 150 | 3.6×10^{-12} | 1.12 | 97 |
| † $\text{OH} + \text{H}_2\text{S} \rightarrow \text{SH} + \text{H}_2\text{O}$ | 1.1×10^{-11} | 220 ± 220 | 5.3×10^{-12} | 1.25 | 98 |
| † $\text{OH} + \text{OCS} \rightarrow \text{prod.}$ | - | - | 5.6×10^{-14} | 1.25 | 99 |
| † $\text{OH} + \text{CS}_2 \rightarrow \text{prod.}$ | - | - | 1.9×10^{-13} | 1.25 | 99 |

* Indicates a change from the NASA RP 1010 recommendation.

† Indicates a new entry that was not in NASA RP 1010.

Notes to Table 1

1. Explanatory notes for all third order reactions are listed in the Appendix.
2. This recommendation is slightly different from the NBS TN 866 and NASA RP 1010 recommendation ($k = 1.9 \times 10^{-11} \exp(-2300/T)$) and is based on the measurements of McCrumb and Kaufman (1972) and Davis et al. (1973).
3. Recommended Arrhenius expression is that of Birks et al. (1976). Room temperature value is an average of Birks et al. (1976), Bemand et al. (1974), Becker et al. (1974) and Stedman and Niki (1973). The slightly lower pre-exponential factor recommended in NASA RP-1010 was based on an alternative analysis of the primary data in Birks et al. and inclusion of older room temperature data. The present recommendation accepts the data analysis given in Birks' paper. Independent confirmation of the temperature dependence is needed.
4. Based on results of Davis et al. (1973), Bemand et al. (1974) and Slanger et al. (1973). There may be a slight negative temperature coefficient, but the evidence at low temperature is uncertain. A slightly lower value was recommended in NASA RP-1010 based only on the results of Davis et al. (1973).
5. Activation energy based on Becker et al. (1969). Value and uncertainty at 298 K assigned from average of Clyne and Thrush (1961), Wilson (1967), Becker et al. (1969), Clark and Wayne (1970) and Westenberg et al. (1970). The recommendation in NASA RP-1010 was purely the Becker expression. Inclusion of the other 298 K data results in the lower pre-exponential factor of the present recommendation. Independent confirmation of the temperature dependence is needed.
6. Recommendation is based on the results of Lee et al. (1978c) and is significantly different from that in NASA RP-1010 which accepted the results of Clyne and McDermid (1975). Based on our critical re-examination of the high temperature data reported by those authors, their derived temperature dependence is rejected. Independent confirmation is needed.
7. Recommended value is a simple average of the results reported by Smith and Zellner (1975) and Margitan et al. (1975). A slightly lower value was recommended in NASA RP-1010 based only on the results of Smith and

7. (Cont.)

Zellner, considered as confirmed by the results of Margitan et al. Products are unknown--reaction may proceed by addition mechanism. The apparent A-factor is low for an abstraction reaction.

8. Accepts the 298 K results of Clyne and McDermid (1975)--both the value of the rate constant and the identity of the products. A pre-exponential factor of 2×10^{-11} was chosen as a reasonable estimate and the temperature dependence was derived from a fit to the room temperature rate constant. Clearly, temperature dependent studies are needed.
9. New recommendation based on results of Stief et al. (1978). Note that this is an upper limit based on instrumental sensitivity. NASA RP-1010 recommended an estimated temperature dependent expression based on the room temperature value of Phillips and Schiff (1962) which was about a factor of 500 greater than the upper limit recommended here. Results of Garvin and Broida (1963) cast doubt on the fast rate reported by Phillips and Schiff and as such support Stief's results. Independent confirmation is needed.
10. Based on least squares fit to data in studies of Davis et al. (1974b), Graham and Johnston (1974) and Hue and Herron (1974).
11. Reactions of $O(^1D)$

The recommendations adopt the time-resolved $O(^1D)$ emission measurements at the National Oceanic and Atmospheric Administration (NOAA) Laboratories for the reactions with N_2O , H_2O , CH_4 , H_2 , N_2 , O_2 , O_3 , HCl , $CFCl_3$, CF_2Cl_2 , NH_3 and CO_2 (Streit et al. (1976), Davidson et al. (1977) and Davidson et al. (1978b).

Rate constants for all the above reactions (except the reaction with HCl) have also been measured at the Cambridge Laboratory (Heidner and Husain (1973), Heidner, Husain and Wiesenfeld (1973), and Fletcher and Husain (1976a, 1976b). These results are based on time resolved $O(^1D)$ resonance absorption measurements. Data analysis uses the modified Lambert-Beer law $I_t/I_o = \exp(-\epsilon(Cl)^\gamma)$ where $\gamma = 0.41$.

11. (Cont.)

The analysis of the latter results is less straightforward than that of the time resolved emission measurements since an independent calibration of the value of γ is required. Additionally, the results from the NOAA Laboratories for N_2O , H_2O , CH_4 , N_2 , O_2 , O_3 and CO_2 have been confirmed very recently by a completely independent technique of J. R. Wiesenfeld, private communication (1978).

Branching ratio for reaction of $O(^1D)$ with N_2O to give $N_2 + O$ or $NO + NO$ is based on the results of Davidson et al. (1978a) and Pirkel et al. (1977).

Branching ratio for reaction of $O(^1D)$ with CH_4 to give $OH + CH_3$ or $H_2 + CH_2O$ is from Lin and DeMore (1973).

Recommendation of $k(O(^1D) + N_2 + M \rightarrow N_2O + M)$ is based on study by Kajimoto and Cvetanovic (1976) relative to $k_{O(^1D) + N_2}$. Uncertainty reflects comparison with results of Gaedtke et al. (1973) and Simonaitis et al. (1972).

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. (1974).

For the reactions of $O(^1D)$ with CCl_2O , CFC_2O and CF_2O , rate constants are reported only by the Cambridge Laboratory (Fletcher and Husain (1978)). Thus, for consistency, the recommended values for these rate constants had to be derived using a scaling procedure. This procedure preserves the relative placement of these rate constants among the set of Cambridge Laboratory data but employs an average ratio (0.50) of the NOAA to Cambridge Laboratory rate constants for those reactions studied by both groups.

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 $k_{298 K}$.

11. (Cont.)

The chlorocarbon rate constants are for total disappearance of $O(^1D)$ and probably include physical quenching. Lower limits have been reported for the fraction of the total rate of disappearance of $O(^1D)$ proceeding through the reactive channel forming ClO for $CFCl_3$ (≥ 0.39) and CF_2Cl_2 (≥ 0.49) (Gillespie et al. (1977)). It is not possible to give corresponding values for the reaction $O(^1D)$ with CCl_2O and $CFClO$.

There are significant changes from the recommendations given in NASA RP-1010 for the values of the rate constants for the reactions of $O(^1D)$ with CF_2Cl_2 , CCl_2O , $CFClO$ and CF_2O since the studies upon which the present recommendations are based did not exist at the time of the previous evaluation. There are minor changes in the values recommended for each of the reactive channels with N_2O based on new measurements of the branching ratio.

In view of the fact that there are two disparate sets of data and that the recommendations are based primarily on one of these, the error limits cited (1σ) are somewhat larger than reported in the NOAA studies.

12. Based on study of Graham and Johnston (1978) and 298 K and 329 K. While limited in temperature range, the data indicate no temperature dependence. Furthermore by analogy with the reaction of O with NO_2 it is assumed that this rate constant is in fact independent of temperature. Clearly, temperature dependent studies are needed.
13. Based on Kaiser and Japar (1978).
14. Based on Kaiser and Japar (1977).
15. The recommended value is derived from the upper limit of Chang and Kaufman (1978) and the measurement of Burrows et al. (1977) and is within the experimental accuracy of both studies although it is not compatible with the DeMore and Tschuikow-Roux (1974) value of $1 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ derived from their rate constant ratio.
16. This is the room temperature value of Hamilton and Lii (1977) and Cox (1978a). Both studies found the rate constant to be sensitive to the presence of water vapor (at the torr level). There is preliminary evidence in the Cox study for a very strong negative temperature

16. (Cont.)

dependence ($E/R = -1245$ K) although the data are very limited. However, there is evidence that the strong temperature dependence does not obtain at low pressure. Thus for the time being, we recommend $E/R = 0$, with a lower uncertainty bound of -1245 . Preliminary evidence of a pressure dependence (Burrows et al. (1978); Cox (1978a)) would, if confirmed, require a further change in the recommendation.

17. The recommended value for this reaction is that of Howard et al. (Howard and Evenson (1977); Zahniser and Howard (1978)). These studies are also confirmed at room temperature by Margitan and Anderson (1978) and Burrows et al. (1978), with all four determinations lying in the range of $8.0 \pm 0.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.
18. The room temperature value is an average of the four reported determinations (Zahniser and Howard (1978); Margitan and Anderson (1978); DeMore and Tschuikow-Roux (1974); and Simonaitis and Heicklen (1973)). The Zahniser and Howard work is the most direct and, presumably, the best determination and gives $E/R = 580$. This temperature dependence is confirmed by the last two studies, which were ratios relative to $k_{\text{HO}_2 + \text{HO}_2}$, when the Cox (1978a) E/R value recently reported for that reaction is used, thus lending additional credence to that determination. The A-factor is unusually low.
19. The room temperature value is an average of five studies (Anderson and Kaufman (1973); Kurylo (1973); DeMore (1975); Margitan and Anderson (1978); and Ravishankara et al. (1978b)). The Anderson and Kaufman and Ravishankara et al. studies are in excellent agreement on the temperature dependence ($E/R = 955$ and 930 , respectively) and are confirmed by DeMore's data over a more limited range.
20. This value is based on the work of Kaufman (1964), Clyne (1963) and Westenberg et al. (1970).
21. This is the recent measurement of Burrows et al. (1977). There are no T dependence data.

22. This expression is that of Davis et al. (1974a). In view of the difficulties in studying H_2O_2 reactions, another study is needed to confirm the rate constant, especially at low temperatures. A-factor seems low.
23. The recommendation is an average of the recent results of Lee et al. (1978b) and Keyser (1979a), 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.
24. This value is based on a re-evaluation of the recent measurements of Westenberg and de Haas (1973a), McKenzie et al. (1973), Clyne and Down (1974) and Trainor and von Rosenberg (1974). There are no T dependence data around room temperature.
25. This value is a composite of a recent Hack et al. (1975) measurement of $8 \times 10^{-12} \exp(-\frac{670}{T}) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ with earlier work of Greiner (1968). Although the two studies are in relatively good agreement, there are reasons to question both determinations. The Greiner work involved a large temperature increase due to absorption of flash energy. The Hack et al. study used radical densities of $3 \times 10^{13} \text{cm}^{-3}$ and may have been complicated by the back reaction between the product HO_2 and residual NO from the OH formation step. The new value for $k(\text{HO}_2 + \text{NO})$ of 8×10^{-12} implies a very rapid reconversion. Additional studies are needed. The A-factor seems unreasonably high for this type of reaction.
26. The recommended expression is $k = 1.35 \times 10^{-13} \times [1 + P(\text{atm})]$, which allows for the factor of 2 increase in k seen in several studies at 1 atm pressures of non-inert gases. The most detailed study (Biermann et al. (1978)) found that the pressure effect requires either (a) small amounts of O_2 (> 0.25 torr) or (b) the presence of other impurities. Further study of the combined pressure and temperature effects is needed.
27. This reaction is one of the few not requiring further work. All four T dependence studies are in excellent agreement. The recommendation is unchanged from other evaluations (NBS, NASA).

28. This reaction is new to the NASA table. The recommendation is based on three T dependence studies which are in very good agreement (Smith and Zellner (1974); Greiner (1969); and Atkinson et al. (1975). The $k(298)$ is based on these studies plus other room temperature determinations (see NBS SP 513). Because of the wider temperature range of the Smith and Zellner study, this evaluation weights their results heavily. We are aware, however, that this procedure results in a surprisingly high A-factor for this reaction.
29. Unchanged from NASA 1010. The results reported for $k(298\text{ K})$ by Watson et al. (1976), Zahniser et al. (1976), Kurylo and Braun (1976a) and Clyne and Nip (1976a) are in good agreement, and have been used to determine the preferred value at this temperature. The values reported by Leu and DeMore (1976) (due to the wide error limits) and Clyne and Watson (1974a) (the value is inexplicably high) are not considered. The four Arrhenius expressions are in fair agreement within the temperature range 205-300 K. In this temperature range, the rate constants at any particular temperature agree to within (30-40%). Although the values of the activation energy obtained by Watson et al., and Kurylo and Braun are in excellent agreement, the value of k in the study of Kurylo and Braun is consistently (~17%) lower than that of Watson, et al. This may suggest a systematic underestimate of the rate constant, as the value of the other three studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (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 298 K. Inclusion of higher temperature ($\leq 466\text{ K}$) experimental data would yield the following Arrhenius expression: $k = (3.34 \pm 1.0) \times 10^{-11} \exp(-(310 \pm 76)/T)$.
30. Unchanged from NASA 1010. The preferred values were derived in the same manner as the previous NASA evaluation. This expression is based on values of $5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 and 230 K, respectively. These values were deduced from 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 reaction can be considered to be well understood, additional data are required.

31. Changed from NASA 1010. The results of the three mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978b) and Watson and Ray (1978)) are in excellent agreement at 298 K. However, unless it can be shown that the value reported by Zahniser and Kaufman (1977) is in error, the preferred value at 298 K is taken to be the mean of all of these results. The magnitude of the temperature dependence reported by Leu and DeMore, and Zahniser and Kaufman is in good agreement. The Arrhenius expression was derived by taking the average of the two values of E/R, and the pre-exponential A-factor was adjusted so that the expression yielded the preferred value of 1.8×10^{-11} at 298 K.
32. Unchanged from NASA 1010. There is good agreement between all six groups of workers at ~ 298 K (Takacs and Glass (1973c), Zahniser et al. (1974), Smith and Zellner (1974), Ravishankara et al. (1977a), Davis et al. (1975b), and Hack et al. (1976)) 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.
33. New entry. There are no experimental data for this reaction. This is an estimated value based on observed rates of OH reaction with similar compounds, combined with an estimated A-factor.
34. Changed from NASA 1010. The values reported from the absolute rate coefficient studies for k at 298 K range from 0.99 to 1.48×10^{-13} with a mean value of 1.16×10^{-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 1.05×10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weighting to the values reported in (Lin et al. (1978a), Watson et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977a), Zahniser et al. (1977), Michael and Lee (1977), and Keyser (1978)). The values derived for k at 298 K from the competitive chlorination studies (Lin et al. (1978a), Pritchard et al. (1954), Knox and Nelson (1959), Knox (1955), and Pritchard et al. (1955)) range from 0.95 - 1.13×10^{-13} , with an average value of 1.02×10^{-13} . The preferred value was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies.

34. (Cont.)

There have been eight absolute studies of the activation energy. In general the agreement between most of these studies can be considered to be quite good. However, for a meaningful analysis of the reported values 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 between ~ 200 and 500 K (Whytock et al. (1977a), Zahniser et al. (1977), and Keyser (1978)) and in each case a strong nonlinear Arrhenius behavior was observed. This behavior tends to partially explain the large variance in the values of E/R reported between those other investigators who only 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 below 300 K is very good, with values of (a) E/R ranging from 1229-1320 K, and (b) k (230 K) ranging from $(2.64 - 3.32) \times 10^{-14}$. The mean of the two discharge flow (Zahniser et al. (1977) and Keyser (1978) results is 2.67×10^{-14} , while the mean of the three flash photolysis (Watson et al. (1976), Manning and Kurylo (1977) and Whytock et al. (1977a)) results is 3.19×10^{-14} . There have not been any absolute studies at stratospheric temperatures other than those which utilized the resonance fluorescence technique. 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 $(7.74 - 8.76) \times 10^{-13}$. Three mass spectrometric studies have been performed above 300 K with E/R values ranging from 1409-1790 K. The data of Poulet et al. (1974) are sparse and scattered, that of Clyne and Walker (1973) show too strong a temperature dependence (compared to all other absolute and competitive studies) and k (298) is ~ 20% higher than the preferred value at 298 K, while that of Lin et al. is in fair agreement with the resonance fluorescence results. In conclusion, it should be stated that the best value of k from the absolute studies, both above and below 300 K, is 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 $(2.11 - 2.54) \times 10^{-14}$ with a mean value of 2.27×10^{-14} . The preferred value is an expression which attempts to best fit the results obtained between 200 and 300 K

34. (Cont.)

from all sources. The average value of k at 298 K is 1.04×10^{-13} , and at 230 K is 2.70×10^{-14} . (These averages include results from the three competitive chlorination systems): $k = 9.94 \times 10^{-12} \exp(-1359/T)$. This expression essentially yields values similar to those obtained in the discharge flow-resonance fluorescence studies.

