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LEVEL II

Chemical Kinetic and Photochemical Data Sheets for Atmospheric Reactions

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Center for Thermodynamics
and Molecular Science
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16. Abstract

A set of individual data sheets for gas phase chemical reactions and photochemistry of neutral species is presented. These data sheets give preferred values for reaction rate constants, photoabsorption cross sections and quantum yields with a brief statement discussing the basis for the preferred value. Recent experimental results are also given. The coverage of this initial set of data sheets issued in February 1980 corresponds to the approximately 400 reactions listed in NBS Special Publication 513, R. F. Hampson and D. Garvin, May 1978. For approximately one quarter of these reactions the data entry has been updated to include the 1979 recommendations of the NASA Panel for Data Evaluation and the CODATA Task Group on Chemical Kinetics. They are intended to provide the basic physical chemical data needed as input data for calculations modeling atmospheric chemistry.

Revisions and additions for specific reactions will be published as new information becomes available.

17. Key Words	18. Distribution Statement
Air pollution; atmospheric chemistry; chemical kinetics; data evaluation, gas phase; photoabsorption cross section; photochemistry; quantum yield; rate constant.	Available through the National Technical Information Service, Springfield, Virginia 22161.

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1. Introduction

A set of individual data sheets on the chemical kinetics and photochemistry of neutral species is presented. They are designed for use in modeling the chemistry of the stratosphere and, to a more limited extent, the polluted troposphere and also the interpretation of laboratory experiments.

The coverage of this initial set of data sheets issued in February 1980 corresponds to the approximately 400 reactions listed in NBS Special Publication 513, "Reaction Rate and Photochemical Data for Atmospheric Chemistry - 1977", R. F. Hampson and D. Garvin, May 1978. Approximately one quarter of these reactions were among those considered by the NASA Panel for Data Evaluation in June 1979 at the Stratosphere Workshop in Harpers Ferry, West Virginia. The Panel recommendations are given in NASA Reference Publication 1049, "The Stratosphere: Present and Future", R. D. Hudson and E. I. Reed editors, December 1979. For these reactions the data entry has been updated to include the NASA 1979 recommendation and explanatory note. The date of preparation of these data sheets is shown as June 1979. For the remaining reactions the data entry itself has not been updated from that given in NBS Special Publication 513 and therefore the date shown on these data sheets is May 1978, the publication date for NBS SP 513.

The Chemical Kinetics Data Center has issued four versions of a table of rate data in the following National Bureau of Standards publications: NBSIR 73-203 (1973); NBSIR 74-430 (1974); NBS Technical Note 866 (1975); and NBS Special Publication 513 (1978). The present data sheets supersede all these earlier publications.

Rate data evaluation is a small but growing branch of physical chemistry. Evaluations and compilations of rate data and on-going programs in these areas have been described in the review paper "Evaluation and Compilation of Reaction Rate Data" by R. F. Hampson and D. Garvin, Journal of Physical Chemistry 81, 2317-2319 (1977). An extensive listing of sources of evaluated rate data, NBS List of Publications 73 "Chemical Kinetics Tables, Data Evaluations and Bibliographies. A Guide to the Literature" is available on request from the NBS Chemical Kinetics Data Center.

In addition to the data evaluation activities at the National Bureau of Standards, these are major ongoing rate data evaluation efforts by two panels of which the present author is a member. One is the NASA Panel for Data Evaluation which as mentioned previously has published its 1979 recommendations in NASA Reference Publication 1049, December 1979. The other is the CODATA Task Group on Chemical Kinetics whose recommendations will be published in 1980 in the Journal of Physical and Chemical Reference Data. Recommendations of both panels are included in these data sheets where appropriate. The only significant difference in recommendations by these panels is for the reactions of $O(^1D)$ atoms. In these cases the present author has chosen to accept the recommendations of the NASA panel.

In addition to recommendations on rate and photochemical data the data sheets include listings of current research results. These data listings serve several puposes. Some simply record measurements, usually limited in number, on reactions for which it is not yet practical to give recommended values. Others show the data upon which a new recommendation is based. Still others show what has been done on a

reaction since its rate constant was last evaluated. These new data may support the recommendation or suggest the need for modifications in the future.

2. Guide to the Data Sheets

2.1 General

These data sheets provide current information on reaction rate constants, quantum yields and absorption cross sections. For many reactions, preferred values are given. The reactions included in this initial set of data sheets are summarized in the index of reactions given in section 3.

Each data sheet contains the following items:

a. A statement of the chemical reaction.

b. The value of the enthalpy of the reaction calculated from the table of thermochemical data in the forthcoming report of the CODATA Task Group on Chemical Kinetics.

c. The data entry for each reaction as given in NBS Special Publication 513 but revised to include the 1979 recommendations of the NASA Panel for Data Evaluation and the CODATA Task Group on Chemical Kinetics where pertinent.

d. Where a recommended value is given, there is a brief statement discussing the basis for the recommendation. In those instances where the recommendation is that of the NASA Panel for Data Evaluation, the statement given in the note of the NASA panel for that reaction as given or cited in NASA Reference Publication 1049.

e. A list of references.

f. The date of the recommendation or the date through which the literature coverage extends. As indicated earlier the date shown is either May 1978 or June 1979.

Recommended values are usually indicated by an asterisk placed ahead of the entry in the reference column. However in those instances where the first entry is either "NASA (1979) eval" or "CODATA (1979) eval" the asterisk has been omitted and it is simply implied that this entry is the recommended value.

2.2 Uncertainty in Recommended Value of a Rate Constant

The uncertainty assigned here to the recommended value of a rate constant is given in the column "Uncert. Factor at 298 K, notes". This is an estimate by the evaluator of the absolute accuracy of the preferred value. It is a subjective judgment derived from intercomparison of data sets, consideration of related reactions studied with the same technique, estimates of how well the parameters could have been controlled, and comparison with theory. It means that in the evaluators judgment, the true value will lie within the indicated limits to a high level of confidence.

The uncertainty factor is given for the value of the rate constant at 298 K. The statement that the rate constant k has the central value k_0 and is uncertain to a factor f means that the true value of k lies in the range between k_0/f and $k_0 f$. An estimate of the uncertainty factor for temperatures below 298 K is given by the following expression:

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

At times a rate constant expression is quoted with individual uncertainties for the rate parameters as $k = (A \pm a) \exp(-B \pm b/T)$. These measures are those provided by the author of the paper and often are indications of precision, not overall reliability.

2.3 Conventions Concerning Rate Constants

a. General Convention. Almost all of the reactions listed here are elementary processes. For them the rate expression is derivable from a statement of the reaction, e.g.

$$A + 2B \rightarrow AB_2$$

$$-d[A]/dt = -(1/2)\, d[B]/dt = d[AB_2]/dt = k[A][B]^2$$

Note that the stoichiometric coefficient for B, i.e. 2, appears in the denominator before B's rate of change (which is equal to $2k[A][B]^2$) and as a power on the right hand side.

b. Combination Reactions. Some reactions of this type are not of integral kinetic order over the stratospheric pressure and temperature range. That is, although they require an energy transfer agent, "M", they are in the "pressure fall-off region". For some such reactions we tabulate the low pressure limiting third order rate constant k_0 in units of $cm^6 molecule^{-2} s^{-1}$ and the high pressure limiting second order rate constant k_∞ in units of $cm^3 molecule^{-1} s^{-1}$. The expression for the value of the rate constant in the pressure fall-off range is given by the expression developed by J. Troe in J. Phys. Chem. 83, 114 (1979):

$$\log k = \log[k_0[M]/(1 + k_0[M[/k_\infty)] + \log F_c/(1 + [\log k_0[M]/k_\infty]^2)$$

For the recommendations of the CODATA panel the value of F_c is 0.8; the recommendations of the NASA panel are based on the value of 0.6 for F_c.

c. Forward and Reverse Reactions. In some cases there are no data on a reaction of interest but there are data on the reverse reaction. Occasionally, an evaluation will use the data on the reverse reaction together with the equilibrium constant to calculate the rate constant.

Obviously this is an approximation but it often is a useful method of estimating non-measured physical properties. The entry contains notations to tell the reader when this procedure has been used, such as "based on reverse reaction", or when both reactions f and r are listed together "$k_f = k_r K_{eq}$" or $k_r = k_f/K_{eq}$. These expressions, which are those used in the analyses, are based on equating the two rates at equilibrium.

2.4 Convention Concerning Optical Absorption Coefficients

These are reported as "absorption cross sections per molecule, base e". They are defined by the equation:

$$\sigma = (1/([N]\ell))\ln (I_0/I)$$

where I_0 and I are the intensities of incident and transmitted light, σ is the absorption cross section, $cm^2 molecule^{-1}$, [N] is the concentration of absorbers, molecules cm^{-3}, and ℓ is the path length, cm. Other definitions and units are frequently used. The terms "absorption coefficient" and "extinction coefficient" are common. It is always necessary to know what concentration units, path length units and type of logarithm (base e or base 10) are used in the definition. To convert "cross-sections" to absorption coefficients in $(atm \text{ at } 273 \text{ K})^{-1} cm^{-1}$, base e, multiply by 2.69×10^{19}.

3. Ordering of the Data Sheets

Data on a reaction appear only once in these data sheets. The normal location for a reaction is determined by its reactants. Each species has been assigned a sequence number (1 to 65) as shown in the index that follows. These sequence numbers are the same as those used in NBS Special Publication 513. The ordering of reactions is the same as in NBS SP 513 but with two exceptions - more pairs of forward and reverse reactions

have been combined into one entry, and all the photochemical data sheets have been consolidated and placed after the data sheets for chemical reactions. A reactions is filed under the lower numbered species. That is, the reaction of ozone (7) with an oxygen atom (1) is filed under reactions of oxygen atoms. The numbers for the reactants appear at the left margin of the table, preceding the statement of the reaction, e.g. 1,7 $O + O_3 \rightarrow O_2 + O_2$. These number pairs run in ascending order through the table. If a reaction is not found in the location described above, the reader should look for it under the reverse reaction. The usual rule is that exothermic reactions are given as the "forward" reactions.

In the index that follows, bimolecular reactions are listed under both reactants. Frequently the listing of reaction partners for a particular species is divided into two parts by three dashes, separating species earlier in the list than the species indexed from those later in the list. Reactions of the particular species with those species listed before the three dashes should be sought under those reaction partners. There is no indexing of products of reactions. A few species are listed in the index for which there are no reactions in the table, in anticipation of expansion of the data set.

ACKNOWLEDGMENT

This work was supported, in part, by the High Altitude Pollution Program of the Office of Environment and Energy, Federal Aviation Administration and the Upper Atmosphere Research Office of the National Aeronautics and Space Administration. It was also supported, in part by the Office of Standard Reference Data, National Bureau of Standards.

REACTION INDEX

1. O — Rxn with: O, $O(^1S)$, O_2, O_3, N, NO, NO_2, NO_3, N_2, N_2O, N_2O_5, NH_2, NH_3, H, HO, HO_2, H_2, H_2O, H_2O_2, HNO_2, HNO_3, HNO_4, SO, SO_2, SO_3, HS, H_2S, CS, CS_2, COS, ClO, BrO, FO, OClO, FO_2, HCl, HBr, HOCl, NO_3Cl, Cl_2, Cl_2O, CO, CO_2, CN, CHO, CH_2O, CH_3, CH_3NO_2, CH_3ONO, CH_4, C_2H_4, C_2H_6, C_3H_6, alkane, C_6H_6, $C_6H_5CH_3$, CH_3Cl

2. $O(^1D)$ — Rxn with: O_2, O_3, NO, NO_2, N_2, N_2O, NH_3, H_2, H_2O, H_2O_2, HCl, HF, CO_2, CH_4, C_2H_6, CF_2Cl_2, $CFCl_3$, CF_2O, $CFClO$, CCl_2O

3. $O(^1S)$ — Rxn with: O, O_2, O_3, NO, NO_2, N_2, N_2O, NH_3, H_2O, CO_2, CH_4

4. O_2 — Rxn with: O, $O(^1D)$, $O(^1S)$ - - -
N, NO, NO_2, NO_3, N_2, H, H_2, H_2O, H_2O_2, HNO, SO, HS, Cl, F, CN, CHO, CH_3, CH_3O

5. $O_2(^1\Delta)$ — Rxn with: O_2, O_3, N, NO, N_2, H, SO, SO_2, H_2S, CO, CF_2Cl_2, CCl_4, CH_3Cl, CH_2Cl_2, $CHCl_3$

6. $O_2(^1\Sigma)$ — Rxn with: O_2, N_2, H_2O

7. O_3 — Rxn with: O, $O(^1D)$, $O(^1S)$, $O_2(^1\Delta)$ - - -
M, N, NO, NO_2, H, HO, HO_2, HNO_2, SO, SO_2, H_2S, Cl, Br, F, ClO, BrO, FO, CO, CH_2O, CH_3, CH_3O_2, CH_3ONO, CH_4, C_2H_4, C_3H_6, allene, butenes, butadiene, $C_2Cl_2H_2$

8. N — Rxn with: O, O_2, $O_2(^1\Delta)$, O_3 - - -
N, NO, NO_2, HO, SO, SO_3, OClO

9. NO — Rxn with: O, $O(^1D)$, $O(^1S)$, O_2, $O_2(^1\Delta)$, O_3, N - - -
M, NC, NO_2 + H_2O, NO_3, NH, NH_2, H, HC,
HO_2, H_2, H_2O, H_2O_2, Cl, F, ClO, BrO, FO,
OClO, CH_3, CH_3O, CH_3O_2

10. NO_2 — Rxn with: O, $O(^1D)$, $O(^1S)$, O_2, O_3, N, NO + H_2O - - -
M, NC_2, NO_3, NH_2, NH_3, H, HO, HO_2, SO_2,
Cl, F, ClO, BrO, FO, CH_3, CH_3O, CH_3O_2

11. NO_3 — Rxn with: O, O_2, NO, NO_2 - - -
M, NO_3, H_2O, SO_2

12. N_2 — Rxn with: O, $O(^1D)$, $O(^1S)$, O_2, $O_2(^1\Delta)$, $O_2(^1\Sigma)$ - - -
M, HC

13. N_2O — Rxn with: O, $O(^1D)$, $O(^1S)$ - - -
M, H, HC, ClO, CO

14. N_2O_5 — Rxn with: O - - - M, H_2O, SO_2

15. NH — Rxn with: NO - - -

16. NH_2 — Rxn with: O, NO - - - H, HO, H_2, H_2O

17. NH_3 — Rxn with: O, $O(^1D)$, $O(^1S)$, NO_2 - - -
M, H, HO, ClO

17. N_2H_4 Rxn with: H

18. H Rxn with: O, O_2, $O_2(^1\Delta)$, O_3, NO, NO_2, N_2O, NH_2, NH_3, N_2H_4 - - -
H, HC, HO_2, H_2O, H_2O_2, HNO, HNO_2, HNO_3, SO_2, HS, H_2S, COS, OClO, HCl, NOCl, Cl_2, CO, CO_2, CH_2O, CH_3OOH, CH_3CNO, CH_3Cl

19. HO Rxn with: O, O_3, N, NO, NO_2, N_2, N_2O, NH_2, NH_3, H - - -
M, HC, HO_2, H_2, D_2, H_2O, H_2O_2, HNO, HNO_2, HNO_3, HNO_4, SO_2, H_2S, CS_2, COS, Cl, ClO, BrO, HCl, DCl, HBr, HOCl, NO_3Cl, CO, CH_2O, CH_3OH, CH_3OOH, CH_3NO_2, CH_3ONO, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_4H_{10}, alkane, C_6H_6, $C_6H_5CH_3$, CF_2Cl_2, $CFCl_3$, CCl_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, $C_iCl_jF_k$

20. HO_2 Rxn with: O, O_3, NO, NO_2, H, HO - - -
M, HO_2, H_2, H_2O, SO_2, Cl, Br, ClO, BrO, CO, CH_2O, CH_3O_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}

21. H_2 Rxn with: O, $O(^1D)$, O_2, NO, NH_2, HO, HO_2 - - -
M, Cl, F, ClO

22. H_2O Rxn with: O, $O(^1D)$, $O(^1S)$, O_2, $O_2(^1\Sigma)$, NO, NO_3, N_2O_5, NH_2, H, HO, HO_2 - - - SO_3, F

23. H_2O_2 Rxn with: O, $O(^1D)$, O_2, NO, H, HO - - -
M, Cl, Br

24. HNO Rxn with: O_2, H, HO - - - M, HNO

25. HNO_2 Rxn with: O, O_3, H, HO - - -

26. HNO_3 Rxn with: O, H, HO - - - M, Cl

26a. HNO_4 Rxn with: O, HO - - -

26b. S Rxn with: CS_2, COS

27. SO Rxn with: O, O_2, $O_2(^1\Delta)$, O_3, N - - - SO, SO_3

28. SO_2 Rxn with: O, $O_2(^1\Delta)$, O_3, NO_2, NO_3, N_2O_5, H, HO, HO_2 - - - CH_3

29. SO_3 Rxn with: O, N, H_2O, SO - - -

30. S_2O Rxn with:

31. HS Rxn with: O, O_2, H - - - HS

32. H_2S Rxn with: O, $O_2(^1\Delta)$, O_3, H, HO - - -

33. HSO_2 Rxn with:

34. H_2ZO_4 Rxn with:

34a. CS Rxn with: O - - -

34b. CS_2 Rxn with: O, HO, S - - -

34c. COS Rxn with: O, H, HO, S - - -

38. Cl Rxn with: O_2, O_3, NO, NO_2, NO, NO_2, H_2, H_2O_2, HNO_3 - - - Cl, OClO, ClOO, HOCl, NO_2Cl, NO_3Cl, Cl_2O, CH_2O, CH_4, C_2H_6, CH_3Cl

38Br. Br Rxn with: O_3, NO_2, H_2O_2 - - -

38F. F Rxn with: O_2, O_3, NO, NO_2, H_2, H_2O - - - CH_4

36. ClO Rxn with: O, O_2, NO, NO_2, H_2O, NH_3, NO, NO_2, H_2 - - - ClO, BrO, CO, CH_4, C_2H_2, C_2H_4

36Br. BrO Rxn with: O, O_3, NO, NO, NO_2, ClO - - - BrO

36F. FO Rxn with: O, O_3, NO, NO_2 - - - FO

37. ClOO Rxn with: Cl - - - N

37. OClO Rxn with: O, N, NO, N, Cl - - -

37F. FO_2 Rxn with: O

38. ClO_3 Rxn with:

39. HCl Rxn with: O, $O(^1D)$, H, NO - - -

39Br. HBr Rxn with: O, NO - - -

39F. HF Rxn with: $O(^1D)$

40. HOCl Rxn with: O, NO - - -

41. HOClO Rxn with:

42. HOCl Rxn with: H, Cl - - -

43. HO_2Cl Rxn with: Cl - - -

43a. HO_3Cl Rxn with: O, HO, Cl - - -

44. Cl_2 Rxn with: O, H - - -

44a. Cl_2O Rxn with: O, Cl - - -

45. CO Rxn with: O, $O_2(^1\Delta)$, O_3, N_2O, H, HO, HO_2, ClO - - -
CH_3O

46. CO_2 Rxn with: O, $O(^1D)$, $O(^1S)$, H - - - H

46a. CH Rxn with: O, O_2 - - -

47. CHO Rxn with: O, O_2 - - -

48. CH_2O Rxn with: O, O_2, H, HO, HO_2, Cl - - -

49. CH_3 Rxn with: O, O_2, O_3, HO, HO_2, HO_2 - - -

50. CH_3O Rxn with: O_2, HO, HO_2, CO

51. CH_3O_2 Rxn with: O_3, HO, HO_2, HO_2 - - - CH_3O_2

52. CH_3CH Rxn with: HO - - -

53. CH_3COH Rxn with: H, HO - - -

54. CH_3HO_2 Rxn with: O, HO - - -

54a. CH_3OHO Rxn with: O, O_2, H, HO - - -

55. CH_3HO_3 Rxn with:

56. CH_4 Rxn with: O, $O(^1D)$, $O(^1S)$, O_3, HO, Cl, F, ClO - - -

56a. C_2H_2 Rxn with: HO, ClO - - -

57. C_2H_4 Rxn with: O, O_3, HO, HO_2, ClO - - -

58. C_2H_6 Rxn with: O, $O(^1D)$, HO, HO_2, Cl - - -

*59. C_3H_6 Rxn with: O, O_3, HO - - -

†60. C_3H_8 Rxn with: O, HO, HO_2 - - -

▼60a. C_6H_6 Rxn with: O, HO - - -

61. CF_2Cl_2 Rxn with: $O(^1D)$, $O_2(^1\Delta)$, HO - - -

62. $CFCl_3$ Rxn with: $O(^1D)$, HO - - -

63. CCl_4 Rxn with: HO - - -

64. CH_iCl_j Rxn with: O, $O_2(^1\Delta)$, O_3, H, HO, Cl - - -

◊65. $CH_iCl_jF_k$ Rxn with: $O(^1D)$, HO - - -

* and higher alkenes
† and higher alkanes
▼ and other aromatics
◊ and other halocarbons

PHOTOCHEMISTRY INDEX

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$		Uncert. Factor at 298K, notes
1.1N	$O + O + M \rightarrow O_2 + M$		$\Delta H (298) = -498$ kJ/mol		
	*Campbell, Gray (1973)	200-300	$4.9 \times 10^{-33} (T/300)^{-2}$	$M = N_2$	1.3
	*Baulch, et al (1976) review	190-4000	$5.2 \times 10^{-35} \exp(900/T)$	$M = Ar$	1.3
	Johnston (1968) review	1000-8000	$3.80 \times 10^{-30} T^{-1} \exp(-170/T)$	$M = O_2$	
	Taylor (1975) review	2000-10000	$1.7 \times 10^{-32} T^{-1/2}$	$M = N_2$	
			$2.2 \times 10^{-28} T^{-3/2}$	$M = O_2$	
			$6.2 \times 10^{-28} T^{-3/2}$	$M = O$	
			$8.3 \times 10^{-33} T^{-1/2}$	$M = N$, NO	

This evaluation accepts the results of Campbell and Gray (1973) at low temperature and with $M = N_2$ as most applicable to stratospheric chemistry and also accepts the recent recommendation of Baulch, et al (1976) for an extended temperature range with $M = Ar$

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R. F. Hampson

May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
1.4M 7.M	$O(^3P) + O_2 + M \rightarrow O_3 + M$ (f) $O_3 + M \rightarrow O + O_2 + M$ (r)		ΔH (298) = -106 kJ/mol	
	NASA (1979) eval	200-300	$k_f = (6.2 \pm 0.9) \times 10^{-34} (T/300)^{-2.0 \pm 0.5}$, M = N_2	
	CODATA (1979) eval	220-300	$k_f = 5.6 \times 10^{-34} (T/300)^{-2.4}$, M = N_2	1.3
		298	$k_{f,0} = 2.8 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$	3
	Klais, et al (1979)	219-368	$k_f = (6.2 \pm 0.9) \times 10^{-34} (T/300)^{-2.0 \pm 0.5}$, M = N_2	
		219-368	$k_f = (6.9 \pm 1.0) \times 10^{-34} (T/300)^{-1.25 \pm 0.2}$, M = O_2	
		219-368	$k_f = (3.9 \pm 0.5) \times 10^{-34} (T/300)^{-1.9 \pm 0.3}$, M = Ar	
	Arnold, Comes (1979)	262-308	$k_f = 1.8 \times 10^{-35} \exp(995/T)$, M = N_2	
		262-318	$k_f = 6.8 \times 10^{-35} \exp(635/T)$, M = O_2	
		263-298	$k_f = 6.2 \times 10^{-35} \exp(525/T)$, M = Ar	
	Baulch, et al (1976) review	300	$k_f = 5.5 \times 10^{-34}$ M = N_2	
		200-1000	$k_r = 4.1 \times 10^{-10} \exp(-11430/T) cm^3 molecule^{-1} s^{-1}$, M = Ar	
	Johnston (1968) eval	200-1000	$k_f = 4.6 \times 10^{-35} \exp(1050/T)$, M = Ar	
			$k_r = 1.65 \times 10^{-9} \exp(-11400/T) cm^3 molecule^{-1} s^{-1}$	
			Rel. M eff.: O_3(1.0), Ar(0.25), O_2(0.44), N_2(0.39)	
	Buie, Herron, Davis (1972)	200-346	$k_f = 6.6 \times 10^{-35} \exp(510/T)$ M = Ar	
			Rel. M efficiencies: Ar(1.0), He(0.9), N_2(1.7)	
	Mulcahy, Williams (1968)	213-386	$k_f = 4.7 \times 10^{-35} \exp(840/T)$ M = Ar	
			Rel. M eff.: Ar(1.0), He(0.8), CO_2(3.4), O_2(1.1)	
	Meaburn, et al (1968)	300	$k_f = 1.0 \times 10^{-33}$ M = CO_2	
			Rel. M eff.: CO_2(1.0), CO(0.44), N_2O(0.88)	
	Stuhl, Niki (1971)	300	$k_f = 5.4 \times 10^{-34}$ M = N_2	
			Rel. M efficiencies: N_2(1.0) O_2(1.18), CO(1.24)	
	Donovan, Husain, Kirsch (1970)	300	$k_f = 5.0 \times 10^{-34}$ M = Ar	
			Rel. M efficiencies: Ar(1.0), Kr(0.98), He(0.92)	
	Hippler, Troe (1971)	300	$k_f = 8 \times 10^{-34}$ M = N_2	
	Slanger, Black (1970)	300	$k_f = 4.4 \times 10^{-34}$ M = Ar, Rel. eff. Ar(1.0), N_2(1.6)	
	Francis (1969)	300	$k_f = 1.24 \times 10^{-34}$ M = O_2	
	Sauer (1967)	300	$k_f = 2.28 \times 10^{-34}$ M = Ar	
	Ball and Larkin (1973)	295	$k_f = 5.4 \pm 1.2 \times 10^{-34}$ M = N_2	
			Rel. efficiencies: N_2(1.0), O_2(1.09), Ar(0.78)	
	Hippler, Schippert, Troe (1975)	300	$k_f = 8 \times 10^{-34}$ M = N_2 (a)	
			$k_{f(\infty)} = 2.8 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ (a)	
			(a) Reevaluation of work in Hippler, Troe (1971)	
	Hogan, Burch (1976)	300	6.3×10^{-34} M = O_2	

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,4M	$O + O_2 + M \rightarrow O_3^* + M$		ΔH (298) = -106 kJ/mol	
	This survey	300	4×10^{-34} $cm^6 molecule^{-2} s^{-1}$ M = O_2	1.5
	Bevan, Johnson (1973)	300	$5.4 \times 10^{-34} cm^6 molecule^{-2} s^{-1}$ M = O_2 Rel. efficiencies: O_2(1.0), Ar(0.50), N_2O(2.4), CO_2(2.5), SF_6(5.7)	(a)
	von Rosenberg, Trainor (1974)	300	3×10^{-34} $cm^6 molecule^{-2} s^{-1}$ M = O_2, N_2	(b)

(a) Vibrationally excited O_3 followed as fn. of time using abs. $250 < \lambda < 330$nm.

(b) Vibrationally excited O_3 followed as fn. of time using i.r. emission at 9.6 and 14.3 μm. Also see von Rosenberg, Trainor (1975)

Recommended value averages the two reported experimental values

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R. F. Hampson

May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.7	$O(^3P) + O_3 \rightarrow O_2 + O_2$		$\Delta H\ (298) = -392$ kJ/mol	
	NASA (1979) eval	200-300	$1.5 \times 10^{-11} \exp(-(2218 \pm 150)/T)$	1.15
	CODATA (1979) eval	220-1000	$2.0 \times 10^{-11} \exp(-(2280 \pm 130)/T)$	1.25
	Hampson (1973) eval.	220-1000	$1.9 \times 10^{-11} \exp(-2300/T)$	
	Baulch, et al (1976) review	200-500	$8.6 \times 10^{-12} \exp(-2090/T)$	
	McCrumb, Kaufman (1972)	269-409	$1.1 \times 10^{-11} \exp(-2155/T)$	
	Lundell, Ketcheson, Schiff (1969)	300	1.5×10^{-14}	
	Husain, Kirsch, Donovan (1972)	300	1.3×10^{-14}	
	Davis, Wong, Lephardt (1973)	220-353	$2.0 \times 10^{-11} \exp(-2280/T)$	

This recommendation is slightly different from the NBS SP 513 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)

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,8M	$O + N + M \rightarrow NO + M$ (f)		ΔH (298) = -632 kJ/mol	
9,M	$NO + M \rightarrow N + O + M$ (r)			
	*Baulch, et al (1973) review	200-400	$k_f = 1.8 \times 10^{-31}(T)^{-0.5} cm^6 molecule^{-2} s^{-1}$, $M = N_2$	1.5
		4200-6700	$k_r = 6.6 \times 10^{-4} T^{-1.5} \exp(-75500/T) cm^3 molecule^{-1} s^{-1}$	(a)
			(M = Ar, O_2, N_2) $k(M = NO, N, O)/k(Ar) \sim 18$	
			(a) Estimate only due to insufficient data	
	Taylor (1975)	2000-10000	$k_f = 2.8 \times 10^{-28} T^{-3/2}$ $M = N_2, O_2, N, O$	
			$k_f = 5.5 \times 10^{-27} T^{-3/2}$ $M = NO$	
	Campbell, Gray (1973)	298	$k_f = 9.2 \times 10^{-33}$	
		196	$k_f = 12.1 \times 10^{-33}$	

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

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R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,9	$O + NO \rightarrow NO_2 + h\nu$		ΔH (298) = -306 kJ/mol	
	Becker, et al (1973)	300	4.2×10^{-18}	

No recommendation

REFERENCES

Becker, K. H., *Groth, W., and Thran, D.*, "Mechanism of the Air Afterglow $NO + O \rightarrow NO_2 + h\nu$," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 353-363

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^6molecule^{-2}s^{-1}$	Uncert Factor at 298K, notes
1,9M	$O + NO + M \rightarrow NO_2 + M$ (f)		ΔH (298) = -306 kJ/mol	
10,M	$NO_2 + M \rightarrow NO + O + M$ (r)			
	NASA (1979) eval	200-300	$k_f = (1.2 \pm 0.3) \times 10^{-31} (T/300)^{-1.8 \pm 0.5}$, M = N_2	
			$k_{f,\infty} = (3.0 \pm 1.0) \times 10^{-11} (T/300)^{0.3 \pm 1} cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	200-300	$k_f = 1.2 \times 10^{-31} (T/300)^{-1.82}$, M = N_2	1.3
		300-1500	$k_{f,\infty} = 3.0 \times 10^{-11} (T/300)^{0.3} cm^3 molecule^{-1} s^{-1}$	1.6
	Whytock, Michael, Payne (1976)	220-500	$k_f = 1.55 \times 10^{-32} exp(584/T)$, M = N_2	
			$k_f = 1.18 \times 10^{-31} (T/300)^{-1.82}$	
	Baulch, et al (1973) review	200-500	$k_f = 3.0 \times 10^{-33} exp(940/T)$, M = O_2	
			Rel. M efficiencies: O_2(1.0), Ar(1.0), N_2(1.4)	
		1400-2400	$k_f = 1.8 \times 10^{-8} exp(-33000/T) cm^3 molecule^{-1} s^{-1}$	
			M = Ar	
	Slanger, Wood, Black (1973)	296	$k_f = 6.0 \times 10^{-32}$ M = Ar	
		241	$k_f = 13.0 \times 10^{-32}$ M = Ar	
	Hippler, Schippert, Troe (1975)	300	$k_f = 7.4 \times 10^{-32}$, M = N_2	
			$k_{f(\infty)} = 3.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$	
	Atkinson, Pitts (1974)	300-392	$k_f = 2.6 \times 10^{-32} exp(450 \pm 100/T)$ M = N_2O	
	Singleton, et al (1975)	298-473	$k_f = 1.7 \times 10^{-32} exp(620/T)$, M = N_2O	
	Campbell, Handy (1975)	285-425	$k_f = 5.0 \times 10^{-33} exp(900/T)$, M = N_2	
	Michael, Payne, Whytock (1976)	217-500	$k_f = 1.08 \times 10^{-32} exp(520/T)$, M = He	
			$k_f = 9.33 \times 10^{-33} exp(515/T)$, M = Ne	
			$k_f = 9.01 \times 10^{-33} exp(590/T)$, M = Ar	
			$k_f = 9.52 \times 10^{-33} exp(570/T)$, M = Kr	

Recommendation for k_f based on results of Whytock et al (1976).
Recommendation for $k_{f,\infty}$ based on results of Hippler et al (1975).

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,9M	$O + NO + M \rightarrow NO_2 + M + h\nu$		ΔH (298) = -306 kJ/mol	
	Becker, et al (1973)	300	7×10^{-32} $cm^6 molecule^{-2} s^{-1}$	

No recommendation

REFERENCES

Becker, K. H., Groth, W., and Thran, D., "Mechanism of the Air Afterglow $NO + O \rightarrow NO_2 + h\nu$," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 353-363

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,10 4,9	$O(^3P) + NO_2 \rightarrow NO + O_2$ (f) $O_2 + NO \rightarrow NO_2 + O$ (r)		ΔH (298) = -192 kJ/mol	
	NASA (1979)	200-300	$k_f = 9.3 \times 10^{-12}$ $\Delta(E/R) = +0, -150$	1.1
	CODATA (1979)	230-340	$k_f = 9.3 \times 10^{-12}$ $\Delta(E/R) = +0, -150$	1.15
	Davis, Herron, Huie (1973)	230-339	$k_f = 9.1 \times 10^{-12}$	
	Baulch, et al (1973) review	300-550	$k_f = 1.7 \times 10^{-11} \exp(-300/T)$	
			$k_r = k_f/K_{eq} = 2.8 \times 10^{-12} \exp(-23400/T)$	
	Clyne, Cruse (1971)	300	$k_f = 8.3 \times 10^{-12}$	
	Harker, Johnston (1973)	300	$k_f = 9.2 \times 10^{-12}$	(a)
	Clyne, Cruse (1972)	298	$k_f = 6.1 \times 10^{-12}$	
	Slanger, et al (1973)	300	$k_f = 9.3 \times 10^{-12}$	(b)
		240	$k_f = 10.5 \times 10^{-12}$	
	Stuhl, Niki (1970)	300	$k_f = 4.4 \times 10^{-12}$	(b)
	Bemand, Clyne, Watson (1974)	230-1055	$k_f = 1.75 \times 10^{-10} \times (T)^{-0.52}$	(c)
		298	$k_f = 9.54 \pm 0.1 \times 10^{-12}$	

(a) $k/k(O + NO + M)$ measured, where $k(ref) = 6.9 \times 10^{-32}$

(b) Similar techniques were used by Slanger and by Stuhl and Niki: Flash Photolysis - chemiluminescence.

(c) Based on this work ($298 < T/K < 1055$) and other recent work.