35. Changed from NASA 1010. The values of $k(\text{Cl} + \text{HO}_2)/k(\text{Cl} + \text{H}_2\text{O}_2)$ reported by Leu and DeMore (1976), Poulet et al. (1978) and Thrush (1978) are in poor agreement. The discrepancy between the two mass-spectrometric results may be attributed to inaccurate estimations of the mass-spectrometric sensitivity for HO_2 . If the NASA preferred value of 4.7×10^{-13} for $k(\text{Cl} + \text{H}_2\text{O}_2)$ at 298 K is combined with the experimentally determined ratios, then values of 2.3, 8.0 and 4.9×10^{-11} are obtained for $k(\text{Cl} + \text{HO}_2)$. The preferred value was obtained by averaging these three "re-evaluated" values with the value reported by Cox and Derwent (1977). The temperature dependence for such an atom-radical process is expected to be weak. Based upon the data reported by Thrush (1978) an upper limit of 4.5×10^{-13} has been placed on the rate constant for production of $\text{ClO} + \text{OH}$ (1% total rate constant).
36. Unchanged from NASA 1010. The results reported by Molina et al. (1977a) and Kurylo (1977) are in good agreement, and this data has been used to derive the preferred Arrhenius expression. The value reported by Ravishankara et al. (1977b) at 245 K is a factor of 2 greater than those from the other studies and this may possibly be attributed to (a) secondary kinetic complications, (b) presence of NO_2 as a reactive impurity in the ClONO_2 , or (c) formation of reactive photolytic products. None of the studies reported identification of the reaction products.
37. Unchanged from NASA 1010. The results reported by Zahniser et al. (1977) and Ravishankara et al. (1977b) are in good agreement at ~ 245 K (within 25%) considering the difficulties associated with handling ClONO_2 . The preferred value is that of Zahniser et al. Neither study reported any data on the reaction products.
38. Unchanged from NASA 1010. Considering the experimental difficulties associated with handling ClONO_2 , and the low precision of the data of Ravishankara et al. (1976), the results are in fair agreement at 245 K.

38. (Cont.)

Therefore, the preferred value is taken to be that reported by Kurylo and Manning (1977). Neither study reported any information which could be used to identify products.

39. Unchanged from NASA 1010. Fair agreement exists between the results of Brown and Smith (1975), Wong and Belles (1971), Ravishankara et al. (1977a) and Hack et al. (1976) at 300 K (some of the values quoted for k (300 K) were obtained by extrapolation of the experimentally determined Arrhenius expressions), but these are a factor of ~ 7 lower than that of Balakhnin et al. (1971). Unfortunately the values reported for E/R are in complete disagreement, ranging from 2260-3755 K. The preferred value was based on the results reported by Brown and Smith, Wong and Belles, Ravishankara et al., and Hack et al. but not those reported by Balakhnin et al.
40. New entry. There are no experimental data; this is an estimated value based on rates of O-atom reactions with similar compounds.
41. Unchanged from NASA 1010. This value is based on the results obtained below 300 K by Watson et al. (1975) and Whytock et al. (1977b). Although the results of these two studies are in agreement below 300 K, the data at higher temperatures are in somewhat poorer agreement. Further, the combined expression, when combined with relative rate data for the reaction of atomic chlorine with H_2 and CH_4 , gives rates for $Cl + CH_4$ at 300 K and above which are significantly lower than those measured directly. The combined expression also is in poor agreement with the high temperature measurements of $k(Cl + H_2)$ by Benson et al. (1969). Thus, although this reaction is not important in the stratosphere, additional studies are needed particularly in the temperature region above 300 K.
42. Unchanged from NASA 1010 (despite new data). The preferred value at 298 K was obtained by taking the mean of all reported values (Watson et al. (1976), Leu and DeMore (1976), Michael et al. (1977), Poulet et al. (1978) and Keyser (1979b)). The agreement between the absolute and "relative" values reported by Poulet et al. should be considered fortuitous as their value of $k(Cl + CH_4)$ is $\sim 20\%$ greater than that preferred by the NASA panel. The Arrhenius expression is based on the activation energy reported by Michael et al. and an A-value that has

42. (Cont.)

been modified to yield the preferred value at 298 K. A large uncertainty has been placed on E/R due to the lack of data below 265 K, and the lack of confidence in the low A-factor (significantly lower than expected on theoretical grounds).

43. Unchanged from NASA 1010. Neither study (Leu and DeMore (1976), and Poulet et al. (1978)) can be considered to be definitive. Poulet et al. postulated that Leu and DeMore were observing removal of HNO_3 via a heterogeneous process. While this hypothesis is certainly tenable, the value of E/R reported by Poulet et al. is much higher than would be expected (resulting in a surprisingly low value for k at 298 K). Although this reaction is not important in atmospheric chemistry, additional studies are required to provide accurate Arrhenius parameters. Until further data becomes available the preferred value is based on assuming that the data of Leu and DeMore represents an upper limit. The uncertainties in k (298 K) and E/R allow for the data of Poulet et al. to be correct.
44. New entry. The results of the three studies (Michael et al. (1978b), Kurylo and Anderson (1978), Niki et al. (1978a)) are in good agreement at ~ 298 K. The preferred value at 298 K was obtained by combining the absolute values reported by Michael et al. (7.48×10^{-11}), and Kurylo and Anderson (7.18×10^{-11}), with the value obtained by combining the ratio of $k(\text{H}_2\text{CO})/k(\text{C}_2\text{H}_6)$ reported by Niki et al. (1.3 ± 0.1) with the NASA preferred value of $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k(\text{C}_2\text{H}_6)$ at 298 K (7.4×10^{-11}). The value of E/R was based on averaging the results of Michael et al. (E/R = 0) and Kurylo and Anderson (E/R = 131).
45. New entry. The results reported by all three groups (Clyne and Walker (1973), Watson et al. (1978) and Manning and Kurylo (1976)) are in good agreement at 298 K. However, the value of the activation energy measured by Watson et al. and Manning et al. is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for the $\text{Cl} + \text{CH}_4$ and similarly, the activation energy measured by Watson et al. and Manning et al. was significantly lower than that measured by Clyne and Walker. It is suggested that the discharge flow-mass spectrometric technique is 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 $\text{Cl} + \text{CH}_4$ studies). In the discussion of the $\text{Cl} + \text{CH}_4$ reaction it was suggested that some of the apparent discrepancy between the results of

45. (Cont.)

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 ($> 2 \times 10^{-10}$).

46. Unchanged from NASA 1010. Value based on the data of Clyne and Cruse (1972). No reliable data on the temperature dependence.
47. Changed from NASA 1010 due to new data. Cox et al. (1978) reported a value of $3.7 \times 10^{-28} \times T \times \exp(3217/T)$ for $K = k(\text{Cl} + \text{O}_2 + \text{M})/k(\text{ClOO} + \text{M})$. This corresponds to a value of $94.8^{+1.6}_{-1.0}$ kJ mol⁻¹ for $\Delta H_f^\circ(\text{ClOO})$, which is just within the uncertainty limits placed on the earlier estimated value for $\Delta H_f^\circ(\text{ClOO})$ of 89 ± 5 kJ mol⁻¹ (Watson, 1977).
48. Changed from NASA 1010 due to new data. Cox et al. (1978) reported values for $k_a(\text{Cl} + \text{ClOO} \rightarrow \text{Cl}_2 + \text{O}_2)$, and $k_b(\text{Cl} + \text{ClOO} \rightarrow 2 \text{ClO})$ of 9.8×10^{-11} and 4.7×10^{-12} , respectively, resulting in a ratio of ~ 20.9 for k_a/k_b . This compares with values previously reported for k_a/k_b of 108 (Johnston et al. (1969)) and 15 (Nicholas and Norrish (1968)). The absolute values of k_a and k_b are dependent upon the choice of $\Delta H_f^\circ(\text{ClOO})$. The preferred values are taken to be those reported by Cox et al. The previous NASA 1010 values were based on the data reported by Johnston et al. for k_a (in good agreement with Cox et al.), and the ratio of k_a/k_b reported by Nicholas and Norrish. The Arrhenius parameters are estimated.
49. Changed from NASA 1010 - previous value was estimated. The preferred value was obtained by taking a simple mean of the results reported by Birks and Leck (1978), Stimpfle et al. (1978) and Reimann and Kaufman (1978). This procedure was adopted because the value reported by Poulet et al. (1978) is significantly lower than those reported by the other groups. Because not all of the studies have yet been published, some of the values may change prior to publication. As for any radical-radical reaction the magnitude of the temperature dependence is expected to be small.

50. Unchanged from NASA 1010. 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.
51. Unchanged from NASA 1010. The results reported by Clyne and Watson (1977) and Basco and Dogra (1971) 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 $\text{BrO} + \text{BrO}$. Although the second reaction channel is shown proceeding directly to $\text{Br} + \text{Cl} + \text{O}_2$, it may proceed through $\text{Br} + \text{ClOO} (\Delta H^\circ = -27.5 \text{ kJ mol}^{-1})$ or $\text{Cl} + \text{BrOO} (\Delta H^\circ \text{ unknown})$.
52. No recommendation at present; however, if values are needed for modelling purposes, use those shown in NASA 1010, i.e., $k(\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClOO}) = 1 \times 10^{-12} \exp(-1238/T)$; $k(\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2) = 5 \times 10^{-13} \exp(-1238/T)$. The data base used for this evaluation has been discussed in detail by Watson (1977). At present no recommendation is given for the $\text{ClO} + \text{ClO}$ reaction as the partitioning between the channels (especially the temperature dependence of the partitioning) is not well established. Cox *et al.* (1978) have recently published a paper concerning the absolute values of the following channels: $\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClOO}$; $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$; $\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OClO}$; $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$. This data needs to be thoroughly evaluated before recommending any new values for these reaction pathways.
53. Unchanged from NASA 1010. The branching ratio between the two channels is not well-defined, but, for the present discussion, is assumed to be unity. The Arrhenius expressions were estimated on the basis of data reported by DeMore, Lin and Jaffe (1976).
54. Unchanged from NASA 1010. Data reported by Bemand, Clyne and Watson (1973).
55. Unchanged from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).
56. Minor modification from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973).

57. Unchanged from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), Davis et al. (1976) and Perry et al. (1976a)). The studies (Davis et al. (1975) and Butler et al. (1978)) which determined $k(\text{HO} + \text{CO})/k(\text{HO} + \text{CH}_3\text{Cl})$ are excluded until the kinetic behavior between HO + CO is better understood, and the accuracy of the HO + CH₄ : HO + CH₃Cl study (Cox et al. (1976a)) was probably no better than a factor of 2. Within the temperature range covered by Davis et al. (1976) and Perry et al. (298-400 K) the results agree to within 20%. However, the value of k obtained by using the Arrhenius expression of Perry et al. at 240 K would be ~ 40% lower than the value obtained directly at that temperature by Davis et al. (1976). The preferred value was obtained from a least squares fit to the data reported by Davis et al. (1975a) and Perry et al. Equal weighting was given to each of the biomolecular rate constants.
58. Minor modification to the A-factor from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), Davis et al. (1976) and Perry et al. (1976a)). The accuracy of the OH + CH₄ : OH + CH₂Cl₂ study (Cox et al. (1976a)) was probably no better than a factor of 2. The agreement at 298 K is good. The Arrhenius expression is based on the value of E/R reported by Davis et al., and an A-factor modified to fit the preferred value at 298 K.
59. Unchanged from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), and Davis et al. (1976)). The accuracy of the OH + CH₄ : OH + CHCl₃ study (Cox et al. (1976a)) was probably no better than a factor of 2. As the agreement at 298 K is excellent the preferred Arrhenius expression is that reported by Davis et al.
60. Changed from NASA 1010. The preferred values were derived using the data reported by Howard and Evenson (1976a), Watson et al. (1977), Perry et al. (1976a) and Chang and Kaufman (1977). The data of Clyne and Holt (1978) 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.
61. Minor modification from NASA 1010 due to new data. The values reported by Howard and Evenson (1976a) (298 K data only), Watson et al. (1977), Atkinson et al. (1975), Chang and Kaufman (1977), Handwerk and Zellner (1978) and Clyne and Holt (1978) for k at 298 K are in good agreement. Consequently the preferred value is a simple mean of all the results.

61. (Cont.)

However, the Arrhenius expression reported by Clyne and Holt is in very poor agreement with all other expressions, and as such the data reported by Clyne and Holt is not considered when deriving the preferred Arrhenius expression. The preferred Arrhenius expression was derived to best fit the data reported from all studies except that of Clyne and Holt.

62. Minor modification from NASA 1010 due to new data. The 298 K values reported by Howard and Evenson (1976a), Watson et al. (1977) and Handwerk and Zellner (1978) are in good agreement and have been averaged to obtain the preferred 298 K value. The Arrhenius expression of Watson et al. and Handwerk and Zellner are in excellent agreement. The preferred Arrhenius parameters were obtained from a least squares treatment of all published data.
63. Changed from NASA 1010. The preferred value is derived by giving equal weighting to all of the absolute rate coefficient data. At present no explanation can be given to the difference at 298 K between the data reported by Howard and Evenson (1976b) and Watson et al. (1977) and that reported by Chang and Kaufman (1977) and Clyne and Holt (1978). The pre-exponential A-factors reported in the latter two studies appear to be somewhat lower than might be expected for abstraction from a carbon containing three hydrogen atoms.
64. Unchanged from NASA 1010. The preferred value at 298 K is a mean of the values reported by Howard (1976), Chang and Kaufman (1977) and Davis et al. (1978). As these values are in excellent agreement (better than 10%), the value reported by Winer et al. (1976) which is more than a factor of 10 greater must be rejected. The results of the temperature dependence studies reported by Chang and Kaufman, and Davis et al. are in excellent agreement (better than 30% at all temperatures between 220 and 425 K). The preferred Arrhenius parameters are those of Chang and Kaufman as the data of Davis et al. has yet to be published.
65. Changed from NASA 1010 due to new data. The results of the three absolute rate coefficient studies (Howard (1976), Chang and Kaufman (1977), and Davis et al. (1978)) are in excellent agreement at 298 K. The value derived from a relative rate coefficient study by Winer et al. (1976) is a factor of ~ 2 greater than the other values and is not considered in deriving the preferred value at 298 K. The Arrhenius parameters are those reported by Chang and Kaufman.

66. Unchanged from NASA 1010. The A-factor was estimated, and a lower limit derived for E/R by using the upper limits reported for the rate constants by Chang and Kaufman (1977) at ~ 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 (1978). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes.
67. Changed from NASA 1010 due to new data. The results reported for k (298 K) by Clyne and Watson (1975), Leu and DeMore (1977), Michael et al. (1978a) and Michael and Payne (1978) 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 220 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 should be synthesized to best fit all the data reported from these four studies.
68. Unchanged from NASA 1010. 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 such an atom-radical process, e.g., $O + ClO$.
69. Changed from NASA 1010 due to new data. The results of the three low pressure mass spectrometric studies (Clyne and Watson (1975), Ray and Watson (1978) and Leu (1978)) and the high pressure uv absorption study (Watson and Sander, (1978)), 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 (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 and Sander 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 dependence of k for the analogous ClO and HO₂ reactions are also negative, and are similar in magnitude.

70. Changed from NASA 1010 due to new data. Four of the five studies (Clyne and Coxon (1968), Clyne and Cruse (1970a), Basco and Dogra (1971), and Sander and Watson (1978), monitored the BrO radical concentration using ultraviolet absorption spectrometry. As the reaction being studied was second order in [BrO] knowledge of σ was required in order to determine k . There is substantial disagreement between the values of σ . Although the magnitude of σ is dependent upon the particular transition, and instrumental parameters such as spectral bandwidth, the most probable reason for the differences is that the techniques (based on reaction stoichiometries) used to determine σ in the early studies (Clyne and Coxon, Clyne and Cruse, and Basco and Dogra) was used incorrectly (discussed by Clyne and Watson (1975)). The most recent study (Sander and Watson (1978) used the same technique to determine σ , but avoided the problems. In three of the studies (Clyne and Coxon, Basco and Dogra, and Sander and Watson) there is good agreement in the reported values of k/σ ; however, this may be somewhat fortuitous as σ is expected to vary somewhat from study to study. The preferred value for k at 298 K is taken to be an average of the values reported by Clyne and Watson (the mass spectrometric study where knowledge of σ is not required) and Sander and Watson (the recent absorption study). There was no observable pressure dependence (50-600 torr) in the recent flash photolysis study. From the values of k reported by Clyne and Watson and Sander and Watson, it can be stated that the BrO + BrO reaction exhibits no pressure dependence within the range 1-600 torr. The recent flash photolysis study determined the temperature dependence of both k/σ and σ independently. The preferred Arrhenius expression uses the temperature dependence reported by Sander and Watson, and the pre-exponential A-factor was adjusted to yield the preferred value at 298 K. Although the partitioning of the total rate constant into its two components, k_1 and k_2 , was quantitatively studied at 298 K by Sander and Watson, and the ratio $k_1/(k_1 + k_2)$ reported to be 0.85 ± 0.5 , it is not clear whether this ratio would be expected to exhibit a temperature dependence (the values shown in the table assume the partitioning is invariant with temperature). Whereas the ratio of k_1/k_2 reported by Sander and Watson is in good agreement with that estimated by Cruse (1971), the temperature dependence of $k_1 + k_2$ disagrees (Clyne and Cruse incorrectly assumed that σ was independent of temperature).
71. Changed from NASA 1010. Based on a study reported by Sander and Watson (1978). Clyne and Cruse (1970a) also reported an upper limit of $8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of $\sim 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

72. Changed from NASA 1010. Re-evaluation of unpublished upper limit reported for k (298 K) by Leu and DeMore (1978a). No temperature dependent data available. An estimate for the Arrhenius expression would be: $k < 2 \times 10^{-12} \exp(-1400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The pre-exponential A-factor was chosen purely to be consistent with that determined for $\text{Cl} + \text{H}_2\text{O}_2$ reaction.
73. Changed from NASA 1010. Revised estimate of the rate constant, as there are still no experimental data. The rate constant for such an atom-radical process is expected to be rapid and relatively insensitive to temperature.
74. Changed from NASA 1010 due to new data. Takacs and Glass (1973a) combined their results with those of Wilson et al. (1969) and obtained the following Arrhenius expression $(3.7 \pm 0.7) \times 10^{-11} \exp(-579 \pm 70)/T$. However, this expression is not recommended as the extrapolation is over too wide a temperature range, and the value reported by Wilson et al. is questionable. The values reported for k (298 K) by Takacs and Glass, and Ravishankara et al. (1978b) differ by a factor of 2.4; therefore, until another study is performed the preferred value should be taken to be a simple mean of these values. The data reported by Ravishankara et al. shows that the rate constant exhibits no temperature dependence between 249-416 K. This observation is compatible with the estimated pre-exponential A-factor being comparable to the value of k at 298 K.
75. Unchanged from NASA 1010. As the values reported for k at 298 K (Takacs and Glass (1973b), Brown and Smith (1975) and Singleton and Cvetanovic (1976)) are in fair agreement, the mean is taken to be the preferred value. The agreement between the values deduced from the Arrhenius expressions reported in stratospheric temperatures is rather poor, e.g., the values differ by $\sim 70\%$ at 250 K. The preferred value has been synthesized to best fit both sets of data between 250 and 400 K. The A-factor derived for the preferred expression and that reported by Brown and Smith appear to be lower than would be expected. This, combined with the absence of data at stratospheric temperature, leads to considerable uncertainty in the values of k between 200 and 260 K.
76. New entry. No experimental data. Estimate based on the rate constant for $\text{ClO} + \text{HO}_2$.

77. Unchanged from NASA 1010. The preferred value at 298 K is the mean of the two results (Howard and Evenson (1976a) and Davis et al. (1976)) which are in excellent agreement. The A-factor of the Arrhenius expression looks a little low considering that there are three abstractable hydrogen atoms (the Arrhenius expression is that reported by Davis et al.).
78. New entry. 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 O₃.
79. New entry. The value of k at ~ 298 K seems to be fairly well established with the results of Homan et al. (1970), Dodonov et al. (1971), Clyne et al. (1973), Bozzelli (1973), and Igoshin et al. (1974) being in excellent agreement considering the diverse nature of the experimental techniques used. The value reported by Kompa and Wanner (1972) appears to be too high by a factor of ~ 2.5, whereas the values reported by Rabideau et al. (1972) and Lam et al. (1974) are too low by factors of 4 and 10, respectively. Therefore, the preferred value at 298 K is taken to be a mean of the five studies which are in good agreement. However, the magnitude of the temperature dependence cannot be considered to be well established with values of E/R of 805 (Homann et al.) and 544 (Igoshin et al.) being reported. The preferred Arrhenius parameters were derived by calculating A to be 2×10^{-10} , and calculating an E/R value to yield a value of 2.5×10^{-11} at 298 K. For detailed comments refer to reviews by Jones and Skolnik (1976) and Foon and Kaufman (1975). A-factor seems high.
80. New entry. 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 0.188. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0×10^{-11} for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al., and Foon and Reid, and the preferred Arrhenius parameters of the F + H₂ reaction. This reaction has recently been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). A-factor may be too high.

81. This is the value of Zetsch (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)).
82. New entry. 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 $(5.2 \pm 0.5) \times 10^{-11}$ Watson (1977) and $(2.5^{+2.5}_{-1.0}) \times 10^{-11}$ Clyne et al. (1976), respectively. 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).
83. New entry. Although there have been no experimental studies of this reaction, it has been used as a rapid titration reaction by Clyne and Watson (1974b). The 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 1.8×10^{-11} and 2.12×10^{-11} , respectively (NASA evaluations). 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 values of -200 K Zahniser and Kaufman (1977) and -300 K Leu and DeMore (1978b) for ClO, and -296 K Leu (1978) and -180 K Watson and Sander (1978) for BrO.
84. New entry. 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.
85. New entry. The FO + O₃ reaction has two possible pathways which are exothermic, resulting in the production of F + 2 O₂ or FO₂ + O₂. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical

85. (Cont.)

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 $FO + O_3 \rightarrow F + 2 O_2$ 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 $[F]_{\text{produced}}/[FO]_{\text{consumed}}$ is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al. whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2 O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al. utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and $FO + FO$ reactions by directly monitoring the time history of the concentrations of F , FO and O_3 . They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of $k(FO + FO)$ of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$ or 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 ($\sim 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) DeMore et al. (1976), and an upper limit of 8×10^{-14} Clyne and Cruse (1970a) and $5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ Sander and Watson (1978) have been reported for $BrO + O_3$.

86. New entry. 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.
87. New entry. No experimental data. k is assumed to be comparable to most other O^1D rate constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence.

88. This is an estimate (significantly higher than that in NASA 1010) based on an assumed similarity to the rapid $\text{HO}_2 + \text{NO}$ reaction. Cox et al. (1976b) give a lower limit of $1.2 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. Anastasi et al. (1978) also give a lower limit of $1 \times 10^{-12} \text{cm}^3 \text{sec}^{-1}$. There are no direct studies.
89. This estimate for k (298 K) is the geometric mean of the values for $\text{HO}_2 + \text{HO}_2$ and $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2$. There are no experimental values, direct or indirect.
90. The values for k (298 K) and E/R are from the Arrhenius expression determined by Barker et al. (1977) who measured the ratio $k(\text{CH}_3\text{O} + \text{O}_2)/k(\text{CH}_3\text{O} + \text{NO}_2 + \text{M})$ from 396 to 442 K. There are no direct studies.
91. The value for k (298 K) is the average of those determined by Atkinson and Pitts (1978) and Niki et al. (1978b). The E/R value is that of Atkinson and Pitts (1978). Evidence for the mechanism given is provided by Morris and Niki (1971). Further measurements are needed.
92. The values for k (298 K) and E/R are based on a recent study by Klemm et al. (1978) who studied the reaction using both discharge flow-resonance fluorescence (298-748 K) and flash photolysis-resonance fluorescence (250-498 K) techniques.
93. The value for k (298 K) is the average of the determinations by Washida et al. (1974), Shibuya et al. (1977) and Clark et al. (1978). Inclusion of the latter two measurements results in a value lower than that recommended in NASA 1010.
94. This estimate for k (298 K) is based on an assumed similarity to the $\text{OH} + \text{H}_2\text{O}_2$ and $\text{OH} + \text{C}_2\text{H}_6$ reactions. The E/R value is assumed to be the same as that for $\text{OH} + \text{H}_2\text{O}_2$. The latter value is, at present, somewhat uncertain.
95. The recommended value for k (298) is the average of the values determined by Hollinden et al. (1970), Whytock et al. (1976) and Slagle et al. (1978). $\Delta \log K$ was chosen to include the value of Cupitt and Glass (1970, 1975) within 2σ . The E/R value is the average of that determined by Hollinden et al. (1970) in the range 205 to 300 K and the mean of the two higher temperature studies (260-500 K) by Whytock et al. (1976) and Slagle et al. (1978). This procedure was adopted due to the possibility of a nonlinear Arrhenius plot and a change to an addition mechanism at low temperature as evidenced for other sulfur compounds (see Slagle et al. 1978). Further study in the 200 to 300 K range is recommended.

96. The value for k (298 K) is the average of five different studies of this reaction: Westenberg and de Haas (1969), 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.
97. The value of k (298 K) is the average of six determinations: Wei and Timmons (1975), Westenberg and de Haas (1969), Slagle et al. (1974), Callear and Smith (1967), Callear and Hedges (1970) and Homann et al. (1968). The E/R value is that of Wei and Timmons (1975). $\Delta E/R$ has been set to encompass within a 2σ error band the limited temperature data of Westenberg and de Haas (1969).
98. The recommended values for k (298 K) and E/R are the average of the values determined by Westenberg and de Haas (1973) and Perry et al. (1976b). $\Delta \log k$ has been chosen to encompass the value of Stuhl (1974) within the 2σ error band. $\Delta E/R$ was chosen to encompass both the 440 value of Westenberg and de Haas (1973b) and the zero value of Perry et al. (1976b). Although $2 \times \Delta E/R(2\sigma)$ allows for a negative value, we do not expect E/R to be less than zero.
99. The k (298 K) value is that reported by Kurylo (1978). The observations in this study at higher reactant pressures (a nonlinear dependence of first-order OH decay rates on reactant concentration) were similar to those of Atkinson et al. (1978) who set an upper limit considerably below the value recommended here. Kurylo attributed these observations to complications associated with secondary reactions. Under more stringent experimental conditions (lower reactant concentration and lower free radical concentrations), well-behaved kinetic results were obtained. These latter results were interpreted as being free from secondary reaction complications. Further study is recommended to determine the validity of this interpretation.

There are no measurements of the temperature dependence of these reactions. In the absence of any direct mechanistic information, no estimate of E/R or the A-factor can be given.

Kurylo and Laufer (1979) suggest the possibility of an addition mechanism in these reactions.

Table 2

Rate Constants for Third Order Reactions

| Reaction | Low Pressure Limit | | High Pressure Limit | |
|---|--|------------------------------|--|----------------------------|
| | $k_o(300)$ | n | $k_\infty(300)$ | m |
| $\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2\text{NO}_2$ | $(2.1 \pm 0.4)(-31)$ | 5 ± 2 | $(6.5 \pm 3.3)(-12)$ | 5 ± 2 |
| $\text{OH} + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_3$ | $(2.6 \pm 0.3)(-30)$ | 2.9 ± 0.7 | $(2.4 \pm 1.2)(-11)$ | 1.3 ± 1 |
| $\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_3$ (Two recommendations) | $(1.6 \pm 0.2)(-31)$ $(3.5 \pm 1.7)(-32)$ | 3.4 ± 0.3 3.8 ± 1 | $(1.5 \pm 0.7)(-11)$ $(1.5 \pm 0.7)(-11)$ | 1.9 ± 1 1.9 ± 1 |
| $\text{CH}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{O}_2$ | $(2.2 \pm 1.1)(-31)$ | 2.2 ± 1 | $(2 \pm 1) (-12)$ | 1.7 ± 1 |
| $\text{O} + \text{O}_2 \xrightarrow{\text{M}} \text{O}_3$ | $(6.2 \pm 0.8)(-34)$ | 2.1 ± 0.7 | - | - |
| $\text{O}(^1\text{D}) + \text{N}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}$ | $(3.5 \pm 3) (-37)$ | 0.45^{+2} $-.45$ | - | - |
| $\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$ | $(9 \pm 2) (-32)$ | 1.8 ± 0.5 | - | - |
| $\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_2$ (ClONO) | $(1.6 \pm 1.0)(-30)$ | 1.9 ± 1 | $(3.0 \pm 1.5)(-11)$ | 1 ± 1 |
| $\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClOO}$ | $(2 \pm 1) (-33)$ | 1.3^{+2} -1.3 | - | - |
| $\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$ | $(5.5 \pm 0.5)(-32)$ | 1.4 ± 1 | - | - |
| $\text{OH} + \text{NO} \xrightarrow{\text{M}} \text{HONO}$ | $(6.7 \pm 1.2)(-31)$ | 3.3 ± 1 | $(3.0 \pm 1.5)(-11)$ | 1 ± 1 |
| $\text{F} + \text{O}_2 \xrightarrow{\text{M}} \text{FO}_2$ | $(1.1 \pm 0.3)(-32)$ | 1.7 ± 1 | - | - |
| $\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$ | $(2.5 \pm 1.3)(-31)$ | 0.8^{+2} -0.8 | $(3.0 \pm 1.5)(-11)$ | 1 ± 1 |
| $\text{CH}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{O}_2\text{NO}_2$ | $(4.2 \pm 2.1)(-30)$ | 3.8 ± 2 | $(1.0 \pm 0.5)(-11)$ | 4 ± 2 |
| $\text{F} + \text{NO} \xrightarrow{\text{M}} \text{FNO}$ | $(6.6 \pm 3.3)(-32)$ | 1^{+2} -1 | - | - |

Table 2 (Cont.)

| <u>Reaction</u> | <u>k_o(300)</u> | <u>n</u> | <u>k_∞(300)</u> | <u>m</u> |
|--|--------------------------------------|---------------------------|---------------------------|-----------|
| FO + NO ₂ \xrightarrow{M} FNO ₃ | (8.3 ± 6) (-31) | 0.7 ⁺³ -0.7 | (2 ± 1) (-11) | 1.5 ± 1.5 |
| F + NO ₂ \xrightarrow{M} FNO ₂ (FONO) | (1.3 ± 0.7) (-30) | 1.7 ⁺² -1.7 | (3.0 ± 1.5) (-11) | 1 ± 1 |
| BrO + NO ₂ \xrightarrow{M} BrNO ₃ | Use 2 × k(ClO + NO ₂ + M) | | | |

Note: $k(z) = k(M, T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)} \right) 0.8 \left\{ 1 + \left[\log_{10}(k_o(T)[M]/k_\infty(T)) \right]^2 \right\}^{-1}$

Table 3. Photochemical Reactions of Stratospheric Interest

| | |
|---|--|
| * $O_2 + h\nu \rightarrow O + O$ (a) | $ClO_2 + h\nu \rightarrow$ products (c) |
| $O_3 + h\nu \rightarrow O + O_2$ (a) | $OCIO + h\nu \rightarrow O + ClO$ (c) |
| * $O_3 + h\nu \rightarrow O(^1D) + O_2$ | $ClO_3 + h\nu \rightarrow$ products |
| * $NO + h\nu \rightarrow N + O$ (a) | $HCl + h\nu \rightarrow H + Cl$ (c) |
| * $NO_2 + h\nu \rightarrow NO + O$ | * $HOCl + h\nu \rightarrow OH + Cl$ |
| * $NO_3 + h\nu \rightarrow NO + O_2$ | $ClNO + h\nu \rightarrow Cl + NO$ |
| * $NO_3 + h\nu \rightarrow NO_2 + O$ | $ClNO_2 + h\nu \rightarrow$ products |
| * $N_2O + h\nu \rightarrow N_2 + O(^1D)$ | $ClONO + h\nu \rightarrow$ products |
| $N_2O_5 + h\nu \rightarrow$ products | * $ClONO_2 + h\nu \rightarrow$ products |
| $NH_3 + h\nu \rightarrow NH_2 + H$ (a) | $Cl_2 + h\nu \rightarrow Cl + Cl$ (c) |
| $HO_2 + h\nu \rightarrow$ products (b) | $Cl_2O + h\nu \rightarrow Cl + ClO$ (c) |
| $H_2O + h\nu \rightarrow H + OH$ (a) | $CCl_4 + h\nu \rightarrow$ products (c) |
| * $H_2O_2 + h\nu \rightarrow OH + OH$ (a) | $CCl_3F + h\nu \rightarrow$ products |
| * $HNO_2 + h\nu \rightarrow OH + NO$ | * $CCl_2F_2 + h\nu \rightarrow$ products |
| $HNO_3 + h\nu \rightarrow OH + NO_2$ (a) | $CClF_3 + h\nu \rightarrow$ products |
| * $SO_2 + h\nu \rightarrow SO + O$ (a) | $CHCl_2F + h\nu \rightarrow$ products (c) |
| $H_2S + h\nu \rightarrow HS + H$ (b) | $CHClF_2 + h\nu \rightarrow$ products (c) |
| $CO + h\nu \rightarrow C + O$ (a) | $CH_2ClF + h\nu \rightarrow$ products (c) |
| $CO_2 + h\nu \rightarrow CO + O$ (a) | $CH_3Cl + h\nu \rightarrow$ products (c) |
| $CH_4 + h\nu \rightarrow$ products (b) | $CCl_2FCClF_2 + h\nu \rightarrow$ products |
| * $CH_2O + h\nu \rightarrow$ products (a) | $CClF_2CClF_2 + h\nu \rightarrow$ products |
| $ClO + h\nu \rightarrow Cl + O$ | $CClF_2CF_3 + h\nu \rightarrow$ products |

Table 3. Photochemical Reactions of Stratospheric Interest
(continued)

| | |
|--|---|
| $\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{products}$ | $\dagger \text{CH}_3\text{COOH} + h\nu \rightarrow \text{products}$ |
| $\text{CCl}_2\text{O} + h\nu \rightarrow \text{products}$ | $\dagger \text{COS} + h\nu \rightarrow \text{products}$ |
| $\text{CClFO} + h\nu \rightarrow \text{products}$ | $\dagger \text{BrONO}_2 + h\nu \rightarrow \text{products}$ |
| $\text{CF}_2\text{O} + h\nu \rightarrow \text{products}$ | |

* New data or comment.