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)

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W. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^6molecule^{-2}s^{-1}$	Uncert Factor at 298K, notes
1,19M	$O + NO_2 + M \rightarrow NO_3 + M$ (f)		ΔH (298) = -210 kJ/mol	
11,M	$NO_3 + M \rightarrow NO_2 + O + M$ (r)			
	NASA (1979) eval	200-300	$k_f = (9.0 \pm 1.0) \times 10^{-32}(T/300)^{-2.0 \pm 1.0}$, $M = N_2$	
			$k_{f\infty} = (2.2 \pm 0.3) \times 10^{-11}$ $cm^3molecule^{-1}s^{-1}$	
	CODATA (1979) eval	298	$k_f = 9 \times 10^{-32}$, $M = N_2$	1.3
			$k_{f,\infty} = 2.2 \times 10^{-11} cm^3molecule^{-1}s^{-1}$	1.3
	Hampson, et al (1973a) review	298	$k_f = 1.0 \times 10^{-31}$, $M = N_2$	
	Baulch, et al (1973) review	295	$k_f = 6.3 \times 10^{-32}$ $M = N_2$	
			$k_r = 8 \times 10^{-42}$ $cm^3molecule^{-1}s^{-1}$, $k_r = k_f/K_{eq}$	
	Hippler, Schippert, Troe (1975)	300	$k_f = 8.0 \times 10^{-32}$, $M = N_2$	
			$k_{f(\infty)} = 2.0 \times 10^{-11}$ $cm^3molecule^{-1}s^{-1}$	
	Harker, Johnston (1973)	297	$k_f = 8.2 \times 10^{-32}$, $M = N_2$	

Recommended values based on results of Harker and Johnston (1973) and Hippler et al (1975)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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Harker, A., and Johnston, H. S., "Photolysis of Nitrogen Dioxide to Produce Transient O, NO_3 and N_2O_5." J. Phys. Chem. 77, 1153-1156 (1973)

Hippler, H., Schippert, C., and Troe, J., "Photolysis of NO_2 and Collisional Energy Transfer in the Reactions O + NO → NO_2 and O + NO_2 → NO_3." Int. J. Chem. Kinet., Symp. No. 1, 27-38 (1975)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,11	$O + NO_3 \rightarrow O_2 + NO_2$		ΔH (298) = -287 kJ/mol	
	NASA (1979) eval	200-300	$1 \times 10^{-11} \exp((0 \pm 150)/T)$	1.6
	CODATA (1979) eval	298	1×10^{-11}	3
	Graham, Johnston (1978)	298-329	$(1.0 \pm 0.4) \times 10^{-11}$	

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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,12M 13,M	$O + N_2 + M \rightarrow N_2O + M$ (f) $N_2O + M \rightarrow N_2 + O + M$ (r)		ΔH (298) = -167 kJ/mol	
	*Baulch, et al (1973) review	1300-2500	$k_f = 3.9 \times 10^{-35} \exp(-10400/T)$ $cm^6 molecule^{-2} s^{-1}$ M = Ar	1.5 (a)
			$k_r = 8.3 \times 10^{-10} \exp(-29000/T)$ $cm^3 molecule^{-1} s^{-1}$ M = Ar	1.5
		900-2100	$k_f = 5.5 \times 10^{-15} \exp(-11330/T)$ $cm^3 molecule^{-1} s^{-1}$	1.5 (a,b)
			$k_r = 1.3 \times 10^{+11} \exp(-30000/T) s^{-1}$	1.5 (c)
			(a) $k_f = k_r K_{eq}$ (b) 2d order high pressure limit (c) 1st order high pressure limit	
	Schofield (1973) review	300-568	$k_f \leq 5 \times 10^{-38}$ $cm^6 molecule^{-2} s^{-1}$	upper limit only
		800-2100	$k_{r\infty} = 1.4 \times 10^{11} \exp(-30,000/T) s^{-1}$	1st order limit

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,13	$O + N_2O \rightarrow N_2 + O_2$ (1)		ΔH (298) = -331 kJ/mol	
4,12	$O_2 + N_2 \rightarrow O + N_2O$ (1r)			
1,13	$O + N_2O \rightarrow NO + NO$ (2)		= -151 kJ/mol	
9,9	$NO + NO \rightarrow N_2O + O$ (2r)			
	*Baulch, et al (1973) review	1200-2000	$k_1 = 1.7 \times 10^{-10} \exp(-14100/T)$	2.5
			$k_{1r} = 1.0 \times 10^{-10} \exp(-55200/T)$	2.5 (a)
			(a) $k_f = k_r K_{eq}$	
			$k_2 = 1.7 \times 10^{-10} \exp(-14100/T)$	2
			$k_{2r} = 2.2 \times 10^{-12} \exp(-32100/T)$	2
	Taylor (1975) review	2000-10000	$k_{2r} = 0.4 T^{-5/2} \exp(-43000/T)$	

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
1,14	$O + N_2O_5 \rightarrow$ products			
	NASA (1979) eval	298	$< 3 \times 10^{-16}$	
	CODATA (1979) eval	220-300	$< 3 \times 10^{-16}$	
	Kaiser, Japar (1978)	223,300	$< 3 \times 10^{-16}$	
	Graham, Johnston (1978)	300	$< 2 \times 10^{-14}$	

This recommendation is based on the upper limit reported by Kaiser and Japar (1978)

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

Kaiser, E. W., and Japar, W. M., "The Kinetics of the Gas Phase Reaction of $O(^3P)$ with N_2O_5." Chem. Phys. Lett. 54, 265-268 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,16	$O + NH_2 \rightarrow HNO + H$ (a) $\rightarrow NO + NH$ (b)		$\Delta H\,(298) = -116$ kJ/mol $= -52$ kJ/mol	
	Gehring, et al (1973)	300	3.5×10^{-12} $(k_a + k_b)$	

Only reported value - no recommendation

REFERENCES

Gehring, M., Hoyermann, K., Schacke, H., and Wolfrum, J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 99-105

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.17 16.19	$O + NH_3 \rightarrow HO + NH_2$ (f) $HO + NH_2 \rightarrow O + NH_3$ (r)		ΔH (298) = 21 kJ/mol	
	*Baulch, et al (1973) review	300-1000	$k_f = 2.5 \times 10^{-12} \exp(-3020/T)$	1.5
		300-1000	$k_r = k_f/K_{eq} = 1 \times 10^{-13}$	1.5 (a)
	Kurylo, et al (1969)	361-677	$k_f = 6.6 \times 10^{-12} \exp(-3300/T)$	
	Albers, et al (1969)	300-1000	$k_f = 2.5 \times 10^{-12} \exp(-3020/T)$	
	Kondratiev (1970) review	350-1000	$k_f = 1.8 \times 10^{-12} \exp(-2500/T)$	

(a) $HO + NH_2 \rightarrow NH + H_2O$ may be preferred channel.

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

Albers, E. A., Hoyermann, K., Wagner, H. Gg., and Wolfrum J., "Study of the Reaction of Ammonia with Oxygen Atoms," Symp. Combust. 12th (Combustion Institute, Pittsburgh, 1969) 313-321

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Kondratiev, V. N., "Konstanty Skorosti Gazofaznykh Reaktsij Spravochnik," (Izdatelstvo "Nauka", Moskva, 1970); also issued as "Rate Constants of Gas Phase Reactions, Reference Book," R. M. Fristrom, Ed., Translated by L. J. Holtschlag CCM-72-10014, Office of Standard Reference Data, NBS (1972) (Distributed by National Technical Information Service, Springfield, Va. 22151)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Uncert. Factor at 298K, notes
1,18M	$O + H + M \rightarrow HO + M$ (f)		ΔH (298) = -428 kJ/mol		
19,M	$HO + M \rightarrow H + O + M$ (r)				
	Schofield (1973) review	1000-3000	$k_f \sim 2 \times 10^{-32}$ $cm^6 molecule^{-2} s^{-1}$	M = Ar	10
	Baulch, et al (1972) review		No recommendation for k_f or k_r		

This evaluation accepts the recommendation for k_f given in the review of Schofield (1973).
No recommendation for k_r but note that E/R > 50000 K

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,19 4,18	$O + HO \rightarrow H + O_2$ (f) $O_2 + H \rightarrow O + HO$ (r)		ΔH (298) = - 70 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 4 \times 10^{-11} \exp((0{\cdot}4300)/T)$	1.5
	CODATA (1979) eval	298	$k_f = 3.8 \times 10^{-11}$	2
	Kaufman (1964)	310	$k_f = (5 \pm 2) \times 10^{-11}$	
	Clyne (1963)	265,293	$k_f = (5 \pm 2) \times 10^{-11}$	
	Westenberg et al (1970)	228-340	$k_f = (3.2 \pm 0.5) \times 10^{-11}$	
	Wilson (1972) review	300-2000	$k_f = (4.2 \pm 1.7) \times 10^{-11}$	
	Baulch, et al (1972) review	300	$k_f = (3.8 \pm 1.7) \times 10^{-11}$	
	*Baulch, et al (1972) review	700-2500	$k_r = 3.7 \times 10^{-10} \exp(-8450/T)$	

This value is based on the work of Kaufman (1964), Clyne (1963) and Westenberg et al (1970)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Clyne, M. A. A., "Rates of Some Atomic Reactions Involving Hydrogen and Oxygen," Symp. Combust. 9th (Academic Press, New York, 1963) 211-219

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Kaufman, F., "Aeronomic Reactions Involving Hydrogen

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,19M	$O + HO + M \rightarrow HO_2 + M$ (f)		ΔH (298) = -286 kJ/mol	
20,M	$HO_2 + M \rightarrow O + HO + M$ (r)			
	Baulch, et al (1972) review		no recommendation for forward or reverse rxn	

See the review of Baulch, et al (1972) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,20	$O + HO_2 \rightarrow HO + O_2$		$\Delta H\ (298) = -212$ kJ/mol	
	NASA (1979) eval	200-300	$3.5 \times 10^{-11} \exp((0\pm350)/T)$	1.5
	CODATA (1979) eval	298	3.1×10^{-11}	3
	Burrows, Harris, Thrush (1977)	293	3.5×10^{-11}	(a)
			(a) Based on value for $k(O + HO)$ and $k(HO + H_2O_2)$	

This is the recent measurement of Burrows et al (1977). There are no T dependence data

REFERENCES

Burrows, J. P., Harris, G. W., and Thrush, B. A., "Rates of Reaction of HO_2 with HO and O studied by Laser Magnetic Resonance," Nature 267, 233-234 (1977)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,21 18,19	$O + H_2 \rightarrow HO + H$ (f) $H + HO \rightarrow O + H_2$ (r)		ΔE (298) = 8 kJ/mol	
	*Dubinsky, McKenney (1975)	350-830	$k_f = 1.6 \times 10^{-11} \exp(-4570/T)$	1.5 (a)
	Baulch, et al (1972) review	400-2000	$k_f = 3.0 \times 10^{-14}(T)\exp(-4480/T)$ $k_r = k_f/K_{eq} = 1.4 \times 10^{-14}(T)\exp(-3500/T)$	
	Schott, et al (1974)	1400-1900	$k_f/k_{ref} = 3.6 \pm 0.7$ Ref rxn is $O_2 + H \rightarrow O + HO$	
	Campbell, Handy (1975)	363-490	$k_f = 5.1 \times 10^{-11} \exp(-4950/T)$ (a) Authors' recommended expression based on all low temperature data	

This evaluation accepts the recommendation of Dubinsky and McKenney (1975) for k_f over this temperature range. For k_f at higher temperatures and for k_r use the recommended expressions in Baulch, et al (1972)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Campbell, I. M., and Handy, B. J., "Studies of Reactions of Atoms in a Discharge Flow Stirred Reactor Part 1 - The $O + H_2 + NO$ System," J. Chem. Soc., Faraday Trans. I 71, 2097-2106 (1975)

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Schott, G. L., Getzinger, R. W., and Seitz, W. A., "Transient Oxygen Atom Yields in H_2O_2 Ignition and the Rate Coefficient for $O + H_2 \rightarrow OH + H$," Int. J. Chem. Kinet. 6, 921-943 (1974)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
1,23	$O(^3P) + H_2O_2 \rightarrow HO_2 + OH$ (a) $\rightarrow H_2O + O_2$ (b)		ΔH (298) = - 72 kJ/mol = -355 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 2.8 \times 10^{-12} \exp(-(2125\pm400)/T)$	1 4
	CODATA (1979) eval	283-368	$k = 2.7 \times 10^{-12} \exp(-(2100\pm500)/T)$	2
	Davis, Wong, Schiff (1974)	283-368	$k = 2.75 \times 10^{-12} \exp(-2125/T)$	(a)
	Foner, Hudson (1962)	300	$\leq 4 \times 10^{-15}$	
	Albers, et al (1971)	370-800	$k = 4.6 \times 10^{-11} \exp(-3220/T)$	

(a) Although there is no evidence, products are most likely $OH + HO_2$ as the channel to produce $H_2O + O_2$ requires a complex rearrangement.

This expression is that of Davis et al (1974). 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.

REFERENCES

Albers, E. A., Hoyermann, K., Wagner, H. Gg., and Wolfrum J., "Absolute Measurements of Rate Coefficients for the Reactions of H and O Atoms with H_2O_2 and H_2O," Symp. Combust. 13th (Combustion Institute, Pittsburgh, 1971) 81-88

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Foner, S. N., and Hudson, R. L., "Mass Spectrometry of the HO_2 Free Radical," J. Chem. Phys. 36, 2681-2688 (1962)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,25	$O + HNO_2 \rightarrow HO + NO_2$		$\Delta H (298) = -97$ kJ/mol	
	*Kaiser, Japar (1978a)	300	$< 1 \times 10^{-15}$	

Note that this is an upper limit only

REFERENCES

Kaiser, E. W., and Japar, S. M., "Upper Limits to the Gas Phase Reaction Rates of HONO with NB_3 and $O(^3P)$ Atoms" J. Phys. Chem. 82, 2753-2754 (1978a)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
1.26	$O + HNO_3 \rightarrow OH + NO_3$		$\Delta H(298) = -4$ kJ/mol	
	NASA (1979) eval	298	$< 3 \times 10^{-17}$	
	Chapman, Wayne (1974)	300	$< 3 \times 10^{-17}$	
	Hampson, et al (1973) review	300	$< 1.5 \times 10^{-14}$	
	Morley, Smith (1972)	300	$< 1.3 \times 10^{-14}$	

This recommendation accepts the upper limit reported by Chapman and Wayne (1974)

REFERENCES

Chapman, C. J., and Wayne, R. P., "The Reaction of Atomic Oxygen and Hydrogen with Nitric Acid," Int. J. Chem. Kinet. 6, 617-630 (1974)

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Morley, C., and Smith, I. W. M., "Rate Measurements of Reactions of OH by Resonance Absorption. Part I. Reactions of OH with NO_2 and NO," J. Chem. Soc., Faraday Trans. II 68, 1016-1030 (1972)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.26a	$C + HC_2NC_2 \rightarrow$ products NASA (1979) eval	298	1×10^{-15}	5

Preliminary value of Trevor, Chang, Barker and Chang.

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Trevor, Chang, Barker and Chang, private communication (1979).

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,27	$C + SC \rightarrow SC_2 + h\nu$ Baulch, et al (1976) review		ΔH (298) = -550 kJ/mol no recommendation	

See the review of Baulch, et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

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May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,27M 28,M	$O + SO + M \rightarrow SO_2 + M$ (f) $SO_2 + M \rightarrow O + SO + M$ (r)		$\Delta H\,(298) = -550$ kJ/mol	
	eBaulch, et al (1976) review	298	$k_f = 1.9 \times 10^{-31}$ $cm^6 molecule^{-2} s^{-1}$ M = Ar k_r no recommendation	1.3
	Schofield (1973) review	300	$k_f = 8.8 \times 10^{-31}$, M = Ar	
		4500-7500	$k_r = 4.2 \times 10^{-10} \exp(-55000/T)$	

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

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Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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R. F. Hampson

May 1978

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant k/cm^{6}molecule^{-2}s^{-1}	Uncert Factor at 298K, notes
1,28M	$O + SO_2 + M \rightarrow SO_3 + M$		ΔH (298) = -348 kJ/mol	
	CODATA (1979) eval	200-400	$k = 4.0 \times 10^{-32} \exp(-1000/T)$, $M = N_2$ no recommendation for k_∞	2
	Davis (1976)	220-353	$3.4 \times 10^{-32} \exp(-1130/T)$, $M = N_2$ $N_2(1.0)$, $He(.45)$, $Ar(.87)$, $SO_2(56)$	
	Schofield (1973) review	250-1000	$1 \times 10^{-33} \exp(+500/T)$ $M = O_2$, N_2, Ar, He	
	Atkinson, Pitts (1974)	299-392	$9.2 \times 10^{-32} \exp(-1000/T)$, $M = N_2O$	
	Westenberg, deHaas (1975d)	248-415	$1.07 \times 10^{-31} \exp(-1400/T)$, $M = He$ Rel. eff: $He(1.0)$, $N_2(2.4)$, $SO_2(.95)$	
	Baulch, et al (1976) review		no recommendation	

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,29	$O + SO_3 \rightarrow$ products			
	sBaulch, et al (1976) review		no recommendation	
	Westenberg, deHaas (1975c)	298-507	$1.4 \times 10^{-31} \exp(785/T)$ $cm^6 molecule^{-2} s^{-1}$	(a)
			Rel. eff: He(1.0), N_2(1.4)	
			(a) Reaction $O + SO_3 + M \rightarrow$ products found to be 3rd order up to P = 7 Torr; SO_4 not detected	
	Schofield (1973) review	1480-1550	$5 \times 10^{-10} \exp(-6000/T)$	uncertain
	Jacob, Winkler (1972)	300-500	$3 \times 10^{-16} \exp(-500/T)$	

See the review of Baulch, et al (1976) for a discussion of reported results. However, because of total lack of agreement of all studies, no recommendation can be made

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,31	O + HS → H + SO		ΔH (298) = -172 kJ/mol	
	*Cupitt, Glass (1975)	295	$1.6 \pm 0.5 \times 10^{-10}$	2
	Baulch, et al (1976)		no recommendation	

This evaluation accepts the result of Cupitt and Glass with increased error limits. See the review of Baulch, et al (1976) for a discussion of reported results

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,32	$O + H_2S \rightarrow HO + HS$		$\Delta H(298) = -44$ kJ/mol	
	NASA (1979) eval	200-300	$2.6 \times 10^{-11} \exp(-(2170 \pm 750)/T)$	2
	CODATA (1979) eval	250-500	$7.2 \times 10^{-12} \exp(-(1660 \pm 150)/T)$	1.3
	Singleton, et al (1979)	297-502	$2.6 \times 10^{-11} \exp(-2170/T)$	
	Slagle, et al (1978)	281-497	$k(301\ K) = 3.6 \times 10^{-14}$	
	Whytock, et al (1976)	263-495	$7.24 \times 10^{-12} \exp(-1660/T)$	
	Hollinden, Kurylo Timmons (1970)	205-300	$2.9 \times 10^{-13} \exp(-750/T)$	(a)
			(a) Assumes stoichiometry of 3.5	

This recommendation accepts the recent determination by Singleton et al (1979). The uncertainty factor in k(298) was chosen to encompass the values of k(298) determined by Hollinden et al (1970), Whytock et al (1976) and Slagle et al (1978). The E/R value is that of the Singleton study as confirmed by the higher temperature data of Whytock et al and the measurements of Slagle et al. It should be emphasized that the Singleton determination did not extend below 298K. The only existing data below 298K appear to indicate a dramatic change in E/R in this temperature region. Thus $\Delta E/R$ was set to account for these observations. Such a nonlinearity in the Arrhenius plot might indicate a change in reaction mechanism from abstraction (as writtenn) to addition. An addition channel has been proposed for $O + H_2S$ by Slagle et al (1978) as well as Singleton, and addition products from this reaction have been seen in a matrix. (Smardzewski and Lin (1977)). Further kinetic study is recommended in the 200 to 300K range. Direct mechanistic information is needed

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,34a	O + CS → CO + S		ΔH (298) = -355 kJ/mol	
	CODATA (1979) eval	150-300	$2.7 \times 10^{-10} \exp(-(760 \pm 250)/T)$	1.25
	Lilenfeld, Richardson (1977)	150-300	$2.6 \times 10^{-10} \exp(-760/T)$	
	Baulch, et al (1976) review	300	2.2×10^{-11}	
	Bida, et al (1976)	300	2.24×10^{-11}	
	Slagle, et al (1975)	305	2.06×10^{-11}	

Recommendation accepts the temperature dependence of Lilenfeld and Richardson (1977) and averages the room temperature values from this and other recent studies

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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June 1979

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.34b	$O + CS_2 \rightarrow CS + SO$ (a) $\rightarrow OCS + S$ (b)		ΔH (298) = - 89 kJ/mol = -231 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 3.1 \times 10^{-11} \exp(-(640 \pm 150)/T)$	1.12
	CODATA (1979) eval	200-500	$k = 5.8 \times 10^{-11} \exp(-(700 \pm 100)/T)$	1.5
	Baulch, et al (1976) review	200-1000	$k_a = 3.7 \times 10^{-11} \exp(-700/T)$	
	Wei, Timmons (1975)	218-293	$k = 2.8 \times 10^{-11} \exp(-640/T)$	
	Slagle, Gilbert, Gutman (1974)	302	$k = 4.0 \times 10^{-12}$ $k_b/k = 0.093$	
	Graham, Gutman (1977)	249-500	k_b/k decreases from 0.098 at 249K to 0.081 at 500K. Overall rate also reported.	
	Westenberg, deHaas (1969)	227-538	$2.0 \times 10^{-11} \exp(-530/T)$	
	Callear, Hedges (1970)	298	3.7×10^{-12}	
	Callear, Smith (1967)	305	4.2×10^{-12}	
	Homann, et al (1968)	300-920	$8.3 \times 10^{-12} \exp(-950/T)$	

The value of k(298 K) is the average of six determinations: Wei and Timmons (1975), Westenberg and deHaas (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). Δ E/R has been set to encompass within a 2 σ error band the limited temperature data of Westenberg and deHaas (1969)

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Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-C_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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Westenberg, A. A., and DeHaas, N., "Atom-Molecule Kinetics using ESR Detection. V. Results for O + OCS, O + CS_2, O + NO_2, and F + C_2H_4," J. Chem. Phys. 50, 707-719 (1969).

W. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
			ΔH (298) = -213 kJ/mol	
1,34c	O + OCS → SO + CO			1.12
	NASA (1979) eval	200-300	$2.1 \times 10^{-11} \exp(-(2200 \pm 150)/T)$	1.5
	CODATA (1979) eval	220-600	$2.6 \times 10^{-11} \exp(-(2250 \pm 150)/T)$	
	Manning, et al (1976)	296	$(1.39 \pm 0.14) \times 10^{-14}$	
	Wei, Timmons (1975)	239-404	$2.0 \times 10^{-11} \exp(-2150/T)$	
	Klemm, Stief (1974)	263-502	$1.65 \times 10^{-11} \exp(-2165/T)$	
	Baulch, et al (1976) review	190-1200	$2.6 \times 10^{-11} \exp(-2250/T)$	
	Breckenridge, Miller (1972)	297	1.19×10^{-14}	
	Westenberg, deHaas (1969)	273-808	$3.2 \times 10^{-11} \exp(-2280/T)$	

The value for k(298 K) is the average of five different studies of this reaction: Westenberg and deHaas (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

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,36	$O + ClO \rightarrow Cl + O_2$		ΔH (298) = -230 kJ/mol	
	NASA (1979) eval	200-300	$7.7 \times 10^{-11} \exp(-(130\pm130)/T)$	1.2
	CODATA (1979) eval	220-425	$7.5 \times 10^{-11} \exp(-(120\pm120)/T)$	1.25
	Clyne, Nip (1976)	220-426	$1.07 \times 10^{-10} \exp(-224/T)$	(a)
			(a) Selected by Watson (1977) review	
	Zahniser, Kaufman (1977)	218-295	$k/k_{ref} = (1.55\pm0.17)\exp(246\pm30/T)$	(b)
			(b) $k_{ref} = k(Cl + O_3)$	
	Bemand, et al (1973)	298	5.3×10^{-11}	

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 $5.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ and $4.4 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ at 298 and 230K, respectively. These values were deduced from the experimental data of Bemand et al (1973), Clyne and Nip (1976), 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.

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R. F. Hampson
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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,36Br	$O + BrO \rightarrow Br + O_2$		$\Delta H (298) = -263$ kJ/mol	
	NASA (1979) eval	200-300	$3 \times 10^{-11} \exp((0\pm250)/T)$	3
	CODATA (1979) eval	298	3×10^{-11}	3
	Clyne, et al (1976)	298	2.5×10^{-11}	

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., $O + ClO$

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,36F	$O + FO \rightarrow F + O_2$		ΔH (298) = -279 kJ/mol	
	NASA (1979) eval	200-300	$5 \times 10^{-11} \exp((0 \pm 250)/T)$	3
	CODATA (1979) eval	298	5×10^{-11}	3

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 (5.2×10^{-11} Watson (1977) and (2.5×10^{-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 (1976).

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Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., "Reactions of O ^3P_J Atoms with Halogens: The Rate Constants for the Elementary Reactions O + BrCl, O + Br_2, and O + Cl_2," Int. J. Chem. Kinet. 8, 425-449 (1976)

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Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

Zahniser, M. S., and Kaufman, F., "Kinetics of the Reactions of ClO with O and with NO," J. Chem. Phys. 66, 3673-3681 (1977)

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,37	$O + OClO \rightarrow ClO + O_2$		$\Delta H\ (298) = -244$ kJ/mol	
	NASA (1979) eval	200-300	$2.5 \times 10^{-11} \exp(-(1166 \pm 300)/T)$	1.5
	Bemand, et al (1973)	298	5×10^{-13}	

Minor modification from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973)

REFERENCES

Bemand, P. P., Clyne, M. A. A., and Watson, R. T., "Reactions of Chlorine Oxide Radicals. Part 4.-Rate Constants for the Reaction Cl + OClO, O + OClO, H + OClO, NO + OClO and O + ClO," J. Chem. Soc., Faraday Trans. I 69, 1356-1374 (1973)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

J. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,37F	$O + FO_2 \rightarrow FO + O_2$		ΔH (298) = -153 kJ/mol	
	NASA (1979) eval	200-300	$5 \times 10^{-11} \exp((0.250)T)$	5
	CODATA (1979) eval	298	5×10^{-11}	5

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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,39	O + HCl → HO + Cl		ΔH (298) = 3 kJ/mol	
	NASA (1979) eval	200-300	$1.14 \times 10^{-11} \exp(-(3370 \pm 350)/T)$	2
	CODATA (1979) eval	293-718	$1.1 \times 10^{-11} \exp(-(3370 \pm 350)/T)$	2
	Ravishankara, et al (1977)	350-454	$5.2 \times 10^{-11} \exp(-3755/T)$	
	Hack, et al (1977)	293-718	$8.5 \times 10^{-12} \exp(-3220/T)$	
	Brown, Smith (1975)	293-440	$2.5 \times 10^{-12} \exp(-2970 \pm 150/T)$	
	Wong, Belles (1972)	356-628	$1.9 \pm 0.3 \times 10^{-11} \exp(-3580/T)$	
	Balakhnin, et al (1971)	295-371	$1.74 \pm 0.6 \times 10^{-12} \exp(-2260/T)$	

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 (1977) 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 etal, and Hack et al but not those reported by Balakhnin et al

REFERENCES

Balakhnin, V. P., Egorov, V. I., and Intezarova, E. I., "Kinetics Investigation of the Elemental Reactions of Oxygen Atoms in the Gas Phase by EPR. II. The Reaction O + HCl = OH + Cl," Kinet. Catal. 12, 258-262 (1971); tr. of: Kinet. Katal. 12, 299-303 (1971)

Brown, R. D. H., and Smith, I. W. M., "Absolute Rate Constants for the Reactions $O(^3P)$ Atoms with HCl and HBr," Int. J. Chem. Kinet 7, 301-315 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Hack, W., Wex, G., and Wagner, H. Gg., "Bestimmung der Geschwindigkeitskonstanten der Reaktionen O + HCl im Temperaturbereich 293 bis 718 K und OH + HCl bei 293 K," Ber. bunsenges. Phys. Chem. 81, 677-684 (1977)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

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Ravishankara, A. R., Smith, G., Watson, R. T., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reactions of HCl with OH and O(^{3}P)," J. Phys. Chem. 81, 2220-2225 (1977)

Wong, E. L., and Belles, F. E., "Rate Measurements for the Reaction of Hydrogen Chloride and Deuterium Chloride with Atomic Oxygen," Lewis Research Center, NASA, Cleveland, Ohio, NASA Tech. Note, NASA TN-D-6495 (1971); Chem. Abstr. 76:18326q (1972)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,39	$O + HCl(v = 1) \rightarrow HO + Cl$ (a) $\rightarrow O + HCl(v = 0)$ (b)		ΔH (298) = - 31 kJ/mol = - 34 kJ/mol	
	*Brown, Glass, Smith (1975)	196-400	$6.2 \times 10^{-12} \exp(-530/T)$	3 (a)
	Arnoldi, Wolfrum (1974)	300	$3.6 \pm 1.2 \times 10^{-12}$	(a)
			(a) Total rate constant for sum of two reaction paths.	

This evaluation accepts the results of the temperature dependent study of Brown, Glass and Smith (1975), but with increased error limits because of the large discrepancy with the room temperature results of Arnoldi and Wolfrum (1974)

REFERENCES

Arnoldi, D., and Wolfrum, J., "The Reaction of Vibrationally Excited HCl with Oxygen and Hydrogen Atoms," Chem. Phys. Lett. 24, 234-238 (1974)

Brown, R. D. B., Glass, G. P., and Smith, I. W. M., "The Relaxation of HCl(v=1) and DCl (v=1) by O Atoms Between 196 and 400 K," Chem. Phys. Lett. 32, 517-520 (1975)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.39Br	$Cl + HBr \rightarrow HCl + Br$		$\Delta H (298)^\circ = -62$ kJ/mol	
	NASA (1979) eval	200-300	$7.6 \times 10^{-12} \exp(-(1571 \pm 300)/T)$	1.5
	CODATA (1979) eval	250-400	$7.0 \times 10^{-12} \exp(-(1560 \pm 300)/T)$	1.5
	Singleton, Cvetanovic (1978)	298-554	$1.34 \times 10^{-11} \exp(-1807/T)$	
	Brown, Smith (1975)	267-430	$4.0 \times 10^{-12} \exp(-1360 \pm 50/T)$	
	Takacs, Glass (1973c)	298	$(4.4 \pm 1.0) \times 10^{-14}$	

Unchanged from NASA 1010. As the values reported for k at 298 K (Takacs and Glass (1973c), Brown and Smith (1975) and Singleton and Cvetanovic (1978)) are in fair agreement, the mean is taken to be the preferred value. The agreement between the values deduced from the Arrhenius expressions reported in stratospheric temperatures is rather poor, e.g., the values differ by ≈ 70% at 250K. 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

REFERENCES

Brown, R. D. H., and Smith, I. W. M., "Absolute Rate Constants for the Reactions $Cl(^2P)$ Atoms with HCl and HBr," Int. J. Chem. Kinet 7, 301-315 (1975)

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NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains

the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Singleton, D. L., and Cvetanovic, R. J., "Temperature Dependence of Rate Constants for the Reactions of Oxygen Atoms, O(^{3}P), with HBr and HI," Can. J. Chem. 56, 2934-2939 (1978)

Takacs, G. A., and Glass, G. P., "Reaction of Atomic Oxygen with Hydrogen Bromide," J. Phys. Chem. 77, 1182-1186 (1973c)

R. F. Hampson
June 1979

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,40	$O + HOCl \rightarrow OH + ClO$		$\Delta H (298) = -30$ kJ/mol	
	NASA (1979) eval	200-300	$1 \times 10^{-11} \exp(-(2200 \pm 800)/T)$	10

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

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.43a	$O + NO_3Cl \rightarrow$ products			
	NASA (1979) eval	200-300	$3.0 \times 10^{-12} \exp(-(808 \pm 200)/T)$	1.5
	CODATA (1979)	213-295	$3.0 \times 10^{-12} \exp(-(808 \pm 200)/T)$	1.25
	Molina, et al (1977a)	213-295	$3.4 \times 10^{-12} \exp(-840/T)$	
	Kurylo (1977)	225-273	$1.9 \times 10^{-12} \exp(-692/T)$	
	Ravishankara, et al (1977)	245	2×10^{-13}	

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 (1977) 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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Kurylo, M. J., "Flash Photolysis Resonance Fluorescence Investigation of the Reaction of $O(^3P)$ Atoms with $ClONO_2$," Chem. Phys. Lett. 49, 467-470 (1977)

Molina, L. T., Spencer, J. E., and Molina, M. J., "The Rate Constant for the Reaction of $O(^3P)$ Atoms with $ClONO_2$," Chem. Phys. Lett. 45, 168-162 (1977a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere"

R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Ravishankara, A. R., Davis, D. D., Smith, G., Tesi, G., and Spencer, J., "A Study of the Chemical Degradation of $ClONO_2$ in the Stratosphere," Geophys. Res. Lett. 4, 7-9 (1977)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.44	$O + Cl_2 \rightarrow ClO + Cl$		$\Delta H(298) = -26$ kJ/mol	
	Clyne, et al (1976)	174-602	$4.2 \times 10^{-12} \exp(-1370/T)$	1.6

This recommended expression was derived by Clyne, et al [1976] on the basis of results in this study (299-602K) and other recent work. It is also recommended in the Watson (1977) review

REFERENCES

Clyne, M. A. A., Monkhouse, P. B., and Townsend, L. W., "Reactions of O ^3P_J Atoms with Halogens: The Rate Constants for the Elementary Reactions O + BrCl, O + Br_2, and O + Cl_2." Int. J. Chem. Kinet. 8, 425-445 (1976)

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.44a	$O + Cl_2O \rightarrow 2ClO$		ΔH (298) = -126 kJ/mol	
	*Watson (1977) review	300	1.4×10^{-11}	1.5

This evaluation accepts the recommendation in the Watson (1977) review

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,45M	$C + CO + M \rightarrow CO_2 + M$ (f)		ΔH (298) = -532 kJ/mol	
46M	$CO_2 + M \rightarrow C + CO + M$ (r)			
	*Baulch, et al (1976) review	250-500	$k_f = 6.5 \times 10^{-33} \exp(-2180/T)$ $cm^6 molecule^{-2} s^{-1}$	1.2 at 250K
			M = CO	inc. to 2.0 at 500K
		296	$k_f = 2.3 \times 10^{-36}$ M = N_2	1.2
			no recommendation for k_r	

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

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May 1978

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.46	$O + CO_2 \rightarrow CO + O_2$ (f)		ΔH (298) = 34 kJ/mol	
4.45	$O_2 + CO \rightarrow O + CO_2$ (r)			
	*Baulch, et al (1976) review	1500-3000	$k_f = 2.8 \times 10^{-11} \exp(-26500/T)$	2 (a)
		1500-3000	$k_r = 4.2 \times 10^{-12} \exp(-24000/T)$	2
			(a) $k_f = k_r K_{eq}$	

This evaluation accepts the recommendations in the review of Baulch, et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson

May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,46a	O + CN → CO + N		ΔH (298) = -322 kJ/mol	
	*Albers, et al (1975)	275-387	2.0×10^{-11}	1.4
	Schmatjko, Wolfrum (1976)	295	1.8×10^{-11}	

This evaluation accepts the temperature independent result of Albers, et al (1975). The room temperature result of Schmatjko and Wolfrum (1976) is in good agreement

REFERENCES

Albers, E. A., Hoyermann, K., Schacke, H., Schmatjko, K. J., Wagner, H. Gg., and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-Atoms with N_2O and Some Reactions of CN Radicals," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 765-773

Schmatjko, K. J., and Wolfrum, J., "Reaction of Flash Photolytically Produced $CN(X^2\Sigma^+, v)$ Radicals with $O(^3P)$ Atoms," Photochem. Conference 12th (National Bureau of Standards, Washington, D. C. 20234 1976) R5-1

B. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,47	$G + CHG \rightarrow CG_2 + H$ (a) $\rightarrow CG + HG$ (b)		ΔH (298) = -462 kJ/mol = -358 kJ/mol	
	Washida, et al (1974)	297	$2.140.4 \times 10^{-10}$ $(k_a + k_b)$	

Only reported value - no recommendation

REFERENCES

Washida, N., Martinez, R. I., and Bayes, K. D., "The Oxidation of Formyl Radicals," Z. Naturforsch. A 29, 251-255 (1974)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.48	O + CH_2O → products			1.25
	NASA (1979) eval	200-300	$3.2 \times 10^{-11} \exp(-(1550\pm250)/T)$	
	Klemm (1979)	250-498	$(2.78\pm0.32) \times 10^{-11} \exp(-(1525\pm40)/T)$	
	Klemm, et al (1979)	298-748	$(3.03\pm0.79) \times 10^{-11} \exp(-(1554\pm125)/T)$	
	Chang, Barker (1979)	296-437	$(3.8\pm0.8) \times 10^{-11} \exp(-(1583\pm73)/T)$	
	Herron, Penzhorn (1969)	300	1.5×10^{-13}	
	Herron, Huie (1973) review	300	1.5×10^{-13}	
	Mack, Thrush (1973)	300	1.5×10^{-13}	

The recommended values for A, E/R and k(298) are the averages of those determined by Klemm (1979) using flash photolysis - resonance fluorescence (250-498K), Klemm et al (1979) using discharge flow - resonance fluorescence (298-748K), and Chang and Barker (1979) using discharge flow - mass spectrometry (296-437K). All three studies are in good agreement. The k(298) value is also consistent with the results of Niki et al (1969), Herron and Penzhorn (1969) and Mack and Thrush (1973). While the mechanism for O + H_2CO has been considered to be the abstraction reaction yielding OH + HCO, Chang and Barker suggest that an addition channel yielding H + HCO_2 may be occurring to the extent of 30% of the the total reaction. This conclusion is based on an observation of CO_2 as a product of the reaction under conditions where reactions such as O + HCO → H + CO_2 and O + HCO → OH + O_2 do not occur. This interesting suggestion needs independent confirmation

REFERENCES

Chang, J. S., and Barker, J. R., "Reaction Rate and Products for the Reaction $O(^3P)$ + H_2CO," J. Phys. Chem. (submitted for publication, 1979)

Herron, J. T., and Huie R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467-518 (1973)

Herron, J. T., and Penzhorn, R. D., "Mass Spectrometric Study of the Reactions of Atomic Oxygen with Ethylene and Formaldehyde," J. Phys. Chem. 73, 191-196 (1969)

Klemm, R. B., "Absolute Rate Parameters for the Reactions of Formaldehyde with O-Atoms and H-Atoms over the Temperature Range 250-500K," J. Chem. Phys. 71, 1987-1993 (1979)

Klemm, R. B., Skolnik, E. G., and Michael, J. V., Manuscript in preparation (1979)

Mack, G. P. R., and Thrush, B. A., "Reaction of Oxygen Atoms with Carbonyl Compounds. Part 1. Formaldehyde," J. Chem. Soc., Faraday Trans I 69, 208-215 (1973)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Niki, H., Daby, E. E., and Weinstock, B., "Mass Spectrometric Study of the Kinetics and Mechanism of the Ethylene-Atomic Oxygen Reaction by the Discharge-Flow Technique at 300°K," Symp. Combust. 12, (Combustion Institute Pittsburgh, Pa., 1969) 277-285

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.49	$O + CH_3 \rightarrow CH_2O + H$ (a) $\rightarrow CHO + H_2$ (b)		ΔH (298) = -285 kJ/mol = -318 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 1.0 \times 10^{-10} \exp((0 \pm 250)/T)$	1.4
	Washida, Bayes (1976)	259-341	$k_a = 1.0 \pm 0.2 \times 10^{-10}$	
	Washida, et al (1974)	300	k_b negligible $k_b/k_a < 0.05$	
	Slagle, Pruss, Gutman (1974)	300	$k_a = 1.85 \pm 0.28 \times 10^{-10}$	
	Morris, Niki (1972)	300	$k_a/k(O + tetramethylethylene) = 1.5$	
	Peeters, Mahnen (1973)	1100-1900	$k_a = 2.2 \times 10^{-10} \exp(-1000/T)$	
	Bowman (1975)	1875-2240	$k_a = 1.7 \times 10^{-10}$	
	Biordi, et al (1975)	1550-1725	$k_a = 1.7 \times 10^{-10}$	