† New entry.

(a) Hudson and Kieffer, 1975. Also see Hampson and Garvin, 1975.

(b) Turco, 1975.

(c) Watson, 1977.

Table 4. Reliability Estimates for Photochemical Rates

| Species | | Uncertainty Factor |
|---------------------------------|--|-----------------------|
| O ₂ | Schumann-Runge bands | 1.4 |
| O ₂ | Continua | 1.15 |
| O ₃ | | 1.12 |
| O ₃ | → O(¹ D); (T) | 1.4 |
| NO ₂ | (T) | 1.25 |
| NO ₃ | | 2.0 |
| NO ₃ | → { NO + O ₂ NO ₂ + O | 3.0 |
| N ₂ O | (T) | 1.2 |
| N ₂ O ₅ | | 2.0 |
| HO ₂ | | 2.0 |
| H ₂ O ₂ | | 1.4 |
| HNO ₂ | | 1.4 |
| HNO ₃ | | 1.15 |
| CH ₂ O | → { H + HCO H ₂ + CO (T) | 1.4 |
| HCl | | 1.12 |
| ClONO ₂ | (T) | 1.25 |
| CCl ₄ | | 1.1 |
| CCl ₃ F | | 1.05 |
| CCl ₂ F ₂ | (T) | 1.15 |
| CH ₃ Cl | | 1.1 |
| CF ₂ O | | 2.0 |

Table 4. Reliability Estimates for Photochemical Rates
(continued)

| Species | Uncertainty Factor |
|---------------------|-----------------------|
| CH ₃ OOH | 10 |
| COS | 1.25 |
| BrONO ₂ | (T)? |

(T) Temperature dependent

Table 5. Experimental and Calculated $O(^1D)$ Quantum Yields*

| (nm) | 230 K | | 263 K | | 298 K | | | 320 K | |
|------|--------------|-------|--------------|-------|-----------------|--------|---------------|--------------|-------|
| | E | C | E | C | E | C | L | E | C |
| 300 | 1.00 ± 0.03 | 1.00 | 1.00 ± 0.02 | 1.00 | 1.00 ± 0.01 | 1.00 | 0.966 ± 0.078 | 1.00 ± 0.02 | 1.00 |
| 301 | 0.995 ± 0.03 | 1.00 | 1.00 ± 0.02 | 1.00 | 1.00 ± 0.01 | 1.00 | 1.008 ± 0.047 | 1.00 ± 0.02 | 1.00 |
| 302 | 0.99 ± 0.035 | 0.997 | 1.00 ± 0.02 | 1.00 | 1.00 ± 0.01 | 1.00 | 1.001 ± 0.059 | 1.00 ± 0.02 | 1.00 |
| 303 | 0.98 ± 0.04 | 0.979 | 0.99 ± 0.03 | 1.00 | 1.00 ± 0.01 | 1.00 | 1.019 ± 0.024 | 1.00 ± 0.02 | 1.00 |
| 304 | 0.97 ± 0.045 | 0.953 | 0.98 ± 0.035 | 0.979 | 1.00 ± 0.015 | 1.00 | 1.000 ± 0.045 | 1.00 ± 0.02 | 1.00 |
| 305 | 0.94 ± 0.05 | 0.914 | 0.96 ± 0.04 | 0.949 | 0.98 ± 0.02 | 0.983 | 1.016 ± 0.005 | 1.00 ± 0.025 | 1.00 |
| 306 | 0.87 ± 0.06 | 0.851 | 0.91 ± 0.045 | 0.907 | 0.95 ± 0.03 | 0.942 | 0.960 ± 0.056 | 0.997 ± 0.03 | 0.991 |
| 307 | 0.72 ± 0.7 | 0.741 | 0.87 ± 0.05 | 0.847 | 0.90 ± 0.04 | 0.889 | 0.941 ± 0.015 | 0.96 ± 0.035 | 0.932 |
| 308 | 0.55 ± 0.07 | 0.560 | 0.76 ± 0.055 | 0.756 | 0.83 ± 0.05 | 0.819 | 0.855 ± 0.072 | 0.89 ± 0.04 | 0.861 |
| 309 | 0.36 ± 0.06 | 0.359 | 0.61 ± 0.06 | 0.626 | 0.73 ± 0.06 | 0.729 | 0.715 ± 0.039 | 0.78 ± 0.045 | 0.774 |
| 310 | 0.23 ± 0.05 | 0.222 | 0.45 ± 0.05 | 0.468 | 0.60 ± 0.055 | 0.619 | 0.567 ± 0.035 | 0.66 ± 0.05 | 0.674 |
| 311 | 0.15 ± 0.04 | 0.143 | 0.34 ± 0.05 | 0.326 | 0.49 ± 0.05 | 0.497 | 0.406 ± 0.055 | 0.53 ± 0.05 | 0.566 |
| 312 | 0.10 ± 0.04 | 0.097 | 0.22 ± 0.04 | 0.223 | 0.38 ± 0.05 | 0.378 | 0.242 ± 0.051 | 0.44 ± 0.055 | 0.458 |
| 313 | 0.07 ± 0.03 | 0.067 | 0.16 ± 0.035 | 0.153 | 0.29 ± 0.04 | 0.277 | 0.193 ± 0.008 | 0.38 ± 0.06 | 0.359 |
| 314 | 0.046 ± 0.02 | 0.046 | 0.12 ± 0.03 | 0.107 | 0.21 ± 0.03 | 0.197 | 0.091 ± 0.034 | 0.30 ± 0.055 | 0.274 |
| 315 | 0.026 ± 0.02 | 0.031 | 0.08 ± 0.025 | 0.074 | 0.14 ± 0.02 | 0.136 | 0.106 ± 0.013 | 0.22 ± 0.05 | 0.204 |
| 316 | 0.00 | 0.019 | 0.052 ± 0.02 | 0.049 | 0.078 ± 0.015 | 0.089 | 0.039 ± 0.043 | 0.14 ± 0.04 | 0.147 |
| 317 | 0.00 | 0.010 | 0.015 ± 0.02 | 0.031 | 0.037 ± 0.01 | 0.052 | 0.036 ± 0.180 | 0.095 ± 0.03 | 0.101 |
| 318 | 0.00 | 0.003 | 0.00 | 0.017 | 0.011 ± 0.01 | 0.024 | 0.047 ± 0.024 | 0.055 ± 0.02 | 0.064 |
| 319 | 0.00 | 0.00 | 0.00 | 0.005 | 0.0005 ± 0.0008 | 0.0007 | 0.011 ± 0.025 | 0.032 ± 0.02 | 0.033 |
| 320 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.005 ± 0.02 | 0.007 |
| 321 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

* From Moortgat and Kudszus (1978).

ϕ_E refers to the data obtained with the Xe-arc lamp/monochromator (Moortgat et al., 1977).

ϕ_L refers to the data obtained with the laser (Arnold et al., 1977).

ϕ_C are the calculated quantum yields using the cited formula (see text).

Table 6. Quantum Yields for NO₂ Photolysis*

| λ | ϕ | λ | ϕ | λ | 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 |

*From Harker et al. (1977).
 λ :nm.

Table 7. NO₂ Absorption Cross Sections at 235 and 298 K

| λ (nm) | σ (cm ²) | | λ (nm) | σ (cm ²) | |
|-------------------|-----------------------------|------------|-------------------|-----------------------------|------------|
| | 235 K | 298 K | | 235 K | 298 K |
| 185 | | 2.60 (-19) | 300 | 1.09 (-19) | 1.17 (-19) |
| 190 | | 2.93 | 305 | 1.67 | 1.66 |
| 195 | | 2.42 | 310 | 1.83 | 1.76 |
| 200 | | 2.50 | 315 | 2.19 | 2.25 |
| 205 | | 3.75 | 320 | 2.35 | 2.54 |
| 210 | | 3.85 | 325 | 2.54 | 2.79 |
| 215 | | 4.02 | 330 | 2.91 | 2.99 |
| 220 | | 3.96 | 335 | 3.14 | 3.45 |
| 225 | | 3.24 | 340 | 3.23 | 3.88 |
| 230 | | 2.43 | 345 | 3.43 | 4.07 |
| 235 | | 1.48 | 350 | 3.11 | 4.10 |
| 240 | | 6.70 (-20) | 355 | 4.37 | 5.13 |
| 245 | | 4.35 | 360 | 3.90 | 4.51 |
| 250 | | 2.83 | 365 | 5.37 | 5.78 |
| 255 | | 1.45 | 370 | 4.87 | 5.42 |
| 260 | | 1.90 | 375 | 5.00 | 5.35 |
| 265 | | 2.01 | 380 | 5.93 | 5.99 |
| 270 | | 3.13 | 385 | 5.79 | 5.94 |
| 275 | | 4.02 | 390 | 5.49 | 6.00 |
| 280 | | 5.54 | 395 | 5.62 | 5.89 |
| 285 | | 6.99 | 400 | 6.66 | 6.76 |
| 290 | 6.77 (-20) | 8.18 | 405 | 5.96 | 6.32 |
| 295 | 8.52 | 9.67 | 410 | 5.32 | 5.77 |

Table 8. NO₃ Absorption Cross Sections*

| λ (nm) | $10^{20}\sigma$ (cm ²) | λ (nm) | $10^{20}\sigma$ (cm ²) | λ (nm) | $10^{20}\sigma$ (cm ²) |
|-------------------|---------------------------------------|-------------------|---------------------------------------|-------------------|---------------------------------------|
| 497.8 | 94 | 593.8 | 232 | 629.8 | 358 |
| 502.8 | 47 | 595.8 | 222 | 630.8 | 289 |
| 507.8 | 80 | 597.8 | 207 | 631.8 | 217 |
| 512.8 | 75 | 599.8 | 195 | 632.8 | 162 |
| 517.8 | 70 | 601.8 | 182 | 637.8 | 65 |
| 522.8 | 85 | 603.8 | 238 | 642.8 | 75 |
| 527.8 | 119 | 605.8 | 193 | 647.8 | 33 |
| 532.8 | 90 | 607.8 | 135 | 652.8 | 70 |
| 537.9 | 107 | 609.8 | 95 | 655.8 | 70 |
| 542.8 | 90 | 611.8 | 119 | 657.8 | 115 |
| 547.8 | 163 | 612.8 | 108 | 658.8 | 199 |
| 552.8 | 149 | 613.8 | 108 | 669.8 | 371 |
| 557.8 | 226 | 615.8 | 112 | 660.8 | 604 |
| 562.8 | 178 | 617.8 | 120 | 661.8 | 713 |
| 567.8 | 209 | 619.8 | 202 | 662.8 | 692 |
| 572.8 | 143 | 620.8 | 310 | 663.8 | 604 |
| 577.8 | 177 | 621.8 | 459 | 664.8 | 480 |
| 579.8 | 144 | 622.8 | 521 | 665.8 | 439 |
| 581.8 | 170 | 623.8 | 552 | 666.8 | 344 |
| 583.8 | 131 | 624.8 | 490 | 667.8 | 256 |
| 585.8 | 130 | 625.8 | 453 | 668.8 | 173 |
| 587.8 | 225 | 626.8 | 440 | 669.8 | 123 |
| 589.8 | 280 | 627.8 | 449 | 670.8 | 64 |
| 591.8 | 260 | 628.8 | 413 | | |

*From Wayne et al. (1978).

Table 9. N₂O Absorption Cross Sections*

| Wave-length (nm) | | | | | | Wave-length (nm) | | | | | |
|------------------|-----------|-----------|-----------|-----------|-----------|------------------|-----------|-----------|-----------|-----------|-----------|
| | 194 K | 225 K | 243 K | 263 K | 296 K | | 194 K | 225 K | 243 K | 263 K | 302 K |
| 240 | | 3.83(-24) | 4.60(-24) | 5.00(-24) | 1.01(-23) | 209 | 5.23(-21) | 5.95(-21) | 6.27(-21) | 7.15(-21) | 9.80(-21) |
| 239 | | 4.40 | 5.60 | 5.95 | 1.23 | 208 | 6.50 | 7.35 | 7.82 | 8.75 | 1.16(-20) |
| 238 | | 5.30 | 6.70 | 7.35 | 1.52 | 207 | 7.87 | 8.95 | 9.52 | 1.07(-20) | 1.38 |
| 237 | | 6.60 | 8.25 | 9.50 | 1.91 | 206 | 9.90 | 1.09(-20) | 1.16(-20) | 1.30 | 1.65 |
| 236 | | 7.70 | 9.90 | 1.19(-23) | 2.40 | 205 | 1.19(-20) | 1.33 | 1.40 | 1.57 | 1.95 |
| 235 | | 9.65 | 1.22(-23) | 1.49 | 3.01 | 204 | 1.44 | 1.62 | 1.69 | 1.85 | 2.30 |
| 234 | | 1.21(-23) | 1.54 | 1.93 | 3.60 | 203 | 1.69 | 1.90 | 2.00 | 2.20 | 2.67 |
| 233 | | 1.51 | 1.91 | 2.46 | 4.78 | 202 | 2.04 | 2.26 | 2.40 | 2.60 | 3.09 |
| 232 | | 1.92 | 2.43 | 3.13 | 6.05 | 201 | 2.40 | 2.67 | 2.81 | 3.01 | 3.58 |
| 231 | | 2.50 | 3.06 | 4.05 | 7.60 | 200 | 2.85 | 3.08 | 3.28 | 3.52 | 4.09 |
| 230 | | 3.20 | 3.91 | 5.05 | 9.55 | 199 | 3.36 | 3.64 | 3.86 | 4.06 | 4.70 |
| 229 | | 4.05 | 5.00 | 6.45 | 1.20(-22) | 198 | 3.89 | 4.24 | 4.45 | 4.73 | 5.35 |
| 228 | | 5.25 | 6.40 | 8.35 | 1.51 | 197 | 4.55 | 4.88 | 5.10 | 5.42 | 6.10 |
| 227 | | 6.81 | 8.30 | 1.06(-22) | 1.90 | 196 | 5.18 | 5.53 | 5.83 | 6.14 | 6.82 |
| 226 | | 9.85(-22) | 1.07(-22) | 1.36 | 2.39 | 195 | 5.80 | 6.20 | 6.42 | 6.85 | 7.57 |
| 225 | | 1.16 | 1.37 | 1.75 | 3.03 | 194 | 6.48 | 6.90 | 7.25 | 7.51 | 8.11 |
| 224 | | 1.45 | 1.81 | 2.34 | 3.75 | 193 | 7.20 | 7.64 | 7.95 | 8.32 | 8.95 |
| 223 | | 1.87 | 2.30 | 2.95 | 4.74 | 192 | 7.72 | 8.40 | 8.75 | 9.20 | 9.75 |
| 222 | | 2.39 | 2.93 | 3.76 | 5.88 | 191 | 8.59 | 9.02 | 9.36 | 9.81 | 1.04(-19) |
| 221 | | 3.08 | 3.74 | 4.73 | 7.39 | 190 | 9.38 | 9.85 | 1.01(-19) | 1.06(-19) | 1.11 |
| 220 | | 3.98 | 4.82 | 6.01 | 9.22 | 189 | 9.97 | 1.05(-19) | 1.07 | 1.12 | 1.17 |
| 219 | | 5.19 | 6.14 | 7.58 | 1.15(-21) | 188 | 1.07(-19) | 1.11 | 1.17 | 1.19 | 1.25 |
| 218 | | 6.68 | 7.65 | 9.66 | 1.42 | 187 | 1.12 | 1.17 | 1.19 | 1.23 | 1.31 |
| 217 | | 8.75 | 1.02(-21) | 1.22(-21) | 1.79 | 186 | 1.16 | 1.22 | 1.25 | 1.29 | 1.36 |
| 216 | | 1.13(-21) | 1.29 | 1.54 | 2.23 | 185 | 1.22 | 1.27 | 1.31 | 1.35 | 1.43 |
| 215 | | 1.44 | 1.64 | 1.95 | 2.76 | 184 | 1.26 | 1.30 | 1.32 | 1.36 | 1.44 |
| 214 | | 1.87 | 2.06 | 2.45 | 3.42 | 183 | 1.28 | 1.33 | 1.35 | 1.39 | 1.46 |
| 213 | | 2.36 | 2.62 | 3.05 | 4.21 | 182 | 1.29 | 1.33 | 1.37 | 1.40 | 1.47 |
| 212 | | 3.00 | 3.31 | 3.80 | 5.18 | 181 | 1.32 | 1.34 | 1.36 | 1.39 | 1.46 |
| 211 | | 3.80 | 4.08 | 4.72 | 6.19 | 180 | 1.33 | 1.35 | 1.38 | 1.39 | 1.46 |
| 210 | 4.23(-21) | 4.70 | 5.11 | 5.79 | 7.55 | 179 | 1.30 | 1.32 | 1.34 | 1.37 | 1.44 |
| | | | | | | 178 | 1.28 | 1.28 | 1.29 | 1.31 | 1.39 |
| | | | | | | 177 | 1.27 | 1.28 | 1.29 | 1.31 | 1.40 |
| | | | | | | 176 | 1.24 | 1.23 | 1.25 | 1.27 | 1.34 |
| | | | | | | 175 | 1.16 | 1.15 | 1.17 | 1.18 | 1.26 |
| | | | | | | 174 | 1.14 | 1.14 | 1.15 | 1.17 | 1.19 |
| | | | | | | 173 | 1.07 | 1.08 | 1.10 | 1.11 | 1.13 |

*From Selwyn et al. (1977). 3.83(-24) = 3.83 x 10⁻²⁴ cm²

Table 10. N₂O₅ Absorption Cross Sections from 200 to 400 Nanometers

| λ (nm) | σ (cm ²) | λ (nm) | σ (cm ²) | λ (nm) | σ (cm ²) |
|-------------------|--------------------------------|-------------------|--------------------------------|-------------------|--------------------------------|
| 206 | 6.6(-18) | 246 | 4.3(-19) | 286 | 7.8(-20) |
| 208 | 5.9 | 248 | 3.8 | 288 | 7.1 |
| 210 | 5.2 | 250 | 3.5 | 290 | 6.3 |
| 212 | 4.4 | 252 | 3.0 | 292 | 5.7 |
| 214 | 3.7 | 254 | 2.72 | 294 | 4.9 |
| 216 | 3.0 | 256 | 2.55 | 296 | 4.4 |
| 218 | 2.48 | 258 | 2.33 | 298 | 3.8 |
| 220 | 2.06 | 260 | 2.12 | 300 | 3.2 |
| 222 | 1.71 | 262 | 1.97 | 302 | 2.7 |
| 224 | 1.41 | 264 | 1.86 | 304 | 2.4 |
| 226 | 1.23 | 266 | 1.7 | 306 | 2.1 |
| 228 | 1.06 | 268 | 1.64 | 308 | 1.8 |
| 230 | 9.3(-19) | 270 | 1.52 | 310 | 1.5 |
| 232 | 8.4 | 272 | 1.42 | 320 | 7.5(-21) |
| 234 | 7.5 | 274 | 1.31 | 330 | 4.0 |
| 236 | 6.9 | 276 | 1.2 | 340 | 2.7 |
| 238 | 6.3 | 278 | 1.15 | 350 | 1.8 |
| 240 | 5.7 | 280 | 1.07 | 360 | 1.0 |
| 242 | 5.3 | 282 | 9.9(-20) | 370 | 4.7(-22) |
| 244 | 4.7 | 284 | 8.9 | 380 | 1.3 |

Table 11. Absorption Cross Sections of H₂O₂ Vapor

| λ (nm) | Lin et al. 1978b | 10 ²⁰ σ (cm ²) Molina et al. 1977b | Mean |
|-------------------|---------------------|--|------|
| 210 | 36.3 | 38.3 | 37.3 |
| 220 | 26.4 | 27.5 | 27.0 |
| 230 | 18.7 | 19.6 | 19.2 |
| 240 | 12.9 | 13.5 | 13.2 |
| 250 | 8.9 | 9.0 | 9.0 |
| 260 | 5.5 | 5.7 | 5.6 |
| 270 | 3.4 | 3.6 | 3.5 |
| 280 | 2.1 | 2.1 | 2.1 |
| 290 | 1.14 | 1.3 | 1.2 |
| 300 | 0.66 | 0.76 | 0.71 |
| 310 | 0.38 | 0.45 | 0.42 |
| 320 | 0.21 | 0.27 | 0.24 |
| 330 | 0.13 | 0.17 | 0.15 |
| 340 | 0.08 | 0.10 | 0.09 |
| 350 | 0.04 | 0.06 | 0.05 |

Table 12. 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 |

*From Stockwell and Calvert (1978).

Table 13. Cross Sections and Quantum Yields for the
Photolysis of CH₂O*

| λ (nm) | $10^{20}\sigma$ (cm ²) | ϕ_1 | ϕ_2 |
|-------------------|---------------------------------------|----------|----------|
| 280 | 2.42 | 0.63 | 0.37 |
| 290 | 3.19 | 0.73 | 0.27 |
| 300 | 3.25 | 0.77 | 0.23 |
| 310 | 3.15 | 0.76 | 0.24 |
| 320 | 2.35 | 0.63 | 0.37 |
| 330 | 2.37 | 0.31 | 0.64 |
| 340 | 2.00 | 0 | 0.75 |
| 350 | 0.84 | 0 | 0.47 |
| 360 | 0.18 | 0 | 0.30 |

*From Cox (1978b).

Table 14. ClO₃ Absorption Cross Sections
from 200 to 350 Nanometers

| λ (nm) | $10^{18}\sigma$ (cm ²) | λ (nm) | $10^{18}\sigma$ (cm ²) |
|-------------------|---------------------------------------|-------------------|---------------------------------------|
| 200 | 5.3 | 280 | 4.6 |
| 210 | 5.0 | 290 | 4.3 |
| 220 | 4.8 | 300 | 4.0 |
| 230 | 4.3 | 310 | 3.2 |
| 240 | 3.5 | 320 | 2.5 |
| 250 | 3.7 | 330 | 1.8 |
| 260 | 4.3 | 340 | 1.1 |
| 270 | 4.5 | 350 | 0.76 |

Table 15. HOCl Absorption Cross Sections*

| λ (nm) | $10^{20}\sigma$ (cm ²) | λ (nm) | $10^{20}\sigma$ (cm ²) |
|-------------------|---------------------------------------|-------------------|---------------------------------------|
| 200 | 12.3 | 330 | 4.1 |
| 210 | 7.7 | 340 | 2.5 |
| 220 | 9.1 | 350 | 1.5 |
| 230 | 16.9 | 360 | 0.86 |
| 240 | 27.8 | 370 | 0.47 |
| 250 | 34.5 | 380 | 0.30 |
| 260 | 28.9 | 390 | 0.23 |
| 270 | 21.3 | 400 | 0.22 |
| 280 | 18.1 | 410 | 0.24 |
| 290 | 15.9 | 420 | 0.25 |
| 300 | 13.4 | 430 | 0.22 |
| 310 | 9.7 | 440 | 0.18 |
| 320 | 6.6 | 450 | 0.15 |

*From Molina and Molina (1978a).

Table 16. ClNO Absorption Cross Sections
from 190 to 400 Nanometers

| λ (nm) | σ (cm ²) | | |
|-------------------|-----------------------------|-----------|-----------|
| | (a) | (b) | Mean |
| 190 | 5.34(-17) | 5.20(-17) | 5.27(-17) |
| 200 | 7.19 | 6.74 | 6.97 |
| 210 | 3.36 | 2.99 | 3.18 |
| 220 | 1.26 | 1.07 | 1.17 |
| 230 | 4.36(-18) | 3.17(-18) | 3.77(-18) |
| 240 | 1.91 | 7.68(-19) | 1.34 |
| 260 | 1.99(-19) | 1.61 | 1.80(-19) |
| 280 | 1.13 | 9.35(-20) | 1.03(-20) |
| 300 | 1.03 | 8.67 | 9.49 |
| 320 | 1.33 | 1.08(-19) | 1.21(-19) |
| 340 | 1.50 | 1.24 | 1.37 |
| 360 | 1.30 | 1.13 | 1.22 |
| 380 | 8.86(-20) | 7.78(-20) | 8.32(-20) |
| 400 | 5.12 | 5.15 | 5.14 |

(a) Ballash and Armstrong (1974).

(b) Illies and Takacs (1976).

Table 17. ClNO₂ Absorption Cross Sections
from 190 to 400 Nanometers

| λ (nm) | σ (cm ²) | λ (nm) | σ (cm ²) |
|-------------------|--------------------------------|-------------------|--------------------------------|
| 190 | 2.69(-17) | 300 | 1.54 |
| 200 | 4.55(-18) | 310 | 1.32 |
| 210 | 3.39 | 320 | 1.02 |
| 220 | 3.42 | 330 | 7.11(-20) |
| 230 | 2.36 | 340 | 4.81 |
| 240 | 1.40 | 350 | 3.06 |
| 250 | 9.85(-19) | 360 | 1.82 |
| 260 | 6.37 | 370 | 1.07 |
| 270 | 3.73 | 380 | 0.62 |
| 280 | 2.31 | 390 | 0.38 |
| 290 | 1.80 | 400 | 0.21 |

Table 18. 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 |

Table 19. ClONO₂ Absorption Cross Sections

| λ (nm) | $10^{20} \sigma$ (cm ²) | | |
|-------------------|-------------------------------------|-------|-------|
| | 296 K | 243 K | 227 K |
| 450 | 0.005 | --- | --- |
| 445 | 0.007 | --- | --- |
| 440 | 0.009 | --- | --- |
| 435 | 0.013 | --- | --- |
| 430 | 0.016 | --- | --- |
| 425 | 0.020 | --- | --- |
| 420 | 0.027 | --- | --- |
| 415 | 0.035 | --- | --- |
| 410 | 0.044 | --- | --- |
| 405 | 0.055 | --- | --- |
| 400 | 0.064 | 0.058 | 0.056 |
| 395 | 0.077 | 0.070 | 0.069 |
| 390 | 0.090 | 0.083 | 0.082 |
| 385 | 0.108 | 0.100 | 0.098 |
| 380 | 0.122 | 0.114 | 0.113 |
| 375 | 0.139 | 0.130 | 0.128 |
| 370 | 0.162 | 0.140 | 0.142 |
| 365 | 0.179 | 0.159 | 0.155 |
| 360 | 0.208 | 0.173 | 0.170 |
| 355 | 0.218 | 0.183 | 0.182 |
| 350 | 0.246 | 0.205 | 0.198 |
| 345 | 0.285 | 0.223 | 0.214 |
| 340 | 0.323 | 0.255 | 0.246 |
| 335 | 0.397 | 0.307 | 0.283 |
| 330 | 0.514 | 0.381 | 0.353 |
| 325 | 0.655 | 0.502 | 0.463 |
| 320 | 0.895 | 0.681 | 0.630 |
| 315 | 1.23 | 0.954 | 0.892 |
| 310 | 1.69 | 1.35 | 1.28 |
| 305 | 2.38 | 1.89 | 1.80 |
| 300 | 3.30 | 2.61 | 2.51 |
| 295 | 4.56 | 3.83 | 3.74 |
| 290 | 6.36 | 5.36 | 5.45 |
| 285 | 8.80 | 7.33 | 7.50 |
| 280 | 11.9 | 9.98 | 10.4 |
| 275 | 16.1 | 13.5 | 13.9 |
| 270 | 21.5 | 18.0 | 18.3 |
| 265 | 26.9 | 23.1 | 23.3 |
| 260 | 34.6 | 30.1 | 30.7 |
| 255 | 44.7 | 39.1 | 39.8 |
| 250 | 57.7 | 50.9 | 52.6 |
| 245 | 77.0 | -- | 70.6 |
| 240 | 106 | -- | 98.5 |
| 235 | 149 | -- | 141 |

Table 19. ClONO₂ Absorption Cross Sections (continued)

| λ (nm) | $10^{20}\delta$ (cm ²) | | |
|-------------------|------------------------------------|-------|-------|
| | 296 K | 243 K | 227 K |
| 230 | 210 | -- | 206 |
| 225 | 286 | -- | 282 |
| 220 | 344 | -- | 348 |
| 215 | 360 | -- | 362 |
| 210 | 329 | -- | 330 |
| 205 | 299 | -- | 293 |
| 200 | 307 | -- | 293 |
| 195 | 381 | -- | 358 |
| 190 | 589 | -- | 555 |

Table 20. CCl₃F Absorption Cross Sections at 298 K

| λ (nm) | ν (10 ³ cm ⁻¹) | $10^{20}\sigma$ (cm ²) | | | |
|-------------------|--|------------------------------------|-------|------|-------|
| | | (a) | (b) | (c) | Mean |
| 186.0 | 54.0 | 255.0 | 247.0 | 226 | 243.0 |
| 187.8 | 53.5 | 227.0 | 218.0 | 206 | 217.0 |
| 189.6 | 53.0 | 197.0 | 186.0 | 175 | 186.0 |
| 191.4 | 52.5 | 164.0 | 160.0 | 152 | 159.0 |
| 193.2 | 52.0 | 141.0 | 134.0 | 125 | 133.0 |
| 195.1 | 51.5 | 115.0 | 112.0 | 105 | 111.0 |
| 197.0 | 51.0 | 93.2 | 93.3 | 84.5 | 90.3 |
| 199.0 | 50.5 | 74.3 | 74.2 | 70.6 | 73.0 |
| 201.0 | 50.0 | 59.0 | 58.0 | 55.0 | 57.3 |
| 203.0 | 49.5 | 45.7 | 44.0 | 46.0 | 45.2 |
| 205.1 | 49.0 | 34.1 | 32.9 | 33.0 | 33.3 |
| 207.3 | 48.5 | 24.8 | 23.0 | 23.8 | 23.9 |
| 209.4 | 48.0 | 17.3 | 16.2 | 16.8 | 16.8 |
| 211.6 | 47.5 | 11.6 | 11.2 | 11.8 | 11.5 |
| 213.9 | 47.0 | 7.8 | 7.3 | 7.8 | 7.6 |
| 216.2 | 46.5 | 4.9 | | 5.0 | 5.0 |
| 218.6 | 46.0 | 3.0 | | 3.2 | 3.1 |
| 221.0 | 45.5 | 2.1 | | 1.9 | 2.0 |
| 223.5 | 45.0 | 1.2 | | 1.2 | 1.2 |
| 226.0 | 44.5 | 0.8 | | 0.8 | 0.8 |
| | 44.0 | | | | |

(a) Chou et al. (1976).