This recommendation is based on the results of Washida and Bayes (1976). This reaction is probably only important in the vicinity of the stratopause

REFERENCES

Biordi, J. C., Lazzara, C. P., and Papp, J. F. "Flame Structure Studies of CF_3Br-Inhibited Methane Flames. II. Kinetics and Mechanisms," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 917-932

Bowman, C. T., "Non-Equilibrium Radical Concentrations in Shock-Initiated Methane Oxidation," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 869-882

Morris, E. D., Jr., and Niki, H., "Reaction of Methyl Radicals with Atomic Oxygen," Int. J. Chem. Kinet. 5, 47-53 (1972)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Peeters, J., and Mahnen, G., "Reaction Mechanisms and Rate Constants of Elementary Steps in Methane-Oxygen Flames," Symp Combust. 14th (Combustion Institute, Pittsburgh, 1973) 133-141

Slagle, I. B., Pruss, F. J., Jr., and Gutman, D., "Kinetics into the Steady State. I. Study of the Reaction of Oxygen Atoms with Methyl Radicals,"

Int. J. Chem. Kinet. 6, 111-123 (1974)

Washida, N., and Bayes, K. D., "The Reactions of Methyl Radicals with Atomic and Molecular Oxygen," Int. J. Chem. Kinet. 8, 777-794 (1976)

Washida, N., Martinez, R. I., and Bayes, K. D., "The Oxidation of Formyl Radicals," Z. Naturforsch. A 29, 251-255 (1974)

W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

[illegible] AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

[illegible]/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
[illegible] products			
[illegible] (1975a)	295	3.3×10^{-15}	

[illegible] reported value - no recommendation

REFERENCES

[illegible], I. W., and Goodman, K., "Reaction of O(^{3}P) Atoms with Nitromethane Vapour at 295 K," Chem. Phys. Lett. 34, 105-108 (1975a)

D. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.54	O + CH_3ONO → products			
	Davidson, Thrush (1975)	300-410	$2.3 \times 10^{-11} \exp(-2620/T)$	

Only reported value - no recommendation

REFERENCES

Davidson, J. A., and Thrush, B. A., "Reaction of Oxygen Atoms with Methyl and Ethyl Nitrites," J. Chem. Soc., Faraday Trans. I 71, 2413-2420 (1975)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,56	$O + CH_4 \rightarrow$ products •Herron, Huie (1973) review	350-1000	$3.5 \times 10^{-11} \exp(-4550/T)$	1.3

This evaluation accepts the recommendation in the review of Herron and Huie (1973)

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Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467-518 (1973)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.57	$O + C_2H_4 \rightarrow CH_3 + HCO$ (a) $\rightarrow CH_2CO + H_2$ (b)		ΔH (298) = -118 kJ/mol = -349 kJ/mol	
	Herron, Huie (1973) evaluation	200-500	$5.5 \times 10^{-12} \exp(-565/T)$ $(k_a + k_b)$	1.2
	Pruss, Slagle, Gutman (1974)	300	$k_b = 3.81 \pm 0.95 \times 10^{-14}$ $k_b/(k_a + k_b) = 0.05$	(a)
	Atkinson, Pitts (1974)	300-392	$5.6 \times 10^{-12} \exp(-640 \pm 100/T)$ $(k_a + k_b)$	
	Singleton, Cvetanovic (1976)	298-486	$1.16 \times 10^{-11} \exp(-845/T)$ a) Calculated using above recommended value for $(k_a + k_b)$	

No recommendation

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R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.58	$C + C_2H_6 \rightarrow$ products			
	aHerron, Huie (1973) evaluation	300-650	$4.1 \times 10^{-11} \exp(-3200/T)$	1.3

This evaluation accepts the recommendation in the review of Herron and Huie (1973)

REFERENCES

Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467-518 (1973)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.59	$O + C_3H_6 \rightarrow$ products			
	Herron, Huie (1973) evaluation	200-500	$4.1 \times 10^{-12} \exp(-38/T)$	1.2
	Atkinson, Pitts (1974)	300-392	$3.45 \times 10^{-12} \exp(0.4150/T)$	
	Singleton, Cvetanovic (1976)	298-483	$1.26 \times 10^{-11} \exp(-363/T)$	

No recommendation

REFERENCES

Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Reaction Rate Constants for $O(^3P)$ Atoms with C_2H_4, C_3H_6 and NO(M = N_2), Determined by a Modulation Technique," Chem. Phys. Lett. 27, 467-470 (1974)

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1,60	O + alkane → HO + alkyl radical *Herron, Huie (1969)	250-600	$k = [0.8 \exp(-2900/T) N_p + 2.2 \exp(-2250/T) N_s + 2.6 \exp(-1650/T) N_t] \times 10^{-11}$ Where N_p, N_s, and N_t are the number of primary, secondary, and tertiary hydrogen atoms, respectively. Do not use formula for CH_4.	3

This evaluation accepts the general rate expression developed by Herron and Huie (1969) which agrees with a large body of rate data to within a factor of 3

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.60a	$O + C_6H_6 \rightarrow$ products			1.3
	This survey	300-460	$1.6 \times 10^{-11} \exp(-2000/T)$	
	Colussi, et al (1975)	298-462	$1.8 \times 10^{-11} \exp(-2115/T)$	
	Atkinson, Pitts (1975a)	300-392	$1.8 \times 10^{-11} \exp(-2000/T)$	
	Atkinson, Pitts (1979)	299-440	$1.7 \times 10^{-11} \exp(-2010/T)$	

The recommended expression is derived from a least squares fit to the data points in these three studies

REFERENCES

Atkinson, R., and Pitts, J. N., Jr., "Temperature Dependence of the Absolute Rate Constants for the Reaction of $O(^3P)$ Atoms with a Series of Aromatic Hydrocarbons over the Range 299-392°K," J. Phys. Chem. 79, 295-297 (1975a)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.60a	O + $C_6H_5CH_3$ → products			
	This survey	300-460	$2.4 \times 10^{-11} \exp(-1730/T)$	1.4
	Colussi, et al (1975)	298-462	$3.8 \times 10^{-11} \exp(-1940/T)$	
	Atkinson, Pitts (1975a)	300-392	$1.4 \times 10^{-11} \exp(-1560/T)$	
	Atkinson, Pitts (1979)	299-440	$1.6 \times 10^{-11} \exp(-1530/T)$	

The recommended expression is derived from a least squares fit to the data points in these three studies

REFERENCES

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R. F. Hampson

June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1.64	$O + CH_3Cl \rightarrow HO + CH_2Cl$		$\Delta H (298) = -3$ kJ/mol	
	*Herron, Huie (1973) eval	350-1000	$2.8 \times 10^{-11} \exp(-3690/T)$	1.6
	Westenberg, deHaas (1975b)	500-1000	$5.8 \times 10^{-11} \exp(-4560/T)$	(a)
	Barassin, Combourieu (1974)	298-443	$2.2 \times 10^{-11} \exp(-3470/T)$	

(a) Also measured $k(O + CH_3Br)/k(O + CH_3Cl)$ to be unity over same temp. range

This evaluation accepts the recommendation in the review of Herron and Huie (1973) with increased error limits to encompass the results of Barassin and Combourieu (1974)

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R. F. Hampson
May 1978

Comments on the NASA(1979) recommended values for reactions of $O(^1D)$ atoms

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, (1978)).

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 used the modified Lambert-Beer law $I_t/I_0 = \exp(-\sigma(Cl)^\gamma)$ where $\gamma = 0.41$. 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, CH_4, N_2, O_2, O_3 and CO_2 have been confirmed very recently by a completely independent technique, Amimoto et al, (1978,1979), although in this same study the value for N_2O is 40% higher than the result from the NOAA Laboratory. These same studies report significant quenching components in the reactions with N_2O, H_2O and CH_4. Further studies are needed to confirm this result.

New studies of $O(^1D)$ reactions with O_2 and H_2O have been reported by Lee and Slanger (1978, 1979). These values are in good agreement with the results recommended here.

The branching ratio for the reaction of $O(^1D)$ with N_2O to give $N_2 + O_2$ or $NO + NO$ is an average of the values reported by Davidson et al (1979), Pirkle et al (1977) and the very recent result of Marx et al (1979). This latest result is significantly different from the earlier results. Further study is needed. The 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). The branching ratio for reaction of $O(^1D)$ with O_3 to give $O_2 + O_2$ or $O_2 + O + O$ is from Davenport et al (1974).

For the reactions of $O(^1D)$ with CCl_2O, $CFClO$ 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

these reactions studied by both groups.

These reactions have been studied only at 298K. 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). 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 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.

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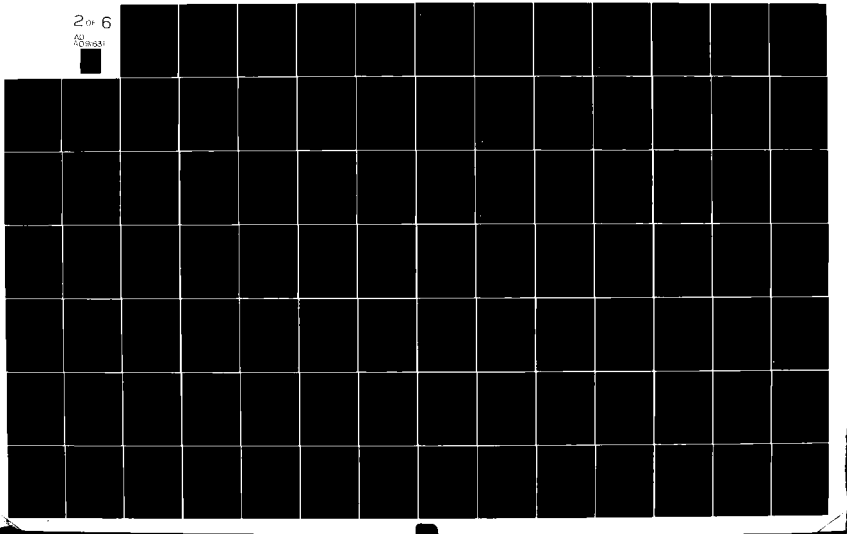

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.4	$O(^1D_2) + O_2 \rightarrow O_2(^1\Sigma_g^+) + O(^3P)$		ΔH (298) = - 33 kJ/mol	
	NASA (1979) eval	200-300	$2.9 \times 10^{-11} \exp((67 \pm 50)/T)$	
		298	3.6×10^{-11}	1.3
	Streit, et al (1976)	104-354	$(2.9 \pm 0.6) \times 10^{-11} \exp(67/T)$	
	Fletcher, Husain (1976a)	300	$(5.3 \pm 0.6) \times 10^{-11}$	
	Lee, Slanger (1978)	298	$(4.0 \pm 0.6) \times 10^{-11}$	
	Amimoto, et al (1979)	298	$(4.2 \pm 0.2) \times 10^{-11}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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P. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.7	$O(^1D_2) + O_3 \rightarrow O_2 + O_2$ (a) $\rightarrow O_2 + 2O$ (b)		ΔH (298) = -582 kJ/mol = - 83 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 1.2 \times 10^{-10} \exp((0\pm50)/T)$	1.3
			$k_b = 1.2 \times 10^{-10} \exp((0\pm50)/T)$	1.3
	Streit, et al (1976)	103-393	$(2.4\pm0.5) \times 10^{-10}$ $(k_a + k_b)$	
	Heidner, et al (1973)	300	$(2.7\pm0.2) \times 10^{-10}$ $(k_a + k_b)$	
	Cvetanovic (1974) review	300	$k_a/k_b \sim 1$	
	Amimoto, et al (1978)	298	$(2.4\pm0.1) \times 10^{-10}$ $(k_a + k_b)$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.9	$O(^1D_2) + NO \rightarrow NO + O(^3P)$		ΔH (298) = -190 kJ/mol	
	This survey	300	4.2×10^{-11}	2
	Heidner, Husain (1973)	300	$(8.5 \pm 1.0) \times 10^{-11}$	

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $O(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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Heidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(2^1D_2)$. A Time-Resolved Study of the Collisional Quenching by the Gases H_2, D_2, NO, N_2O, NO_2, CH_4, and C_3O_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int. J. Chem. Kinet. 5, 819-831 (1973)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.10	$O(^1D_2) + NO_2 \rightarrow NO + O_2$		ΔH (298) = -382 kJ/mol	
	This survey	300	1.2×10^{-10}	2
	Heidner, Husain (1973)	300	$(2.3 \pm 0.2) \times 10^{-10}$	

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $O(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2,12	$O(^1D_2) + N_2 \rightarrow N_2 + O(^3P)$		ΔH (298) = -190 kJ/mol	
	NASA (1979) eval	200-300	$2.0 \times 10^{-11} \exp((107 \pm 50)T/)$	
		298	2.9×10^{-11}	1.3
	Streit, et al (1976)	104-354	$(2.0 \pm 0.4) \times 10^{-11} \exp(107/T)$	
	Heidner, et al (1973)	300	$(6.9 \pm 0.6) \times 10^{-11}$	
	Amimoto, et al (1979)	298	$(2.9 \pm 0.1) \times 10^{-11}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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Amimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)

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Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A., and Schiff, H. I., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with O_2, N_2, CO_2, O_3, and H_2O," J. Chem. Phys. 65, 4761-4764 (1976)

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert. Factor at 298K, notes
2.12N	$O(^1D_2) + N_2 + M \rightarrow N_2O + M$		ΔH (298) = -357 kJ/mol	
	NASA (1979) eval	200-300	$3.5 \times 10^{-37} (T/300)^{-0.45}$ cm^{6}molecule^{-2}s^{-1}	5
	Kajimoto, Cvetanovic (1976)	296	3.5×10^{-37}	(a)
	Gaedtke, et al (1973)	298	3×10^{-36}	
	Simonaitis, et al (1972)	298	$< 2 \times 10^{-36}$	(a)

(a) adjusted value based on k($O(^1D) + M$) this survey

This recommendation is based on the results reported in Kajimoto and Cvetanovic (1976)

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2,13	$O(^1D_2) + N_2O \rightarrow N_2 + O_2$ (a) $\rightarrow 2NO$ (b)		ΔH (298) = -521 kJ/mol = -340 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 4.8 \times 10^{-11} \exp((0\pm50)/T)$	1.5
			$k_b = 6.2 \times 10^{-11} \exp((0\pm50)/T)$	1.5
	Davidson, et al (1977)	204-355	$(1.1\pm0.2) \times 10^{-10}$ $(k_a + k_b)$	
	Heidner, Husain (1973)	300	$(2.2\pm0.2) \times 10^{-10}$ $(k_a + k_b)$	
	Amimoto, et al (1979)	298	$(1.5\pm0.1) \times 10^{-10}$ $(k_a + k_b)$	
	Davidson, et al (1979)	170-434	$k_a/k_b = (0.72\pm0.11) + (21.6\pm7)/T$	
	Pirkle, et al (1977)	290	$k_a/k_b = 0.92\pm0.10$	
	Marx, et al (1979)	298	$k_a/k_b = 0.62\pm0.04$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Amimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)

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Heidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(2^1D_2)$. A Time-Resolved Study of the Collisional Quenching by the Gases H_2, D_2, NO, N_2O, NO_2, CH_4, and C_3O_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int. J. Chem. Kinet. 5, 819-831 (1973)

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.17	$O(^1D_2) + NH_3 \rightarrow NH_2 + HO$		ΔH (298) = -169 kJ/mol	
	NASA (1979) eval	200-300	$2.5 \times 10^{-10} \exp((0\pm50)/T)$	1.3
	Davidson, et al (1977)	204-354	$(2.5\pm0.5) \times 10^{-10}$	
	Fletcher, Husain (1976a)	300	$(6.3\pm0.7) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L., and Howard, C. J. "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with N_2O, H_2, CH_4, HCl, and NH_3," J. Chem. Phys. 67, 5021-5025 (1977)

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $O(2^1D_2)$ by the Gases NH_3, H_2O_2, C_2H_6, C_3H_8, and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. 54, 1765-1770 (1976a)

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2,21	$O(^1D_2) + H_2 \rightarrow OH + H$		ΔH (298) = -182 kJ/mol	
	NASA (1979) eval	200-300	$9.9 \times 10^{-11} \exp((0\pm50)/T)$	1.3
	Davidson, et al (1977)	204-352	$(9.9\pm3.0) \times 10^{-11}$	
	Heidner, Husain (1973)	300	$(2.7\pm0.3) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L., and Howard, C. J., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with N_2O, H_2, CH_4, HCl, and NH_3," J. Chem. Phys. 67, 5021-5025 (1977)

Heidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(2^1D_2)$. A Time-Resolved Study of the Collisional Quenching by the Gases H_2, D_2, NO, N_2O, NO_2, CH_4, and C_3H_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int J. Chem. Kinet. 5, 819-831 (1973)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.22	$O(^1D_2) + H_2O \rightarrow 2HO$		ΔH (298) = -119 kJ/mol	
	NASA (1979) eval	200-300	$2.3 \times 10^{-10} \exp((0\pm50)/T)$	1.3
	Streit, et al (1976)	253-353	$(2.3\pm0.4) \times 10^{-10}$	
	Heidner, et al (1973)	300	$(3.0\pm0.3) \times 10^{-10}$	
	Lee, Slanger (1979)	300	$(2.6\pm0.5) \times 10^{-10}$	
	Amimoto, et al (1979)	298	$(2.0\pm0.3) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Amimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)

Heidner, R. F., III, Husain, D., and Wiesenfeld, J. R., "Kinetic Investigation of Electronically Excited Oxygen Atoms, $O(2^1D_2)$, by Time-resolved Attenuation of Atomic Resonance Radiation in the Vacuum Ultra-violet. Part 2.-Collisional Quenching by the Atomospheric Gases N_2, O_2, CO, CO_2, H_2O and O_3," J. Chem. Soc., Faraday Trans. II 69, 927-938 (1973)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2,23	$O(^1D_2) + H_2C_2 \rightarrow HO + HO_2$		ΔH (298) = -262 kJ/mol	
	This survey	300	2.6×10^{-10}	2
	Fletcher, Husain (1976a)	300	$(5.2 \pm 0.6) \times 10^{-10}$	

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $O(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $O(2^1D_2)$ by the Gases NH_3, H_2O_2, C_2H_6, C_3H_8, and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. 54, 1765-1770 (1976a)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.39	$O(^1D_2) + HCl \rightarrow HO + Cl$		ΔH (298) = -186 kJ/mol	
	NASA (1979) eval	200-300	$1.4 \times 10^{-10} \exp((0.50)/T)$	1.3
	Davidson, et al (1977)	199-379	$(1.4 \pm 0.4) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Davidson, J. A., Schiff, H. I., Streit, G. E., McAfee, J. R., Schmeltekopf, A. L., and Howard, C. J., "Temperature Dependence of $O(^1D)$ Rate Constants for Reactions with N_2O, H_2, CH_4, HCl, and NH_3," J. Chem. Phys. 67, 5021-5025 (1977)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.39F	$O(^1D_2) + HF \rightarrow HO + F$		$\Delta H (298)^\circ = -47$ kJ/mol	
	NASA (1979) eval	200-300	$1 \times 10^{-10} \exp((0 \pm 100)/T)$	3

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.

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA PP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.45	$O(^1D_2) + CO \rightarrow CO + O(^3P)$		ΔH (298) = -190 kJ/mol	
	•Davidson, et al (1978a)	113-333	$(4.7 \pm 0.9) \times 10^{-11} \exp(63/T)$	1.4
	Heidner, et al (1973)	300	$(7.3 \pm 0.7) \times 10^{-11}$	

This evaluation accepts the results of the temperature dependent study of Davidson, et al (1978a)

REFERENCES

Davidson, J. A., and Schiff, H. I., "Temperature Dependence of the Deactivation of $O(^1D)$ by CO from 113-333 K," J. Chem. Phys. 69, 1216-1217 (1978a)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2,46	$O(^1D_2) + CO_2 \rightarrow CO_2 + O(^3P)$		ΔH (298) = -190 kJ/mol	
	NASA (1979) eval	200-300	$6.8 \times 10^{-11} \exp((117\pm50)/T)$	
		298	1.0×10^{-10}	1.3
	Streit, et al (1976)	139-200	1.2×10^{-10}	
		200-354	$(6.8\pm1.4) \times 10^{-11} \exp(117/T)$	
	Fletcher, Husain (1976a)	300	$(1.7\pm0.2) \times 10^{-10}$	
	Amimoto, et al (1979)	298	$(1.28\pm0.07) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Amimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $O(2^1D_2)$ by the Gases NH_3, H_2O_2, C_2H_6, C_3H_8, and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. 54, 1765-1770 (1976a)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2,56	$O(^1D_2) + CH_4 \rightarrow CH_3 + HO$ (a) $\rightarrow CH_2O + H_2$ (b)		ΔH (298) = -180 kJ/mol = -473 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 1.3 \times 10^{-10} \exp((0\pm50)/T)$	1.3
			$k_b = 1.4 \times 10^{-11} \exp((0\pm50)/T)$	1.3
	Davidson, et al (1977)	198-357	$(1.4\pm0.4) \times 10^{-10}$ $(k_a + k_b)$	
	Heidner, Husain (1973)	300	$(3.1\pm0.4) \times 10^{-10}$ $(k_a + k_b)$	
	Amimoto, et al (1979)	298	$(1.57\pm0.14) \times 10^{-10}$ $(k_a + k_b)$	
	Lin and DeMore (1973)	295	$k_b/k_a = 0.1$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Amimoto, S. T., Force, A. P., and Wiesenfeld, J. R., results presented at the National Meeting, American Chemical Society, Honolulu, April (1979)

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Heidner, R. F., III, and Husain, D., "Electronically Excited Oxygen Atoms, $O(2^1D_2)$. A Time-Resolved Study of the Collisional Quenching by the Gases H_2, D_2, NO, N_2O, NO_2, CH_4, and C_3O_2 Using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," Int J. Chem. Kinet. 5, 819-831 (1973)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.58	$O(^1D_2) + C_2H_6 \rightarrow$ products			
	This survey	300	3.6×10^{-10}	2
	Fletcher, Husain (1976a)	300	$(7.3 \pm 0.8) \times 10^{-10}$	

The recommended value has been derived from the reported value by use of the scaling factor 0.50 for consistency with other recommended $O(^1D)$ rates. See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of Electronically Excited Oxygen Atoms, $O(2^1D_2)$ by the Gases NH_3, H_2O_2, C_2H_6, C_3H_8, and $C(CH_3)_4$ Using Time-Resolved Attenuation of Atomic Resonance Radiation," Can. J. Chem. 54, 1765-1770 (1976a)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.61	$O(^1D_2) + CF_2Cl_2$ - products			
	NASA (1979) eval	200-300	$1.4 \times 10^{-10} \exp((0\pm50)/T)$	1.3
	Davidson, et al (1978)	173-343	$(1.45\pm0.5) \times 10^{-10}$	
	Fletcher, Husain (1976b)	300	$(4.8\pm0.5) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Davidson, J. A., Schiff, A. I., Brown, T. J., and Howard, C. J., "Temperature Dependence of the Rate Constants for Reactions of $O(^1D)$ Atoms with a number of Halocarbons," J. Chem. Phys. 69, 4277-4279 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.62	$O(^1D_2) + CFCl_3 \rightarrow$ products			
	NASA (1979) eval	200-300	$2.2 \times 10^{-10} \exp((0\pm50)/T)$	1.3
	Davidson, et al (1978)	173-343	$(2.2\pm0.7) \times 10^{-10}$	
	Fletcher, Husain (1976b)	300	$(5.5\pm0.7) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Davidson, J. A., Schiff, A. I., Brown, T. J., and Howard, C. J., "Temperature Dependence of the Rate Constants for Reactions of $O(^1D)$ Atoms with a number of Halocarbons," J. Chem. Phys. 69, 4277-4279 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.65	$O(^1D_2) + CCl_2O \rightarrow$ products			
	NASA (1979) eval	200-300	$3.6 \times 10^{-10} \exp((0\pm50)/T)$	1.4
	Fletcher, Husain (1978)	300	$(7.1\pm0.9) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

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Fletcher, I. S., and Husain, D., "The Collisional Quenching of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2 using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," J. Photochem. 8, 355-361 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.65	$O(^1D_2)$ + $CFClO$ → products			
	NASA (1979) eval	200-300	$1.9 \times 10^{-10} \exp((0\pm50)/T)$	1.4
	Fletcher, Husain (1978)	300	$(3.7\pm0.4) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2 using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," J. Photochem. 8, 355-361 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
2.65	$O(^1D_2) + CF_2O \rightarrow$ products			
	NASA (1979) eval	200-300	$2.3 \times 10^{-10} \exp((0\pm50)/T)$	1.4
	Fletcher, Husain (1978)	300	$(4.6\pm0.4) \times 10^{-10}$	

See comments on NASA (1979) recommended values for reactions of $O(^1D)$ atoms

REFERENCES

Fletcher, I. S., and Husain, D., "The Collisional Quenching of $O(2^1D_2)$ by $COCl_2$, $COFCl$ and COF_2 using Atomic Absorption Spectroscopy in the Vacuum Ultraviolet," J. Photochem. 8, 355-361 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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June 1979

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.1	$O(^1S) + O(^3P) \rightarrow$ products			
	*Slanger, Black (1976a)	200-365	$5 \times 10^{-11} \exp(-305/T)$	1.5
	Schofield (1978) review	298	1.8×10^{-11}	

This evaluation accepts the results of the temperature dependent study of Slanger and Black (1976a). The room temperature value is the same as that recommended in Schofield's (1978) review. It is three orders of magnitude greater than the value calculated by Krauss and Neumann (1975) for the specific channel yielding 2 $O(^1D)$, suggesting the importance of other channels

REFERENCES

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Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Black, G., "$O(^1S)$ Quenching by $O(^3P)$," J. Chem. Phys. 64, 3763-3766 (1976a)

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June 1979

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.4	$O(^1S) + O_2 \rightarrow$ products			
	*Slanger, Welge (1973) review	200-377	$4.3 \times 10^{-12} \exp(-850/T)$	1.4
	Schofield (1978) review	298	2.8×10^{-13}	

This evaluation accepts the recommendation of Slanger and Welge (1973). Slanger and Black (1978b) measured the branching ratio for the production of $O(^1D)$ and $O(^3P)$. The fraction yielding $O(^1D)$ is 0.31±0.07, the remainder yielding $O(^3P)$

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Black, G., "Products of the $O(^1S) - O_2$ Interaction," J. Chem. Phys. 68, 998-1000 (1978b)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.7	$O(^1S) + O_3 \rightarrow$ products			
	*Schofield (1978) review	298	5.8×10^{-10}	1.4

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits. The same value was recommended in the review of Slanger and Welge (1973).

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.9	$O(^1S) + N_2O \rightarrow$ products			
	*Slanger, Welge (1973) review	200-300	$3.2 \times 10^{-11} (T)^{0.5}$	1.2
	Schofield (1978) review	298	5.7×10^{-10}	

This evaluation accepts the recommendation of Slanger and Welge (1973) which agrees with Schofield's (1978) recommendation at room temperature. Slanger and Black (1978a) measured the branching ratio for the production of $O(^1D)$ and $O(^3P)$. The fraction yielding $O(^1D)$ is 0.64 ± 0.06, the remainder yielding $O(^3P)$

REFERENCES

Schofiel , K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Black, G., "$O(^1S)$ Interactions - The Product Channels," J. Chem. Phys. 68, 989-997 (1978a)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.10	$O(^1S) + N_2 \rightarrow$ products *Schofield (1978) review	298	5×10^{-10}	1.5

This evaluation accepts the recommendation in Schofield's (1978) review. The same value was recommended in the review of Slanger and Welge (1973)

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.12	$O(^1S) + N_2 \rightarrow$ products			
	*Slanger, Welge (1973) review	200-380	$< 5 \times 10^{-17}$	
	Schofield (1978) review	298	$< 5 \times 10^{-17}$	

This evaluation accepts the recommendation in the review of Slanger and Welge (1973)

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C. (1973) pages 22-32

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.13	$O(^1S) + N_2O \rightarrow$ products			
	*Slanger, Black (1976b)	200-368	$3.8 \times 10^{-11} \exp(-420/T)$	1.3
	Schofield (1978) review	298	9.4×10^{-12}	

This evaluation accepts the results of the temperature dependent study of Slanger and Black (1976b). The room temperature value is the same as that recommended in Schofield's (1978) review. Slanger and Black (1978a) measured the relative importance of the interaction pathways. The fraction yielding $O(^1D)$ is 0.33±0.07, the remainder yielding $O(^3P)$, with no chemical reaction

REFERENCES

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Slanger, T. G., and Black, G., "Temperature Dependence for Quenching of $O(^1S)$ by N_2O," J. Chem. Phys. 65, 2025-2026 (1976b)

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June 1979

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.17	$O(^1S) + NH_3$ → products •Schofield (1978) review	298	5×10^{-10}	1.5

This evaluation accepts the recommendation in Schofield's (1978) review. The same value was recommended in the review of Slanger and Welge (1973)

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1\Sigma_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3,22	$O(^1S) + N_2O \rightarrow$ products			
	*Schofield (1978) review	298	5×10^{-10}	3

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits. Slanger and Black (1978a) measured the relative importance of the interaction pathways. The fraction yielding $O(^1D)$ is 0.30 ± 0.06, that yielding $O(^3P)$ is 0.09 ± 0.06, with the major fraction (0.61 ± 0.06) being the chemical interaction to give $OH + OH$

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Black, G., "$O(^1S)$ Interactions - The Product Channels," J. Chem. Phys. 68, 989-997 (1978a)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.46	$O(^1S) + CO_2 \rightarrow$ products			1.4
	*Slanger, Welge (1973) review	200-450	$3 \times 10^{-11} \exp(-1320/T)$	
	Schofield (1978) review	298	3.6×10^{-13}	

This evaluation accepts the recommendation in the review of Slanger and Welge (1973) which agrees with Schofield's (1978) recommendation at room temperature. Slanger and Black (1978a) measured the branching ratio for the production of $O(^1D)$ and $O(^3P)$. The fraction yielding $O(^1D)$ is 0.63 ± 0.05, the remainder yielding $O(^3P)$

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

Slanger, T. G., and Black, G., "$O(^1S)$ Interactions - The Product Channels," J. Chem. Phys. 68, 989-997 (1978a)

Slanger, T. G., and Welge, K. H., "Rate Constants for Reactions of $O(^1S)$," in Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C., (1973) pages 22-32

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June 1979

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3.56	$O(^1S) + CH_4 \rightarrow$ products Schofield (1978) review	298	2.7×10^{-14}	2.5

This evaluation accepts the recommendation in Schofield's (1978) review with increased error limits

REFERENCES

Schofield, K., "Rate Constants for the Gaseous Interactions of $O(2^1D_2)$ and $O(2^1S_0)$ - A Critical Evaluation," J. Photochem. 9, 55-68 (1978)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
4,8 1,9	$O_2 + N \rightarrow NO + O$ (f) $O + NO \rightarrow O_2 + N$ (r)		ΔH (298) = -133 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 4.4 \times 10^{-12} \exp(-(3220 \pm 340)/T)$	1.25
	CODATA (1979) eval	280-333	$k_f = 4.4 \times 10^{-12} \exp(-(3220 \pm 350)/T)$	1.25
	Becker, Groth, Kley (1969)	280-333	$k_f = 5.5 \times 10^{-12} \exp(-3220/T)$	
	Clyne, Thrush (1961)	412-755	$k_f = 1.4 \times 10^{-11} \exp(-3570/T)$	
	Wilson (1967)	300-910	$k_f = 2.3 \times 10^{-11} \exp(-3975/T)$	
	Clark, Wayne (1970)	302	$k_f = 10.8 \times 10^{-17}$	
	Westenberg, et al (1970)	298	$k_f = 7.5 \times 10^{-17}$	
	Taylor (1975)	2000-10000	$k_f = 2.2 \times 10^{-14}(T) \exp(-3560/T)$	
	Baulch, et al (1973) review	1000-3000	$k_r = k_f/K_{eq} = 2.5 \times 10^{-15}(T) \exp(-19500/T)$	2

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

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
4.9.9 10.10	$O_2 + NO + NO \rightarrow NO_2 + NO_2$ (f) $NO_2 + NO_2 \rightarrow NO + NO + O_2$ (r)		ΔH (298) = -114 kJ/mol	
	*Baulch, et al (1973) review	273-660	$k_f = 3.3 \times 10^{-39} \exp(530/T)$ $cm^6 molecule^{-2} s^{-1}$	1.5
		600-2000	$k_r = 3.3 \times 10^{-12} \exp(-13500/T) cm^3 molecule^{-1} s^{-1}$	1.4
	Stedman, Niki (1973)	300	$k_f = 2.0 \times 10^{-38}$	

This evaluation accepts the recommendations in the review of Baulch, et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Stedman, D. H., and Niki, H., "Kinetics and Mechanism for the Photolysis of Nitrogen Dioxide in Air," J. Phys. Chem. *77*, 2604-2609 (1973)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
4.9N	$C_2 + NC + N \rightarrow NC_3 + N$ Baulch, et al (1973) review		ΔH (298) = - 19 kJ/mol No recommendation	

See the review of Baulch, et al (1973) for a discussion of reported results. However, there is no direct evidence for the occurrence of this reaction and no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-C_2 System," (Butterworths, London, 1973)

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May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
4,18M 2r,M	$C_2 + B + M \rightarrow BC_2 + M$ (f) $BC_2 + M \rightarrow C_2 + B + M$ (r)		ΔH (298) = -216 kJ/mol	
	NASA (1979) eval	200-300	$k_f = (5.5 \pm 0.5) \times 10^{-32} (T/300)^{-1.4 \pm 0.5}$, M = N_2	
	CODATA (1979) eval	200-400	$k_f = 5.9 \times 10^{-32} (T/300)^{-1.0}$, M = N_2	1.6
	Eurylo (1972)	203-404	$k_f = 6.7 \times 10^{-33} \exp(235/T)$ Rel. M eff.: Ar(1.0), He(1.0), N_2(3.4)	
	Wong, Davis (1974)	220-360	$k_f = 6.8 \times 10^{-33} \exp(340/T)$ Rel. M efficiencies: Ar(1.0), He(0.93) N_2(2.6), H_2(3.0), CH_4(21.5)	
	Baulch, et al (1972) eval	300-2000	$k_f = 4.1 \times 10^{-33} \exp(500/T)$ M = Ar Rel. M eff.: Ar(1.0), He(1.0), N_2(1.3), O_2(1.3), H_2O(21) $k_r = k_f/K_{eq} = 3.5 \times 10^{-9} \exp(-23000/T)$ M = Ar	
	Bishop, Dorfman (1970)	300	$k_f = 2.35 \times 10^{-32}$ M = Ar	
	Hikida, Eyre, Dorfman (1971)	300	$k_f = 1.64 \times 10^{-32}$ M = Ar	
	Ahumada, Michael, Osborne (1972)	300	$k_f = 0.75 \times 10^{-32}$ M = He Rel. M efficiencies: He(1.0), Ar(0.8)	
	Westenberg, deHaas (1972a)	300	$k_f = 1.9 \times 10^{-32}$ M = Ar or He	
	Slack (1977)	980-1176	$k_f = (9.1 \pm 1.6) \times 10^{-33}$ M = N_2	
		964-1075	$k_f = (6.1 \pm 1.1) \times 10^{-33}$ M = Ar	(a)
		200-2000	$k_f = 1.85 \times 10^{-28} T^{-1.42}$ M = N_2	(b)
		200-2200	$k_f = 5.8 \times 10^{-30} T^{-1}$ M = Ar	(b)

(a) reanalysis of literature
(b) recommendation based on this work and data from literature

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June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
4,24	$O_2 + HNO \rightarrow NO + HO_2$		$\Delta H (298) = -7$ kJ/mol	
	Demerjian, et al (1974) review	300	$< 2 \times 10^{-20}$, $E/R > 5000K$	

No data; estimated value

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
4,27 1,28	$O_2 + SO \rightarrow O + SO_2$ (f) $O + SO_2 \rightarrow O_2 + SO$ (r)		ΔH (298) = - 53 kJ/mol	
	CODATA (1979) eval	300-1000	$k_f = 6 \times 10^{-13} \exp(-(3300 \pm 500)/T)$	3
	Homann, Krome, Wagner (1968)	580-1145	$k_f = 5.8 \times 10^{-13} \exp(-3270/T)$	
	Baulch, et al (1976) review	440-2100	$k_f = 7.5 \times 10^{-13} \exp(-3250/T)$	
		440-2100	$k_r = k_f/K_{eq} = 2.1 \times 10^{-10} T^{-0.5} \exp(-9980/T)$	
	Breckenridge, Miller (1972)	300	$k_f < 8 \times 10^{-17}$	
	Schofield (1973) review	400-2500	$k_f = 3.0 \times 10^{-13} \exp(-2800/T)$	

Recommendation is based largely on the results reported by Homann, Krome and Wagner (1968) with increased error limits. See the review of Baulch, et al (1976)

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Breckenridge, W. H., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of $SO(^1\Delta)$ in the Reaction of $O_2(^1\Delta_g)$ with $SO(^3\Sigma^-)$," J. Chem. Phys. 56, 465-474 (1972)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
4.31	$O_2 + HS \rightarrow SO + HO$		ΔH (298) = -101 kJ/mol	
	CODATA (1979) eval		no recommendation	
	Cupitt, Glass (1975)	295	$< 10^{-13}$	

No recommendation

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CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.

Cupitt, L. T., and Glass, G. P., "Reactions of SH with Atomic Oxygen and Hydrogen," Int. J. Chem. Kinet., Symp. No. 1, 39-50 (1975)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
4,35M	$O_2 + Cl + M \rightarrow ClOO + M$ (f)		ΔH (298) = - 32 kJ/mol	
37,M	$ClOO + M \rightarrow Cl + O_2 + M$ (r)			
	NASA (1979) eval	200-300	$k_f = (2.0 \pm 1.0) \times 10^{-33} (T/300)^{-1.3}$	
			$k_r = 2.7 \times 10^{-9} \exp(-(2650 \pm 800)/T)$ $cm^3 molecule^{-1} s^{-1}$	7 (a)
			(a) $k_r = k_f / K_{eq}$	
	Nicholas, Norrish (1968)	293	$k_f = 1.7 \times 10^{-33}$	
	Clyne and Coxon (1968)	300	$k_f = < 5.5 \times 10^{-33}$	
	Stedman (1968)	200-300	$k_f = 5.5 \times 10^{-34}$	(b)
			(b) As quoted by Clyne and Coxon (1968).	

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert. Factor at 298K, notes
4.35F	$C_2 + F + M \rightarrow FC_2 + M$		ΔH (298) = - 25 kJ/mol	
	NASA (1979) eval	200-300	$k = (1.1 \pm 0.3) \times 10^{-32} (T/300)^{-1.7 \pm 1}$, $M = N_2$	
	CODATA (1979) eval	270-360	$k = 1.1 \times 10^{-32} (T/300)^{-2}$, $M = N_2$	2
	Zetzsch (1973)		$k_\infty = 3 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$	3
	Arutyunov, et al (1976)	270-360	$k = 5.2 \times 10^{-34} \exp(656/T)$, $M = He$	
		293	$k = 7 \times 10^{-33}$, $M = He$	
			Rel. M eff: He(1.0), N_2(2.4), Ar(0.5)	
	Chen, et al (1977)	298	$k = 5.4 \times 10^{-33}$, $M = He$	
			Rel. M eff: He(1.0), C_2(2.8), Ar(1.6)	

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
4.46a	$C_2 + CN \rightarrow NCC + C$		$\Delta H(298) = -27$ kJ/mol	
	Albers, et al (1975)	275-398	$5.3 \times 10^{-11} \exp(-500 \pm 170/T)$	1-3

These results are in agreement with earlier work for room temperature value but not for temperature dependence

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
4.47	$O_2 + CHO \rightarrow CO + HO_2$		$\Delta H(298) = -146$ kJ/mol	
	NASA (1979) eval	200-300	$5 \times 10^{-12} \exp((0 \pm 250)/T)$	1.4
	CODATA (1979) eval	298	5.1×10^{-12}	1.25
	Shibuya, et al (1977)	300	$(5.6 \pm 0.9) \times 10^{-12}$	
	Clark, et al (1978)	300	$(4.0 \pm 0.8) \times 10^{-12}$	
	Washida, et al (1974)	297	$(5.7 \pm 1.2) \times 10^{-12}$	
	Peeters, Mahnen (1973)	1400-1800	5×10^{-11}	

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 (1978a). Inclusion of the latter two measurements results in a value lower than that recommended in NASA 1010

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert Factor at 298K, notes
4.49	$O_2 + CH_3 \rightarrow CH_2O + HO$		ΔH (298) = -215 kJ/mol	
	CODATA (1979) eval		No recommendation	
	Washida, Bayes (1976)	259-341	$2.9 \times 10^{-13} \exp(-940/T)$	
	Basco, et al (1972)	295	$\leq 3 \times 10^{-16}$	estimated (a)
			a. Based on negative result and sensitivity limit. Other measurements at higher T suggest an appreciable activation energy.	

No recommendation

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Washida, N., and Bayes, K. D., "The Reactions of Methyl Radicals with Atomic and Molecular Oxygen," Int. J. Chem. Kinet. 8, 777-794 (1976)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
4.49M	$C_2 + CH_3 + M \rightarrow CH_3C_2 + M$		ΔH (298) = -139 kJ/mol	
	NASA (1979) eval	200-300	$k = (2.2 \pm 1.1) \times 10^{-31}(T/300)^{-2.2 \pm 1.0}$, $M = N_2$	
			$k_\infty = (2.0 \pm 1.0) \times 10^{-12}(T/300)^{-1.7 \pm 1.0}$	(b)
	CODATA (1979) eval	260-340	$k = 2.6 \times 10^{-31}(T/300)^{-3}$, $M = N_2$	2
		200-400	$k_\infty = 2 \times 10^{-12}$	2(b)
	Parkes (1977)	298	$k = 3.1 \times 10^{-31}$, $M = N_2$	
			$k_\infty = 1.2 \times 10^{-12}$	(b)
	Laufer, Bass (1975)	298	$10^{12} \times k_{bi}$ / $P(N_2)$/torr: 0.45 / 50; 0.7 / 100; 1.2 / 700	(a)
			1.7	(b)
	Washida, Bayes (1976)	300	5.0×10^{-13}	(b)
			1.9×10^{-31} $M = N_2$	
	Hochanadel, et al (1977)	295	2.2×10^{-12}	(b)
	Basco, et al (1972)	295	5.1×10^{-13}	(b)
			2.6×10^{-31} $M = N_2$	
	van den Bergh, Callear (1971)	295	1.8×10^{-12} preliminary	(b)
			6×10^{-31} $M = C_3H_8$ preliminary	

(a) Values are based on $k(CH_3 + CH_3) = 9.5 \times 10^{-11}$, given in Bass, Laufer (1973).

(b) 2nd order high pressure limit in $cm^3 molecule^{-1} s^{-1}$

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Basco, N., James, D. G. L., and James, F. C., "A Quantitative Study of Alkyl Radical Reactions by Kinetic Spectroscopy. II. Combination of the Methyl Radical with the Oxygen Molecule," Int. J. Chem. Kinet. 4, 129-149 (1972)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
5,M	$O_2(^1\Delta) + M \rightarrow O_2 + M$		ΔH (298) = - 94 kJ/mol	
	*Hampson, et al (1973) review	285-322	$2.2 \times 10^{-18} (T/300)^{0.8}$ M = O_2	1.3
	Huestis, et al (1974)	77	1.1×10^{-18} M = O_2	(a)
			(a) Liquid phase. When combined with gas phase data of Findlay and Snelling (1971a) (summarized in Hampson, et al (1973) $k = 2.2 \times 10^{-18} (T/300)^{0.5}$	
	*Hampson, et al (1973) review	300	$< 2 \times 10^{-20}$ M = N_2	
	Collins, et al (1973)	300	1.4×10^{-19}, M = N_2	
	*Penzhorn, et al (1974)	300	3.9×10^{-20} M = SO_2	
		300	2.1×10^{-19} M = H_2S	
	*Penzhorn, et al (1975)	300	$k \times 10^{18}$ / M: 0.4 / CF_2Cl_2; ≤0.08 / CCl_4; 1.01 / CH_3Cl; 0.87 / CH_2Cl_2; 0.92 / $CHCl_3$	
	Fisher, McCarty (1966)	300	$< 3 \times 10^{-16}$ M = CO	(b)
			(b) total rate, quenching and reaction	

For M = O_2 and N_2 use the recommendations in the review of Hampson, et al (1973). For sulfur compounds and for halocarbons use the values reported by Penzhorn et al (1974) and (1975) respectively

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Collins, R. J., Husain, D., and Donovan, R. J., "Kinetic and Spectroscopic Studies of $O_2(a^1\Delta_g)$ by Time-Resolved Absorption Spectroscopy in the Vacuum Ultra-violet," J. Chem. Soc., Faraday Trans. II 69, 145-157 (1973)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
5,7	$O_2(^1\Delta) + O_3 \rightarrow 2O_2 + O$		ΔH (298) = 12 kJ/mol	
	This survey	200-350	$1.2 \times 10^{-11} \exp(-2400/T)$	1,2
	Clark, Jones, Wayne (1970)	195-439	$6.6 \times 10^{-13} \exp(-1560/T)$	
	Findlay, Snelling (1971)	283-321	$4.5 \times 10^{-11} \exp(-2830/T)$	
	Becker, et al (1972)	296-360	$6.0 \times 10^{-11} \exp(-2850/T)$	
	Collins, et al (1973)	300	4.4×10^{-15}	
	Schofield (1972) review	283-321	$4.5 \times 10^{-11} \exp(-2830/T)$	

This evaluation recommends a room temperature value which is the average of the four reported values. The temperature dependence is taken as the average of the reported values, and the pre-exponential factor derived to fit the room temperature value

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
5,6	$O_2(^1\Delta) + N \rightarrow NO + O$		$\Delta H\,(298) = -228$ kJ/mol	
	Schmidt, Schiff (1973)	300	$k < k(N + O_2 \rightarrow NO + O)$	probably
	Westenberg, et al (1970)	195-300	$k << k(N + O_2 \rightarrow NO + O)$	
	Clark, Wayne (1970)	195-431	$k = 2 \times 10^{-14} \exp(-600/T)$	(a)
			(a) probably refers to physical deactivation, not chemical reaction; see above refs	

No recommendation

REFERENCES

Clark, I. D., and Wayne, R. P., "Kinetics of the Reaction between Atomic Nitrogen and Molecular Oxygen in the Ground ($^3\Sigma_g^-$) and First Excited ($^1\Delta_g$) States," Proc. Roy. Soc. London A 316, 539-550 (1970)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
5.9	$O_2(^1\Delta) + NO \rightarrow O_2 + NO(v = 4)$		ΔH (298) = - 6 kJ/mol	
	*Becker, et al (1971)	300	4.5×10^{-17}	1.4
	Yaron, et al (1976)	300	2.5×10^{-17}	
	Giachardi, et al (1976)	293	$(4.5 \pm 1) \times 10^{-17}$	
	Ogryzlo, Thrush (1973)	300	NO(v = 4) observed	

This evaluation selects the value reported by Becker, et al (1971). It is confirmed by the results of Giachardi, et al (1976). Ogryzlo and Thrush concluded that all the observed NO excitation is due to the indicated process followed by vibrational relaxation

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert Factor at 298K, notes
5,18	$O_2(^1\Delta) + H \rightarrow$ products			
	Schmidt, Schiff (1973)	300	$(2.5 \pm 0.5) \times 10^{-14}$ (a) expt could not distinguish between chemical rxn and physical quenching	(a)
	Westenberg, et al (1970)	300	rxn to give HO + O as products not observed	

No recommendation

REFERENCES

Schmidt, C., and Schiff, H. I., "Reactions of $O_2(^1\Delta_g)$ with Atomic Nitrogen and Hydrogen," Chem. Phys. Lett. 23, 339-342 (1973)

Westenberg, A. A., Roscoe, J. M., and DeHaas, N., "Rate Measurements on $N + O_2(^1\Delta_g) \rightarrow NO + O$ and $H + O_2(^1\Delta_g) \rightarrow OH + O$," Chem. Phys. Lett. 7, 597-599 (1970)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
5.27	$O_2(^1\Delta) + SO \rightarrow O_2 + SO(^1\Delta)$		ΔH (298) = - 20 kJ/mol	
	Breckenridge, Miller (1972)	300	$3.5 \pm 0.36 \times 10^{-13}$	

No recommendation

REFERENCES

Breckenridge, W. H., and Miller, T. A., "Kinetic Study by EPR of the Production and Decay of $SO(^1\Delta)$ in the Reaction of $O_2(^1\Delta_g)$ with $SO(^3\Sigma^-)$," J. Chem. Phys. 56, 465-474 (1972)

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CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
6,M	$O_2(^1\Sigma) + M \rightarrow O_2 + M$		ΔH (298) = -157 kJ/mol	
	*Hampson, et al (1973) review	300	1.5×10^{-16}, M = O_2	1-3
			2.0×10^{-15}, M = N_2	1-3
			4×10^{-12}, M = H_2O	1-5

Use these recommendations from the review of Hampson, et al (1973)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
7.8	$O_3 + N \rightarrow NO + O_2$		$\Delta H(298) = -525$ kJ/mol	
	NASA (1979) eval	298	$< 1 \times 10^{-15}$	
	CODATA (1979) eval	298	$< 5 \times 10^{-16}$	
	Stief, et al (1979)	300	$< 5 \times 10^{-16}$	
	Phillips, Schiff (1962)	300	5.7×10^{-13}	

New recommendation based on results of Stief et al (1979). 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

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,9 4,10	$O_3 + NO \rightarrow NO_2 + O_2$ (f) $O_2 + NO_2 \rightarrow NO + O_3$ (r)		ΔH (298) = -200 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 2.3 \times 10^{-12} \exp(-(1450 \pm 200)/T)$	1 2
	CODATA (1979) eval	200-360	$k_f = 2.3 \times 10^{-12} \exp(-(1450 \pm 200)/T)$	1 15
	Birks, et al (1976)	203-361	$k_f = 2.34 \pm 0.23 \times 10^{-12} \exp(-1450 \pm 50/T)$	
	Stedman, Niki (1973)	298	$k_f = 1.73 \pm 0.1 \times 10^{-14}$	
	Baulch, et al (1973) review	200-350	$k_f = 1.5 \times 10^{-12} \exp(-1330/T)$	
		200-350	$k_r = k_f/K_{eq} = 2.8 \times 10^{-12} \exp(-25400/T)$	
	Ghormley, et al (1973)	298	$k_f = 1.41 \times 10^{-14}$	
	Bemand, et al (1974)	300	$k_f = 1.81 \pm 0.13 \times 10^{-14}$	
	Becker, Schurath, Seitz (1974)	290	$k_f = 1.70 \times 10^{-14}$	

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

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
7.9	$O_3^* + NO \rightarrow NO_2^*(^2B_{1,2}) + O_2$ (1) $\rightarrow NO_2^*(^2A_1) + O_2$ (2) $\rightarrow O_3 + NO$ (3)			
	Kurylo, et al (1975)	153-373	see discussion	
	Bar-Ziv, Moy, Gordon (1978)	158-437	see discussion	
	Hui, Cool (1978)	138-410	$k_1 = 1.0 \times 10^{-12} \exp(-1450/T)$	
			$k_2 = 3.8 \times 10^{-13} \exp(-520/T)$	
			$k_3 = 1.1 \times 10^{-13}$ at 333 K and at 143 K with minimum value of 0.62×10^{-13} at approx 230K	

Measured quantity in all studies is $(k_1 + k_2 + k_3)$. Values of this quantity measured by Kurylo et al and by Hui, Cool are in good agreement; values reported by Bar-Ziv, Moy and Gordon are systematically higher below 300K.

Hui and Cool derived values as a function of temperature for k_1, k_2, and k_3 given above from an analysis of the temperature dependent data for $(k_1 + k_2 + k_3)$ reported by the three groups, the temperature dependence of the enhancement factor for rxn channel (1) reported by Moy, Bar-Ziv and Gordon (1977), their own temperature dependent data for the ratio of the enhancement factors for rxn channels (1) and (2) and the rate constant for channels (1) and (2) for thermal ozone reported by Clough and Thrush (1967)

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.10 4.11	$O_3 + NO_2 \rightarrow NO_3 + O_2$ (f) $O_2 + NO_3 \rightarrow O_3 + NO_2$ (r)		ΔH (298) = -105 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 1.2 \times 10^{-13} \exp(-(2450 \pm 140)/T)$	1.15
	CODATA (1979) eval	230-360	$k_f = 1.2 \times 10^{-13} \exp(-(2450 \pm 150)/T)$	1.15
	Davis, Prusazcyk, Dwyer, Kim (1974)	260-343	$k_f = 9.76 \pm 0.54 \times 10^{-14} \exp(-2427 \pm 140/T)$	
	Graham, Johnston (1974)	231-298	$k_f = 1.34 \pm 0.11 \times 10^{-13} \exp(-2466 \pm 30/T))$	
	Huie, Herron (1974a)	259-362	$k_f = 1.57 \pm 0.41 \times 10^{-13} \exp(-2509 \pm 76/T)$	
	Baulch, et al (1973) review	300	$k_r = 7 \times 10^{-34}$ based on k_f	
	Wu, Morris, Niki (1973)	299	$k_f = 4.4 \times 10^{-17}$	
	Ghormley, et al (1973)	298	$k_f = 3.2 \times 10^{-17}$	
	Stedman, Niki (1973)	298	$k_f = 6.5 \pm 0.8 \times 10^{-17}$	
	Becker, Schurath, Seitz (1974)	289	$k_f = 3.24 \times 10^{-17}$	

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

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
7,18	$O_3 + H \rightarrow HO + O_2$		ΔH (298) = -322 kJ/mol	
	NASA (1979) eval	200-300	$1.4 \times 10^{-10} \exp(-(470\pm200)/T)$	1.25
	CODATA (1979) eval	220-360	$1.4 \times 10^{-10} \exp(-(480\pm100)/T)$	1.5
	Keyser (1979a)	196-424	$(1.54\pm0.2) \times 10^{-10} \exp(-(499\pm32)/T)$	
	Lee, et al (1978b)	219-360	$(1.3 \pm 0.3) \times 10^{-10} \exp(-(449\pm58)/T)$	
	Clyne, Monkhouse (1977)	298-638	$(1.0 \pm 0.2) \times 10^{-10} \exp(-(516 \pm 60)/T)$	
	Phillips, Schiff (1962)	300	$2.6 \pm 0.5 \times 10^{-11}$	

This 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.

Recent results by Finlayson-Pitts and Kleindienst (1979) agree well with the present recommendation although they do indicate a second reaction channel to give $HO_2 + O$ (~ 25%). Confirmation is needed

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,19	$O_3 + HO \rightarrow HO_2 + O_2$		$\Delta H\,(298) = -180$ kJ/mol	
	NASA (1979) eval	200-300	$1.6 \times 10^{-12} \exp(-(940 \pm 300)/T)$	1.25
	CODATA (1979) eval	220-450	$1.9 \times 10^{-12} \exp(-1000/T)$	1.4
			$\Delta(E/R) = +250, -100$	
	Ravishankara, et al (1979)	238-357	$1.8 \times 10^{-12} \exp(-930/T)$	
	Anderson, Kaufman (1973)	220-450	$1.3 \times 10^{-12} \exp(-956/T)$	
	Baulch, et al (1976) review	300	6.5×10^{-14}	
	DeMore (1975)	271-333	$k/k(OH + CO) = 16.8 \exp(-1230/T)$ at 700 torr CO_2	
	Kurylo (1973)	298	6.5×10^{-14}	

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 (1979). 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

A recent determination by Zahniser and Howard (1979) is in excellent agreement with our recommendation below room temperature. Their measured rate constants also agree very well with our recommended values at higher temperatures although their data indicates a curved Arrhenius plot over the entire T range

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Uncert Factor at 298K, notes
7.19	$O_3 + HO(v_1 > 0) \rightarrow$ products				
	Coltharp, Worley, Potter (1971)	300	$v_1(HO)$	$10^{12} \times k(300\ K)$	
				CSP	SJ
	Streit, Johnston (1976)		2	1.9±1.1	
			3	2.4±0.9	
			4	2.8±0.8	3.7±0.1
			5	3.4±0.7	4.5±0.1
			6	5.3±0.6	7.1±0.2
			7	6.5±0.5	8.5±0.2
			8	6.7±0.5	8.9±0.2
			9	7.7±0.3	11 ±0.4

The values reported by Streit and Johnston (1976) are 35% higher than the corresponding values of Coltharp, et al (1971). No selection is made

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
			ΔH (298) = -106 kJ/mol	
7.20	$O_3 + HO_2 \rightarrow HO + 2O_2$			
	NASA (1979) eval	200-300	$1.1 \times 10^{-14} \exp(-580/T)$	1-4
			$\Delta(E/R) = \pm 500, -100$	
	CODATA (1979) eval	250-400	$1.4 \times 10^{-14} \exp(-(600 \pm 200)/T)$	1-5
	Zahniser, Howard (1979)	250-370	$(1.4 \pm 0.4) \times 10^{-14} \exp(-(580 \pm 100)/T)$	
	DeMore (1979)	230-334	$k/(k_{ref})^{0.5} = 6.4 \times 10^{-8} \exp(-1220/T)$	(a)
	Simonaitis, Heicklen (1973b)	225-298	$k/(k_{ref})^{0.5} = 1.9 \times 10^{-8} \exp(-1000/T)$	(a)
	DeMore, Tschuikow-Roux (1974)	273-332	$k/(k_{ref})^{0.5} = 1.1 \times 10^{-7} \exp(-1550 \pm 250/T)$	(a)
			(a) $k_{ref} = k(HO_2 + HO_2 \rightarrow H_2O_2 + O_2)$	

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 (1973b). The Zahniser and Howard work is the most direct and, presumably, the best detemination and gives E/R = 580. This temperature dependence is confirmed by the last two studies, which were ratios relative to $k(HO_2 + HO_2)$, when the Cox (1978) E/R value recently reported for that reaction is used, thus lending additional credence to that determination. The A-factor is unusually low. Recent rate constant ratio measurements by DeMore (1979) confirm this recommendation

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
7.25	$O_3 + HNO_2 \rightarrow O_2 + HNO_3$		ΔH (298) = -198 kJ/mol	
	NASA (1979) eval	298	$<5 \times 10^{-19}$	
	Kaiser, Japar (1977)	226	$<5 \times 10^{-19}$	
		300	$<1 \times 10^{-19}$	
	Streit, et al (1979)	300	$<5 \times 10^{-19}$	

This recommendation is based on the upper limits reported by Kaiser and Japar (1977) and by Streit et al (1979)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.27	$O_3 + SO \rightarrow O_2 + SO_2$		$\Delta H(298) = -445$ kJ/mol	
	CODATA (1979) eval	220-300	$2.5 \times 10^{-12} \exp(-(1100 \pm 400)/T)$	2
	Schofield (1973) review	223-303	$2.5 \times 10^{-12} \exp(-1050/T)$	
	Baulch et al (1976) review		no recommendation	

There is only one reported value for this rate constant. See the reviews by Schofield (1973) and Baulch, et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

CODATA(1979): Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
7,28	$O_3 + SO_2 \rightarrow SO_3 + O_2$		ΔH (298) = -242 kJ/mol	
	*Davis, Prusazcyk, Dwyer, Kim (1974)	300	$k < 2 \times 10^{-22}$	
	Daubendiek, Calvert (1974)	300	$k < 8 \times 10^{-24}$	preliminary

Note that this is an upper limit only

REFERENCES

Daubendiek, R. L., and Calvert, J. G., "A Study of the N_2O_5-SO_2-O_3 Reaction System," Environ. Lett. 8, 103-116 (1975)

Davis, D. D., Prusazcyk, J., Dwyer, M., and Kim, P., "A Stop-Flow Time of Flight Mass Spectrometry Kinetics Study. Reaction of Ozone with Nitrogen Dioxide and Sulfur Dioxide," J. Phys. Chem. 78, 1775-1779 (1974)

R. F. Hampson
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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,32	$O_3 + H_2S \rightarrow$ products			
	Glavas, Toby (1975)	298-343	$7 \times 10^{-14} \exp(-3400/T)$	
	Becker, Inocencio, Schurath (1975)	300	$< 2 \times 10^{-20}$	

No recommendation is made because of the disagreement between these results - the room temperature value of Glavas and Toby (1975) is a factor of 40 higher than the upper limit reported by Becker, et al (1975)

REFERENCES

Becker, K. H., Inocencio, M., and Schurath, U., "The Reaction of Ozone with Hydrogen Sulfide and its Organic Derivatives," Int. J. Chem. Kinet., Symp. No. 1, 205-220 (1975)

Glavas, S., and Toby, S., "The Reaction between Ozone and Hydrogen Sulfide: Kinetics and Effect of Added Gases," Am. Chem. Soc., ACS Symp. Series 17, 122-131 (1975)

R. F. Hampson

May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
7.35	$O_3 + Cl \rightarrow ClO + O_2$		ΔH (298) = -162 kJ/mol	
	NASA (1979) eval	200-300	$2.8 \times 10^{-11} \exp(-(257 \pm 100)/T)$	1.15
	CODATA (1979)	205-298	$2.7 \times 10^{-11} \exp(-(257 \pm 100)/T)$	1.15
	Watson (1977) review	205-298	$2.7 \times 10^{-11} \exp(-257/T)$	
	Clyne, Nip (1976a)	221-629	$5.18 \times 10^{-11} \exp(-418/T)$	
	Kurylo, Braun (1976)	213-298	$2.72 \times 10^{-11} \exp(-298/T)$	
	Watson, et al (1976)	220-350	$3.08 \times 10^{-11} \exp(-290/T)$	
	Zahniser, et al (1976)	210-360	$2.17 \times 10^{-11} \exp(-171/T)$	

Unchanged from NASA 1010. The results reported for k(298 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 (≤ 466 K) experimental data would yield the following Arrhenius expression: $k = (3.34 \pm 1.0) \times 10^{-11} \exp(-(310 \pm 76)/T)$

REFERENCES

Clyne, M. A., and Nip, W. S., "Study of Elementary Reactions by Atomic Resonance Absorption with a Non-Reversed Source Part 1 - The Reaction $Cl + O_3 \rightarrow ClO + O_2$," J. Chem. Soc., Faraday Trans. II 72, 838-847 (1976a)

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions involving the ClO $X^2\Pi$ Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Kurylo, M. J., and Braun, W., "Flash Photolysis Resonance Fluorescence Study of the Reaction Cl + O_3 → ClO + O_2 over the Temperature Range 213-298 K," Chem. Phys. Lett. 37, 232-235 (1976)

Lou, M-T., and DeMore, W. B., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H_2O_2, HO_2, O_3, CH_4 and HNO_3," Chem. Phys. Lett. 41, 121-124 (1976)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R., Machado, G., Fischer, S., and Davis, D. D., "A Temperature Dependence Kinetics Study of the Reaction of Cl($^2P_{3/2}$) with O_3, CH_4 and H_2O_2," J. Chem. Phys. 65, 2126-2138 (1976)

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

Zahniser, M. S., Kaufman, F., and Anderson, J. G., "Kinetics of the Reaction Cl + O_3 → ClO + O_2," Chem. Phys. Lett 37, 226-231 (1976)

R. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,35Br	$O_3 + Br \rightarrow BrO + O_2$		$\Delta H (298) = -129$ kJ/mol	
	NASA (1979) eval	200-300	$1.4 \times 10^{-11} \exp(-(755\pm200)/T)$	1.2
	CODATA (1979) eval	220-360	$1.4 \times 10^{-11} \exp(-(760\pm200)/T)$	1.25
	Leu, DeMore (1977)	224-422	$3.34 \times 10^{-11} \exp(-978/T)$	
	Michael, et al (1978)	200-360	$7.74 \times 10^{-12} \exp(-603/T)$	
	Michael, Payne (1979)	234-360	$9.45 \times 10^{-12} \exp(-659/T)$	
	Clyne, Watson (1975)	298	1.2×10^{-12}	

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 (1978) 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

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetics Studies for Diatomic Free Radicals using Mass Spectrometry Part 3 - Elementary Reactions Involving BrO $X^2\Pi$ Radicals," J. Chem. Soc., Faraday Trans. I 71, 336-350 (1975)

CODATA(1979) Recommendations of the CODATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data

Leu, M.-T., and DeMore, W. B., "Rate Constant for the Reaction of Atomic Bromine with Ozone," Chem. Phys. Lett. 48, 317-320 (1977)

Michael, J. V., Lee, J. H., Payne, W. A., and Stief, L. J., "Absolute Rate of the Reaction of Bromine Atoms with Ozone from 200-360 K," J. Chem. Phys. 68, 4093-4097 (1978)

Michael, J. V., and Payne, W. A., "Absolute Rate Constants for the Reaction of Bromine Atoms with Ozone from 234 to 360K," Int. J. Chem. Kinet. 11, 799-809 (1979)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
7.35F	$ClO_3 + F \rightarrow FO + ClO_2$		ΔH (298) = -114 kJ/mol	
	NASA (1979) eval	200-300	$2.8 \times 10^{-11} \exp(-(226 \pm 200)/T)$	2
	CODATA (1979) eval	250-365	$2.8 \times 10^{-11} \exp(-(226 \pm 200)/T)$	2
	Wagner, et al (1972)	253-365	$2.8 \times 10^{-11} \exp(-(226 \pm 200)/T)$	

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 ClO_3

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

Wagner, H. Gg., Zetzsch, C., and Warnatz, J. "Gas-Phase Preparation of OF Radicals by Reaction of Fluorine Atoms with Ozone," Ber. Bunsenges. Phys. Chem. 76, 526-530 (1972)

R. F. Hampson

June 1979

CHEMICAL KINETICS DATA SURVEY

[illegible] AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

[illegible]/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
[illegible] (a)		ΔH (298) = -148 kJ/mol	
[illegible] (b)		= -156 kJ/mol	
[illegible] (1979) eval	200-300	$k_a < 1 \times 10^{-12} \exp(-4000/T)$	
	200-300	$k_b < 1 \times 10^{-12} \exp(-4000/T)$	
[illegible] (1977) review	300	$< 5 \times 10^{-15}$	

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)

REFERENCES

DeMore, W. B., Lin, C. L., and Jaffe, S., Results presented at 12th Informal Conference on Photochemistry, Washington, D.C. (1976)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,36Br	$O_3 + BrO \rightarrow Br + 2O_2$		ΔH (298) = -157 kJ/mol	
	NASA (1979) eval	200-300	$k < 1 \times 10^{-12} \exp(-1600/T)$	3
	CODATA (1979) eval	298	$k < 5 \times 10^{-15}$	3
	Sander, Watson (1978)	298	$k < 5 \times 10^{-15}$	
	Clyne, Cruse (1970)	293	$k < 8 \times 10^{-14}$	

Changed from NASA 1010. Based on a study reported by Sander and Watson (1978). Clyne and Cruse (1970a) also reported an upper limit of $8 \times 10^{-14} cm^3 molecule^{-1} s^{-1}$ for this reaction. Both studies reported that there is no evidence for this reaction. The analogous ClO reaction has a rate constant of ~ 10-18cm3molecule-1s-1

REFERENCES

Clyne, M. A. A., and Cruse, H. W., "Rates of Elementary Reaction Involving the $BrO(X^2\Pi)$ and $IO(X^2\Pi)$ Radicals. Part 1.-Formation and Decay of the BrO Radical," Trans. Faraday Soc. 66, 2214-2226 (1970a)

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Sander, S. P., and Watson, R. T., 1978c., Manuscript in preparation

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
7.36F	$ClO + O_3 \rightarrow F + 2O_2$ (a) $\rightarrow FO_2 + O_2$ (b)		Δ (298) = -172 kJ/mol = -239 kJ/mol	
	NASA (1979) eval		no recommendation; see note	
	CODATA (1979) eval		No recommendation	

New entry. The $FO + O_3$ reaction has two possible pathways which are exothermic, resulting in the production of $F + 2O_2$ or $FO_2 + O_2$. Although this reaction has not been studied in a single direct manner, two studies of complex chemical systems have inferred some kinetic information about it. Starrico et al (1962) measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~4600, to be due to the rapid regeneration of atomic fluorine via the $FO + O_3 \rightarrow F + 2O_2$ reaction. However, their results are probably also consistent with the chain propagation process being $FO + FO \rightarrow 2F + O_2$ (the latter reaction has been studied twice (Wagner et al (1972), Clyne and Watson (1974b)), but although the value of $[F]_{produced}/[FO]_{consumed}$ is known to be close to unity, it has not been accurately determined. Consequently it is impossible to ascertain from the experimental results of Starrico et al whether or not the high quantum yields for ozone destruction should be attributed to the $FO + O_3$ reaction producing either $F + 2O_2$ or $FO_2 + O_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner et al utilized a low pressure discharge flow-mass spectrometric system to study the $F + O_3$ and $FO + FO$ reactions by directly monitoring the time history of the concentrations of F, FO and O_3. They concluded that the $FO + O_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of k(FO + FO) of 3×10^{-11} is about a factor of 4 greater than that reported by Clyne and Watson, which may possibly be attributed to either reactive impurities being present in their system, e.g., $O(^3P)$ or that the $FO + O_3$ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the $FO + O_3$ reaction rate constant from existing experimental data. It is worth noting that the analogous $ClO + O_3$ reactions are extremely slow (~$10^{-18} cm^3 molecule^{-1} s^{-1}$) DeMore et al (1976), and an upper limit of 8×10^{-14} Clyne and Cruse (1970a) and $5 \times 10^{-15} cm^3 molecule^{-1} s^{-1}$ Sander and Watson (1978) have been reported for $BrO + O_3$

REFERENCES

Clyne, M. A. A., and Cruse, H. W., "Rates of Elementary Reaction Involving the BrO($X^2\Pi$) and IO ($X^2\Pi$) Radicals. Part 1.-Formation and Decay of the BrO Radical," Trans. Faraday Soc. 66, 2214-2226 (1970a)

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 1. System Description and Applications to F Atoms and FO Radicals," J. Chem. Soc., Faraday Trans. I 70, 1109-1123 (1974)

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DeMore, W. B., Lin, C. L., and Jaffe, S., Results presented at 12th Informal Conference on Photochemistry, Washington, D.C. (1976)

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Sander, S. P., and Watson, R. T., 1978, Manuscript in preparation.

Stericco, E. B., Sicre, J. E., and Schumacher, H. J., "Die Photochemische Reaktion Zwischen Fluor und Ozon," Z. Phys. Chemie. N.F. 31, 385-396 (1962)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.45	$O_3 + CO \rightarrow CO_2 + O_2$		ΔH (298) = -426 kJ/mol	
	*Arin, Warneck (1972)	296	$< 4 \times 10^{-25}$	

Note that this is an upper limit only

REFERENCES

Arin, L. M., and Warneck, P., "Reaction of Ozone with Carbon Monoxide," J. Phys. Chem. 76, 1514-1515 (1972)

R. F. Hampson
May 1978

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.48	$O_3 + CH_2O \rightarrow$ products			
	Braslavsky, Heicklen (1976)	300	$\leq 2 \times 10^{-24}$	

Note that this is an upper limit only for the gas phase reaction

REFERENCES

Braslavsky, S., and Heicklen, J., "The Gas-Phase Reaction of O_3 with H_2CO," Int. J. Chem. Kinet. 8, 801-808 (1976)

D. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.49	$O_3 + CH_3 \rightarrow CH_3O + O_2$ (a) $\rightarrow CH_2O + HO_2$ (b) Simonaitis, Heicklen (1975)	221-298	ΔH (298) = -274 kJ/mol = -395 kJ/mol $(k_a + k_b)/k_{ref} = 12 \exp(-525/T)$ (a) k_{ref} is 2nd order high pressure limit for $CH_3 + O_2(+M) \rightarrow CH_3O_2(+M)$	(a)

Only reported value - no recommendation. Authors suggest that channel (a) is major, if not exclusive, reaction pathway

REFERENCES

Simonaitis, R., and Heicklen, J., "Reactions of CH_3, CH_3O, and CH_3O_2 Radicals with O_3," J. Phys. Chem. 79, 298-302 (1975)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,51	$O_3 + CH_3O_2 \rightarrow$ products Simonaitis, Heicklen (1975)	300	$<2.4 \times 10^{-17}$	

Note that this is an upper limit only

REFERENCES

Simonaitis, R., and Heicklen, J., "Reactions of CH_3, CH_3O, and CH_3O_2 Radicals with O_3," J. Phys. Chem. 79, 298-302 (1975)

R. P. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.54	$O_3 + CH_3ONO \rightarrow CH_3ONO_2 + O_2$		$\Delta H (298) = -197$ kJ/mol	
	Hastie, et al (1976)	298-325	$6.2 \times 10^{-13} \exp(-5315/T)$	

Only reported value - no recommendation

REFERENCES

Hastie, D. R., Freeman, C. G., McEwan, M. J., and Schiff, H. I., "The Reactions of Ozone with Methyl and Ethyl Nitrites," Int. J. Chem. Kinet. 8, 307-313 (1976)

W. P. Wampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
*,56	$O_3 + CH_4 \rightarrow$ products Dillemuth, et al (1960)	310-340	$2.7 \times 10^{-13} \exp(-7700/T)$	

*only reported value - no recommendation

REFERENCES

Dillemuth, F. J., Skidmore, D. R., and Schubert, C. C., "The Reaction of Ozone with Methane," J. Phys. Chem. 64, 1496-1495 (1960)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.57	$O_3 + C_2H_4 \rightarrow$ products			1.3
	Herron, Huie (1974)	235-362	$9.0 \times 10^{-15} \exp(-2560/T)$	
	Demerjian, et al (1974) review	300	2.7×10^{-18}	
	DeMore (1969)	178-233	$3.2 \times 10^{-15} \exp(-2400/T)$	
	Stedman, et al (1973)	300	$1.55 \pm 0.15 \times 10^{-18}$	
	Becker, Schurath, Seitz (1974)	280-360	$1.2 \times 10^{-14} \exp(-2490 \pm 100/T)$	
	Japar, Wu, Niki (1974)	298	$1.9 \pm 0.1 \times 10^{-18}$	
	Toby, et al (1976)	303	$1.7 \pm 0.1 \times 10^{-18}$	

This evaluation accepts the results of Herron and Huie (1974), which were determined in the presence of excess O_2. Dioxirane has been identified as a product at low temperature; *see* Lovas and Suenram (1977) and Martinez et al (1977)

REFERENCES

Becker, K. H., Schurath, U., and Seitz, H., "Ozone-Olefin Reactions in the Gas Phase. I. Rate Constants and Activation Energies," Int. J. Chem. Kinet. 6, 725-739 (1974)

Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," Adv. Environ. Sci. Technol. 4, 1-262 (1974) J. N. Pitts, Jr., and R. L. Metcalf, editors, Wiley-Interscience

DeMore, W. B., "Arrhenius Constants for the Reactions of Ozone with Ethylene and Acetylene," Int. J. Chem. Kinet. 1, 209-220 (1969)

Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Ozone with Ethene and Propene, from 235.0 to 362.0 K," J. Phys. Chem. 78, 2085-2088 (1974)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

Lovas, F. J., and Suenram, R. D., "Identification of Dioxirane ($H_2C\overline{O}\overline{O}$) in Ozone-Olefin Reactions Via Microwave Spectroscopy," Chem. Phys. Lett. 51, 453-456 (1977)

Martinez, F. Y., Wuie, E. E., and Herron, J. T., "Mass Spectrometric Detection of Dioxirane, $H_2C\overline{O}\overline{O}$, and its Decomposition Products, H_2 and $C\overline{O}$, from the Reaction of Ozone with Ethylene," Chem. Phys. Lett. 51, 457-459 (1977)

Stedman, D. H., Wu, C. H., and Niki, H., "Kinetics of Gas-Phase Reactions of Ozone with Some Olefins," J. Phys. Chem. 77, 2511-2514 (1973)

Toby, F. S., Toby, S., and O'Neal, H. E., "The Kinetics of the Gas-Phase Reaction between Ozone and Alkenes," Int. J. Chem. Kinet. 8, 25-35 (1976)

W. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert at 298K, notes	Factor
7.59	$O_3 + C_3H_6$ → products				
	*Herron, Huie (1974)	235-362	$6.1 \times 10^{-15} \exp(-1900/T)$	1 3	
	Demerjian et al (1974) review	300	1.0×10^{-17}		
	DeMore (1969)	183, 193, 300	$1.6 \times 10^{-15} \exp(-1600/T)$		(a)
	Stedman, et al (1973)	300	$1.25 \pm 0.1 \times 10^{-17}$		
	Becker, Schurath, Seitz (1974)	280-360	$1.1 \times 10^{-14} \exp(-1970 \pm 100/T)$		
	Japar, Wu, Niki (1974)	298	1.30×10^{-17}		

(a) Includes 300 K point of Hanst et al (1958).