(b) Robbins et al. (1975).

(c) Bass (private communication, 1976).

Table 21. Low-Temperature Absorption Cross Sections for CCl₃F

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20} \sigma$ (cm ²) | | | |
|-------------------|-------------------------------------|-------------------------------------|-----------|-----------|-----------|
| | | 252 K (a) | 232 K (a) | 213 K (a) | 222 K (b) |
| | 54.0 | | | | |
| 186.0 | 53.5 | | | | 233.0 |
| 187.8 | 53.0 | | | | 202.0 |
| 189.6 | 52.5 | | | | 176.0 |
| 191.4 | 52.0 | 164.0 | 161.0 | 161.0 | 143.0 |
| 193.2 | 51.5 | 141.0 | 137.0 | 137.0 | 120.0 |
| 195.1 | 51.0 | 114.0 | 110.0 | 110.0 | 97.0 |
| 197.0 | 50.5 | 91.3 | 88.5 | 88.5 | 79.8 |
| 199.0 | 50.0 | 72.1 | 69.1 | 69.1 | 62.6 |
| 201.0 | 49.5 | 56.6 | 54.3 | 53.1 | 50.8 |
| 203.0 | 49.0 | 43.0 | 41.1 | 40.2 | 38.9 |
| 205.1 | 48.5 | 31.7 | 30.0 | 28.6 | 28.6 |
| 207.3 | 48.0 | 22.6 | 21.1 | 19.8 | 19.6 |
| 209.4 | 47.5 | 15.2 | 14.2 | 13.3 | 13.5 |
| 211.6 | 47.0 | 9.9 | 9.1 | 8.5 | 8.7 |
| 213.9 | 46.5 | 6.4 | 5.7 | | 5.4 |
| 216.2 | 46.0 | 3.9 | 3.4 | | 3.3 |
| 218.6 | 45.5 | 2.3 | 2.0 | | 1.9 |
| 221.0 | 45.0 | | | | 1.2 |
| 223.5 | 44.5 | | | | 0.68 |
| 226.0 | 44.0 | | | | 0.40 |

(a) Chou et al. (1976).

(b) Bass (private communication, 1976).

Table 22. CCl_2F_2 Absorption Cross Sections at 298 K

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20} \sigma (\text{cm}^2)$ | | | Mean |
|-------------------|-------------------------------------|--------------------------------|-------|-------|--------|
| | | (a) | (b) | (c) | |
| 186.0 | 54.0 | 105.0 | 108.0 | 104.0 | 106.0 |
| 187.8 | 53.5 | 86.5 | 84.5 | 85.1 | 85.4 |
| 189.6 | 53.0 | 66.1 | 62.8 | 64.8 | 64.6 |
| 191.4 | 52.5 | 51.4 | 46.0 | 48.7 | 48.7 |
| 193.2 | 52.0 | 36.7 | 34.0 | 35.3 | 35.3 |
| 195.1 | 51.5 | 24.9 | 24.3 | 24.3 | 24.5 |
| 197.0 | 51.0 | 16.8 | 16.5 | 16.6 | 16.6 |
| 199.0 | 50.5 | 10.9 | 11.0 | 10.5 | 10.8 |
| 201.0 | 50.0 | 6.96 | 7.00 | 6.65 | 6.87 |
| 203.0 | 49.5 | 4.37 | 4.40 | 4.32 | 4.36 |
| 205.1 | 49.0 | 2.66 | 2.60 | 2.52 | 2.59 |
| 207.3 | 48.5 | 1.53 | 1.50 | 1.47 | 1.50 |
| 209.4 | 48.0 | 0.90 | 0.87 | 0.90 | 0.89 |
| 211.6 | 47.5 | 0.53 | 0.49 | 0.50 | 0.51 |
| 213.9 | 47.0 | 0.32 | 0.27 | 0.28 | 0.29 |
| 216.2 | 46.5 | 0.19 | 0.17 | 0.16 | 0.17 |
| 218.6 | 46.0 | 0.10 | | 0.089 | 0.095 |
| 221.0 | 45.5 | 0.05 | | | 0.05 |
| 223.5 | 45.0 | < 0.05 | | | < 0.05 |
| 226.0 | 44.5 | < 0.05 | | | < 0.05 |
| | 44.0 | | | | |

(a) Chou et al. (1976).

(b) Robbins et al. (1975).

(c) Bass (private communication, 1976).

Table 23. Low-Temperature Absorption Cross Sections of CCl_2F_2

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma(\text{cm}^2)$ | | |
|-------------------|-------------------------------------|------------------------------|-----------|-----------|
| | | 252 K (a) | 230 K (a) | 222 K (b) |
| 186.0 | 54.0 | | | |
| 186.0 | 53.5 | 103.0 | 102.0 | 99.7 |
| 187.8 | 53.0 | 83.0 | 80.4 | 81.7 |
| 189.6 | 52.5 | 61.5 | 58.8 | 60.7 |
| 191.4 | 52.0 | 46.3 | 44.2 | 42.1 |
| 193.2 | 51.5 | 32.3 | 30.1 | 29.3 |
| 195.1 | 51.0 | 21.2 | 19.4 | 19.2 |
| 197.0 | 50.5 | 13.9 | 12.6 | 12.4 |
| 199.0 | 50.0 | 8.72 | 7.85 | 7.49 |
| 201.0 | 49.5 | 5.36 | 4.80 | 4.39 |
| 203.0 | 49.0 | 3.28 | 2.84 | 2.58 |
| 205.1 | 48.5 | 1.94 | 1.65 | 1.46 |
| 207.3 | 48.0 | 1.07 | 0.90 | 0.76 |
| 209.4 | 47.5 | 0.61 | 0.50 | 0.44 |
| 211.6 | 47.0 | 0.35 | 0.28 | 0.25 |
| 213.9 | 46.5 | 0.21 | 0.16 | 0.13 |
| 216.2 | 46.0 | 0.12 | 0.09 | 0.07 |
| 218.6 | 45.5 | 0.06 | 0.05 | 0.04 |

(a) Chou et al. (1976).

(b) Bass (private communication, 1976).

Table 24. Absorption Cross Sections for CClF_3 and $\text{CCl}_2\text{FCClF}_2$

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma(\text{cm}^2)$ | |
|-------------------|-------------------------------------|------------------------------|------------------------------|
| | | CClF_3 | $\text{CCl}_2\text{FCClF}_2$ |
| 184.6 | | 0.36 | 116.0 |
| 186.0 | 54.0 | 0.31 | 105.0 |
| 187.8 | 53.5 | 0.23 | 85.0 |
| 189.6 | 53.0 | 0.168 | 68.9 |
| 191.4 | 52.5 | 0.126 | 53.8 |
| 193.2 | 52.0 | 0.090 | 41.0 |
| 195.1 | 51.5 | 0.064 | 30.0 |
| 197.0 | 51.0 | 0.041 | 21.3 |
| 199.0 | 50.5 | 0.026 | 14.9 |
| 201.0 | 50.0 | 0.017 | 10.4 |
| 203.0 | 49.5 | 0.012 | 7.0 |
| 205.1 | 49.0 | | 4.7 |
| 207.3 | 48.5 | | 3.2 |
| 209.4 | 48.0 | | 2.05 |
| 211.6 | 47.5 | | 1.26 |
| 213.9 | 47.0 | | 0.78 |
| 216.2 | 46.5 | | 0.47 |
| 218.6 | 46.0 | | 0.29 |
| 221.0 | 45.5 | | 0.18 |
| 223.5 | 45.0 | | 0.11 |
| | 44.5 | | |

Table 25. Absorption Cross Sections for $\text{CClF}_2\text{CClF}_2$ and CClF_2CF_3

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma(\text{cm}^2)$ | | | | | |
|-------------------|-------------------------------------|------------------------------|-------|-------|----------------------------|-------|-------|
| | | $\text{CClF}_2\text{CClF}_2$ | | | CClF_2CF_3 | | |
| | | (a) | (b) | Mean | (a) | (b) | Mean |
| 186.0 | 54.0 | | | | | | |
| | 53.4 | 10.0 | 10.5 | 10.0 | 0.67 | 0.54 | 0.61 |
| 187.8 | 53.0 | 7.71 | 8.10 | 7.91 | 0.58 | 0.40 | 0.49 |
| 189.6 | 52.5 | 5.84 | 6.10 | 5.97 | 0.44 | 0.28 | 0.36 |
| 191.4 | 52.0 | 4.36 | 4.52 | 4.44 | 0.33 | 0.20 | 0.27 |
| 193.2 | 51.5 | 3.18 | 3.08 | 3.13 | 0.24 | 0.15 | 0.20 |
| 195.1 | 51.0 | 2.81 | 2.22 | 2.52 | 0.17 | 0.10 | 0.14 |
| 197.0 | 50.5 | 1.44 | 1.63 | 1.54 | 0.11 | 0.075 | 0.093 |
| 199.0 | 50.0 | 0.97 | 1.03 | 1.00 | 0.077 | 0.055 | 0.066 |
| 201.0 | 49.5 | 0.66 | 0.67 | 0.67 | 0.050 | | |
| 203.0 | 49.0 | 0.43 | 0.45 | 0.44 | 0.032 | | |
| 205.1 | 48.5 | 0.28 | 0.31 | 0.30 | | | |
| 207.3 | 48.0 | 0.18 | 0.18 | 0.18 | 0.012 | | |
| 209.4 | 47.5 | 0.12 | 0.10 | 0.11 | | | |
| 211.6 | 47.0 | 0.070 | 0.055 | 0.063 | | | |
| 213.9 | 46.5 | 0.044 | 0.041 | 0.043 | | | |
| 216.2 | 46.0 | 0.027 | | | | | |
| 218.6 | 45.5 | 0.015 | | | | | |

(a) Chou et al. (1978).

(b) Robbins (private communication, 1976).

Table 26. Absorption Cross Sections for CH_3CCl_3

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma$ (cm^2) | λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma$ (cm^2) |
|-------------------|-------------------------------------|--------------------------------------|-------------------|-------------------------------------|--------------------------------------|
| | 54.0 | | | 49.0 | |
| 186.0 | 53.5 | 325.0 | 205.1 | 48.5 | 80.5 |
| 187.8 | 53.0 | 284.0 | 207.3 | 48.0 | 63.9 |
| 189.6 | 52.5 | 246.0 | 209.4 | 47.5 | 51.1 |
| 191.4 | 52.0 | 215.0 | 211.6 | 47.0 | 39.4 |
| 193.2 | 51.5 | 189.0 | 213.9 | 46.5 | 28.1 |
| 195.1 | 51.0 | 168.0 | 216.2 | 46.0 | 19.6 |
| 197.0 | 50.5 | 148.0 | 218.6 | 45.5 | 12.5 |
| 199.0 | 50.0 | 128.0 | 221.0 | 45.0 | 8.3 |
| 201.0 | 49.5 | 111.0 | 223.5 | 44.5 | 5.1 |
| 203.0 | 49.0 | 95.4 | 226.0 | 44.0 | 2.9 |

Table 27. Absorption Cross Sections for CCl₂O, CClFO, and CF₂O

| λ (nm) | ν (10^3 cm^{-1}) | $10^{20}\sigma \text{ (cm}^2\text{)}$ | | |
|-------------------|-------------------------------------|---------------------------------------|-------|-------------------|
| | | CCl ₂ O | CClFO | CF ₂ O |
| 184.9 | | 204.0 | | 4.7 |
| 186.0 | 54.0 | 189.0 | 15.6 | 5.5 |
| 187.8 | 53.5 | 137.0 | 14.0 | 5.2 |
| 189.6 | 53.0 | 117.0 | 13.4 | 4.5 |
| 191.4 | 52.5 | 93.7 | 12.9 | 4.0 |
| 193.2 | 52.0 | 69.7 | 12.7 | 3.3 |
| 195.1 | 51.5 | 52.5 | 12.5 | 2.8 |
| 197.0 | 51.0 | 41.0 | 12.4 | 2.3 |
| 199.0 | 50.5 | 31.8 | 12.3 | 1.9 |
| 201.0 | 50.0 | 25.0 | 12.0 | 1.4 |
| 203.0 | 49.5 | 20.4 | 11.7 | 1.1 |
| 205.1 | 49.0 | 16.9 | 11.2 | 0.86 |
| 207.3 | 48.5 | 15.1 | 10.5 | 0.65 |
| 209.4 | 48.0 | 13.4 | 9.7 | 0.48 |
| 211.6 | 47.5 | 12.2 | 9.0 | 0.36 |
| 213.9 | 47.0 | 11.7 | 7.9 | 0.26 |
| 216.2 | 46.5 | 11.6 | 6.9 | 0.21 |
| 218.6 | 46.0 | 11.9 | 5.8 | 0.15 |
| 221.0 | 45.5 | 12.3 | 4.8 | 0.12 |
| 223.5 | 45.0 | 12.8 | 4.0 | 0.10 |
| 226.0 | 44.5 | 13.2 | 3.1 | 0.08 |

Table 28. OCS Absorption Cross Sections*

| λ (nm) | $10^{20}\sigma$ (cm ²) | | |
|-------------------|------------------------------------|-------|-------|
| | 296 K | 251 K | 232 K |
| 226.0 | 28.3 | 28.0 | 27.3 |
| 223.5 | 30.6 | 29.5 | 29.1 |
| 221.0 | 27.0 | 26.9 | 26.7 |
| 218.6 | 25.1 | 24.9 | 24.5 |
| 216.2 | 23.2 | 23.1 | 22.8 |
| 213.9 | 20.8 | 20.1 | 19.9 |
| 211.6 | 16.1 | 16.1 | 16.0 |
| 209.4 | 12.2 | 12.1 | 12.0 |
| 207.3 | 9.6 | 9.9 | 9.3 |
| 205.1 | 7.2 | 7.2 | 7.0 |
| 203.0 | 5.3 | 5.4 | 5.2 |
| 201.0 | 4.1 | 4.0 | 3.7 |
| 199.0 | 2.8 | 2.9 | 2.7 |
| 197.0 | 2.0 | 2.1 | 1.9 |
| 195.1 | 1.4 | 1.5 | 1.2 |
| 193.2 | 1.2 | 1.1 | 0.9 |
| 191.4 | 1.5 | 1.3 | 1.0 |
| 189.6 | 3.4 | 2.5 | 2.0 |
| 187.8 | 9.8 | 6.6 | 5.6 |
| 186.0 | 13.8 | 10.6 | 9.8 |

*From Chou et al. (1978).

Table 29. Ultraviolet Absorption Cross Sections (186-390 nm) of Bromine Nitrate

| λ (nm) | σ^a (cm ²) | λ (nm) | σ (cm ²) |
|----------------|-------------------------------|----------------|-----------------------------|
| 390 | 2.8(-20) | 250 | 7.8(-19) |
| 380 | 4.0 | 245 | 1.0(-18) |
| 370 | 4.9 | 240 | 1.3 |
| 360 | 6.2 | 235 | 1.7 |
| 350 | 7.7 | 230 | 1.9 |
| 345 | 8.5 | 225 | 2.1 |
| 340 | 8.7 | 220 | 2.4 |
| 335 | 9.5(-20) | 215 | 2.7 |
| 330 | 1.0(-19) | 210 | 3.2 |
| 325 | 1.1 | 205 | 4.3 |
| 320 | 1.2 | 200 | 7.2(-18) |
| 315 | 1.4 | 195 | 1.0(-17) |
| 310 | 1.5 | 190 | 1.3 |
| 305 | 1.8 | 186 | 1.5(-17) |
| 300 | 1.9 | | |
| 295 | 2.2 | | |
| 290 | 2.4 | | |
| 285 | 2.7 | | |
| 280 | 2.9 | | |
| 275 | 3.1 | | |
| 270 | 3.4 | | |
| 265 | 3.9 | | |
| 260 | 4.8 | | |
| 255 | 6.1(-19) | | |

^a2.8(-20) signifies $\sigma = 2.8 \times 10^{-20}$ cm².