This evaluation accepts the results of Herron and Huie (1974), which were determined in the presence of excess O_2

REFERENCES

Becker, K. H., Schurath, U., and Seitz, H., "Ozone-Olefin Reactions in the Gas Phase. 1. Rate Constants and Activation Energies," Int. J. Chem. Kinet. 6, 725-739 (1974)

Demerjian, K. L., Kerr, J. A., and Calvert, J. G., "The Mechanism of Photochemical Smog Formation," Adv. Environ. Sci. Technol. 4, 1-262 (1974) J. N. Pitts, Jr., and R. L. Metcalf, editors, Wiley-Interscience

DeMore, W. B., "Arrhenius Constants for the Reactions of Ozone with Ethylene and Acetylene," Int. J. Chem. Kinet. 1, 209-220 (1969)

Hanst, P. L., Stephens, E. R., Scott, W. E., and Doerr, R. C., "Atmospheric Ozone-Olefin Reactions," (The Franklin Institute, Philadelphia, Pa. 1958)

Herron, J. T., and Huie, R. E., "Rate Constants for the Reactions of Ozone with Ethene and Propene, from 235.0 to 362.0 K," J. Phys. Chem. 78, 2085-2088 (1974)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

Stedman, D. H., Wu, C. H., and Niki, H., "Kinetics of Gas-Phase Reactions of Ozone with Some Olefins," J. Phys. Chem. 77, 2511-2514 (1973)

W. F. Hampson

June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.59	C_3 + allene → products Toby, Toby (1974)	226-325	$1.6 \times 10^{-15} \exp(-2750/T)$ (a) Mechanism discussed in Toby and Toby (1975) and Toby, et al (1976)	(a)

Only one reported value - no recommendation

REFERENCES

Toby, F. S., and Toby, S., "Reaction between Ozone and Allene in the Gas Phase," Int. J. Chem. Kinet. 6, 417-428 (1974)

Toby, F. S., and Toby, S., "The Reaction of Ozone with 1,3-Butadiene and with Allene," Int. J. Chem. Kinet., Symp. No 1, 197-204 (1975)

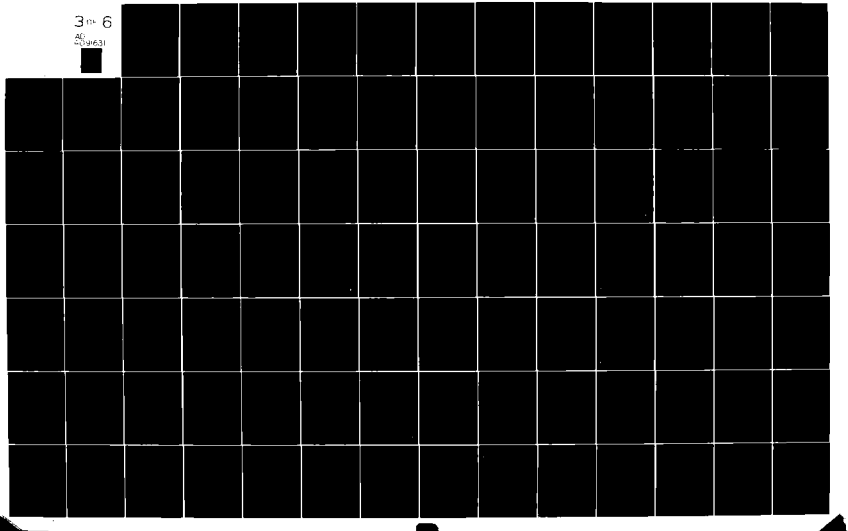
Toby, F. S., Toby, S., and O'Neal, H. E., "The Kinetics of the Gas-Phase Reaction between Ozone and Alkenes," Int. J. Chem. Kinet. 8, 25-35 (1976)

R. F. Hampson

June 1979

AD-A091 631 NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC(U)
APR 80 R F HAMPSON DOT-FA79WAI-005

UNCLASSIFIED FAA/EE-80-17 NL



CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.59	O_3 + 1-butene → products			
	*Huie, Herron (1975)	225-363	$2.9 \times 10^{-15} \exp(-1690/T)$	1.3
	Japar, Wu, Niki (1974)	298	1.23×10^{-17}	

This evaluation accepts the results of the temperature dependent study of Huie and Herron (1975) with error limits to encompass the 20% higher room temperature result of Japar, et al (1974)

REFERENCES

Huie, R. E., and Herron, J. T., "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet., Symp. No. 1, 165-181 (1975)

Japar, S. M., Wu, C. E., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

W. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7,59	O_3 + cis-2-butene → products			
	*Huie, Herron (1975)	225-363	$3.1 \times 10^{-15} \exp(-960/T)$	1-3
	Japar, Wu, Niki (1974)	298	1.61×10^{-16}	

This evaluation accepts the results of the temperature dependent study of Huie and Herron (1975) with error limits to encompass the 50% higher room temperature result of Japar, et al (1974)

REFERENCES

Huie, R. E., and Herron, J. T., "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet., Symp. No. 1, 165-181 (1975)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert Factor at 298K, notes
7,59	O_3 + trans-2-butene → products			1-5
	*Huie, Herron (1975)	225-363	$6.0 \times 10^{-15} \exp(-1050/T)$	
	Japar, Wu, Niki (1974)	298	2.60×10^{-16}	

This evaluation accepts the results of the temperature dependent study of Huie and Herron (1975) with error limits to encompass the 50% higher room temperature result of Japar, et al (1974)

REFERENCES

Huie, R. E., and Herron, J. T., "Temperature Dependence of the Rate Constants for Reactions of Ozone with Some Olefins," Int. J. Chem. Kinet., Symp. No. 1, 165-181 (1975)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318 (1974)

R. F. Hampson

May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
7.59	O_3 + 1,3-butadiene → products			
	This survey	270-360	$8 \times 10^{-14} \exp(-2800/T)$	1.3
	Toby, Toby (1975)	273-343	$1 \times 10^{-13} \exp(-2900/T)$	a0.5
	Becker, Schurath, Seitz (1974)	280-360	$5.4 \times 10^{-14} \exp(-2680/T)$	
	Japar, Wu, Niki (1974)	298	8.4×10^{-18}	

The recommended expression was derived by averaging the three room temperature values and averaging the two temperature dependences. The preexponential factor was then derived to fit the room temperature value

REFERENCES

Becker, K. H., Schurath, U., and Seitz, H., "Ozone-Olefin Reactions in the Gas Phase. 1. Rate Constants and Activation Energies," Int. J. Chem. Kinet. 6, 725-739 (1974)

Japar, S. M., Wu, C. H., and Niki, H., "Rate Constants for the Reaction of Ozone with Olefins in the Gas Phase," J. Phys. Chem. 78, 2318-2320 (1974)

Toby, F. S., and Toby, S., "The Reaction of Ozone with 1,3-Butadiene and with Allene," Int. J. Chem. Kinet., Symp. No 1, 197-204 (1975)

R. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
7.64	O_3 + cis-$C_2Cl_2H_2$ → products Blume et al (1976)	296	3.7×10^{-20}	

Only reported value - no recommendation

REFERENCES

Blume, C. W., Hisatsune, I. C., and Heicklen, J., "Gas-Phase Ozonolysis of Cis- and Trans-Dichloroethylene," Int. J. Chem. Kinet. 8, 235-258 (1976)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
7.64	O_3 + trans-$C_2Cl_2H_2$ → products Blume et al (1976)	296	2.5×10^{-19}	

Only reported value - no recommendation

REFERENCES

Blume, C. W., Hisatsune, I. C., and Heicklen, J., "Gas-Phase Ozonolysis of Cis- and Trans-Dichloroethylene," Int. J. Chem. Kinet. 8, 235-258 (1976)

R. F. Hampson
May 1978

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8,8W 12,W	$N + N + M \rightarrow N_2 + M$ (f) $N_2 + M \rightarrow N + N + M$ (r)		ΔH (298) = -945 kJ/mol	
	eBaulch, et al (1973) review	100-600	$k_f = 8.3 \times 10^{-34} \exp(+500/T) cm^6 molecule^{-2} s^{-1}$ $M = N_2$	1.5
		8000-15000	$k_f = 6.4 \times 10^{-28} T^{-1.6}$ $M = N_2$	3
			$k_r = 6.1 \times 10^{-3} T^{-1.6} \exp(-113,200/T) cm^3 molecule^{-1} s^{-1}$ $M = N_2$	3
	Taylor (1975) review	2000-10000	$k_f = 7.6 \times 10^{-32} T^{-1/2}$ $M = N_2$	
			$k_f = 3.0 \times 10^{-32} T^{-1/2}$ $M = O_2$, O, NO	
			$k_f = 6.5 \times 10^{-27} T^{-3/2}$ $M = N$	

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DOT-TST-75-51, Department of Transportation, Washington D.C., September 1975

R. F. Hampson

May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8,9	$N + NO \rightarrow N_2 + O$ (f)		ΔH (298) = -314 kJ/mol	
1,12	$O + N_2 \rightarrow N + NO$ (r)			
	NASA (1979) eval	200-300	$k_f = 3.4 \times 10^{-11} \exp((0\pm100)/T)$	1.4
	CODATA (1979) eval	200-400	$k_f = 3.4 \times 10^{-11} \exp((0\pm100)/T)$	1.4
	Lee, et al (1978)	196-400	$k_f = 3.4 \times 10^{-11}$	
	Clyne, McDermid (1975)	298-670	$k_f = 8.2 \times 10^{-11} \exp(-410/T)$	
	Baulch, et al (1973) review	2000-5000	$k_r = 1.3 \times 10^{-10} \exp(-38000/T)$	
	Taylor (1975) review	2000-10000	$k_f = 2.7 \times 10^{-11}$	

Recommendation is based on the results of Lee et al (1978) 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

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Clyne, M. A. A., and McDermid, I. S., "Mass Spectrometric Determinations of Rates of Elementary Reactions of NO and of NO_2 with Ground State N^4S Atoms," J. Chem. Soc., Faraday Trans I 71, 2189-2208 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.

Lee, J. H., Michael, J. V., Payne, W. A., and Stief, L. J., "Absolute Rate of the Reaction of $N(^4S)$ with NO from 196-400 K with DF-RF Techniques," J. Chem. Phys. 69, 3069-3076 (1978)

NASA RP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Taylor, R. L., "High Temperature Reactions of Air" pages 5-154 to 5-157 in "The Natural Stratosphere of 1974" Climatic Impact Assessment Program Monograph 1, DOT-TST-75-51, Department of Transportation, Washington D.C., September 1975

R. F. Hampson
June 1979

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8,1*	$N + NO_2 \rightarrow N_2O + O$		ΔH (298) = -175 kJ/mol	
	NASA (1979) eval	200-300	$2.1 \times 10^{-11} \exp(-(890 \pm 350)/T)$	1.25
	CODATA (1979) eval	298	1.4×10^{-12}	1.5
	Clyne, McDermid (1975)	298	1.4×10^{-12}	

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

REFERENCES

Clyne, M. A. A., and McDermid, I. S., "Mass Spectrometric Determinations of Rates of Elementary Reactions of NO and of NO_2 with Ground State $N(^4S)$ Atoms," J. Chem. Soc., Faraday Trans. I 71, 2189-2208 (1975)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
8,19	N + NO → NO + N		ΔH (298) = -203 kJ/mol	
	*Baulch, et al (1973) review	300	5.3×10^{-11}	2
			(a) Based on $k/k(O + NO \rightarrow O_2 + N) = 1.4$	

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8,27	N + SO → NO + S Baulch, et al (1976) review		ΔH (298) = -110 kJ/mol no recommendation	

See the review of Baulch et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8.29	$N + SO_3 \rightarrow NO + SO_2$ Baulch, et al (1976) review		$\Delta H (298) = -283$ kJ/mol no recommendation	

See the review of Baulch et al (1976) for a discussion of reported results. However, because of an insufficient data base, no recommendation can be made

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
8,37	N + OClO → NO + ClO Watson (1977) review	298	ΔH (298) = -377 kJ/mol $k < 6 \times 10^{-13}$	preliminary value

No recommendation

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9,9	$NO + NO \rightarrow N + NO_2$ Baulch, et al (1973) review		ΔH (298) = 325 kJ/mol Endothermic. Unimportant compared to $NO + NO \rightarrow N_2O + O$	

There is no evidence for this reaction

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9,1*,22	$NO + NO_2 + H_2O \rightarrow 2HNO_2$ (f) $2HNO_2 \rightarrow NO + NO_2 + H_2O$ (r)		ΔH (298) = - 41 kJ/mol	
	Chan, et al (1976)	296	$k_f = 6.0 \times 10^{-38} cm^6 molecule^{-2} s^{-1}$ $k_r = 9.5 \times 10^{-19} cm^3 molecule^{-1} s^{-1}$	
	Kaiser, Wu (1977)	300	$k_f \leq 4.4 \times 10^{-40} cm^6 molecule^{-2} s^{-1}$ $k_r \leq 1 \times 10^{-20} cm^3 molecule^{-1} s^{-1}$	
	Hampson, et al (1973) review	300	Reviewed earlier work, probably heterogeneous	

No recommendation

REFERENCES

Chan, W. H., Nordstrom, R. J., Calvert, J. G., and Shaw, J. H., "An IRFTS Spectroscopic Study of the Kinetics and the Mechanism of the Reactions in the Gaseous System, HONO, NO, NO_2, H_2O," Chem. Phys. Lett. 37, 441-446 (1976)

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

Kaiser, E. W., and Wu, C. H., "A Kinetic Study of the Gas Phase Formation and Decomposition Reactions of Nitrous Acid," J. Phys. Chem. 81, 1701-1706 (1977)

R. F. Hampson
May 1978

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9,11 10,10	$NO + NO_3 \rightarrow 2NO_2$ (f) $NO_2 + NO_2 \rightarrow NO + NO_3$ (r)		ΔH (298) = - 95 kJ/mol	
	NASA (1979) eval	298	$k_f = 2 \times 10^{-11}$	3
	CODATA (1979) eval	298	$k_f = 2 \times 10^{-11}$	3
	Graham, Johnston (1978)	300	$k_f = (1.9 \pm 0.4) \times 10^{-11}$	
	Baulch, et al (1973) review	300	$k_f \sim 2 \times 10^{-11}$ k_r no recommendation	

This recommendation accepts the value reported by Graham and Johnston (1978) with increased error limits

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the N_2-N_2-O_2 System," (Butterworths, London, 1973)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9.15	NO + NH → products			
	Hansen, et al (1976)	300	$(4.7 \pm 1.2) \times 10^{-11}$	
	Gordon, et al (1971)	300	3.8×10^{-11}	
	Mulvihill, Phillips (1975)	1500	N_2 + O + H identified as products of major rxn channel	

No recommendation

REFERENCES

Hansen, I., Heinghaus, K., Zetzsch, C., and Stuhl, F., "Detection of NH($X^3\Sigma^-$) by Resonance Fluorescence in the Pulsed Vacuum UV Photolysis of NH_3 and Its Application to Reactions of NH Radicals," Chem. Phys. Lett. 42, 370-372 (1976)

Gordon, S., Mulac, W., and Nangia, P., "Pulse Radiolysis of Ammonia Gas. II-Rate of Disappearance of the $NH_2(X^2B_1)$ Radical," J. Phys. Chem. 75, 2087-2093 (1971)

Mulvihill, J. N., and Phillips, L. F., "Products of Reaction of NH with NO," Chem. Phys. Lett. 35, 327-329 (1975)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
9.16	$NO + NH_2 \rightarrow N_2 + H_2O$*		$\Delta H(298) = -517$ kJ/mol	
	*Hancock, et al (1975)	298	2.1×10^{-11}	1.5
	Lesclaux, et al (1975)	300	1.8×10^{-11}	(a)
			(a) $T^{-1.25}$ dependence observed 300-500K	
	Gehring, et al (1973)	300	8×10^{-12}	
	Gordon, et al (1971)	300	2.7×10^{-11}	

This evaluation accepts the results of Hancock et al (1975) which are confirmed by the results of Lesclaux et al (1975)

REFERENCES

Gehring, M., Hoyermann, K., Schacke, H., and Wolfrum, J., "Direct Studies of Some Elementary Steps for the Formation and Destruction of Nitric Oxide in the H-N-O System," Symp. Combust. 14th (Combustion Institute, Pittsburgh, 1973) 99-105

Gordon, S., Mulac, W., and Nangia, P., "Pulse Radiolysis of Ammonia Gas. II. Rate of Disappearance of the $NH_2(X^2B_1)$ Radical," J. Phys. Chem. 75, 2087-2093 (1971)

Hancock, G., Lange, W., Lenzi, M., and Welge, K. H., "Laser Fluorescence of NH_2 and Rate Constant Measurement of NH_2 + NO," Chem Phys. Lett. 33, 168-172 (1975)

Lesclaux, R., van Khe, P., Dezauzier, P., and Soulignac, J. C., "Flash Photolysis Studies of the Reaction of NH_2 Radicals with NO," Chem. Phys. Lett. 35, 493-497 (1975)

R. F. Hampson

May 1976

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Uncert Factor at 298K, notes
9,18M	$NO + H + M \rightarrow HNO + M$ (f)		ΔH (298) = -209 kJ/mol		
24,M	$HNO + M \rightarrow H + NO + M$ (r)				
	*Baulch, et al (1973) review	230-700	$k_f = 1.5 \times 10^{-32} \exp(300/T) cm^6 molecule^{-2} s^{-1}$	$M = N_2$	1.5
			$k_r = k_f/K_{eq} = 5 \times 10^{-8} \exp(-24500/T)$	$M = N_2$	1.5
	Atkinson, Cvetanovic (1973)	286-390	$k_f = 2.5 \times 10^{-32} \exp(270/T)$	$M = N_2$	
	Allen, Moortgat (1973)	180-300	$k_f = 5.6 \times 10^{-33} \exp(375/T)$,	$M = Ar$	

This evaluation accepts the recommendations in the review of Baulch et al (1973)

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R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
9,19M	$NO + NO(+M) \rightarrow ONO_2(+M)$		ΔH (298) = -209 kJ/mol	
	NASA (1979) eval	200-300	$k = (6.7 \pm 1.2) \times 10^{-31}(T/300)^{-3.3 \pm 1}$, M = N_2	
			$k_\infty = (3.0 \pm 1.5) \times 10^{-11}(T/300)^{-1 \pm 1}$ $cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	220-440	$k = 6.5 \times 10^{-31}(T/300)^{-2.4}$, M = N_2	1.3
			$k_\infty = 1.0 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$	1.6
	Baulch, et al (1973) review	273-395	$2.2 \times 10^{-32} \exp(+1110/T)$ M = He	1.6
		300	2×10^{-12} $cm^3 molecule^{-1} s^{-1}$ (2d order high pressure limit)	2
	Anderson, et al. (1974)	295,439	$5.8 \pm 1.2 \times 10^{-31} \times (295/T)^{+2.4}$ M = N_2	
			Relative efficiencies: N_2(1.0), Ar(0.58), He(0.57)	
	Howard, Evenson (1974)	296	$7.8 \pm 1.2 \times 10^{-31}$ M = N_2	
			Relative efficiencies: N_2(1.0), Ar(0.56), He(0.51)	
	Cox (1974)	294	$k/k(HO + CO) = 40 \pm 7$	
			$k = 1.2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$	(a)
			(a) 2nd order rate constant, [M] = 1 atm $N_2 + O_2$; $k_{ref} = 3 \times 10^{-13}$, this survey	
	Harris, Wayne (1975)	300	$7 \pm 2 \times 10^{-31}$, M = Ar	
			$15 \pm 5 \times 10^{-31}$, M = N_2	
	Gordon, Mulac (1975)	435	$7.5 \pm 0.3 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$ (2nd order rate constant at 1 atm H_2O vapor)	
	Atkinson, Hansen, Pitts (1975a)	298	$4.94 \pm 0.5 \times 10^{-13}$ M = 25 Torr N_2	(b)
			(b) also data for M = Ar at 25-655 torr	
	Cox, Derwent, Holt (1976)	298	1.17×10^{-11} M = 1 atm $N_2 + O_2$	(c)
			(c) relative to $k(HO + H_2) = 7 \times 10^{-15}$	
	Overend, et al (1976)	295	$0.956 \pm 0.05 \times 10^{-12}$ M = 25 torr N_2	
			$6.89 \pm 0.68 \times 10^{-12}$ M = 770 torr N_2	
	Sie, et al (1976b)	298	$k/k_{ref} = 16.1$ at 95 torr and = 22 at 408 and 768 torr total pressure, mostly H_2 where ref rxn is $HO + CO \rightarrow CO_2 + H$	

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R. P. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
9,20	$NO + HO_2 \rightarrow NO_2 + HO$		ΔH (298) = - 20 kJ/mol	
	NASA (1979) eval	200-300	$4.3 \times 10^{-12} \exp((200\pm200)/T)$	1.2
	CODATA (1979) eval	230-425	$4.3 \times 10^{-12} \exp((200\pm200)/T)$	1.2
	Zahniser, Howard (1978)	230-400	$3.3 \times 10^{-12} \exp(254/T)$	
	Leu (1979)	270-425	$5.7 \times 10^{-12} \exp(130/T)$	
	Marsitan, Anderson (1978)	298	8.0×10^{-12}	
	Kaufman, Reimann (1978)	298	7.9×10^{-12}	
	Burrows, et al (1978)	298	8.2×10^{-12}	
	Howard, Evenson (1977)	296	$(8.1 \pm 1.5) \times 10^{-12}$	
	Hack, et al (1975)	298-670	$2.0 \times 10^{-11} \exp(-1200/T)$	
	Simonaitis, Heicklen (1977)	245-328	$k/(k_{ref})^{0.5} = 6.4 \times 10^{-6} \exp(-700/T)$	(a)
			(a) ref rxn: $2HO_2 \rightarrow H_2O_2 + O_2$	
	Cox, Derwent (1975)	296	1.2×10^{-12}	
	Payne, Stief, Davis (1973)	300	3×10^{-13}	
	Glanzer, Troe (1975)	1350-1700	7.5×10^{-12}	

The recommendation is based on Zahniser and Howard (1978) and Leu (1979) and the room temperature determinations of Marsitan and Anderson (1978) and Kaufman and Reimann (1978) and the ratio determination by Burrows et al (1978) relative to $OH + H_2O_2$. The agreement is excellent

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9.23	$HO + H_2O_2 \rightarrow H_2O + HO_2$		$\Delta H(298) = 6$ kJ/mol	
	*Hampson, et al (1973) review	300	$< 5 \times 10^{-20}$	
		500	$\sim 2 \times 10^{-20}$	
	Gray, et al (1972)	300	$< 5 \times 10^{-20}$	

This evaluation accepts the recommendations in the review of Hampson et al (1973)

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R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
9,35M	NO + Cl + M → ClNO + M		ΔH (298) = -160 kJ/mol	
	NASA (1979) eval	200-300	$k = (9 \pm 2) \times 10^{-32} (T/300)^{-1.8 \pm 0.5}$, M = N_2	
	Lee, et al (1978a)	200-400	$k = 1.18 \times 10^{-32} \exp(532/T)$, M = N_2	
			$k = 7.15 \times 10^{-32} (T/300)^{-1.91}$, M = N_2	
	Watson (1977) review	293	$k = 1.1 \times 10^{-31}$, M = N_2	

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert. Factor at 298K, notes
9.35F	$NO + F + M \rightarrow FNO + M$ NASA (1979) eval	200-300	$k = (6.6 \pm 3.3) \times 10^{-32}(T/300)^{-1}$, $M = N_2$	

Estimated value; no data

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9,36	$NO + ClO \rightarrow NO_2 + Cl$		$\Delta H(298) = -38$ kJ/mol	
	NASA (1979) eval	200-300	$7.8 \times 10^{-12} \exp((250 \pm 100)/T)$	1.25
	CODATA (1979) eval	227-415	$8.9 \times 10^{-12} \exp((210 \pm 100)/T)$	1.25
	Leu, DeMore (1978)	227-415	$5.7 \times 10^{-12} \exp(296/T)$	
	Watson, Ray (1979)	298	1.75×10^{-11}	
	Clyne, Watson (1974a)	298	1.7×10^{-11}	
	Watson (1977) review	220-298	$8 \times 10^{-12} \exp(250/T)$	
	Zahniser, Kaufman (1977)	230-298	$k/k_{ref} = (0.52 \pm 0.05)\exp(373 \pm 23/T)$	(a)
			(a) $k_{ref} = k(Cl + O_3)$	

Changed from NASA 1010. The results of the three mass spectrometric studies (Clyne and Watson (1974a), Leu and DeMore (1978) and Watson and Ray (1979)) 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

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R. P. Wayne
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
9,36Br	$NO + BrO \rightarrow NO_2 + Br$		ΔH (298) = - 71 kJ/mol	
	NASA (1979) eval	200-300	$8.7 \times 10^{-12} \exp((265\pm130)/T)$	1.15
	CODATA (1979) eval	224-425	$8.7 \times 10^{-12} \exp((260\pm100)/T)$	1.25
	Leu (1979)	230-425	$7.1 \times 10^{-12} \exp(296/T)$	
	Watson, Sander, Yung (1979)	224-396	$1.3 \times 10^{-11} \exp(181/T)$	
	Ray, Watson (1979)	298	2.3×10^{-11}	
	Clyne, Watson (1975)	298	2.2×10^{-11}	
	Clyne, Cruse (1970)	298	2.5×10^{-12}	

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 (1979) and Leu (1979)) and the high pressure uv absoprtion study (Watson, Sander and Yung (1979), which all used pseudo first-order conditions, are in excellent agreement at 298 K, and are thought to be much more reliable than the earlier low pressure uv absorption (Clyne and Cruse(1970)). 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, Sander and Yung (1979) 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 NO_2 reactions are also negative, and are similar in magnitude

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Watson, R. T., Sander, S. P., and Yung, Y. L., 1979, Manuscript in preparation

W. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
9,36F	NO + FO → NO_2 + F		ΔH (298) = -239 kJ/mol	
	NASA (1979) eval	200-300	$2 \times 10^{-11} \exp((0 \pm 250)/T)$	3
	CODATA (1979) eval	298	2×10^{-11}	3

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 (1974). 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 2.1×10^{-11}, respectively (this evaluation). 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 (1978) for ClO, and -296 K (Leu (1979) and -180 K (Watson and Sander (1978) for BrO

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 1. System Description and Applications to F Atoms and FO Radicals," J. Chem. Soc., Faraday Trans. I 70, 1109-1123 (1974)

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Watson, R. T., and Sander, S. P., 1978, Manuscript in preparation.

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R. P. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert Factor at 298K, notes
9.37	NO + ClO → NO_2 + Cl		ΔH (298) = - 52 kJ/mol	
	NASA (1979) eval	200-300	2.5×10^{-12} exp(-(600±300)/T)	1.5
	Bemand, Clyne, Watson (1973)	300	3.4×10^{-13} (a) Based on room temp. value of Bemand, Clyne, Watson; temp dependence estimated	

Unchanged from NASA 1010. Arrhenius expression was estimated based on 298 K data reported by Bemand, Clyne and Watson (1973)

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
9.49M	$NO + CH_3$ (+M) → CH_3NO (+M)			
	Laufer, Bass (1975)	298	$10^{11} \times k$ / $P(N_2)$/torr: 0.3 / 50; 0.45 / 100; 1.1 / 700	(a)
	Basco, et al (1970)	298	4×10^{-12}	(b)
	van den Bergh, Callear (1971)	295	1.7×10^{-11}	(b)

(a) Values are based on $k(CH_3 + CH_3) = 9.5 \times 10^{-11}$ given in Bass, Laufer (1973).

(b) 2nd order high pressure limit

No recommendation

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
9.51	$NO + CH_3O_2 \rightarrow CH_3O + NO_2$ (a) $\rightarrow CH_2O + HONO$ (b) $\rightarrow CH_3O_2NO$ (c)		ΔH (298) = - 50 kJ/mol ΔH (298) = -286 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 7 \times 10^{-12} \exp((0.500)/T)$	3
	CODATA (1979) eval	298	$k_a = 7.5 \times 10^{-12}$	2
	Plumb, et al (1979)	295	$k_a = (8 \pm 2) \times 10^{-12}$	
	Cox, Tyndall (1979)	298	$k_a = (6.5 \pm 2) \times 10^{-12}$	
	Cox, et al (1976a)	298	$k_a \geq 1.2 \times 10^{-12}$ (a) based on value of $k(CH_3O_2 + CH_3O_2)$	lower limit (a)
	Pate, Finlayson, Pitts (1974)	296	Reaction proceeds exclusively through channel (a)	
	Simonaitis, Heicklen (1974)	298	$k_a/k = 0.80 \pm 0.15$ $(k = k_a + k_b + k_c)$	

The value for k(298) is the average of those reported by Plumb et al (1979), and by Cox and Tyndall (1979). Preliminary data of Sander and Watson (1979) supports the recommendation

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R. F. Hampson
June 1979

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Uncert Factor at 298K, notes
10, 10W	$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$ (f) $N_2O_4 + M \rightarrow NO_2 + NO_2 + M$ (r)		ΔH (298) = - 57 kJ/mol		
	eBaulch, et al (1973) review	250-350	$k_f = 3.0 \times 10^{-35} \exp(1040/T) cm^6 molecule^{-2} s^{-1}$	$M = N_2$	1.3 (a)
			(a) corrected expression; $k_f = k_r k_{eq}$		
			$k_r = 4.2 \times 10^{-7} \exp(-5550/T)$	$M = N_2$	1.3
	Schofield (1973) review	250-350	$k_r = 3.3 \times 10^{-7} \exp(-5540/T)$	$M = N_2$	

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- Factor at 298K, notes
1^,11	$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ (f)		ΔH (298) = 19 kJ/mol	
4,9,1^	$O_2 + NO + NO_2 \rightarrow NO_2 + NO_3$ (r)			
	*Baulch, et al (1973) review	300-850	$k_f = 2.3 \times 10^{-13} \exp(-1000/T)$	2-5 (a)
		300-500	$k_r = k_f/K_{eq} = 8 \times 10^{-41} \exp(400/T) cm^6 molecule^{-2} s^{-1}$	2.5
	Graham, Johnston (1978)	338-396	$k_f = 2.5 \times 10^{-14} \exp(-1230/T)$	

(a) Based on $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ and $2NO_2 \rightarrow 2NO + O_2$

This evaluation accepts the recommendations in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
10, 11M 14, M	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (f) $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ (r)		ΔH (298) = - 93 kJ/mol	
	NASA (1979) eval	200-300	$k_f = (1.4 \pm 0.7) \times 10^{-30} (T/300)^{-2.8 \pm 1.0}$, M = N_2	
			$k_{f,\infty} = (9.0 \pm 4.5) \times 10^{-13} (T/300)^{0.7} cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	300-340	$k_f = 1.5 \times 10^{-30} (T/300)^{-4.6}$, M = N_2	2
		200-400	$k_{f,\infty} = 5 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$	2
		300-340	$k_r = 8.8 \times 10^{-6} exp(-9700/T)$ $cm^3 molecule^{-1} s^{-1}$	2
		273-300	$k_{r,\infty} = 5.7 \times 10^{14} exp(-10600/T)$ s^{-1}	2
	Baulch, et al (1973) review	300	$k_f = 2.8 \times 10^{-30}$	2 (a)
		300	$k_{f,\infty} = 3.8 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$	2.5 (a)
		300-340	$k_r = 2.2 \times 10^{-5} exp(-9700/T)$ $cm^3 molecule^{-1} s^{-1}$	2 (a)
		273-300	$k_{r,\infty} = 5.7 \times 10^{14} exp(-10600/T)$ s^{-1}	2.5 (a)
	Graham, Johnston (1978)	298-329	$K_{eq} = 1.2 \times 10^{-27} exp(+11180/T) cm^3 molecule^{-1}$	
		273-300	$k_f = 1.48 \times 10^{-13} exp(+861/T) cm^3 molecule^{-1} s^{-1}$	(b)
			$k_r = 1.24 \times 10^{14} exp(-10317/T) s^{-1}$	(c)
	Connell, Johnston (1979)	262-307	$k_r = 6.1 \times 10^{-6} exp(-9570/T)$ $cm^3 molecule^{-1} s^{-1}$	
			$k_{r,\infty} = 1.78 \times 10^{17} exp(-12540/T) s^{-1}$	

(a) $k_f = K_{eq} k_r$, M = N_2O_5 + NO
(b) 2d order rate const at 1 atm
(c) 1st order rate const at 1 atm

Recommendation is based on results reported by Connell and Johnston (1979) and private communication from D. Albritton, F. Fehsenfeld and A. Viggiano (1979)

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Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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June 1979

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert- at 298K,	Factor notes
1[c],16	$NO_2 + NH_2 \rightarrow$ products Jayanty, et al (1975d)	300	$k > k(NO + NH_2)$		

No recommendation

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May 1978

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
16,17	$NO_2 + NH_3 \rightarrow NH_2 + HNO_2$		ΔH (298) = 118 kJ/mol	
	Bedford, Thomas (1972)	615-660	$6.7 \times 10^{-12} \exp(-13900/T)$	

No recommendation

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May 1978

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
1*,18 9,19	$NO_2 + H \rightarrow NO + OH$ (f) $NO + HO \rightarrow NO_2 + H$ (r)		ΔH (298) = -122 kJ/mol	
	This survey	250-500	$k_f = 5.8 \times 10^{-10} \exp(-450/T)$	1.3
	Wagner, et al (1976a)	243-461	$k_f = 7.1 \times 10^{-10} \exp(-505 \pm 84/T)$	
	Clyne, Monkhouse (1977)	298-653	$k_f = 4.80 \times 10^{-10} \exp(-400 \pm 70/T)$	
	Bemand, Clyne (1977)	298	$k_f = 1.13 \pm 0.22 \times 10^{-10}$	
	Baulch, et al (1973) review	298-633	$k_r = 5 \times 10^{-12} \exp(-15100/T)$ (a) $k_r = k_f/K_{eq}$	2 (a)

Recommended expression is based on the results reported in the two temperature dependent studies

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant k/cm^{6}molecule^{-2}s^{-1}	Uncert Factor at 298K, notes
18,19M 26,M	$NO_2 + NO + M \rightarrow HNO_3 + M$ (f) $HNO_3 + M \rightarrow NO + NO_2 + M$ (r)		ΔH (298) = -207 kJ/mol	
	NASA (1979) eval	200-300	$k_f = (2.6 \pm 0.3) \times 10^{-30}(T/300)^{-2.9 \pm 0.7}$, M = N_2	
			$k_{f,\infty} = (2.4 \pm 1.2) \times 10^{-11}(T/300)^{-1.3 \pm 1}$ cm^{3}molecule^{-1}s^{-1}	
	CODATA (1979) eval	220-550	$k_f = 2.6 \times 10^{-30}(T/300)^{-2.7}$, M = N_2	1.3
		220-360	$k_{f,\infty} = 1.6 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}	1.6
	Anastasi, Smith (1976)	296	$k_f = 2.6 \times 10^{-30}$ M = N_2 Rel. Efficiencies: N_2(1.0), He(0.34), Ar(0.42), O_2(0.68), SF_6(2.5)	
		220-550	n = -2.6 for temp dependence of form T^n, M = N_2 values given for bimolecular rate constant over ranges T = 220-550K and [N_2] = 3×10^{17} to 1.6×10^{19} molecule cm^{-3}	
	Baulch, et al (1973) review	273-400	$k_f = 3.6 \times 10^{-32} \exp(+1100/T)$ M = He	1.6
		800-1200	$k_r = 2.7 \times 10^{-9} \exp(-15400/T)$cm^{3}molecule^{-1}s^{-1} M = Ar	2.5
		300	$k_{f,\infty} = 8 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}	2.5
	Anderson, et al (1974)	295-450	$k_f = 2.3 \pm 0.5 \times 10^{-30} \times (295/T)^{+2.5}$ M = N_2 Relative efficiencies: N_2(1.0), Ar(0.43), He(0.43)	
	Howard, Evenson (1974)	296	$k_f = 2.9 \pm 0.4 \times 10^{-30}$ M = N_2	
	Gordon, Mulac (1975)	435	$k_f = 5.3 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} (2nd order rate constant at 1 atm H_2O vapor)	
	Harris, Wayne (1975)	300	$15 \pm 5 \times 10^{-31}$, M = Ar $26 \pm 10 \times 10^{-31}$, M = N_2	
	Atkinson, Perry, Pitts (1976)	298	$k_f = (1.0 \pm 0.1) \times 10^{-30}$ M = Ar Values given for bimolecular rate constant over pressure range 25-646 torr Ar	

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June 1979

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
10,20N	$NO_2 + HO_2 + N \rightarrow HO_2NO_2 + N$		ΔH (298) = -69kJ/mol	
	NASA (1979) eval	200-300	$k = (2.1 \pm 0.4) \times 10^{-31} (T/300)^{-5 \pm 2}$, $M = N_2$	
			$k_\infty = (6.5 \pm 3.3) \times 10^{-12} (T/300)^{-5 \pm 2}$ $cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	300	$k = 2.1 \times 10^{-31}$	
	Howard (1977)	300	$(2.09 \pm 0.52) \times 10^{-31}$ $M = N_2$	
			Rel. eff: N_2(1.0), He(0.48); O_2(0.72); NO_2(3.2)	
			$k(HO_2 + NO_2 \rightarrow HONO + O_2) < 3 \times 10^{-15}$	
	Cox, Patrick (1979)	283	$k = (2.5 \pm 0.5) \times 10^{-31}$	
	Simonaitis, Heicklen (1977)	245	$k[M]/k(HO_2 + NO) = 0.61$	(a)
		295	$k[M]/k(HO_2 + NO) = 0.036$	(a)
			(a) M = 700 torr N_2. Rxn to give HONO + O_2 is negligible	

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
17,28	$NO_2 + SO_2 \rightarrow SO_3 + NO$		$\Delta H(298) = -42$ kJ/mol	
	Davis (1976)	300	$k < 2 \times 10^{-24}$	preliminary

No recommendation

REFERENCES

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

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May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
1C,35M	$NO_2 + Cl + M \rightarrow$ products			
	NASA (1979) eval	200-300	$k = (1.6 \pm 1.0) \times 10^{-30}(T/300)^{-1.9 \pm 1}$ $k_\infty = (3.0 \pm 1.5) \times 10^{-11}(T/300)^{-1 \pm 1}$ $cm^3 molecule^{-1} s^{-1}$	

Reaction proceeds through two reaction channels to give both ClONO and $ClNO_2$ as products; see Niki et al (1978) and Chang et al (1979)

REFERENCES

Chang, J. S., Baldwin, A. C., and Golden, D. M., "An Explanation of the Preferential Formation of Less Stable Isomers in Three-Body Reactions: $Cl + NO_2 + M$; $ClO + NO_2 + M$," J. Chem. Phys. 71, 2021-2024 (1979)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert. Factor at 298K, notes
10.38F	$NO_2 + F + M \rightarrow FNO_2 + M$ $\rightarrow FONO + M$			
	NASA (1979) eval	200-300	$k = (1.3 \pm 0.7) \times 10^{-30}(T/300)^{-1.7}$, $M = N_2$ $k_\infty = (3 \pm 1.5) \times 10^{-11}(T/300)^{-1 \pm 1}$ $cm^3 molecule^{-1} s^{-1}$	

Estimated values; no data

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant k/cm^{6}molecule^{-2}s^{-1}		Uncert Factor at 298K, notes
1c,36N	$NO_2 + ClO + M \rightarrow ClONO_2 + M$		ΔH (298) = -109 kJ/mol		
	NASA (1979) eval	200-300	$k = (1.6\pm0.2) \times 10^{-31}(T/300)^{-3.4\pm0.3}$, M = N_2		
			$k = (3.5\pm1.7) \times 10^{-32}(T/300)^{-3.8\pm1}$, M = N_2		
			$k_\infty = (1.5\pm0.7) \times 10^{-11}(T/300)^{-1.9\pm1}$ cm^{3}molecule^{-1}s^{-1}		
	CODATA (1979) eval	250-400	$k = 1.7 \times 10^{-31}(T/300)^{-3.0}$, M = N_2		1.3
			$k_\infty = 1.2 \times 10^{-11}$ cm^{3}molecule^{-1}s^{-1}		2.5
	Birks, et al (1977)	250-356	$(4.40 \pm 0.66) \times 10^{-33}\exp(1087/T)$	M = N_2	
		297	$9.57 \pm 0.28 \times 10^{-32}$	M = He	
	Leu, Lin, DeMore (1977)	298-417	$(3.69 \pm 0.24) \times 10^{-33}\exp(1150/T)$	M = N_2	
		248-417	$(2.66 \pm 0.35) \times 10^{-33}\exp(1140/T)$	M = He	
	Zahniser, Chang, Kaufman (1977)	251-365	$(3.54 \pm 0.06) \times 10^{-33}\exp(950/T)$	M = He	
		251-365	$5.53 \times 10^{-24}T^{-3.15}$	M = He	
		297	1.52×10^{-31}	M = N_2	

NASA (1979) gives two distinct recommendations for k_∞. The first corresponds to the measured rate constant for disappearance of the reactants. The second has been calculated from the rate of decomposition of $ClONO_2$ (Knauth, 1978) and the equilibrium constant. The discrepancy may be due to the production of isomers through different reaction channels. See the discussion in Chang et al (1979)

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Zahniser, M. S., Chang, J. S., and Kaufman, F., "Chlorine Nitrate: Kinetics of Formation by ClO + NO_2 + M and of Reaction with OH," J. Chem. Phys. 67, 997-1003 (1977)

W. F. Hampson

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CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert. Factor at 298K, notes
10.3ClBr	$NO_2 + BrO + M \rightarrow BrONO_2 + M$		ΔH (298) = -138 kJ/mol	
	NASA (1979) eval	200-300	$k = 3.2 \times 10^{-31}(T/300)^{-3.4}$, $M = N_2$	
	CODATA (1979) eval	200-400	$k = 3 \times 10^{-31}(T/300)^{-3}$, $M = N_2$	2.5
			$k_\infty = 1.2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$	
	Watson, Sander (1978)	298	$k = 3 \times 10^{-31}$, $M = N_2$	provisional data

Estimated value; taken as twice the value for $NO_2 + ClO + M$

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., and Sander, S. P., 1978, Manuscript in preparation.

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert. Factor at 298K, notes
10.36F	$NO_2 + FO + M \rightarrow FNO_2$		ΔH (298) = -132 kJ/mol	
	NASA (1979) eval	200-300	$k = (8.3 \pm 6.0) \times 10^{-31} (T/300)^{-0.7}$, $M = N_2$	
			$k_\infty = (2.0 \pm 1.0) \times 10^{-11} (T/300)^{-1.5 \pm 1.5}$ $cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	200-400	$k = 1.7 \times 10^{-31} (T/300)^{-3}$, $M = N_2$	5
			$k_\infty = 1.2 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$	5

Estimated value; no data

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
1°,49	$NO_2 + CH_3 \rightarrow CH_3O + NO$ Glanzer, Troe (1974)	300-1400	3.3×10^{-11} (a) Based on $k/k(CH_3 + NO) = 3.3$ at room temperature and on shock wave pyrolysis of CH_3NO_2	2 (a)
1°,49W	$NO_2 + CH_3 (+M) \rightarrow CH_3NO_2 (+M)$ Glanzer, Troe (1974)	295	2.8×10^{-11} $cm^3 molecule^{-1} s^{-1}$ (a) Based on high pressure limit rate ratio $k/k(CH_3 + NO) = 1.7$	2 (a)
1°,49M	$NO_2 + CH_3 + M \rightarrow CH_3NO_2 + M$ Glanzer, Troe (1974)	900-1400	$6.9 \times 10^{-31} (T/1000)^{-6}$ $cm^6 molecule^{-2} s^{-1}$, M = Ar (a) $k_f = k_r K_{eq}$	(a)

No recommendations

REFERENCES

Glanzer, K., and Troe, J., "Reactions of Alkyl Radicals in the Shock Wave-Induced Pyrolysis of Nitroalkanes," Ber. Bunsenges. Phys. Chem. 78, 182-184 (1974)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
1C.51	$NO_2 + CH_3O_2 \rightarrow CH_3O_2NO_2$ (a) $\rightarrow CH_2O + HONO_2$ (b) $\rightarrow CH_3O + NO_3$ (c) Heicklen (1973) review	298	ΔH (298) = - 80 kJ/mol = -284 kJ/mol = 45 kJ/mol k_a/k = 0.75 ±0.05 k_b/k = 0.25 ±0.1 k_c/k < 0.1	

No recommendation

REFERENCES

Heicklen, J., "Photochemical and Rate Data for Methyl Nitrite, Methoxy and Methylperoxy," Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C (1973) pages 43-48

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant k/cm^{6}molecule^{-2}s^{-1}	Uncert. Factor at 298K, notes
10.51M	$NO_2 + CH_3O_2 + M \rightarrow CH_3O_2NO_2 + M$		ΔH (298) = - 60 kJ/mol	
	NASA (1979) eval	200-300	$k = (2.0 \pm 1.5) \times 10^{-30}(T/300)^{-4 \pm 2}$, $M = N_2$	
			$k_\infty = (0.5 \pm 3.3) \times 10^{-12}(T/300)^{-4 \pm 2}$	
	CODATA (1979) eval	200-300	1.6×10^{-12} (1 atm air)	3 (a)
	Cox, Tyndall (1979)	276	1.6×10^{-12} (540 torr N_2)	(a)
			1.2×10^{-12} (50 torr Ar)	(a)
			(a) Effective bimolecular rate constant in units of cm^{3}molecule^{-1}s^{-1}	

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Cox, R. A., and Tyndall, G. S., "Rate Constants for Reactions of CH_3O_2 in the Gas Phase," Chem. Phys. Lett. 65, 357-360 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
11,11	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$		$\Delta H^\circ(298) = -76$ kJ/mol	
	Graham, Johnston (1978)	298-329	$8.5 \times 10^{-13} \exp(-2450/T)$	(a)
	Baulch, et al (1973) review	293-309	$5 \times 10^{-12} \exp(-3000/T)$	
			(a) $-d[NO_3]/dt = 2k[NO_3]^2$. Based on rate of O_3 decomp. in presence of N_2O_5	

No recommendation

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
11,28	$NO_3 + SO_2 \rightarrow NO_2 + SO_3$		ΔF (298) = -137 kJ/mol	
	*Daubendiek, Calvert (1975)	300	$k < 7 \times 10^{-21}$	
	Davis (1976)	300	$k < 1 \times 10^{-21}$	preliminary

*Note that this is an upper limit only

REFERENCES

Daubendiek, R. L., and Calvert, J. G., "A Study of the N_2O_5-SO_2-O_3 Reaction System," Environ. Lett. 8, 103-116 (1975)

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
11,28	$NO_3 + SO_2 \rightarrow NO_2 + SO_3$		ΔF (298) = -137 kJ/mol	
	aDaubendiek, Calvert (1975)	300	$k < 7 \times 10^{-21}$	
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Daubendiek, R. L., and Calvert, J. G., "A Study of the N_2O_5-SO_2-O_3 Reaction System," Environ. Lett. 8, 103-116 (1975)

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
13,18	$N_2O + H \rightarrow N_2 + HO$ (f)		ΔH (298) = -261 kJ/mol	
12,19	$N_2 + HO \rightarrow N_2O + H$ (r)			
	Albers, et al (1975)	718-1111	$k_f = (3.6 \pm 1.2) \times 10^{-10} \exp(-8710 \pm 350/T)$	
	Baulch, et al (1973) review	700-2500	$k_f = 1.3 \times 10^{-10} \exp(-7600/T)$	1.5
			$k_r = 5.4 \times 10^{-12} \exp(-40400/T)$	1.5 (a)
			(a) $k_r = k_f/K_{eq}$ corrected expression	
	Baldwin, et al (1973)	773	$k_f = 4.3 \times 10^{-15}$	

No recommendation

REFERENCES

Albers, E. A., Hoyermann, K., Schacke, H., Schmatjko, K. J., Wagner, H. Gg., and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-Atoms with N_2O and Some Reactions of CN Radicals," Symp. Combust. 15th (Combustion Institute, Pittsburgh, 1975) 765-773

Baldwin, R. R., Gethin, A., and Walker, R. W., "Reaction of Hydrogen Atoms with Nitrous Oxide," J. Chem. Soc., Faraday Trans. I 69, 352-358 (1973)

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
13,19	$N_2O + OH \rightarrow$ products			upper limit only
	*Chang, Kaufman (1977)	480	$< 4 \times 10^{-16}$	
	Bierman, et al (1976)	298	$3.8 \pm 1.2 \times 10^{-17}$	
	Atkinson, Perry, Pitts (1976a)	298	$< 2 \times 10^{-16}$	
		443	$< 2 \times 10^{-16}$	
	Gordon, Mulac (1975)	440	$< 2 \times 10^{-14}$	

This evaluation accepts the upper limit reported by Chang and Kaufman. It is consistent with the upper limits reported by Atkinson et al (1976a)

REFERENCES

Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., "Kinetics of the Reactions of OH Radicals with CO and N_2O," Chem. Phys. Lett. 44, 204-208 (1976a)

Biermann, H. W., Zetzsch, C., and Stuhl, F., "Rate Constant for the Reaction of OH with N_2O at 298 K," Ber. Bunsenges. Phys. Chem. 80, 909-911 (1976)

Chang, J. S., and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of $CFCl_3$(F-11), CF_2Cl_2(F-12), and N_2O with OH and Estimates of Corresponding Lower Limit of their Tropospheric Lifetimes," Geophys. Res. Lett. 4, 192-194 (1977)

Gordon, S., and Mulac, W. A., "Reaction of the OH($X^2\Pi$) Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
13,36	N_2O + ClO → products NASA (1979) eval	200-300	≤ 1 x 10^{-12} exp(-4260/T)	

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

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions involving the ClO $X^2\Pi$ Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Fector at 298K, notes
13,45	$N_2O + CH \rightarrow$ products Wilks, Watula (1973)	1169-1655	$3.5 \times 10^{-13} \exp(-8650/T)$	

No recommendation

REFERENCES

Wilks, D., and Watula, R. A., "A Single-Pulse Shock-Tube Study of the Reaction between Nitrous Oxide and Carbon Monoxide," Symp. Combust., 14th (Combustion Institute, Pittsburgh, 1973) 83-96

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
14.22	$N_2O_5 + H_2O \rightarrow 2HNO_3$		$\Delta H (298) = -40$ kJ/mol	
	Morris, Niki (1973)	298	$< 1.3 \times 10^{-20}$	

Note that this is an upper limit only. This result and earlier results are discussed in the review of Hampson et al (1973)

REFERENCES

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

Morris, E. D., Jr., and Niki, H., "Reaction of Dinitrogen Pentoxide with Water," J. Phys. Chem. 77, 1929-1932 (1973)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
14,28	$N_2O_5 + SO_2$ → products			
	*Daubendiek, Calvert (1975)	300	$k < 4 \times 10^{-23}$	
	Davis (1976)	300	$k < 8 \times 10^{-24}$	preliminary

Note that this is an upper limit only

REFERENCES

Daubendiek, R. L., and Calvert, J. G., "A Study of the N_2O_5-SO_2-O_3 Reaction System," Environ. Lett. 8, 103-116 (1975)

Davis, D. D., "Absolute Rate Constants for Elementary Reactions of Atmospheric Importance: Results from the University of Maryland Gas Kinetics Laboratory," Report 3 (Univ. of Maryland, College Park, Md. 20742, 1976)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
16,18W 17,W	$NF_2 + H + M \rightarrow NH_3 + M$ (f) $NF_3 + M \rightarrow NF_2 + H + M$ (r)		ΔH (298) = -449 kJ/mol	
	*Baulch, et al (1973) review	200-3000	$k_f = 1.2 \times 10^{-33} \exp(11200/T)$ cm^6 $molecule^{-2} s^{-1}$, M = Ar (a) $k_f = K_{eq} k_r$ $k_r = 1.5 \times 10^{-8} \exp(-42400/T)$ (M = Ar) (b) To be used when P(M)<4 atm	? (a) 2 (b)

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
16,21 17,18	$NH_2 + H_2 \rightarrow NH_3 + H$ (f) $NH_3 + H \rightarrow NH_2 + H_2$ (r)		ΔH (298) = - 13 kJ/mol	
	Baulch, et al (1973) review	800	$k_f = < 10^{-16}$ $k_f = K_{eq} k_r$ $k_r < 10^{-16}$	approximate approximate

No recommendation

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
17,19 16,22	$NH_3 + HO \rightarrow NH_2 + H_2O$ (f) $NH_2 + H_2O \rightarrow NH_3 + HO$ (r)		ΔH° (298) = - 50 kJ/mol	
	*Smith, Zellner (1975)	228-472	$k_f = 2.3 \times 10^{-12} \exp(-800/T)$	1 25
	Perry, Atkinson, Pitts (1976a)	298-427	$k_f = 2.9 \times 10^{-12} \exp(-860 \pm 150/T)$	
	Cox, Derwent, Holt (1975)	300	$k_f = (1.2 \pm 0.4) \times 10^{-13}$	
	Hack, et al (1974)	298-669	$k_f = 5.3 \pm 0.8 \times 10^{-12} \exp(-920/T)$	
	Stuhl (1973a)	298	$k_f = 1.5 \times 10^{-13}$	
	Kurylo (1973)	298	$k_f = 4.1 \times 10^{-14}$	
	Gordon, Mulac (1975)	418	$k_f = 4.3 \pm 0.5 \times 10^{-13}$	
	Baulch, et al (1973) review		k_r - no data, no recommendation	

This evaluation accepts the results of the low temperature study of Smith and Zellner (1975). The results of Perry et al (1976a) and the room temperature result of Stuhl (1973a) are in good agreement

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Cox, R. A., Derwent, R. G., and Holt, P. M. "The Photo-Oxidation of Ammonia in the Presence of NO and NO_2," Chemosphere, No. 4, 201-205 (1975)

Gordon, S., and Mulac, W. A., "Reaction of the OH($X^2\Pi$) Radical Produced by the Pulse Radiolysis of Water Vapor," Int. J. Chem. Kinet., Symp. No. 1, 289-299 (1975)

Hack, W., Royermann, K., and Wagner, H. Gg., "Reaktionen des Hydroxyl-radikals mit Ammoniak und Hydrazin in der gasphase," Ber. Bunsenges. Physik. Chem. 78, 386-391 (1974)

Kurylo, M. J., "Kinetics of the Reactions OH(v = 0) + NH_3 → H_2O + NH_2 and OH(v = 0) + O_3 → HO_2 + O_2 at 298°K," Chem. Phys. Letts. 23, 467-471 (1973)

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reactions OH + H_2S → H_2O + SH and OH + NH_3 → H_2O + NH_2 over the Temperature Range 297-427°K," J. Chem. Phys. 64, 3237-3239 (1976a)

Smith, I. W. M., and Zellner, R., "Rate Measurements of Reactions of OH by

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
17, 36	NH_2 + ClO → products			
	Watson (1977) review	670	$k < 5 \times 10^{-16}$	

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
17a,18	$N_2H_4 + H \rightarrow H_2 + N_2H_3$			
	Stief, Payne (1976)	228-400	$(9.87 \pm 1.17) \times 10^{-12} \exp(-1200 \pm 50/T)$	

No recommendation

REFERENCES

Stief, L. J., and Payne, W. A., "Absolute Rate Parameters for the Reaction of Atomic Hydrogen with Hydrazine," J. Chem. Phys. 64, 4892-4896 (1976)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$		Uncert. Factor at 298K, notes
18,18M 21,M	$H + H + M \rightarrow H_2 + M$ (f) $H_2 + M \rightarrow H + H + M$ (r)		ΔH (298) = -436 kJ/mol		
	*Baulch, et al (1972) review	300	$k_f = 8.3 \times 10^{-33}$ $cm^6 molecule^{-2} s^{-1}$	$M = H_2$	1.5
		1700-5000	$= 1.8 \times 10^{-30}$ T^{-1}	$M = Ar$	2
			Rel. efficiencies: H_2(1.0), Ar(0.25)		
			$-d[H]/dt = 2k[H]^2[M]$		
		2500-5000	$k_r = 3.7 \times 10^{-10} \exp(-48300/T) cm^3 molecule^{-1} s^{-1}$,	$M = Ar$	2

This evaluation accepts the recommendations in the review of Baulch et al (1972)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,19M 22,M	$H + HO + M \rightarrow H_2O + M$ (f) $H_2O + M \rightarrow H + HO + M$ (r)		ΔH (298) = -499 kJ/mol	
	*Baulch, et al (1972) review	1000-3000	$k_f = 6.1 \times 10^{-26} T^{-2}$ $cm^6 molecule^{-2} s^{-1}$, $M = N_2$	2
		2000-6000	$k_r = 5.8 \times 10^{-9} \exp(-52900/T)$ $cm^3 molecule^{-1} s^{-1}$ $M = N_2$	1.5
	Zellner, Erler, Field (1977)	230-300	$k_f = 4.3 \times 10^{-25} T^{-2.6}$ $M = He$ Rel eff: He(1.0), Ar(1.5), N_2(3.2)	

This evaluation accepts the recommendations in the review of Baulch et al (1972) for high temperature. For low temperatures use the new results of Zellner et al (1977)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Zellner, R., Erler, K., and Field, D., "Kinetics of the Recombination Reaction OH + H + M → H_2O + M at Low Temperatures," Symp. Combust. 16th (Combustion Institute, Pittsburgh, 1977) 939-948

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,20	$H + HO_2 \rightarrow HO + HO$ (1f)		ΔH (298) = -142 kJ/mol	
19,19	$HO + HO \rightarrow H + HO_2$ (1r)			
18,20	$H + HO_2 \rightarrow H_2 + O_2$ (2)		= -220 kJ/mol	
18,20	$H + HO_2 \rightarrow H_2O + O$ (3f)		= -213 kJ/mol	
1,22	$O + H_2O \rightarrow H + HO_2$ (3r)			
	CODATA (1979) eval	298	$k_{1f} = 3.2 \times 10^{-11}$	2.5
			$k_2 = 1.4 \times 10^{-11}$	2.5
			$k_{3f} < 9.4 \times 10^{-13}$	3
	Hack, et al (1979)	293	4.7×10^{-11} ($k = k_{1f} + k_2 + k_{3f}$)	
	Hack, et al (1978)	293	$k_{1f}/k = 0.69$	
			$k_2/k = 0.29$	
			$k_{3f}/k \leq 0.02$	
	Baulch, et al (1972) review	290-800	$k_{1f} = 4.2 \times 10^{-10} \exp(-950/T)$	
			$k_{1r} = k_{1f}/K_{eq} = 2.0 \times 10^{-11} \exp(-20200/T)$	
		290-800	$k_2 = 4.2 \times 10^{-11} \exp(-350/T)$	
			$k_{2r} = k_{2f}/K_{eq} = 9.1 \times 10^{-11} \exp(-29100/T)$	
			k_{3f} and k_{3r} no recommendation	

The preferred values are based on the overall rate reported by Hack et al (1979) and the branching ratio values of Hack et al (1978)

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

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Hack, W., Wagner, H. Gg., and Hoyermann, K., "Reaktionen von Wasserstoffatomen mit Hydroperoxylradikalen I. Bestimmung der spezifischen Geschwindigkeitskonstanten der Reaktionskanale," Ber. Bunsenges. Phys. Chem. 82, 713-719 (1978)

Hack, W., Preuss, A. W., Wagner, H. Gg., and Hoyermann, K., "Reaktionen von Wasserstoffatomen mit Hydroperoxylradikalen II. Bestimmung der Geschwindigkeitskonstanten der Bruttoreaktion," Ber. Bunsenges. Phys. Chem. 83, 212-217 (1979)

H. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,23 20,21 18,23 19,22	$H + H_2O_2 \rightarrow H_2 + HO_2$ (1f) $HO_2 + H_2 \rightarrow H + H_2O_2$ (1r) $H + H_2O_2 \rightarrow HO + H_2O$ (2f) $HO + H_2O \rightarrow H + H_2O_2$ (2r)		ΔH (298) = - 80 kJ/mol = -285 kJ/mol	
	*Klemm, Payne, Stief (1975)	283-353	$k_{1f} + k_{2f} = 5.2 \times 10^{-12} \exp(-1400 \pm 140/T)$	1.5
	Gorse, Volman (1974)	300	$k_{1f} = 3.1 \pm 0.8 \times 10^{-15}$ $k_{2f} = 5.7 \pm 1.4 \times 10^{-15}$	
	Meagher, Heicklen (1975)	298	$k_{2f}/k_{1f} = 1.3$	
	Baulch, et al (1972)	300-800	$k_{1f} = 2.8 \times 10^{-12} \exp(-1900/T)$ $k_{1r} = k_{1f}/K_{eq} = 1.2 \times 10^{-12} \exp(-9400/T)$ k_{2f} and k_{2r}: no recommendation	

This evaluation accepts the results reported in Klemm et al (1975) for the overall rate of the forward reaction channels. Use the calculated expression of Baulch et al (1972) for k_{1r}

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Gorse, R. A., and Volman, D. H., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen Peroxide," J. Photochem. 3, 115-122 (1974)

Klemm, R. B., Payne, W. A., and Stief, L. J., "Absolute Rate Parameters for the Reaction of Atomic Hydrogen with H_2O_2," Int. J. Chem. Kinet., Symp. No. 1, 61-72 (1975)

Meagher, J. F., and Heicklen, J., "The Photolysis of Hydrogen Peroxide in the Presence of Carbon Monoxide," J. Photochem. 3, 455-466 (1975)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,24	$H + HNC \rightarrow H_2 + NC$ (f)		ΔH (298) = -227 kJ/mol	
9,21	$NC + H_2 \rightarrow H + HNC$ (r)			
	*Hampson, et al (1973) review	211-703	$k_f > 5 \times 10^{-14}$	2
		2000	$k_f = 7 \times 10^{-12}$	2
	Baulch, et al (1973) review	300	$10^{-13} < k < 10^{-12}$	
		2000	$k_f = 8 \times 10^{-12}$	
		2000	$k_r = k_f/K_{eq} = 5.3 \times 10^{-18}$	

This evaluation accepts the recommendations in the review of Hampson et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,25	H + HNO_2 → products Hampson, et al (1973) review		No data	

No recommendation since there are no data

REFERENCES

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric *Chemistry*," *J. Phys. Chem. Ref. Data* 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,26	H + HNO_3 → products			
	*Chapman, Wayne (1974)	300	$< 2 \times 10^{-15}$	
	Hampson, et al (1973) review	300	$< 1 \times 10^{-13}$	

Note that this is an upper limit only
Earlier results are discussed in the review of Hampson et al (1973)

REFERENCES

Chapman, C. J., and Wayne, R. P., "The Reaction of Atomic Oxygen and Hydrogen with Nitric Acid," Int. J. Chem. Kinet. 6, 617-620 (1974)

Hampson, R. F., (editor), "Survey of Photochemical and Rate Data for Twenty-Eight Reactions of Interest in Atmospheric Chemistry," J. Phys. Chem. Ref. Data 2, No. 2 pgs. 267-312 (1973). These are revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert. Factor at 298K, notes
18.28M	M + SO_2 + M → HSO_2 + M			
	*Baulch, et al (1976) review	1660-2120	1.4×10^{-32} cm^{6}molecule^{-2}s^{-1}	1.5

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

D. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,31 21,26a	$H + HS \rightarrow H_2 + S$ (f) $H_2 + S \rightarrow H + HS$ (r)		ΔH (298) = - 87 kJ/mol	
	*Baulch, et al (1976) review	298	$k_f = 2.5 \times 10^{-11}$ $k_r = 2.2 \times 10^{-25}$ (a) $k_r = k_f / K_{eq}$	1.5 1.5 (a)
	Cupitt, Glass (1975)	295	$k_f = 2.5 \pm 0.8 \times 10^{-11}$	

This evaluation accepts the recommendation in the review of Baulch et al (1976) which is confirmed by the results of Cupitt and Glass (1975)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

Cupitt, L. T., and Glass, G. P., "Reactions of SH with Atomic Oxygen and Hydrogen," Int. J. Chem. Kinet., Symp. No. 1, 39-50 (1975)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,32	$H + H_2S \rightarrow H_2 + HS$		$\Delta H (298) = -51$ kJ/mol	
	*Kurylo, Peterson, Braun (1971)	190-464	$1.29 \times 10^{-11} \exp(-860/T)$	1.5

This evaluation accepts the results of the temperature dependent study by Kurylo et al (1971). This result was also accepted in the Baulch et al (1976) review

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, The CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

Kurylo, M. J., Peterson, N. C., and Braun, W., "Absolute Rate of the Reaction $H + H_2S$," J. Chem. Phys. 54, 943-946 (1971)

W. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
H + CH_3S → CH_2 + HS		ΔH (298) = - 40 kJ/mol	
*Baulch, et al (1976) review	300	2.2×10^{-14}	1.5

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,37	H + OClO → HO + ClO •Watson (1977) review	298	ΔH (298) = -174 kJ/mol 5.7×10^{-11}	1.3

This evaluation accepts the recommendation in the Watson (1977) review

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

F. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,42	H + NOCl → HCl + NO Wagner, et al (1976a)	255-461	ΔH (298) = -272 kJ/mol $7.6 \times 10^{-11} \exp(-457 \pm 72/T)$	

These are the only temperature dependent results reported - no recommendation

REFERENCES

Wagner, H. Gg., Welzbacher, U., and Zellner, R., "Rate Measurements for the Reactions H + NO_2 → OH + NO and H + NOCl → HCl + NO by Lyman-α Fluorescence," Ber. Bunsenges. Phys. Chem. 80, 1023-1027 (1976)

W. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,44	$H + Cl_2 \rightarrow HCl + Cl$		$\Delta H (298) = -189$ kJ/mol	
	*This survey	250-700	$1.46 \times 10^{-10} \exp(-593/T)$	1.3
	Bemand, Clyne (1977)	300-730	$(1.41 \pm 0.24) \times 10^{-10} \exp(-575 \pm 65/T)$	
	Wagner, et al (1976)	252-458	$(1.44 \pm 0.28) \times 10^{-10} \exp(-600 \pm 70/T)$	
	Ambidge, et al (1976)	292-434	$(7.6 \pm 2.2) \times 10^{-11} \exp(-714 \pm 100/T)$	

The recommended expression is based on the data reported by Bemand and Clyne (1977) and by Wagner et al (1976) which are in good agreement

REFERENCES

Ambidge, P. F., Bradley, J. N., and Whytock, D. A., "Kinetic Study of the Reaction of Hydrogen Atoms with Molecular Chlorine," J. Chem. Soc. Faraday Trans. I 72 1157-1164 (1976)

Bemand, P. P., and Clyne, M. A. A., "Atomic Resonance Fluorescence for Rate Constants of Rapid Bimolecular Reactions. Part 6.-Hydrogen Atom Reactions: $H + Cl_2$ from 300 to 730K and $H + NO_2$ at 298K." J. Chem. Soc., Faraday Trans. II 73, 394-405 (1977)

Wagner, H. Gg., Welzbacher, U., and Zellner, R., "Rate Measurements for the Reaction $H + Cl_2 \rightarrow HCl + Cl$ by Lyman-α Fluorescence," Ber. Bunsenges. Phys. Chem. 80, 902-908 (1976)

F. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,454	H + CO + M → HCO + M *Baulch, et al (1976) review	298-773	ΔH (298) = - 70 kJ/mol $2.0 \times 10^{-33} \exp(-850/T)$ $cm^6 molecule^{-2} s^{-1}$, M = N_2	1.3

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18,48	$H + CH_2O \rightarrow H_2 + CHO$		$\Delta H (298) = -72$ kJ/mol	
	Ridley, et al (1972)	297	5.4×10^{-14}	
	Westenberg, deHaas (1972b)	297-652	$2.2 \times 10^{-11} \exp(-1890/T)$	

No recommendation

REFERENCES

Ridley, B. A., Davenport, J. A., Stief, L. J., and Welge, K. H., "Absolute Rate Constant for the Reaction $H + H_2CO$," J. Chem. Phys. 57, 520-523 (1972)

Westenberg, A. A., and deHaas, N., "Measurement of the Rate Constant for $H + H_2CO \rightarrow H_2 + HCO$ at 297-652°K," J. Phys. Chem. 76, 2213-2214 (1972b)

R. F. Hampson
May, 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18.53	H + CH_3OOH → CH_3O + H_2O (a) → CH_3O_2 + H_2 (b) → CH_2OOH + H_2 (c)		ΔH (298) = -314 kJ/mol = - 80 kJ/mol	
	Slemr, Warneck (1977)	250-358	$k = (2.8 \pm 0.9) \times 10^{-13} \exp(-930 \pm 95/T)$ $k_a/k = 0.43 \pm 0.07$ $k_b/k = 0.52 \pm 0.07$ $k_c/k = 0.05$	overall rate const

Only reported value - no recommendation

REFERENCES

Slemr, F., and Warneck, P., "Kinetics of the Reaction of Atomic Hydrogen with Methylhydroperoxide," Int. J. Chem. Kinet. 9, 267-282 (1977)

F. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
18.64	$H + CH_3Cl \rightarrow HCl + CH_3$		$\Delta H (298) = -83$ kJ/mol	
	Westenberg, deHaas (1975a)	500-800	$6.2 \times 10^{-11} \exp(-4650/T)$	

No recommendation

REFERENCES

Westenberg, A. A., and deHaas, N., "Rates of H + CH_3X Reactions," J. Chem. Phys. 62, 3321-3325 (1975a)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,19 4,21	• HC + H_2 + C_2 (f) C_2 + H_2 + HC • HC (r) Baulch, et al (1972) review		ΔH (298) = - 78 kJ/mol no recommendation given for k_f or k_r	

No recommendation

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,19	$HO_2 + NO \rightarrow H_2O + O_2$ (f)		ΔH (298) = - 71 kJ/mol	
1,22	$O + H_2O \rightarrow HO + HO$ (r)			
	NASA (1979) eval	200-300	$k_f = 1 \times 10^{-11} \exp(-(500\pm400)/T)$	1.25
	CODATA (1979) eval	298	$k_f = 1.8 \times 10^{-12}$	1.5
	Westenberg, deHaas (1973b)	300	$k_f = 2.3 \times 10^{-12}$	
	McKenzie, et al (1973)	298	$k_f = 2.1 \pm 0.5 \times 10^{-12}$	
	Clyne, Down (1974)	300	$k_f = 1.4 \pm 0.2 \times 10^{-12}$	
	Trainor, von Rosenberg (1974)	300	$k_f = 2.1 \pm 0.2 \times 10^{-12}$	
	Baulch, et al (1972) review	300-2000	$k_f = 1.0 \times 10^{-11} \exp(-550/T)$	
		300-2000	$k_r = 1.1 \times 10^{-10} \exp(-9240/T)$	
	Rawlins, Gardiner (1974)	1500-2000	$k_f = 9.1 \times 10^{-11} \exp(-3500/T)$	

This value is based on a re-evaluation of the recent measurements of Westenberg and deHaas (1973b), McKenzie et al (1973), Clyne and Down (1974) and Trainor and von Rosenberg (1974). There are no T dependence data around room temperature

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

Clyne, M. A. A., and Down, S., "Kinetic Behaviour of OH $X^2\Pi$ and $A^2\Sigma^+$ using Molecular Resonance Fluorescence Spectrometry," J. Chem. Soc. Faraday Trans. II 70, 253-266 (1974)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

McKenzie, A., Mulcahy, M. F. R., and Steven, J. R., "Kinetics of Decay of Hydroxyl Radicals at Low Pressure," J. Chem. Phys. 59, 3244-3254 (1973)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Hawlins, W. T., and Gardiner, W. C., Jr., "Rate Constant of $OH + OH = H_2O + O$ from 1500 to 2000 K," J. Chem. Phys. 60, 4676-4681 (1974)

Trainor, D. W., and von Rosenberg, C. W., Jr., "Flash Photolysis Study of the Gas Phase Recombination of Hydroxyl Radicals," J. Chem. Phys. 61, 1010-1015 (1974)

Westenberg, A. A., and deHaas, N., "Rate of the Reaction $OH + OH \rightarrow H_2O + O$," J. Chem. Phys. 58, 4066-4071 (1973b)

W. F. Hampson
June 1979

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
19, 19M 23, M	$HO + HO + M \rightarrow H_2O_2 + M$ (f) $H_2O_2 + M \rightarrow HO + HO + M$ (r)		ΔH (298) = -214 kJ/mol	
	NASA (1979) eval	200-300	$k_f = (2.5 \pm 1.3) \times 10^{-31} (T/300)^{-0.8}$, $M = N_2$ $k_{f,\infty} = (3.0 \pm 1.5) \times 10^{-11} (T/300)^{-1 \pm 1}$ $cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	298	$k_f = 6.5 \times 10^{-31}$, $M = N_2$	2
	Trainor, von Rosenberg (1974)	300	$k_f = 2.5 \pm 0.3 \times 10^{-31}$ $M = N_2$	
	Baulch, et al (1972) revies	700-1500	$k_f = 2.5 \times 10^{-33} \exp(+2550/T)$, $M = N_2$	2
			$k_r = 2.0 \times 10^{-7} \exp(-22900/T) cm^3 molecule^{-1} s^{-1}$, $M = N_2$; $k_f = k_r K_{eq}$	2