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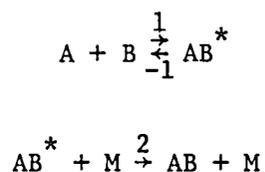
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APPENDIX

Three-Body Reactions

Three-body reactions are best treated as a separate grouping, since they are characterized by competition between energy transfer and chemical bonding. The simple representation of this phenomenon is seen via the "Lindemann Mechanism":



where AB^* represents a molecule with sufficient energy to decompose to A and B, and step 2 represents the collisional removal of this excess energy.

This mechanism yields a rate constant using the steady-state assumption:

$$\frac{d(AB)}{dt} = k_2(AB^*)(M) \quad ; \quad (AB^*) \cong \frac{k_1(A)(B)}{k_{-1} + k_2(M)}$$

$$k_{\text{expt}} \cong \frac{1}{(A)(B)} \frac{d(AB)}{dt} = \frac{k_1 k_2(M)}{k_{-1} + k_2(M)}$$

Two obvious limiting cases can be identified:

$$k_2(M) \gg k_{-1} \quad ; \quad k_{\text{expt}} \cong k_{\infty} = k_1 \quad (\text{chemistry controls})$$

$$k_2(M) \ll k_{-1} \quad ; \quad k_{\text{expt}} \cong k_o(M) = k_1 k_2(M) / k_{-1} \quad (\text{energy transfer controls})$$

expt = experimental

Thus:

$$\frac{1}{k_{\text{expt}}} = \frac{1}{k_1 k_2(M)} = \frac{1}{k_1} = \frac{1}{k_0(M)} = \frac{1}{k_\infty} = \frac{k_\infty + k_0(M)}{k_\infty k_0(M)}$$

and

$$k_{\text{expt}} = \frac{k_\infty k_0(M)}{k_\infty + k_0(M)} = \frac{k_0(M)}{1 + k_0(M)/k_\infty}$$

This last expression, rewritten to express the temperature dependence of the appropriate rate constants, can be used as a zeroth order approximation to the value of the rate constant as a function of T and [M] (or pressure).

$$k(Z) = k(M,T) = k_0(T)[M]/1 + k_0(T)[M]/k_\infty(T)$$

This level of approximation can be substantially improved without the introduction of any new parameters. Troe (1974, and Luther & Troe 1978) has suggested an inherently satisfying way of representing combination rate constants as a function of pressure and temperature (i.e., altitude), and Zellner (1978) has applied this representation to some of the reactions considered herein. (Troe has suggested higher order approximations as well, but we limit ourselves to the expression below.)

The essence of the Troe representation is an analytical form depending only on $k_0(T)[M]$ and $k_\infty(T)$, which connect low-pressure and high-pressure limiting values for the rate constant. Thus, it remains to have good values for these quantities and their temperature dependences. Such values are available from several sources

and it is these which are surveyed herein. We have chosen the best values (in our opinions), and we recommend using Troe's formula as presented by Zellner, viz:

$$k(Z) \equiv k(M,T) = \left(\frac{k_o(T)[M]}{1 + k_o(T)[M]/k_\infty(T)} \right) 0.8 \left\{ 1 + \left[\log_{10} \left(k_o(T)[M]/k_\infty(T) \right) \right]^2 \right\}^{-1} \quad (1)$$

Further, we recommend that the temperature dependences of the two limiting rate constants be written as follows:

$$k_{N_2}^o(T) = k_{N_2}^o(300)[T/300]^{-n} \text{ cm}^6 \text{ s}^{-2} \quad (2)$$

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

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

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

$$k_x^o(T) \equiv k_x^{o,sc}(T) \times \beta_x \quad (4)$$

where sc signifies "strong" collisions and β_x is an efficiency parameter ($0 < \beta < 1$) which provides a measure of energy transfer.

The coefficient β is related to the average energy transferred $\langle \Delta E \rangle$ via:

$$\frac{\beta_x}{1 - \beta_x^{1/2}} = \frac{\langle \Delta E \rangle_x}{F_E kT} \quad (5)$$

F_E is the correction factor of the energy dependence of the density of states (a quality 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 evaluating $k_x^{o,sc}(T)$ for the appropriate bath gas x and compute the value of β_x corresponding to the experimental value. The data is then evaluated based on the values of $\langle \Delta E \rangle_x$. From the evaluation we have selected our best estimate of the value for $\langle \Delta E \rangle_{N_2}$ (and thus β_{N_2}) for use in stratospheric modelling. Values of $k_{N_2}^o(T)$ are computed for $T = 200$ and 300 K by assuming (Troe, 1977) that $\langle \Delta E \rangle_{N_2}$ is temperature dependent, and recast in the form of equation (2) to obtain the recommended values.

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 render reactions of interest much closer to the low-pressure limit, and thus are 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 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.

Error limits were assigned in a subjective way, taking into account the reported precision and the uncertainties in the methods used herein.

This Appendix includes tables which list experimental results for rate constants evaluated (one table for each rate constant) The tables also show the

values of the strong collision rate constant $k_o^x(T)$ and the values of β_T^x implied from the measurements. The β 's lead directly to values of $\langle \Delta E \rangle_x$, the average amount of energy transferred per collision.

Temperature Dependence

In our recommendations we have suggested that the temperature dependences of the low-pressure limit rate constants be expressed as:

$$k_o(T) = k_o(300)(T/300)^{-n}$$

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

This procedure can be directly compared with measured values of $k_o(200 \text{ K})$ when those exist. Unfortunately, very few values of 200 K are available. There are often temperature dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data is to be extrapolated out of the measured temperature range, a choice must be made as to the functional form of the temperature dependence. There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression $k_o(T) = A \exp(-E/RT)$ or the form $k_o(T) = A' \cdot T^{-n}$ is employed. In comparing the reported temperature dependent data with our recommended values at 200 K, we have computed the value of 200 K from a reported Arrhenius expression and from the

other form, defining $n = (E/R)/\langle T \rangle$. We show this comparison in the tables of this Appendix. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the theory of Troe as explained heretofore as the basis for our recommendations.

Notes to Tables:

- (1) $k_0^x(T)$ = Low-pressure limiting rate constant with third-body x at temperature T. (Values in brackets are calculated from the values of $\langle \Delta E \rangle$ listed.)
- (2) T_{dep} = Exp; this is a direct experimental value.
 = T^{-n} ; this value has been extrapolated using either the reported value of n or $n = (E/R)/\langle T \rangle$ using the reported (E/R).
 = Arrhe; this value has been extrapolated using the reported Arrhenius expression.
 = Calc; this value has been calculated from the indicated value of $\langle \Delta E \rangle_x$ as explained in the text.
- (3) $k_0^{\text{sc}}(T)$ = Calculated low-pressure limit recombination rate constant based upon strong collision assumption.
- (4) β_T^x = $k_x^0(T)/k_0^{\text{sc}}(T)$ weak collision parameter.
- (5) $\langle \Delta E \rangle_x$ = Average amount of energy transferred, calculated from β . See text.
 When the entry in the table is bracketed, it is the average of several experiments.

Table A-1. $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|---------------------------------|-----|------------------|---------------|------------------------|-------------|------------------------------|---------------|
| 2.1×10^{-31} | 300 | Exp | N_2 | 5.0×10^{-31} | 0.42 | 0.81 | Howard (1977) |
| 1.0×10^{-31} | 300 | Exp | He | 10.5×10^{-31} | 0.1 | 0.096 | Howard (1977) |
| 1.5×10^{-31} | 300 | Exp | O_2 | 4.5×10^{-31} | 0.34 | 0.54 | Howard (1977) |
| $(6.6 \pm 3.3) \times 10^{-31}$ | 300 | Exp | NO_2 | 4.5×10^{-31} | ~1 | s.c. | Howard (1977) |
| $[1.6 \times 10^{-30}]$ | 200 | Calc | N_2 | 3.2×10^{-30} | 0.5 | $\langle 0.81 \rangle$ | |

Note: This table is presented first to illustrate the fact that β_x and $\langle \Delta E \rangle_x$ have the expected relative values. Absolute values depend strongly on $k_o^{\text{sc}}(T)$, which cannot be claimed to be accurate to more than a factor of two; however, these seem "reasonable" as well.

Recommended values:

$$k_o(300) = 2.1 \times 10^{-31}$$

$$k_\infty(300) = 6.5 \times 10^{-12}$$

$$k_o(T) = 2.1 \times 10^{-31} \left(\frac{T}{300} \right)^{-5}$$

$$k_\infty(T) = 6.5 \times 10^{-12} \left(\frac{T}{300} \right)^{-5}$$

Table A-2. OH + NO₂ + M → HONO₂ + M

| $k_o^x(T)$ | T | T _{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|---|-----|------------------------------------|----------------|-----------------------|--------------|------------------------------|--|
| 2.3×10^{-30} | 300 | Exp | N ₂ | 1.1×10^{-29} | 0.21 | 0.26 | Anderson, et al. (1974) 240-450K T ^{-2.5} or E/R = 900 |
| 6.3×10^{-30} 10.3×10^{-30} | 200 | T ⁻ⁿ reported Arrhe. | N ₂ | 2.8×10^{-29} | 0.23 0.37 | 0.19 0.41 | Anderson, et al. (1974) 240-450K T ^{-2.5} or E/R = 900 |
| 2.9×10^{-30} | 300 | Exp | N ₂ | 1.1×10^{-29} | 0.26 | 0.35 | Howard & Evenson (1974) |
| 2.6×10^{-30} | 300 | Exp | N ₂ | 1.1×10^{-29} | 0.24 | 0.31 | Harris & Wayne (1975) |
| 2.6×10^{-30} | 300 | Exp | N ₂ | 1.1×10^{-29} | 0.24 | 0.31 | Anastasi & Smith (1976) 220-550K T ^{-2.6} E/R = 813 |
| 7.5×10^{-30} 10.0×10^{-30} | 200 | T ⁻ⁿ reported Arrhe. | N ₂ | 2.8×10^{-29} | 0.27 0.37 | 0.25 0.41 | Anastasi & Smith (1976) 220-550K T ^{-2.6} E/R = 813 |
| $[2.6 \times 10^{-30}]$ | 300 | Average | N ₂ | 1.1×10^{-29} | 0.24 | <0.31> | |
| $[8.6 \times 10^{-30}]$ | 200 | Calc. | N ₂ | 2.8×10^{-29} | 0.31 | <0.31> | |

Note: The values of $k_o(200)$ computed from extrapolations of reported temperature dependences illustrate the uncertainty of these extrapolations and underscore our reason for recommending T-dependence as described in the text.

Recommended values:

$$k_o(300) = 2.6 \times 10^{-30}$$

$$k_\infty(300) = 2.4 \times 10^{-11} \text{ (Smith and Golden, 1978; Quack and Troe, 1977)}$$

$$k_o(T) = 2.6 \times 10^{-30} \left(\frac{T}{300} \right)^{-2.9}$$

$$k_\infty(T) = 2.4 \times 10^{-11} \left(\frac{T}{300} \right)^{-1.3}$$

Table A-3. $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-------------------|--------------|-----------------------|-------------|------------------------------|---|
| 1.5×10^{-31} | 300 | Exp | N_2 | 2.6×10^{-31} | 0.58 | 1.6 | Zahniser, et al. (1977) 246-387 K (He) $T^{-3.15}$ or E/R = 950 |
| 5.3×10^{-31} | 200 | T^{-n} reported | N_2 | 9.1×10^{-31} | 0.58 | 1.1 | Zahniser, et al. (1977) 246-387 K (He) $T^{-3.15}$ or E/R = 950 |
| 7.2×10^{-31} | | Arrhe. | | | | | |
| 1.8×10^{-31} | 300 | Exp | N_2 | 2.6×10^{-31} | 0.69 | 2.7 | Birks, et al. (1977) 250-356 K E/R = 1087 |
| 10.1×10^{-31} | 200 | Arrhe | N_2 | 9.1×10^{-31} | 0.85 | 4.6 | Birks, et al. (1977) 250-356 K E/R = 1087 |
| 7.7×10^{-31} | | T^{-n} | | | | | |
| 1.7×10^{-31} | 300 | Exp | N_2 | 2.6×10^{-31} | 0.65 | 2.2 | Leu, et al. (1977) 298-417 K E/R = 1150 |
| 11.6×10^{-31} | 200 | Arrhe | N_2 | 9.1×10^{-31} | 0.68 | 1.7 | Leu, et al. (1977) 298-417 K E/R = 1150 |
| 6.2×10^{-31} | | T^{-n} | | | | | |
| $[1.6 \times 10^{-31}]$ | 300 | Average | N_2 | 2.6×10^{-31} | 0.62 | $\langle 1.9 \rangle$ | |
| $[6.4 \times 10^{-31}]$ | 200 | Calc | N_2 | 9.1×10^{-31} | 0.70 | $\langle 1.9 \rangle$ | |

Recommended values:

$$k_o(300) = 1.6 \times 10^{-31}$$

$$k_{\infty}(300) = 1.45 \times 10^{-11} \text{ (Smith and Golden, 1978)}$$

$$k_o(T) = 1.6 \times 10^{-31} \left(\frac{T}{300}\right)^{-3.4}$$

$$k_{\infty}(T) = 1.45 \times 10^{-11} \left(\frac{T}{300}\right)^{-1.9}$$

Table A-4. $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------------|--------------|-----------------------|-------------|------------------------------|---|
| 3.5×10^{-32} | 300 | Calc. from reverse rxn | N_2 | 2.6×10^{-31} | 0.13 | 0.14 | Knauth (1978) |
| 1.6×10^{-31} | 200 | Calc. from reverse rxn | N_2 | 9.1×10^{-31} | 0.18 | 0.14 | Knauth (1978) |
| $[1.6 \times 10^{-31}]$ | 200 | Calc. | N_2 | 9.1×10^{-31} | 0.18 | $\langle 0.14 \rangle$ | Based on $\langle \Delta E \rangle = \text{const.}$ |

Note: Values obtained by measuring the disappearance of reactants in the indicated direction are about a factor of four higher than those obtained from the temperature dependence of the low-pressure limiting rate constant for the decomposition of ClONO_2 combined with an equilibrium constant calculated from $\Delta S = 40.6$ eu, $\Delta H = 26.12$ kcal mole⁻¹. It has been suggested that there are multiple pathways for the reaction of ClO with NO_2 , thus accounting for both the above discrepancy and the fact that the values of β obtained in the first three references seem high. Thus, we have made two different recommendations.

Recommended values: (2 sets)

$$k_o(300) = 3.5 \times 10^{-32}$$

$$k_\infty(300) = 1.45 \times 10^{-11}$$

$$k_o(T) = 3.5 \times 10^{-32} \left(\frac{T}{300} \right)^{-3.8}$$

$$k_\infty(T) = 1.45 \times 10^{-11} \left(\frac{T}{300} \right)^{-1.9}$$

Table A-5. $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{SC}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------|--------------|-----------------------|-------------|------------------------------|--|
| 1.9×10^{-31} | 300 | Exp. | N_2 | 2.3×10^{-31} | 0.82 | 5.78 | Washida & Bayes (1976) extrapolation to low pressure limit |
| 2.5×10^{-31} | 300 | Exp. | N_2 | 2.3×10^{-31} | 1 | | Basco, James & James (1972) extrapolation to low p |
| 3.1×10^{-31} | 300 | Exp. | N_2 | 2.3×10^{-31} | >1 | | Parkes (1977) extrapolation to low p |
| $[2.5 \times 10^{-31}]$ | 300 | Average | N_2 | 2.3×10^{-31} | 1 | | Average |
| $[5.4 \times 10^{-31}]$ | 200 | Calc. | | 5.4×10^{-31} | 1 | | |

Note: This rate constant (k_o) seems a little high, but since it is the only fate of CH_3 radical, the actual value is not very important. k_∞ is also very low for a radical combination.