REFERENCES

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 1: Homogeneous Gas Phase Reactions of the H_2-O_2 System," (Butterworths, London, 1972)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Trainor, D. W., and von Rosenberg, C. W., Jr., "Flash Photolysis Study of the Gas Phase Recombination of Hydroxyl Radicals," J. Chem. Phys. 61, 1010-1015 (1974)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,20	$HO + HO_2 \rightarrow H_2O + O_2$		$\Delta H(298) = -283$ kJ/mol	
	NASA (1979) eval	200-300	$4 \times 10^{-11} \exp((0\pm250)/T)$	2
	CODATA (1979) eval	298	3.5×10^{-11}	3
	Chang, Kaufman (1978)	295	$2\text{-}3 \times 10^{-11}$	
	DeMore (1979)	298	$\sim 1 \times 10^{-10}$	
	Hack, et al (1978)	293	$(3 \pm 1) \times 10^{-11}$	
	Burrows, Harris, Thrush (1977)	293	5.1×10^{-11}	(a)
			(a) Based on $k(HO + H_2O_2) = 8 \times 10^{-13}$	
	Hochanadel, et al (1972)	300	2×10^{-10}	
	DeMore, Tschuikow-Roux (1974)	300	$\sim 1 \times 10^{-10}$	

The recommended value is derived from the upper limit of Chang and Kaufman (1978), the measurement of Hack et al (1978), and the ratio measurement (relative to $OH + H_2O_2$) by Burrows et al (1977) and is within the experimental accuracy of all three studies, although it is not compatible with the value of $1\text{-}2 \times 10^{-10}$ derived from rate constant ratios in steady state O_3 photolysis experiments by DeMore and Tschuikow-Roux (1974) and DeMore (1979)

REFERENCES

Burrows, J. P., Harris, G. W., and Thrush, B. A., "Rates of Reaction of HO_2 with HO and O studied by Laser Magnetic Resonance," Nature 267, 233-234 (1977)

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R. F. Hampson
June 1979

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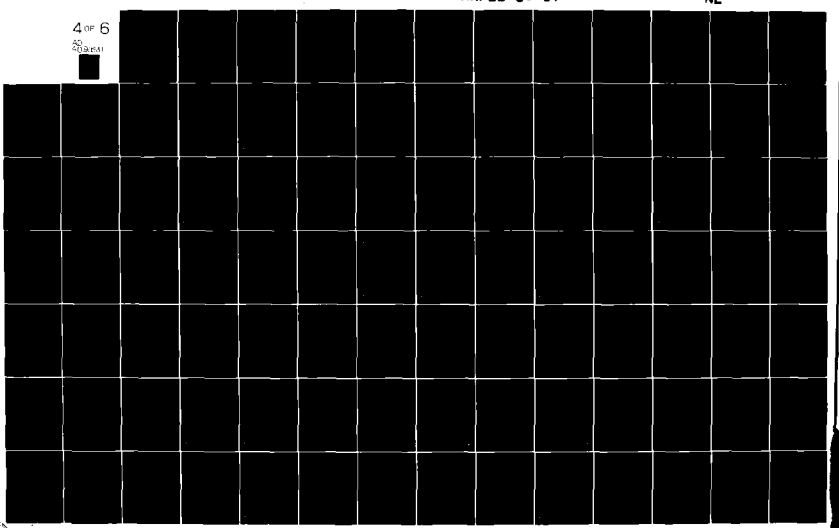

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,21	$HO + H_2 \rightarrow H_2O + H$ (f)		ΔH (298) = - 63 kJ/mol	
18,22	$H + H_2O \rightarrow HO + H_2$ (r)			
	NASA (1979) eval	200-300	$k_f = 1.2 \times 10^{-11} \exp(-(2200 \pm 200)/T)$	1.2
	CODATA (1979) eval	210-300	$k_f = 1.8 \times 10^{-11} \exp(-(2330 \pm 300)/T)$	1.25
	Smith, Zellner (1974a)	210-460	$k_f = 1.8 \times 10^{-11} \exp(-2330/T)$	
	Greiner (1969)	300-500	$k_f = 6.8 \times 10^{-12} \exp(-2020/T)$	
	Atkinson, Hansen, Pitts (1975)	297-434	$k_f = 5.9 \times 10^{-12} \exp(-2008 \pm 150/T)$	
	Overend, et al (1975)	295	$k_f = (5.80 \pm 0.26) \times 10^{-15}$	
	Trainor, von Rosenberg (1975)	300	$k_f = 5.3 \times 10^{-15}$	
	Vandooren, et al (1975)	600-1300	$k_f = 1.2 \times 10^{-11} \exp(-2200/T)$	
	Gardiner, et al (1974)	1350-1600	$k_f = 8.7 \times 10^{-11} \exp(-3250/T)$	
	Baulch, et al (1972) review	300-2500	$k_f = 3.6 \times 10^{-11} \exp(-2590/T)$	
			$k_r = k_f/K_{eq} = 1.5 \times 10^{-10} \exp(-10250/T)$	
	Stuhl, Niki (1972)	298	$k_f = 7.1 \times 10^{-15}$	
	Westenberg (1973a)	298-745	$k_f(298\ K) = 7.6 \times 10^{-15}$	

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

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.21D	$BH + D_2 \rightarrow HDB + D$			
	Smith, Zellner (1974a)	210-460	$1.25 \times 10^{-11} \exp(-2590/T)$	

These are the only temperature dependent results reported. The room temperature value is in good agreement with two earlier studies

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W. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,23 20,22	$HO + H_2O_2 \rightarrow H_2O + HO_2$ (f) $HO_2 + H_2O \rightarrow HO + H_2O_2$ (r)		ΔH (298) = -143 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 1 \times 10^{-11} \exp(-(750\pm350)/T)$	2
	CODATA (1979) eval	200-700	$k_f = 7.6 \times 10^{-12} \exp(-(670\pm200)/T)$	2
	Hack, et al (1975)	298-670	$k_f = 8.0 \times 10^{-12} \exp(-670/T)$	
	Greiner (1968)	300-458	$k_f = 4.1 \times 10^{-13} T^{1/2} \exp(-600/T)$	
	Harris, Pitts (1979)	298	$k_f = 6.8 \times 10^{-13}$	
	Baulch, et al (1972) review	300-800	$k_r = k_f/K_{eq} = 4.7 \times 10^{-11} \exp(-16500/T)$	
	Gorse, Volman (1972)	300	$k_f/k(HO + CO) = 8.1$	
	Meagher, Heicklen (1974)	298	$k_f/k(HO + CO) = 4.1$	

This value is a composite of a recent Hack et al (1975) measurement of $8 \times 10^{-12} \exp(-670/T) cm^3 molecule^{-1} s^{-1}$ 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 $3 \times 10^{13} cm^{-3}$ and may have been complicated by the back reaction between the product HO_2 and residual HO from the OH formation step. The new value for $k(HO_2 + HO)$ of 8×10^{-12} implies a very rapid reconversion. Additional studies are needed. The A-factor seems unreasonably high for this type of reaction. Harris and Pitts (1979) confirm our room temperature recommendation. Preliminary data by Keyser, however, is about a factor of three higher. This reaction clearly requires additional work, especially on the T dependence

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,24 9,22	$HO + HNO \rightarrow H_2O + NO$ (f) $NO + H_2O \rightarrow HO + HNO$ (r)		ΔH (298) = -291 kJ/mol	
	*Hampson, et al (1973) review	1600-2100	$k_f = 7 \times 10^{-11}$	5
	Baulch, et al (1973) revis	2000	$k_f = 6 \times 10^{-11}$ $k_r = k_f/K_{eq} = 4 \times 10^{-18}$ (corrected)	

This evaluation accepts the temperature - independent recommendation in the review of Hampson et al (1973)

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R. F. Hampson
May 1976

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.25	$HO + HNO_2 \rightarrow H_2O + NO_2$		$\Delta H(298) = -169$ kJ/mol	
	*Cox, Derwent, Holt (1976)	296	6.6×10^{-12} ref. rxn is $HO + H_2 \rightarrow H_2O + H$ with $k_{ref} = 7 \times 10^{-15}$	1.5
	Cox (1974)	294	$k/k(HO + CO) = 15 \pm 1$ at 1 atm air	

This evaluation accepts the results of Cox et al (1976) with error limits to encompass the value derived from the ratio reported in Cox (1974) and the value of k(HO + CO) at 1 atm air

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,26 11,22	$HO + HNO_3 \rightarrow H_2O + NO_3$ (f) $NO_3 + H_2O \rightarrow HO + HNO_3$ (r)		ΔH (298) = - 75 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 8.5 \times 10^{-14} \exp((0 \pm 100)/T)$	1.25
	CODATA (1979) eval	240-470	$k_f = 8.5 \times 10^{-14} \exp((0 \pm 300)/T)$	1.25
	Smith, Zellner (1975)	240-406	$k_f = 8 \pm 2 \times 10^{-14}$	
	Margitan, et al (1975)	270-470	$k_f = 8.9 \pm 1.3 \times 10^{-14}$	
	Baulch, et al (1973) review	300	$k_r = k_f/K_{eq} = 2.3 \times 10^{-26}$	

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 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

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,26a	NO + NO_2NO_2 → products			
	NASA (1979) eval	298	5×10^{-13}	10
	CODATA (1979) eval	298	1×10^{-13}	10
	Graham, Winer, Pitts (1978)	298	$<3 \times 10^{-12}$	

Estimated by analogy with the Reaction OH + H_2O_2. This value is consistent with the upper limit reported by Graham, Winer and Pitts (1978)

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^6 molecule^{-2} s^{-1}$	Uncert Factor at 298K, notes
19,28M	$HO + SO_2 + M \rightarrow HSO_3 + M$		ΔH (298) = -223 kJ/mol	
	NASA (1979) eval	200-300	$k = (3.0 \pm 1.5) \times 10^{-31}(T/300)^{-2.9 \pm 1}$, $M = N_2$	
			$k_\infty = (2.0 \pm 1.5) \times 10^{-12}(T/300)^{0 \pm 1}$ $cm^3 molecule^{-1} s^{-1}$	
	CODATA (1979) eval	200-400	$k = 3 \times 10^{-31}(T/300)^{-2.9}$, $M = N_2$	2
			$k_\infty = 2 \times 10^{-12}$ $cm^3 molecule^{-1} s^{-1}$	2.5
	Davis, et al (1979)	300	$10^{13} \times k$ / P(Ar)/torr	(a)
			0.75 ± .07 / 5	
			1.41 ± .08 / 10	
			2.16 ± .20 / 20	
			(a) Effective 2nd order rate constant in $cm^3 molecule^{-1} s^{-1}$ Data also given for M = He and Ar. Authors estimate value of 9×10^{-13} at 1 atm N_2	
	Harris, Wayne (1975)	300	$4.5 \pm 1.5 \times 10^{-31}$, M = Ar	
			$7.2 \pm 2.6 \times 10^{-31}$, M = N_2	
	Cox (1974)	294	$k/k(HO + CO) = 4 \pm 0.5$	(c)
			(c) *2nd order rate constant, [M] = 1 atm. N_2 + O_2* see entry for k(HO + CO)	
	Gordon, Mulac (1975)	435	1.8×10^{-12} $cm^3 molecule^{-1} s^{-1}$ (2d order rate constant at 1 atm. H_2O vapor)	
	Castleman, Tang (1977)	297	1.6×10^{-31}, M = N_2	
			$k/k(HO + CO) = 4.3$	(d)
			(d) Measured ratio of 2d order rate constants at 1 atm N_2. Values for k given in paper assumed $k_{ref} = 1.5 \times 10^{-13}$ over entire pressure range. See entry for k(OH + CO)	
	Atkinson, Perry, Pitts (1976)	298	$10^{13} \times k$ / P(Ar)/torr	(e)
			1.35 / 25	
			2.16 / 50	
			3.10 / 100	
			4.38 / 202	
			5.87 / 402	
			6.55 / 648	
			(e) Effective 2nd order rate constant in $cm^3 molecule^{-1} s^{-1}$	

See the discussion of the rate data for this reaction in the review by Zellner (1978)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.32	$HO + H_2S \rightarrow H_2O + HS$		$\Delta H (298) = -114$ kJ/mol	
	NASA (1979) eval	200-300	$1.1 \times 10^{-11} \exp(-(220 \pm 220)/T)$	1.25
	CODATA (1979) eval	250-400	$1.4 \times 10^{-11} \exp(-(225 \pm 225)/T)$	1.25
	Baulch, et al (1976) review	300-500	$1.05 \times 10^{-11} \exp(-200/T)$	
	Perry, Atkinson, Pitts (1976a)	297-427	$(5.2 \pm 0.5) \times 10^{-12}$	
	Stuhl (1974)	298	$3.1 \pm 0.5 \times 10^{-12}$	
	Westenberg, deHaas (1973)	298-885	$2.3 \times 10^{-11} \exp(-440/T)$	

The recommended values for k (298 K) and E/R are the average of the values determined by Westenberg and deHaas (1973) and Perry et al (1976a). $\Delta \log k$ has been chosen to encompass the value of Stuhl (1974) within the 2 σ error band. Δ E/R was chosen to encompass both the 440 value of Westenberg and deHaas (1973) and the zero value of Perry et al (1976a). Although 2 x Δ E/R(2 σ) allows for a negative value, we do not expect E/R to be less than zero.

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.34b	OH + CS_2 → products			
	NASA (1979) eval	298	1.5×10^{-13}	2
	CODATA (1979) eval	298	$\leq 2 \times 10^{-13}$	5
	Kurylo (1978)	296	$(1.85 \pm 0.34) \times 10^{-13}$	
	Atkinson, et al (1978)	300	$<7 \times 10^{-14}$	

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 this reaction. In the absence of any direct mechanistic information, no estimate of E/R or the A-factor can be given.

The uncertainty factor in k(298 K) has been increased since the evaluation in DeMore et al (1979) to reflect the complexity of the kinetic analysis used to derive k(298 K). This increase does not permit overlap of k(298 K) from both literature studies. Further study is still needed to establish the validity of the interpretation upon which the present recommendation is based. Measurements of both the temperature dependence of k and the mechanism of the reaction are essential. If suggestions regarding a possible addition mechanism (Kurylo and Laufer (1979)) are correct, the reaction may have a negative temperature dependence.

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,34c	OH + CH_3Cl → products			
	NASA (1979) eval	298	5.6×10^{-14}	2
	CODATA (1979) eval	298	4.6×10^{-14}	5
	Kurylo (1978)	296	$(5.66 \pm 1.2) \times 10^{-14}$	
	Atkinson, et al (1978)	299	$< 7 \times 10^{-15}$	

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 this reaction. In the absence of any direct mechanistic information, no estimate of E/R or the A-factor can be given.

The uncertainty factor in k(298 K) has been increased since the evaluation in DeMore et al (1979) to reflect the complexity of the kinetic analysis used to derive k(298 K). This increase does not permit overlap of k(298 K) from both literature studies. Further study is still needed to establish the validity of the interpretation upon which the present recommendation is based. Measurements of both the temperature dependence of k and the mechanism of the reaction are essential. If suggestions regarding a possible addition mechanism (Kurylo and Laufer (1979)) are correct, the reaction may have a negative temperature dependence.

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,36	BG + ClO → products			1.4
	NASA (1979) eval	298	9.1×10^{-12}	2
	CODATA (1979) eval	298	9.1×10^{-12}	
	Leu, Lin (1979)	298	$(9.1 \pm 1.3) \times 10^{-12}$	

Value reported by Leu and Lin (1979). A lower limit of 0.65 was determined for $k_1(BE + ClO \rightarrow BG_2 + Cl)/k(BE + ClO \rightarrow \text{products})$ at 298K. The actual value of k_1/k may possibly be unity

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,36Br	BO + BrO → products NASA (1979) eval	298	5×10^{-12}	5

No data; value chosen to be consistent with k(BO + ClO)

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,39	$BO + HCl \rightarrow H_2O + Cl$		ΔH (298) = - 67 kJ/mol	
	NASA (1979) eval	200-300	$2.8 \times 10^{-12} \exp(-(425\pm100)/T)$	1.15
	CODATA (1979) eval	210-460	$3.0 \times 10^{-12} \exp(-(425\pm100)/T)$	1.15
	Watson (1977) revies	220-300	$3.0 \times 10^{-12} \exp(-425/T)$	
	Smith, Zellner (1974a)	210-460	$4.1 \times 10^{-12} \exp(-530/T)$	
	Zahniser, et al (1974)	224-460	$2.0 \times 10^{-12} \exp(-312/T)$	
	Ravishankara, et al (1977)	250-402	$3.3 \times 10^{-12} \exp(-472/T)$	
	Hack, Nex, Wagner (1977))	293	6.6×10^{-13}	
	Takacs, Glass (1973b)	295	$6.4 \pm 1.5 \times 10^{-13}$	

Unchanged from NASA 1010. There is good agreement between all groups of workers at ~ 298 K (Takacs and Glass (1973b); Zahniser et al (1974), Smith and Zellner (1974), Ravishankara et al (1977a), and Hack et al (1977a) and the preferred value at this temperature is the average . The Arrhenius expression was derived by giving an equal weighting to data reported by Zahniser et al, Ravishankara et al and Smith and Zellner

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R. P. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,39D	Rd + DCl → RDd + Cl Smith, Zellner (1974a)	210-460	$4.7 \times 10^{-12} \exp(-780/T)$	

Only reported value - no recommendation

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,39Br	$BC\ell + HBr \rightarrow B_2\sigma + Br$		$\Delta H\ (298) = -133$ kJ/mol	
	NASA (1979) eval	200-300	$8.5 \times 10^{-12} \exp((0 \pm 250)/T)$	2
	CODATA (1979) eval	249-416	$8.5 \times 10^{-12} \exp((0 \pm 250)/T)$	2
	Ravishankara, et al (1979)	249-416	11.9×10^{-12}	
	Takacs, Glass (1973a)	300	5.1×10^{-12}	
	Wilson, et al (1979)	1875-1975	2.7×10^{-11}	

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 $(3.7 \pm 0.7) \times 10^{-11} \exp(-575 \pm 70)/T)$. 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

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P. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,40	$BG + HGCl \rightarrow B_2C + ClC$		$\Delta H (298) = -101$ kJ/mol	
	NASA (1979) eval	200-300	$3 \times 10^{-12} \exp(-(800 \pm 500)/T)$	10

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

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,43a	$HO + NO_3Cl \rightarrow$ products			
	NASA (1979) eval	200-300	$1.2 \times 10^{-12} \exp(-(333 \pm 200)/T)$	1.5
	CODATA (1979) eval	246-387	$1.2 \times 10^{-12} \exp(-(330 \pm 200)/T)$	1.5
	Zahniser, et al (1977)	246-387	$(1.19 \pm 0.10) \times 10^{-12} \exp(-333 \pm 22/T)$	
	Ravishankara, et al (1977)	245	3.7×10^{-13}	

Unchanged from NASA 1010. The results reported by Zahniser et al (1977) and Ravishankara et al (1977) 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

REFERENCES

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June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factory at 298K, notes
19,45	$HO + CO \rightarrow CO_2 + H$ (f)		ΔH (298) = -104 kJ/mol	
18,46	$H + CO_2 \rightarrow HO + CO$ (r)			
	NASA (1979) eval	200-300	$k_f = 1.35 \times 10^{-13}(1 + P_{atm}) \exp((0 \pm 200))$	1.25
	CODATA (1979) eval	200-300	$k_f = 1.5 \times 10^{-13}$ P ≤ 100 torr	1.15
		298	$k_f = 2.8 \times 10^{-13}$ (1 atm air)	1.25
	Baulch, et al (1976) review	250-2500	$\log k_f = -12.95 + 3.94 \times 10^{-4} \times T$ same as given in Baulch, Drysdale (1974) recommendation based on low pressure studies	
		1000-3000	$k_r = k_f/K_{eq} = 2.5 \times 10^{-10} \exp(-13300/T)$	
			Experiments bearing on the "pressure effect"	
	Biermann, et al (1978)	300	$(1.51 \pm 0.16) \times 10^{-13}$ 25 torr N_2	
			$((2.83 \pm 0.28) \times 10^{-13}$ 750 torr N_2	
			This pressure effect was shown to depend on the amount of O_2 present	
	Butler, et al (1978)	298	k_f/k_{ref} / P/torr / Mole fractions N_2 / O_2 / CO	
			0.094 / 100 / 0.49/0.33/0.15	
			0.10 / 200 / 0.50/0.34/0.15	
			0.17 / 300 / 0.73/0.17/0.08	
			0.15 / 400 / 0.50/0.34/0.15	
			0.16 / 500 / 0.73/0.17/0.07	
			0.18 / 600 / 0.74/0.17/0.08	
			Ref. rxn is HO + isobutane → products, with 6-28% correction for side rxn. Ratios calculated from reported data using authors' value for $k_{ref} = 1.59 \times 10^{-12}$ which was determined in the 100 torr expt. relative to $k(HO + CO) = 1.5 \times 10^{-13}$	
	Chan, et al (1977)	298	k_f/k_{ref} / P/torr	
			0.059 / 100 in "synthetic air"	
			0.127 / 700	
			Ref. rxn is HO + isobutane → products	
	Sie, Simonaitis, Heicklen (1976a)		k_f/k_{ref} / P/torr	
		217-298	$0.2\exp(1700/T)$ high pressure limit in N_2	
		298	14 / 20 (H_2)	
			21 / 83 (H_2)	
			42 / 296 (H_2)	
			49 / 702 (H_2)	
			17 / 605 (He) + 26 (H_2)	
			33 / 550 (SF_6) + 26 (H_2)	
			49 / 605 (SF_6) + 26 (H_2)	
			Ref. rxn is $HO + H_2 \rightarrow H_2O + H$	
	Cox, Derwent, Holt (1976)	296	k_f/k_{ref} / P/torr	
			38.6 / 700 $N_2/O_2 = 2$	
			Ref. rxn. is $HO + H_2 \rightarrow H_2O + H$	
	Atkinson, Perry, Pitts (1976a)	299	$(1.54 \pm 0.16) \times 10^{-13}$ P = 25-654 torr Ar	

Perry, Atkinson, Pitts (1977a)	295	10^{13} x k — P(SF_6)/torr 1.53 — 25 1.93 — 76 2.40 — 208 3.09 — 403 3.43 — 603
Overend, Paraskevopoulos (1977)	296	$(2.03 \pm 0.08) \times 10^{-13}$ at 50 torr He
Gordon, Mulac (1975)	298	$(3.24 \pm 0.20) \times 10^{-13}$ at 200, 350 torr SF_6 1.50×10^{-13} at 710 torr Ar, 10 torr H_2O
		Experiments either at low pressure or for which pressure effects were not studied.
Trainor, von Rosenberg (1975)	300	1.25×10^{-13}
Vandooren, et al (1975)	400-800	1.33×10^{-13}
Biordi, et al (1975)	1000-1800	$3.85 \times 10^{-12} \exp(-2850/T)$
Steinert, Zellner (1975)	1350-1750	7.8×10^{-13}
Wilson (1972) review	300-900	$\log k = -12.93 + 4.0 \times 10^{-4} \times T$
Stuhl, Niki (1972)	300-2000	$5.1 \times 10^{-13} \exp(-300/T)$
Westenberg, deHaas (1973a)	300	1.35×10^{-13}
Davis, Fischer, Schiff (1974)	298-915	$k(298) = 1.33 \times 10^{-13}$
Greiner (1969)	220-373	$2.15 \pm 0.19 \times 10^{-13} \exp(-80 \pm 40/T)$
Smith, Zellner (1973)	300-500	$2.1 \times 10^{-13} \exp(-115/T)$
	300	1.45×10^{-13}
		Data reported 210 <T< 460 K. Slight positive temperature dependence, possibly curved.
Peeters, Mahnen (1973)	1600-1900	4.7×10^{-13}
Gardiner, et al (1973)	1500-2000	$6.7 \times 10^{-12} \exp(-4000/T)$
Howard, Evenson (1974)	296	$1.56 \pm 0.2 \times 10^{-13}$

The recommended expression 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

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W. P. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,48	$HO + CH_2O \rightarrow H_2O + CHO$		ΔH (298) = -135 kJ/mol	
	NASA (1979) eval	200-300	$1.0 \times 10^{-11} \exp((0\pm200)/T)$	1.25
	CODATA (1979) eval	200-400	$1.3 \times 10^{-11} \exp((0\pm200)/T)$	1.4
	Atkinson, Pitts (1978)	299-426	$1.25 \times 10^{-11} \exp(-(90\pm150)/T)$	
	Stief, et al (1979)	228-362	$(1.05\pm0.22) \times 10^{-11}$	
	Morris, Niki (1971)	300	$(1.4\pm0.3) \times 10^{-11}$	
	Niki, et al (1978)	298	$(1.5\pm0.1) \times 10^{-11}$	
	Smith (1978)	298	$(6.5\pm1.5) \times 10^{-12}$	

The value for k(298) is the average of these determined by Atkinson and Pitts (1978) and Stief et al (1979), both using the flash photolysis - resonance fluoresence technique. The value reported by Morris and Niki (1971) agrees within the stated uncertainty. There are two relative values which are not in agreement with the recommendations. The value of Niki et al (1978) relative to $HO + C_2H_4$ is higher while the value of Smith (1978) relative to HO + HO is lower. The latter data is also at variance with the negligible temperature dependence observed in the two flash photolysis studies. Although Atkinson and Pitts assign a small energy barrier (E/R = 90 ± 150), their data at 356K and 426K and that of Stief et al at 228K, 257K and 362K are all within 10% of the k(298) value. Thus the combined data set suggest E/R = 0.

The abstraction reaction given is probably the major channel; other channels may contribute (Horowitz et al 1978).

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.52	OH + CH_3OH → products			
	Overend, Paraskevopoulos (1978)	296	1.06×10^{-12}	
	Campbell, et al (1976)	292	9.5×10^{-13}	

No recommendation

REFERENCES

Campbell, I. M., McLaughlin, D. F., and Handy, B. J., "Rate Constans for Reactions of Hydroxyl Radicals with Alcohol Vapours at 292 K," Chem. Phys. Lett. 38, 362-364 (1976)

Overend, R., and Paraskevopoulos, G., "Rates of OH Radical Reactions. 4. Reactions with Methanol, Ethanol, 1-Propanol, and 2-Propanol at 296 K," J. Phys. Chem. 82, 1329-1333 (1978)

P. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,53	$BO + CH_3OOH \rightarrow$ products			
	NASA (1979) eval	200-300	$1 \times 10^{-11} \exp(-(750 \pm 350)/T)$	5

This estimate is based on an assumed similarity to $OH + H_2O_2$ and $OH + CH_3OH$. The k(298) values for these two reactions are reported to be very similar: $k(OH + H_2O_2) = 8.1 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$ (this evaluation) and $k(OH + CH_3OH) = 9.5 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$ (Campbell et al, 1976). In the absence of temperature dependent data for $OH + CH_3OH$, the A-factor and E/R values are assumed to be the same as those for $OH + H_2O_2$. The latter values are somewhat uncertain at present. The reaction products are not specified since, using the above analogies to CH_3OH and H_2O_2, abstraction of H from either end of the molecules may be equally probable

REFERENCES

Campbell, I. N., McLaughlin, D. F., and Handy, B. J., "Rate Constants for Reactions of Hydroxyl Radicals with Alcohol Vapours at 292 K," Chem. Phys. Lett. 38, 362-364 (1976)

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B. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,54	$NO + CH_3NO_2 \rightarrow$ products			
	Campbell, Goodman (1975b)	292	9.2×10^{-13}	

No recommendation

REFERENCES

Campbell, I. M., and Goodman, K., "Rate Constants for Reactions of Hydroxyl Radicals with Nitromethane and Methyl Nitrite Vapours at 292 K," Chem. Phys. Lett. 36, 382-384 (1975b)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,54	OH + CH_3ONO → products			
	Campbell, Goodman (1975b)	292	1.3×10^{-12}	

No recommendation

REFERENCES

Campbell, I. M., and Goodman, K., "Rate Constants for Reactions of Hydroxyl Radicals with Nitromethane and Methyl Nitrite Vapours at 292 K," Chem. Phys. Lett. 36, 382-384 (1975b)

B. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.56	$HO + CH_4 \rightarrow CH_3 + H_2O$		ΔH (298) = - 60 kJ/mol	
	NASA (1979) eval	200-300	$2.4 \times 10^{-12} \exp(-(1710 \pm 200)/T)$	1.2
	CODATA (1979) eval	200-300	$2.4 \times 10^{-12} \exp(-(1710 \pm 200)/T)$	1.25
	Davis, Fischer, Schiff (1974)	240-373	$2.36 \pm 0.21 \times 10^{-12} \exp(-1710 \pm 88/T)$	
	Margitan, et al (1974)	290-440	$3.23 \times 10^{-12} \exp(-1840 \pm 20/T)$	
	Zellner, Steinert (1976)	300-900	$5.76 \times 10^{-21} T^{3.08} \exp(-1010/T)$	
	Greiner (1970)	300-500	$5.5 \times 10^{-12} \exp(-1900/T)$	
	Overend, et al (1975)	300	$6.51 \pm 0.26 \times 10^{-15}$	
	Peeters, Mahnen (1973)	1100-1900	$5 \times 10^{-11} \exp(-3000/T)$	
	Gordon, Mulac (1975)	381	2.6×10^{-14} (1 atm H_2O vapor)	
		416	5.5×10^{-14} (1 atm H_2O vapor)	
	Howard, Evenson (1976a)	296	$(9.5 \pm 1.4) \times 10^{-15}$	
	Cox, Derwent, Holt (1976)	296	$(7.3 \pm 0.9) \times 10^{-15}$ ref rxn is $HO + H_2 \rightarrow H_2O + H$ with $k_{ref} = 7 \times 10^{-15}$	

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 SP 513, NASA RP-1010)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,56a	OH + C_2H_2 → products			
	Smith, Zellner (1973)	210-460	$2.0 \times 10^{-12} \exp(-250/T)$	
	Pastrana, Carr (1974)	300	$2.0 \pm 0.6 \times 10^{-13}$	
	Davis, et al (1975)	300	$1.65 \pm 0.15 \times 10^{-13}$	

No recommendation

REFERENCES

Davis, D. D., Fischer, S., Schiff, R., Watson, R. T., and Bollinger, W., "A Kinetics Study of the Reaction of OH Radicals with Two C_2 Hydrocarbons: C_2H_4 and C_2H_2," J. Chem. Phys. 63, 1707-1712 (1975)

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W. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,57	$HO + C_2H_4 \rightarrow$ products			
	*Atkinson, Perry, Pitts (1977)	299-425	$2.2 \times 10^{-12} \exp(385 \pm 150/T)$	1.3 (a)
			(a) High pressure values (225-660 torr Ar) Values also given for 25 and 75 torr	
	Howard (1976)	296	pressure dependent values given over range 1 to 7 torr He	
	Overend, Paraskevopoulos (1977)	296	$1.0 \pm 0.2 \times 10^{-11}$	(b)
			(b) Authors' suggested limiting high pressure value based on expts at 400 torr SF_6 and CF_4 and analysis of dependence of k on $[H_2O]$ at low values of $[H_2O]$	
	Stuhl (1973c)	298	3×10^{-12}	
	Smith, Zellner (1973)	210-460	$7.5 \times 10^{-12} \exp(-110/T)$	
			$10^{12} \times k$ / P(He)/torr	
	Davis, et al (1975)	300	2.24 / 3	
			2.78 / 5	
			3.63 / 10	
			4.06 / 20	
			4.72 / 100	
			5.33 / 300	
		300	3.64×10^{-12} at 3 torr N_2	
	Morris, et al (1971)	300	1.8×10^{-12}	
	Bradley, et al (1973)	300	$1.7 \pm 0.5 \times 10^{-12}$	
	Greiner (1970a)	300-500	$1.26 \times 10^{-12} \exp(454/T)$ at 100 torr He	
	Gordon, Mulac (1975)	381	6.2×10^{-12} (1 atm H_2O vapor)	
		416	7.3×10^{-12} (1 atm H_2O vapor)	

Recommendation is to use the temperature dependent results of Atkinson et al (1977) at high pressures. Within reliability factor given they are confirmed at room temperature by high pressure results of Overend and Paraskevopoulos (1977)

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Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with Ethylene Over the Temperature Range 299-425°K," J. Chem. Phys. 66, 1197-1201 (1977)

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P. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.58	$OD + C_2H_6 \rightarrow$ products			
	*Greiner (1970)	300-500	$1.86 \times 10^{-11} \exp(-1230/T)$	1.2
	Overend, et al (1975)	300	$2.64 \pm 0.17 \times 10^{-13}$	
	Howard, Evenson (1976b)	296	$(2.9 \pm 0.6) \times 10^{-13}$	

Recommendation is to use the results of the temperature dependent study by Greiner (1970). Room temperature value is in good agreement with the other reported results

REFERENCES

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," J. Chem. Phys. 53, 1070-1076 (1970)

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Overend, R., Paraskevopoulos, G., and Cvetanović, R. J., "Rates of OH Radical Reactions. I. Reactions with H_2, CH_4, C_2H_6, and C_3H_8 at 295 K," Can. J. Chem. 53, 3374-3382 (1975)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.59	$HO + C_3H_6 \rightarrow$ products			
	*Atkinson, Pitts (1975b)	297-425	$4.1 \times 10^{-12} \exp(540 \pm 150/T)$ 25-100 torr Ar	1.2
	Ravishankara, et al (1978)	298	$(2.56 \pm 0.12) \times 10^{-11}$ 20 torr He	
			$(2.63 \pm 0.12) \times 10^{-11}$ 200 torr He	
	Stuhl (1973c)	298	1.45×10^{-11}	
	Morris, et al (1971)	300	1.7×10^{-11}	
	Bradley, et al (1973)	300	$5.0 \pm 1.7 \times 10^{-12}$	
	Gorse, Volman (1974)	300	$k/k(CO + HO) = 89.3$ (low pressure)	
			$k = 1.2 \times 10^{-11}$	(a)
			(a) $k(CO + HO) = 1.4 \times 10^{-13}$, this survey	
	Gordon, Mulac (1975)	381	1.4×10^{-11} (1 atm H_2O vapor)	
		416	2.0×10^{-11} (1 atm H_2O vapor)	

Results of Atkinson and Pitts (1975b) are confirmed at room temperature by results of Ravishankara et al (1978)

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Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with Propylene and the Butenes over the Temperature Range 297-425°K," J. Chem. Phys. 63, 3591-3595 (1975b)

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R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,60	OH + $n\text{-}C_4H_{10}$ → products			
	*Perry, Atkinson, Pitts (1976b)	297-420	$1.76 \times 10^{-11} \exp(-560/T)$	1.3
	Greiner (1970)	300-500	$1.41 \times 10^{-11} \exp(-524/T)$	
	Stuhl (1973b)	300	2.35×10^{-12}	
	Gorse, Volman (1974)	300	$k/k(CO + H_2) = 19.4$ (low pressure) $k = 2.7 \times 10^{-12}$ (a) $k(CO + H_2) = 1.4 \times 10^{-13}$, this survey	(a)

Good agreement among all these values at room temperature

REFERENCES

Gorse, R. A., and Volman, D. H., "Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System II: Rate Constants for Hydroxyl Radical Reactions with Hydrocarbons and for Hydrogen Atom Reactions with Hydrogen Peroxide," J. Photochem. 3, 115-122 (1974)

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," J. Chem. Phys. 53, 1070-1076 (1970)

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Stuhl, F., "Rate Constant for the Reaction of OH with $n\text{-}C_4H_{10}$," Z. Naturforsch. Pt A 28, 1383-1384 (1973b)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,60	HO + isobutane → products			
	Greiner (1970)	300-500	$8.7 \times 10^{-12} \exp(-387/T)$	
	Gorse, Volman (1974)	300	$k/k(HO + CO) = 23.5$ (low pressure)	
			$k = 3.3 \times 10^{-12}$	(a)
			(a) $k(CO + OH) = 1.4 \times 10^{-13}$, this survey	
	Butler, et al (1978)	300	1.6×10^{-12}	(b)
			(b) Determined in expt. at 100 torr relative to $k(HO + CO) = 1.5 \times 10^{-13}$	

No recommendation

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Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," J. Chem. Phys. 53, 1070-1076 (1970)

R. F. Hampson

May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.60	OH + alkane → H_2O + alkyl radical Greiner (1970)	300-500	$k = [1.0 \exp(-820/T)\ N_p + 2.3 \exp(-430/T)\ N_s + 2.1 \exp(+95/T)\ N_t] \times 10^{-12}$ Where N_p, N_s, and N_t are the number of primary secondary, and tertiary hydrogen atoms respectively. Do not use formula for CH_4 and C_2H_6.	