Recommended values:

$$k_o(300) = 2.5 \times 10^{-31}$$

$$k_\infty(300) = 2 \times 10^{-12} \quad (\text{van den Bergh and Callear, 1971; Washida and Bayes, 1976; Basco et al., 1972; Laufer and Bass, 1978; Hochandal et al., 1977})$$

$$k_o(T) = 2.5 \times 10^{-31} \left(\frac{T}{300} \right)^{-2.2}$$

$$k_\infty(T) = 2 \times 10^{-12} \left(\frac{T}{300} \right)^{-1.7}$$

Table A-6. $O + O_2 + M \rightarrow O_3 + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-----------|-------|-----------------------|-------------|------------------------------|---|
| 5.8×10^{-34} | 300 | Exp | N_2 | 1.1×10^{-32} | 0.053 | 0.043 | Huie, Herron & Davis (1972) 200-346 K (N_2 , Ar) E/R = 507 |
| 1.23×10^{-33} | | T^{-n} | N_2 | | 0.068 | 0.041 | Huie, Herron & Davis (1972) 200-346 K (N_2 , Ar) E/R = 507 |
| 1.4×10^{-33} | 200 | Arrhe | N_2 | 1.8×10^{-32} | 0.077 | 0.045 | |
| 5.9×10^{-34} | | Exp | | | 0.054 | 0.044 | Johnston (1968) |
| 5.4×10^{-34} | 300 | Exp | N_2 | 1.1×10^{-32} | 0.049 | 0.04 | Stuhl & Niki (1971) |
| 8×10^{-34} | 300 | Exp | | | 0.073 | 0.063 | Hippler & Troel (1971); Hippler, et al. (1974) Slanger & Black (1970) |
| 7×10^{-34} | 300 | Exp | N_2 | 1.1×10^{-32} | 0.064 | 0.054 | |
| 5.4×10^{-34} | 300 | Exp | N_2 | 1.1×10^{-32} | 0.049 | 0.04 | Ball & Larkin (1973) |
| $[6.2 \times 10^{-34}]$ | 300 | Average | N_2 | 1.1×10^{-32} | 0.056 | $\langle 0.047 \rangle$ | |
| $[1.4 \times 10^{-33}]$ | 200 | Calc. | N_2 | 1.8×10^{-32} | 0.08 | $\langle 0.047 \rangle$ | |

Note: Low values of β are due to incomplete treatment of rotational effects in calculating $k_o^{sc}(T)$ (see Troe, 1979) is a very important reaction and the variation in measured values at 300 K might cause some concern. This is amplified by the fact that only one temperature-dependent study has been performed in N_2 . There have been temperature-dependent studies in other gases.

Recommended values:

$$k_o(300) = 6.2 \times 10^{-34}$$

$$k_o(T) = 6.2 \times 10^{-34} \left(\frac{T}{300} \right)^{-2.1}$$

Table A-7. $O(^1D) + N_2 + M \rightarrow N_2O + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-----------|-------|-----------------------|--------------------------------------|------------------------------|--|
| 3.5×10^{-37} | 300 | Exp | N_2 | 4.3×10^{-32} | 8.1×10^{-6} | | Kajimoto and Cvetanovic (1976) strange β value due to curve crossing |
| $[4.2 \times 10^{-37}]$ | 200 | Calc | N_2 | 5.3×10^{-32} | $\langle 8.1 \times 10^{-6} \rangle$ | | Based on same β |

Recommended values:

$$k_o(300) = 3.5 \times 10^{-37}$$

$$k_o(T) = 3.5 \times 10^{-37} \left(\frac{T}{300} \right)^{-0.45}$$

Table A-8. $F + O_2 + M \rightarrow FO_2 + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------|-------|-----------------------|-------------|------------------------------|-----------------------------------|
| 1.4×10^{-32} | 300 | Exp | N_2 | 7.7×10^{-32} | 0.18 | 0.21 | Arutyunov, Popov & Chaikin (1976) |
| 1.1×10^{-32} | 300 | Evaluation | N_2 | 7.7×10^{-32} | 0.14 | 0.15 | Watson (1978) |
| 3.3×10^{-32} | | Arrhe | | | 0.30 | 0.29 | |
| 2.5×10^{-32} | 200 | T^{-n} | N_2 | 1.1×10^{-31} | 0.23 | 0.20 | Watson (1978) |
| $[2.2 \times 10^{-32}]$ | 200 | Calc. | N_2 | 1.1×10^{-31} | 0.20 | $\langle 0.15 \rangle$ | |

Recommended values:

$$k_o(300) = 1.1 \times 10^{-32}$$

$$k_o(T) = 1.1 \times 10^{-32} \left(\frac{T}{300} \right)^{-1.7}$$

Table A-9. OH + OH + M → H₂O₂ + M

| $k_o^x(T)$ | T | T _{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-----------------------|-----|------------------|----------------|-----------------------|-------------|------------------------------|--------------------------------|
| 2.5×10^{-31} | 300 | Exp | N ₂ | 2.2×10^{-30} | 0.11 | 0.11 | Trainor & Von Rosenberg (1974) |
| 3.4×10^{-31} | 200 | Calc | N ₂ | 2.2×10^{-30} | 0.15 | <1.11> | |

Recommended values:

$$k_o(300) = 2.5 \times 10^{-31}$$

$$k_\infty(300) = 3 \times 10^{-11}$$

$$k_o(T) = 2.5 \times 10^{-31} \left(\frac{T}{300} \right)^{-0.8}$$

$$k_\infty(T) = 3 \times 10^{-11} \left(\frac{T}{300} \right)^{-1}$$

Table A-10. $C\ell + NO + M \rightarrow C\ell NO + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-----------|-------|-----------------------|-------------|------------------------------|---|
| 7×10^{-32} | 300 | Exp | N_2 | 2.7×10^{-31} | 0.26 | 0.33 | Lee, et al. (1978a) 200-400 K. E/R = 532 |
| 1.7×10^{-31} | | (Exp) | | 4.3×10^{-31} | 0.40 | 0.46 | |
| 1.4×10^{-31} | 200 | T^{-n} | N_2 | 4.3×10^{-31} | 0.47 | 0.64 | Lee, et al. (1978a) 200-400 K. E/R = 532 |
| 9.7×10^{-32} | 300 | Exp | N_2 | 2.7×10^{-31} | 0.36 | 0.57 | Clark, et al. (1968) 270-620 K E/R = 550 |
| 2.3×10^{-31} | | Arrhe | | 4.3×10^{-31} | 0.53 | 0.82 | |
| 1.6×10^{-31} | 200 | T^{-n} | N_2 | | 0.37 | 0.42 | Clark, et al. (1968) 270-620 K E/R = 550 |
| 1.1×10^{-31} | 300 | Exp | N_2 | | 0.41 | 0.72 | Ashmore & Spencer (1959) |
| 8.5×10^{-32} | 300 | Exp | N_2 | 2.7×10^{-31} | 0.31 | 0.44 | Ravishankara, et al. (1978) |
| $[9 \times 10^{-32}]$ | 300 | Average | N_2 | 2.7×10^{-31} | 0.33 | $\langle 0.52 \rangle$ | Average |
| $[1.9 \times 10^{-31}]$ | 200 | Calc. | N_2 | 4.3×10^{-31} | 0.43 | $\langle 0.52 \rangle$ | |

Note: The data presented here illustrate the problem of temperature extrapolation. Our recommended method seems to solve this problem as well as can be expected.

Recommended values:

$$k_o(300) = 9 \times 10^{-32}$$

$$k_o(T) = 9 \times 10^{-32} \left(\frac{T}{300} \right)^{-1.8}$$

Table A-11. $\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-----------------------|-----|------------------|--------------|-----------------------|-------------|------------------------------|---|
| 7.2×10^{-31} | 300 | Exp | Ar | 7.4×10^{-31} | 0.97 | | Clyne & White (1968) |
| 1.6×10^{-30} | 300 | Exp | N_2 | 8.9×10^{-31} | >1 | | Ravishankara, et al. (1978) |
| 3.4×10^{-30} | 200 | T^{-n} | N_2 | 1.3×10^{-30} | >1 | | Ravishankara, et al. (1978) Could mean that $\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO} + \text{M}$ $\rightarrow \text{ClNO}_2 + \text{M}$ |

Note: It is very interesting to notice that all values of β are greater than unity. This could mean that there is more than one path for reaction. See comments on the very similar situation in Tables A-3 and A-4. Recent studies (Niki, 1978) have reported both products.

Recommended values:

$$k_o(300) = 1.6 \times 10^{-30}$$

$$k_\infty(300) = 3 \times 10^{-11}$$

$$k_o(T) = 1.6 \times 10^{-30} \left(\frac{T}{300} \right)^{-1.9}$$

$$k_\infty(T) = 3 \times 10^{-11} \left(\frac{T}{300} \right)^{-1.0}$$

Table A-12. $\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$

| $k_o^x(T)$ | T | T _{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------|----|-----------------------|-------------|------------------------------|---------------------------|
| 5.6×10^{-34} | 300 | Exp | Ar | 5.2×10^{-33} | 0.11 | 0.11 | Stedman et al. (1968) |
| $<5.6 \times 10^{-33}$ | 300 | Exp | Ar | 5.2×10^{-33} | | | Clyne & Coxon (1968) |
| 1.7×10^{-33} | 300 | Exp | Ar | 5.2×10^{-33} | 0.33 | 0.51 | Nicholas & Norrish (1968) |
| $[1.1 \times 10^{-33}]$ | 300 | Average | Ar | 5.2×10^{-33} | 0.21 | [0.26] | Average |
| $[1.9 \times 10^{-33}]$ | 200 | Calc. | Ar | 6.6×10^{-33} | 0.28 | [0.26] | |

Note: Values are for x = Ar. The recommended values in N_2 were arrived at by multiplying by 1.8.

Recommended values:

$$k_o(300) = 2 \times 10^{-33} \text{ (Based on } k_{\text{N}_2}^{\text{N}_2}/k^{\text{Ar}} = 1.8$$

$$k_o(T) = 2 \times 10^{-33} \left(\frac{T}{300}\right)^{-1.3}$$

Table A-13. $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------|--------------|-----------------------|-------------|------------------------------|--|
| 5.6×10^{-32} | 300 | Evaluation | N_2 | 1.1×10^{-30} | 0.05 | 0.04 | NBS Review |
| 9.1×10^{-32} | 200 | | | 1.6×10^{-30} | 0.057 | 0.04 | |
| 5.0×10^{-32} | 300 | Exp | N_2 | 1.1×10^{-30} | 0.05 | 0.04 | Kurylo (1972) 203-404 K (Ar) E/R = 238 |
| 7.5×10^{-32} | 200 | Exp | N_2 | 1.6×10^{-30} | 0.05 | 0.04 | Kurylo (1972) 203-404 K (Ar) E/R = 238 |
| 6.9×10^{-32} | | T^{-n} | | | 0.043 | 0.04 | |
| 5.9×10^{-32} | 300 | Exp | N_2 | 1.1×10^{-30} | 0.05 | 0.04 | Wong & Davis (1974) 220-365K E/R = 344 |
| 9.8×10^{-32} | 200 | Arrhe | N_2 | 1.6×10^{-30} | 0.06 | 0.04 | Wong & Davis (1974) 220-365 K E/R = 344 |
| 8.3×10^{-32} | 200 | T^{-n} | | | 0.05 | 0.04 | |
| $[5.5 \times 10^{-32}]$ | 300 | Average | N_2 | 1.1×10^{-30} | 0.05 | $\langle 0.04 \rangle$ | Average |
| $[9.6 \times 10^{-32}]$ | 200 | Calc. | N_2 | 1.6×10^{-30} | 0.06 | $\langle 0.04 \rangle$ | |

Note: Low values of $\langle \Delta E \rangle$ result from rotational effects.

Recommended values:

$$k_o(300) = 5.5 \times 10^{-32}$$

$$k_o(T) = 5.5 \times 10^{-32} \left(\frac{T}{300} \right)^{-1.4}$$

Table A-14. OH + NO + M → HONO + M

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|--------------------------------|-----|--------------------------|----------------|-----------------------|-------------|------------------------------|--|
| 5.6×10^{-31} | 300 | Exp | N ₂ | 1.6×10^{-30} | 0.36 | 0.59 | Anderson, et al. (1974) 230-450 (He) E/R = 850 or T ^{-2.4} |
| 2.3×10^{-30} | 200 | Arrhe | N ₂ | 4.9×10^{-30} | 0.47 | 0.65 | Anderson, et al. (1974) 230-450 (He) E/R = 850 or T ^{-2.4} |
| 1.5×10^{-30} | | T ⁻ⁿ reported | | | 0.30 | 0.28 | |
| 7.8×10^{-31} | 300 | Exp | N ₂ | 1.6×10^{-30} | 0.50 | 1.13 | Howard & Evenson (1974) |
| $(1.5 \pm .5) \times 10^{-30}$ | 300 | Exp | N ₂ | 1.6×10^{-30} | 0.6~1 | | Harris & Wayne (1975) |
| [6.7×10^{-31}] | 300 | Average | N ₂ | 1.6×10^{-30} | 0.42 | <0.86> | |
| [2.6×10^{-30}] | 200 | Calc | N ₂ | 4.9×10^{-30} | 0.53 | <0.86> | |

Note: Once again the difference between Arrhenius and Tⁿ extrapolation is illustrated.

Recommended values:

$$k_o(300) = 6.7 \times 10^{-31}$$

$$k_\infty(300) = 3 \times 10^{-11}$$

$$k_o(T) = 6.7 \times 10^{-31} \left(\frac{T}{300} \right)^{-3.3}$$

$$k_\infty(T) = 3 \times 10^{-11} \left(\frac{T}{300} \right)^{-1.0}$$

Table A-15. $\text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------|--------------|-----------------------|-----------------------|------------------------------|------------|
| $[4.2 \times 10^{-30}]$ | 300 | Calc | N_2 | 1.4×10^{-29} | $\langle 0.3 \rangle$ | | |
| $[2.2 \times 10^{-20}]$ | 200 | Calc | N_2 | 7.2×10^{-29} | $\langle 0.3 \rangle$ | | |

Note: In the absence of data, we have guessed $\beta = 0.3$ for all situations.

Recommended values:

$$k_o(300) = 4.2 \times 10^{-30}$$

$$k_\infty(300) = 1 \times 10^{-11}$$

$$k_o(T) = 4.2 \times 10^{-30} \left(\frac{T}{300} \right)^{-3.8}$$

$$k_\infty(T) = 1 \times 10^{-11} \left(\frac{T}{300} \right)^{-4}$$

Table A-16. $F + NO + M \rightarrow FNO + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-----------|-------|-----------------------|-----------------------|------------------------------|------------|
| $[6.6 \times 10^{-32}]$ | 300 | Calc | N_2 | 2.2×10^{-31} | $\langle 0.3 \rangle$ | | |
| $[9.9 \times 10^{-32}]$ | 200 | Calc | N_2 | 3.3×10^{-31} | $\langle 0.3 \rangle$ | | |

Recommended values:

$$k_o(300) = 6.6 \times 10^{-32}$$

$$k_o(T) = 6.6 \times 10^{-32} \left(\frac{T}{300} \right)^{-1}$$

Table A-17. $\text{FO} + \text{NO}_2 + \text{M} \rightarrow \text{FONO}_2 + \text{M}$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{\text{sc}}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|------------------|--------------|------------------------|-----------------------|------------------------------|------------|
| $[8.3 \times 10^{-31}]$ | 300 | Calc | N_2 | 2.75×10^{-30} | $\langle 0.3 \rangle$ | | |
| $[1.1 \times 10^{-30}]$ | 200 | Calc | N_2 | 3.6×10^{-30} | $\langle 0.3 \rangle$ | | |

Recommended values:

$$k_o(300) = 8.3 \times 10^{-31}$$

$$k_\infty(300) = 2 \times 10^{-11}$$

$$k_o(T) = 8.3 \times 10^{-31} \left(\frac{T}{300} \right)^{-0.7}$$

$$k_\infty(T) = 2 \times 10^{-11} \left(\frac{T}{300} \right)^{-1.5}$$

Table A-18. $F + NO_2 + M \rightarrow FNO_2 + M$

| $k_o^x(T)$ | T | T_{dep} | x | $k_o^{sc}(T)$ | β_T^x | $\langle \Delta E \rangle_x$ | References |
|-------------------------|-----|-----------|-------|-----------------------|-----------------------|------------------------------|------------|
| $[1.3 \times 10^{-30}]$ | 300 | Calc | N_2 | 4.2×10^{-30} | $\langle 0.3 \rangle$ | | |
| $[2.5 \times 10^{-30}]$ | 200 | Calc | N_2 | 8.3×10^{-30} | $\langle 0.3 \rangle$ | | |

Recommended values:

$$k_o(300) = 1.3 \times 10^{-30}$$

$$k_\infty(300) = 3 \times 10^{-11}$$

$$k_o(T) = 1.3 \times 10^{-30} \left(\frac{T}{300} \right)^{-1.7}$$

$$k_\infty(T) = 3 \times 10^{-11} \left(\frac{T}{300} \right)^{-1}$$

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