This additivity rule can be used to estimate the rate constant for the overall rate of hydrogen atom abstraction from an alkane by hydroxyl radical when there are no direct experimental data

REFERENCES

Greiner, N. R., "Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300-500°K," J. Chem. Phys. 53, 1070-1076 (1970)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.60a	OH + C_6H_6 → products			
	*Perry, Atkinson, Pitts (1977)	298	$(1.20 \pm 0.15) \times 10^{-12}$	total rxn; P = 100 torr Ar
		380-470	$k_1 = 4 \times 10^{-11} \exp(-2000/T)$	(a)
		298	$k_1/k = 0.05$	(b)
			(a) k_1 refers to abstraction rxn	
			(b) Fraction of rxn proceeding by abstraction; expression for k_1 extrapolated to 298K	
	Hansen, Atkinson, Pitts (1975)	298	$(1.24 \pm 0.12) \times 10^{-12}$	total rxn; P = 50-600 torr Ar
	Davis, Bollinger, Fischer (1975)	298	0.85×10^{-12} P = 3 torr He	total rxn
			1.36×10^{-12} P = 20 torr He	total rxn
			1.59×10^{-12} P = 100 torr He	total rxn

The results reported by Perry et al (1977) are the only temperature dependent data available. The room temperature value is in excellent agreement with the results of Hansen et al (1975) but 25% lower than the value of Davis et al (1975) at high pressure

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R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.60a	OH + $C_6H_5CH_3$ → products			
	*Perry, Atkinson, Pitts (1977)	298	$(6.40 \pm 0.64) \times 10^{-12}$	total rxn; P = 200 torr Ar
		380-470	$k_1 = 5 \times 10^{-12} \exp(-450/T)$	(a)
		298	$k_1/k = 0.16$	(b)
			(a) k_1 refers to H atom abstraction	
			(b) Fraction of rxn proceeding by abstraction; expression for k_1 extrapolated to 298K	
	Hansen, Atkinson, Pitts (1975)	298	$(5.78 \pm 0.58) \times 10^{-12}$	total rxn; P = 100-600 torr Ar
	Davis, Bollinger, Fischer (1975)	298	3.60×10^{-12} P = 3 torr He	total rxn
			5.00×10^{-12} P = 20 torr He	total rxn
			6.11×10^{-12} P = 100 torr He	total rxn

The results reported by Perry et al (1977) are the only temperture dependent data available. The room temperature value is in good agreement with the other high pressure results

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W. F. Hampson

May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,61	$HO + CF_2Cl_2 \rightarrow$ products			
	NASA (1979) eval	200-300	$k < 1 \times 10^{-12} \exp(-3560/T)$	(a)
	Atkinson, Hansen, Pitts (1975)	297-424	$k < 1 \times 10^{-15}$	(a)
	Howard, Evenson (1976a)	296	$k < 4 \times 10^{-16}$	(a)
	Chang, Kaufman (1977)	480	$k < 6 \times 10^{-16}$	(a)
	Cox, et al (1976)	298	$k < 1 \times 10^{-16}$	(a)
			(a) upper limit only	

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 (1976) and Clyne and Holt (1978). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes

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Atkinson, R., Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CHF_2Cl, CF_2Cl_2, $CFCl_3$, and H_2 over the Temperature Range 297-434°K," J. Chem. Phys. 63, 1703-1706 (1975)

Chang, J. S., and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of $CFCl_3$(F-11), CF_2Cl_2(F-12), and N_2O with OH and Estimates of Corresponding Lower Limit of their Tropospheric Lifetimes," Geophys. Res. Lett. 4, 192-194 (1977)

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published in NASA RP 1049 "The Stratosphere: Present and Future,"
R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,62	OH + $CFCl_3$ → products			
	NASA (1979) eval	200-300	$k < 1 \times 10^{-12} \exp(-3650/T)$	(a)
	Atkinson, Hansen, Pitts (1975)	297-424	$k < 1 \times 10^{-15}$	(a)
	Howard, Evenson (1976a)	296	$k < 5 \times 10^{-16}$	(a)
	Chang, Kaufman (1977)	480	$k < 5 \times 10^{-16}$	(a)
	Cox, et al (1976)	298	$k < 1 \times 10^{-17}$	(a)
			(a) upper limit only	

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 (1976) and Clyne and Holt (1978). None of the investigators reported any evidence for reaction between OH and these chlorofluoromethanes

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Atkinson, R., Hansen, D. A., and Pitts, J. N., Jr., "Rate Constants for the Reaction of OH Radicals with CHF_2Cl, CF_2Cl_2, $CFCl_3$, and H_2 over the Temperature Range 297-434°K," J. Chem. Phys. 63, 1703-1706 (1975)

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R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the
June 1979 Harpers Ferry Workshop).
D. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.63	$BO + CCl_4$ → products			
	Howard, Evenson (1976a)	296	$k < 4 \times 10^{-15}$	(a)
	Cox, et al (1976)	298	$k < 1 \times 10^{-16}$	(a)
			(a) upper limit only	

Note that these are upper limits only. No evidence for reaction was found

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W. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,64	$HO + CH_3Cl \rightarrow H_2O + CH_2Cl$		ΔH (298) = - 74 kJ/mol	
	NASA (1979) eval	200-300	$2.2 \times 10^{-12} \exp(-(1142 \pm 200)/T)$	1.25
	CODATA (1979) eval	240-422	$2.2 \times 10^{-12} \exp(-(1140 \pm 200)/T)$	1.25
	Davis, et al (1976)	250-350	$(1.84 \pm 0.18) \times 10^{-12} \exp(-1098 \pm 35/T)$	
	Perry, Atkinson, Pitts (1976)	298-423	$4.1 \times 10^{-12} \exp(-1359 \pm 150/T)$	
	Howard, Evenson (1976a)	296	$(3.6 \pm 0.8) \times 10^{-14}$	

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 (1976)). The studies (Davis et al (1975) and Butler et al (1978)) which determined $k(HO + CO)/k(HO + CH_3Cl)$ are excluded until the kinetic behavior between $HO + CO$ is better understood, and the accuracy of the $HO + CH_4$: $HO + CH_3Cl$ study (Cox et al (1976)) 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 (1976) and Perry et al. Equal weighting was given to each of the bimolecular rate constants

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,64	$OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$			
	NASA (1979) eval	200-300	$5.5 \times 10^{-12} \exp(-(1094 \pm 200)/T)$	1.25
	Davis, et al (1976)	245-375	$(4.27 \pm 0.63) \times 10^{-12} \exp(-1094 \pm 81/T)$	
	Perry, Atkinson, Pitts (1976)	298	$(1.45 \pm 0.20) \times 10^{-13}$	
	Howard, Evenson (1976a)	296	$(1.55 \pm 0.34) \times 10^{-13}$	

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 (1976)). The accuracy of the $OH + CH_4$: $OH + CH_2Cl_2$ study (Cox et al (1976)) 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 298K

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1618-1620 (1976)
R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
			ΔH (298) = - 98 kJ/mol	
19,64	$OH + CHCl_3 \rightarrow H_2O + CCl_3$			1.25
	NASA (1979) eval	200-300	$4.7 \times 10^{-12} \exp(-(1134 \pm 200)/T)$	
	Davis, et al (1976)	245-375	$(4.69 \pm 0.71) \times 10^{-12} \exp(-1134 \pm 108/T)$	
	Howard, Evenson (1976a)	296	$1.01 \pm 0.15 \times 10^{-13}$	

Unchanged from NASA 1010. The preferred values were obtained using only absolute rate coefficient data (Howard and Evenson (1976a), and Davis et (1976)). The accuracy of the $OH + CH_4$: $OH + CHCl_3$ 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

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W. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	$BC + CHFCl_2 \rightarrow H_2C + CFCl_2$		$\Delta H (298) = -92$ kJ/mol	
	NASA (1979) eval	200-300	$1.5 \times 10^{-12} \exp(-(1184 \pm 200)/T)$	1.3
	CODATA (1979) eval	240-400	$1.5 \times 10^{-12} \exp(-(1180 \pm 200)/T)$	1.25
	Perry, Atkinson, Pitts (1976)	298-422	$1.75 \times 10^{-12} \exp(-1253 \pm 150/T)$	
	Chang, Kaufman (1977)	241-396	$(1.16 \pm 0.17) \times 10^{-12} \exp(-1073 \pm 40/T)$	
	Watson, et al (1977)	245-375	$(1.87 \pm 0.2) \times 10^{-12} \exp(-1245 \pm 26/T)$	
	Howard, Evenson (1976a)	296	2.6×10^{-14}	
	Clyne, Holt (1979)	294-426	$4.8 \times 10^{-12} \exp(-1400/T)$	

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 (1976) and Chang and Kaufman (1977). The data of Clyne and Holt (1979) 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

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W. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	$H^{\bullet} + CHF_2Cl \rightarrow H_2O + CF_2Cl$		ΔH (298) = - 66 kJ/mol	
	NASA (1979) eval	200-300	$1.2 \times 10^{-12} \exp(-(1666 \pm 200)/T)$	1.25
	CODATA (1979) eval	240-400	$1.3 \times 10^{-12} \exp(-(1670 \pm 200)/T)$	1.25
	Atkinson, Hansen, Pitts (1975)	297-434	$1.21 \times 10^{-12} \exp(-1636 \pm 150/T)$	
	Chang, Kaufman (1977)	253-427	$(1.20 \pm 0.16) \times 10^{-12} \exp(-1657 \pm 39/T)$	
	Watson, et al (1977)	250-350	$(9.25 \pm 1.0) \times 10^{-13} \exp(-1575 \pm 71/T)$	
	Handwerk, Zellner (1978)	263-373	$2.1 \times 10^{-12} \exp(-(1780 \pm 150)/T)$	
	Howard, Evenson (1976a)	296	3.4×10^{-15}	
	Clyne, Holt (1979)	294-426	$9.6 \times 10^{-12} \exp(-(2300 \pm 200)/T)$	

Minor modification from NASA 1010 due to new data. The values reported by Howard and Evenson (1976a), Watson et al (1977), Atkinson et al (1975), Chang and Kaufman (1977), Handwerk and Zellner (1978) and Clyne and Holt (1979) for k at 298 K are in good agreement. Consequently the preferred value is a simple mean of all the results.

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 an 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

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W. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	$BC + CH_2FCl \rightarrow HCl + CHFCl$			
	NASA (1979) eval	200-300	$3.5 \times 10^{-12} \exp(-(1322 \pm 150)/T)$	1.25
	Watson, et al (1977)	245-375	$(2.84 \pm 0.3) \times 10^{-12} \exp(-1259 \pm 50/T)$	
	Howard, Evenson (1976a)	296	$3.7 \pm 0.6 \times 10^{-14}$	
	Handwerk, Zellner (1978)	273-373	$3.1 \times 10^{-12} \exp(-(1320 \pm 100)/T)$	

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

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Handwerk, V., and Zellner, R., "Kinetics of the Reactions of OH Radicals with Some Halocarbons ($CHClF_2$, CH_2ClF, CH_2ClCF_3, CH_3CClF_2, CH_3CHF_2) in the Temperature Range 260-370 K," Ber. Bunsenges. Phys. Chem. 82, 1161-1166 (1978)

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Watson, R. T., Machado, G., Conaway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3 CH_3CF_2Cl, and $CF_2ClCFCl_2$," J. Phys. Chem. 81, 256-262 (1977)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	$BG + CH_3F \rightarrow$ products			
	Howard, Evenson (1976a)	296	$(1643.5) \times 10^{-15}$	

No recommendation

REFERENCES

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	OH + CH_2F_2 → products			
	Clyne, Holt (1979)	293-429	$7.4 \times 10^{-12} \exp(-2100/T)$	
	Howard, Evenson (1976a)	296	$(7.8 \pm 1.2) \times 10^{-15}$	

The results reported by Clyne and Holt (1979) are the only temperature dependent data available. The two room temperature values are in good agreement

REFERENCES

Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground $X^2\Pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 2.-Rate Constants for Reactions of OH $X^2\Pi$ with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II 75, 582-591 (1979)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)

P. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	$OH + CHF_3 \rightarrow$ products			
	Howard, Evenson (1976a)	296	2×10^{-16}	
	Clyne, Holt (1979)	296-430	$(1.3 \pm 0.7) \times 10^{-15}$	

No recommendation

REFERENCES

Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground $X^2\Pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 2.-Rate Constants for Reactions of OH $X^2\Pi$ with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II 75, 582-591 (1979)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)

P. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	$BC + CF_4 \rightarrow$ products			
	Howard, Evenson (1976a)	296	$k < 4 \times 10^{-16}$	upper limit only

No recommendation

REFERENCES

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of B with CF_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	$HO + CF_3Cl \rightarrow$ products			
	Howard, Evenson (1976a)	296	$k < 7 \times 10^{-16}$	upper limit only

No recommendation

REFERENCES

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," *J. Chem. Phys.* **64**, 197-202 (1976a)

R. F. Hampson
May 1978

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	$HO + CH_3Br \rightarrow H_2O + CH_2Br$		$\Delta H(298) = -80$ kJ/mol	
	NASA (1979) eval	200-300	$7.9 \times 10^{-13} \exp(-(889 \pm 200)/T)$	1.25
	CODATA (1979) eval	244-350	$7.6 \times 10^{-13} \exp(-(890 \pm 200)/T)$	1.25
	Davis, et al (1976)	245-350	$(7.93 \pm 0.79) \times 10^{-13} \exp(-(889 \pm 58)/T)$	
	Howard, Evenson (1976a)	296	$(3.54 \pm 0.8) \times 10^{-14}$	

Unchanged from NASA 1010. The preferred value of 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)

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Davis, D. D., Machado, G., Conaway, B., Oh, Y., and Watson, R., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br," J. Chem. Phys. 65, 1268-1274 (1976)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions OH with CH_4 and Fluorine, Chlorine, and Bromine Substituted Methanes at 296 K," J. Chem. Phys. 64, 197-202 (1976a)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
19,65	$HO + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3$		$\Delta H (298)^\circ = -94$ kJ/mol	
	NASA (1979) eval	200-300	$5.4 \times 10^{-12} \exp(-(1820\pm200)/T)$	1,3
	CODATA (1979) eval	250-460	$5.1 \times 10^{-12} \exp(-(1800\pm200)/T)$	1,4
	Kurylo, et al (1979)	253-363	$(5.44\pm1.8) \times 10^{-12} \exp(-(1810\pm100)/T)$	
	Jeong, Kaufman (1979)	278-460	$(5.5\pm1.4) \times 10^{-12} \exp(-(1830\pm100)/T)$	
	Clyne, Holt (1979)	293-430	$(2.4\pm0.8) \times 10^{-12} \exp(-(1394\pm113)/T)$	
	Watson, et al (1977)	260-375	$(3.72\pm0.4) \times 10^{-12} \exp(-1627\pm50/T)$	
	Chang, Kaufman (1977)	275-405	$(1.95\pm0.24) \times 10^{-12} \exp(-1333\pm37/T)$	
	Howard, Evenson (1976b)	296	$(15\pm3) \times 10^{-15}$	

This evaluation is based on the recent data of Kurylo et al (1979) and Jeong and Kaufman (1979). Their results are in excellent agreement. The earlier result of Howard and Evenson (1976b), Watson et al (1977), Chang and Kaufman (1977) and Clyne and Holt (1978) are rejected in favor of the recent results. The CH_3CCl_3 used in the early studies may have been contaminated

REFERENCES

Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: $CHFCl_2$, CHF_2Cl, CH_3CCl_3, C_2HCl_3, and C_2Cl_4," J. Chem. Phys. 66, 4989-4994 (1977)

Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground $X^2\Pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 1. Quenching Kinetics of OH $A^2\Sigma^+$ and Rate Constants for Reactions of OH $X^2\Pi$ with CH_3CCl_3 and CO," J. Chem. Soc., Faraday Trans. II 75, 569-581 (1979)

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Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," J. Chem. Phys. 64, 4303-4306 (1976b)

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Watson, R. T., Machado, G., Conaway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3 CH_3CF_2Cl, and $CF_2ClCFCl_2$." J. Phys. Chem. 81, 256-262 (1977)

R. P. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	$HO + C_2HCl_3 \rightarrow$ products			
	NASA (1979) eval	200-300	$5.0 \times 10^{-13} \exp((445 \pm 200)/T)$	1.25
	Chang, Kaufman (1977)	234-420	$(5.32 \pm 0.71) \times 10^{-13} \exp((445 \pm 41)/T)$	
	Davis, et al (1978)	300	$(2.35 \pm 0.25) \times 10^{-12}$	preliminary
	Howard (1976)	296	$(2.0 \pm 0.4) \times 10^{-12}$	

Changed from NASA 1010 which recommended a temperature independent value. 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

REFERENCES

Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: $CHFCl_2$, CHF_2Cl, CH_3CCl_3, C_2HCl_3, and C_2Cl_4," J. Chem. Phys. 66, 4989-4994 (1977)

Davis, D. D., Machado, W. Smith, G., Wagner, S., and Watson, R. T., Manuscript in preparation, (1978)

Howard, C. J., "Rate Constants for the Gas-Phase Reactions of OH Radicals with Ethylene and Halogenated Ethylene Compounds," J. Chem. Phys. 65, 4771-4777 (1976)

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Winer, A. M., Lloyd, A. C., Darnall, K. R., and Pitts, J. N. Jr., "Relative Rate Constants for the Reaction of the Hydroxyl Radical with Selected Ketones, Chloroethenes, and Monoterpene Hydrocarbons," J. Phys. Chem. 80, 1635-1639 (1976)

R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19.65	$BC + C_2Cl_4$ → products			
	NASA (1979) eval	200-300	$9.4 \times 10^{-12} \exp(-(1199 \pm 200)/T)$	1.25
	Chang, Kaufman (1977)	297-420	$(9.44 \pm 1.34) \times 10^{-12} \exp(-(1199 \pm 55)/T)$	
	Davis, et al (1978)	260-375	$(1.06 \pm 0.5) \times 10^{-11} \exp(-(1300 \pm 150)/T)$	preliminary
	Howard (1976)	296	$(1.70 \pm 0.34) \times 10^{-13}$	

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

REFERENCES

Chang, J. S., and Kaufman, F., "Kinetics of the Reactions of Hydroxyl Radicals with Some Halocarbons: $CHFCl_2$, CHF_2Cl, CH_3CCl_3, C_2HCl_3, and C_2Cl_4," J. Chem. Phys. 66, 4989-4994 (1977)

Davis, D. D., Machado, V. Smith, G., Wagner, S., and Watson, R. T., Manuscript in preparation, (1978)

Howard, C. J., "Rate Constants for the Gas-Phase Reactions of OH Radicals with Ethylene and Halogenated Ethylene Compounds," J. Chem. Phys. 65, 4771-4777 (1976)

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Winer, A. M., Lloyd, A. C., Darnall, K. R., and Pitts, J. N. Jr., "Relative Rate Constants for the Reaction of the Hydroxyl Radical with Selected Ketones, Chloroethenes, and Monoterpene Hydrocarbons," J. Phys. Chem. 80, 1635-1639 (1976)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	OH + CH_3CF_2Cl → products			
	This survey	275-375	$1.5 \times 10^{-12} \exp(-1800/T)$	1.3
	Watson, et al (1977)	273-375	$1.15 \times 10^{-12} \exp(-(1748\pm30)/T)$	
	Clyne, Holt (1979)	293-417	$3.3 \times 10^{-12} \exp(-(1800\pm300)/T)$	
	Handwerk, Zellner (1978)	293-373	$1.8 \times 10^{-12} \exp(-(1790\pm150)/T)$	
	Howard, Evenson (1976b)	296	$(2.8\pm0.4) \times 10^{-15}$	

Recommended expression accepts the reported temperature dependence and averages the room temperature values except for the value of Clyne and Holt (1979) which is much higher than the others

REFERENCES

Clyne, M. A. A., and Holt, P. M., "Reaction Kinetics Involving Ground $X^2\Pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 2.-Rate Constants for Reactions of OH $X^2\Pi$ with Halogenomethanes and Halogenoethanes," J. Chem. Soc. Faraday Trans. II 75, 582-591 (1979)

Handwerk, V., and Zellner, R., "Kinetics of the Reactions of OH Radicals with Some Halocarbons ($CHClF_2$, CH_2ClF, CH_2ClCF_3, CH_3CClF_2, CH_3CHF_2) in the Temperature Range 260-370 K," Ber. Bunsenges. Phys. Chem. 82, 1161-1166 (1978)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," J. Chem. Phys. 64, 4303-4306 (1976b)

Watson, R. T., Machado, G., Conaway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3 CH_3CF_2Cl, and $CF_2ClCFCl_2$," J. Phys. Chem. 81, 256-262 (1977)

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No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
19,65	OH + $CF_2ClCFCl_2$ → products			
	Watson, et al (1977)	298	$k < 3 \times 10^{-16}$	(a)
	Howard, Evenson (1976)	296	$k < 3 \times 10^{-16}$	(a)
			(a) upper limit only	

Note that these are upper limits only. No evidence for reaction was found

REFERENCES

Watson, R. T., Machado, G., Conaway, B., Wagner, S., and Davis, D. D., "A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF, $CHCl_2F$, $CHClF_2$, CH_3CCl_3 CH_3CF_2Cl, and $CF_2ClCFCl_2$," J. Phys. Chem. 81, 256-262 (1977)

Howard, C. J., and Evenson, K. M., "Rate Constants for the Reactions of OH with Ethane and some Halogen Substituted Ethanes at 296 K," J. Chem. Phys. 64, 4303-4306 (1976b)

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May 1978

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
2C, 2C	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$		ΔH (298) = -140 kJ/mol	
	NASA (1979) eval	200-300	2.5×10^{-12}	2
			$\Delta(E/R)$ = 0, -1245	
	CODATA (1979) eval	298	2.3×10^{-12}	2
	Hamilton, Lii (1977)	298	2.5×10^{-12}	P = 1 atm
	Cox (1978)	273-338	$3.8 \times 10^{-14} \exp(1245/T)$	P = 2 torr
	Burrows, et al (1978)	298	$k < 1 \times 10^{-12}$	
	Baulch, et al (1972) review	300	3.3×10^{-12}	

This is the room temperature value of Hamilton and Lii (1977) and Cox (1978). 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 dependence (E/R = -1245K) although the data are very limited However, there is evidence that the strong T dependence is not present at lower pressures. Thus, for the time being, E/R = 0, with a lower uncertainty bound of -1245K is recommended. Preliminary evidence of a pressure dependence (Burrows et al, 1978; Cox, 1978) would, if confirmed, require a further change in the recommendation Recent measurements of the relevant rate constant ratios in a study by DeMore (1979) are consistent with both the water vapor and temperature effects cited by Cox.

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Cox, R. A., 1978a, Paper presented at WMO Symposium on Ozone, Toronto, June, (1978)

DeMore, W. B., "Reaction of HO_2 with O_3 and the Effect of Water Vapor on HO_2 Kinetics," J. Phys. Chem. 83, 1113-1118 (1979)

Hamilton, E. J., Jr., and Lii, R.-R., "The Dependence on H_2O and on NH_3 of the Kinetics of the Self-Reaction of HO_2 in the Gas-Phase. Formation of $HO_2 \cdot H_2O$ and $HO_2 \cdot NH_3$ Complexes," Int. J. Chem. Kinet. 9, 875-885 (1977)

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Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
[illegible]		$\Delta H(298) = -62$ kJ/mol	
[illegible] eval		No recommendation	
Payne, Stief, Davis (1973)	300	9×10^{-16} Relative to $k(HO_2 + HO_2)$	
Graham, et al (1979)	300	$k < 1 \times 10^{-18}$ Relative to $k(HO_2 + NO_2)$	

No recommendation

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., Winer, A. M., Atkinson, R., and Pitts, J. N., Jr., "Rate Constants for the Reaction of HO_2 with HO_2, SO_2, CO, N_2O, trans-2-Butene, and 2,3-Dimethyl-2-butene at 300 K," J. Phys. Chem. 83, 1563-1567 (1979)

Payne, W. A., Stief, L. J., and Davis, D. D., "A Kinetics Study of the Reaction of HO_2 with SO_2 and NO," J. Amer. Chem. Soc. 95, 7614-7619 (1973)

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June 1979

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,35	$HO_2 + Cl \rightarrow HCl + O_2$		ΔH (298) = -216 kJ/mol	
	NASA (1979) eval	200-300	$4.5 \times 10^{-11} \exp((0\pm250)/T)$	1-6
	CODATA (1979) eval	298	4.1×10^{-11}	2
	Leu, DeMore (1976)		3×10^{-11}	
	Poulet, et al (1978)	298	6.8×10^{-11}	
	Burrows, et al (1978)	293	4.1×10^{-11}	
	Cox, Derwent (1977)	306	2.5×10^{-11}	

Changed from NASA 1010. The values of $k(Cl + HO_2)/k(Cl + H_2O_2)$ reported by Leu and DeMore (1976), Poulet et al (1978), and Burrows et al (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 $k(Cl + H_2O_2)$ 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 $k(Cl + HO_2)$. 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 Burrows et al (1978) an upper limit of 4.5×10^{-13} has been placed on the rate constant for production of ClO + OH (1% total rate constant)

REFERENCES

Burrows, J. P., Cliff, D. I., Harris, G. W., Thrush, B. A., and Wilkinson, J. P. T., paper presented at WMO Symposium on Ozone, Toronto, June, (1978)

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NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Poulet, G., Le Bras, G., and Combourieu, J., "Kinetic Study of the Reactions of Cl Atoms with HNO_3, N_2O_2, and HO_2," J. Chem. Phys. 65, 767-773 (1978)

R. F Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,35Br	$HO_2 + Br \rightarrow HBr + O_2$		ΔH (298) = -151 kJ/mol	
	NASA (1979) eval	200-300	$2 \times 10^{-11} \exp((0\pm250)/T)$	3
	CODATA (1979) eval	298	1×10^{-11}	5

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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics To be published in the Journal of Physical and Chemical Reference Data.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

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R. F. Hampson

June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
20.35	$BrO_2 + ClO \rightarrow BrCl + O_2$		ΔH (298) = -182 kJ/mol	
	NASA (1979) eval	298	5.2×10^{-12}	1.5
	CODATA (1979) eval	298	5.2×10^{-12}	1.5
	Reimann, Kaufman (1978)	298	3.8×10^{-12}	
	Howard, et al (1979)	298	6.0×10^{-12}	
	Birks, Lock (1979)	298	5.7×10^{-12}	

The preferred value at 298 K was obtained by taking a simple mean of the results reported by Howard et al (private communication, 1979); Birks and Lock (private communication, 1979); and Reimann and Kaufman (1978). No recommendation is given for the temperature dependence of this reaction. Howard et al have reported that the reaction exhibits nonlinear Arrhenius behavior, with the rate constant increasing as temperature decreases. The magnitude of the temperature dependence below 300 K is similar to that reported by Cox (1978) for $BrO_2 + BrO_2$

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Reimann, B., and Kaufman, F., "Rate Constant of the Reaction $BrO_2 + ClO \rightarrow BrCl + O_2$." J. Chem Phys. 69, 2925-2926 (1978)

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
20,36Br	$HO_2 + BrO \rightarrow HOBr + O_2$		$\Delta H (298) = -207$ kJ/mol	
	NASA (1979) eval	298	5×10^{-12}	5
	CODATA (1979) eval	298	5×10^{-12}	3

No data; value chosen to be consistent with $k(HO_2 + ClO)$

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson

June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,45	$HC_2 + CO \rightarrow CH_2 + H$		$\Delta H^\circ(298) = -246$ kJ/mol	
	*This survey	300	$<10^{-19}$	
	Baulch, et al (1976) review	700-1000	$2.5 \times 10^{-10} \exp(-11900/T)$	a
	Lloyd (1974) eval	300-1000	$1.7 \times 10^{-13} \exp(-5000/T)$	b
	Westenberg, deHaas (1972a)	300	$\sim 1 \times 10^{-12}$	c,d
	Davis, Payne, Stief (1973)	300	$<10^{-20}$	e
	Wyrsch, et al (1974)	300	$<3 \times 10^{-18}$	
	Simonaitis, Heicklen (1973a)	373-473	$<5 \times 10^{-18}$	e
	Volman, Gorse (1972)	330	$<10^{-15}$	f
	Baldwin, Walker, Webster (1970)	713-773	$1 \times 10^{-10} \exp(-11500/T)$	e
	Vardanyan, Dangyan, Sachyan (1972)	878-952	$2.2 \times 10^{-10} \exp(-11500/T)$	

a. Review of all data listed here.
b. Based on Davis, Payne and Stief (1972) and high T results. Temperature coef probably maximum value.
c. Indirect measurement using a low-pressure discharge flow system.
d. Relative rate measurement - reference reaction: $H + HC_2 \rightarrow HC + HC$
e. Relative rate measurement - reference reaction: $HC_2 + HC_2 \rightarrow H_2C_2 + C_2$
f. Relative rate measurement - reference reaction: $HC + CO \rightarrow CH_2 + H$

Upper limit only. The low value of k selected in this evaluation is based on the evaluation by Lloyd and the measurements by Davis, Payne, Stief and Simonaitis, Heicklen

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Lloyd, A. C. "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974) Supersedes NBS Report 10447

Simonaitis, R., and Heicklen, J. "The Reactions of HO_2 with Carbon Monoxide and Nitric Oxide and the Reaction of $O(^1D)$ with Water," J. Phys. Chem. 77, 1096-1102 (1973a)

Westenberg, A. A., and deHaas, N. "Steady-State Intermediate Concentrations and Rate Constants. Some HO_2 Results," J. Phys. Chem. 76, 1586-1593 (1972a)

Pyrsch, D., Wendt, H. R., and Hunziker, H. E., "Modulation Kinetic Spectroscopy of $H_2/O_2/CO$ Mixtures: Reactions of HCH and HO_2," XI. Int. Symp. on Free Radicals (Berchtesgaden-Konigssee, Sept. 4-7, 1973) Paper No. 36; see also, Ber Bunsenges. Physik. Chem. 78, 204 (1974)

Verdanyan, E. A., Danayan, T. M., and Sachyan, G. A., "Rate Constants for the Reaction $HO_2 + CO \rightarrow CO_2 + OH$," Dokl. Phys. Chem. 205, 632-634 (1972); tr. of Dokl. Akad. Nauk SSSR 205, 619-621 (1972)

Volman, D. H., and Gorse, R. A., "Rate Constant for the Reaction of HO_2 with Carbon Monoxide," J. Phys. Chem. 76, 3301-3302 (1972)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,48	$HO_2 + CH_2O \rightarrow H_2O_2 + CHO$		ΔH (298) = 8 kJ/mol	
	*Lloyd (1974) review	300-800	$1.7 \times 10^{-12} \exp(-4000/T)$	>10 at 300K, 1.5 at 800K
	Baldwin, et al (1972)	773	1.6×10^{-15} (a)	(a)

(a) Derived by computer fit to data

This evaluation accepts the recommendation in Lloyd's (1974) review. Note the large error limits at room temperature

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Baldwin, V. R., Fuller, A. V., Longthorn, D., and Walker, R. W., "Addition of Formaldehyde to Slowly Reacting Hydrogen + Oxygen Mixtures," J. Chem. Soc., Faraday Trans. I 68, 1362-1367 (1972)

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974) Supersedes NBS Report 10447

W. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,51	$HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$		ΔH (298) = -140 kJ/mol	
	NASA (1979) eval	298	6×10^{-12}	3
	CODATA (1979) eval	298	6.5×10^{-12}	2
	Cox, Tyndall (1979)	274-338	$7.7 \times 10^{-14} \exp(1296/T)$	

The room temperature value is that of Cox and Tyndall (1979). This study also reports a large negative E/R value over the temperature range 274-338K. This is similar to that found by this group for $HO_2 + HO_2$. This requires independent verification. No recommendations for A or E/R are suggested at the present time

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
2*,57	$HO_2 + C_2H_4 \rightarrow C_2H_4O + HO$?		ΔH (298) = - 68 kJ/mol	
	Walker (1973)	773	2.5×10^{-17}	(a)
			(a) Relative to k (HO_2 + $HCHO$) = 1.6×10^{-15}	
2*,57	$HO_2 + C_2H_4$ → addition products			
	Lloyd (1974) review	300	$\sim 1.7 \times 10^{-17}$	>10 (a)
			(a) Suggestion. Data are irreconcilable.	

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974) Supersedes NBS Report 10447

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R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,58	$HO_2 + C_2H_6 \rightarrow H_2O_2 + C_2H_5$		ΔH (298) = 53 kJ/mol	
	Lloyd (1974) review	300-1000	$\sim 1.7 \times 10^{-12} \exp(-7000/T)$	10 (a)
			(a) Relative rate data versus $2HO_2 \rightarrow H_2O_2 + O_2$ and $HO_2 + CO \rightarrow HO + CO_2$. Temp. coef. estimated.	

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974)
Supersedes NBS Report 10447

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,60	$HO_2 + C_3H_8 \rightarrow H_2O_2 + i\text{-}C_3H_7$		ΔH (298) = 39 kJ/mol	
	Lloyd (1974) review	300-1000	$<3.3 \times 10^{-13} \exp(-5300/T)$	10 (a)
			(a) Based on upper limit meas. Temp coef estimated.	

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974) Supersedes NBS Report 10447

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,6[illegible]	$HO_2 + n\text{-}C_4H_{10} \rightarrow H_2O_2 + n\text{-}C_4H_9$		ΔH (298) = 45 kJ/mol	
	Lloyd (1974) review	300-1000	$8.3 \times 10^{-13} \exp(-5300/T)$	10 (a)
			(a) Based on upper limit meas. Temp coef estimated.	

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974)
Supersedes NBS Report 10447

P. F. Hampson
May 1978

AD-A091 631 NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC(U)
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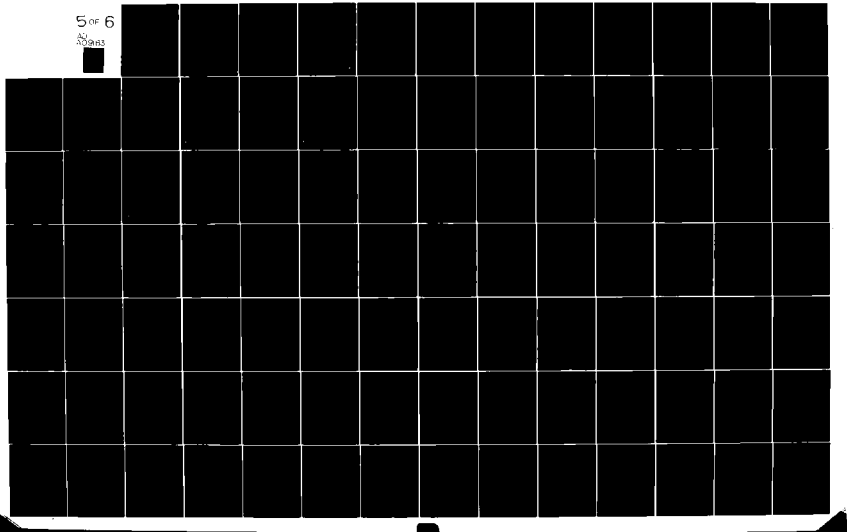

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,60	$HO_2 + i\text{-}C_4H_{10} \rightarrow H_2O_2 + t\text{-}C_4H_9$		$\Delta H^\circ(298) = 32$ kJ/mol	
	Lloyd (1974) review	300-1000	$1.7 \times 10^{-13} \exp(-3500/T)$ (a) Based on upper limit meas. Temp. coef estimated.	10 (a)

No recommendation

REFERENCES

Lloyd, A. C., "Evaluated and Estimated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," Int. J. Chem. Kinet. 6, 169-228 (1974) Supersedes NBS Report 10447

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
20,6c	HO_2 + alkane → H_2O_2 + alkyl radical			
	Walker (1977)	300-800	$k = 8 \times 10^{-14}[N_p \exp(-7520/T) + N_s \exp(-6330/T) + N_t \exp(-4990/T)]$ where N_p, N_s, and N_t are the number of primary, secondary, and tertiary hydrogen atoms respectively	

This additivity rule can be used to estimate the rate constant for the overall rate of hydrogen atom abstraction from an alkane by the hydroperoxyl radical when there are no experimental data.

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Walker, R. W., "Rate Constants for Reactions in Gas-Phase Hydrocarbon Oxidation," Chapter 7 in "Gas Kinetics and Energy Transfer - Volume 2" A Specialist Periodical Report, The Chemical Society, London (1977)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
21,35 18,39	$H_2 + Cl \rightarrow HCl + H$ (f) $H + HCl \rightarrow H_2 + Cl$ (r)		ΔH (298) = 4 kJ/mol	
	NASA (1979) eval	200-300	$k_f = 3.5 \times 10^{-11} \exp(-(2290 \pm 200)/T)$	1 5
	CODATA (1979) eval	210-1070	$k_f = 4.7 \times 10^{-11} \exp(-(2340 \pm 200)/T)$	1-5
	Watson (1977) eval	200-300	$k_f = 3.5 \times 10^{-11} \exp(-2290/T)$	
	Watson, et al (1975)	213-350	$k_f = (5.5 \pm 0.5) \times 10^{-11} \exp(-2375 \pm 100/T)$	
	Lee, et al (1977)	200-500	$k_f = (2.66 \pm 0.42) \times 10^{-11} \exp(-2230 \pm 60/T)$	
	Ambidge, et al (1976a)	298-521	$k_r = 7.8 \times 10^{-12} \exp(-1600 \pm 84/T)$	
	Spencer, Glass (1975)	295	$k_r = 4.3 \times 10^{-14}$	

Unchanged from NASA 1010. This value is based on the results obtained below 300 K by Watson et al (1975) and Lee et al (1977). 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.

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NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

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Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

Watson, R. T., Machado, E. S., Schiff, R. L., Fischer, S., and Davis, D. D., 1975, Proceedings of the 4th CIAP Conference. DOT-TSC-OST-75-38. Cambridge, Mass., February 1975; also manuscript in preparation.

W. F. Wampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
21,35F	$H_2 + F \rightarrow HF + H$		ΔH (298) = -135 kJ/mol	
	NASA (1979) eval	200-300	$2.0 \times 10^{-10} \exp(-(620 \pm 250)/T)$	1.5
	CODATA (1979) eval	200-400	$2.0 \times 10^{-10} \exp(-(620 \pm 250)/T)$	1.5
	Homann, et al (1970)	298-400	$2.66 \times 10^{-10} \exp(-805/T)$	
	Dodonov, et al (1971)	293	3×10^{-11}	
	Clyne, et al (1973)	298	2.8×10^{-11}	
	Bozzelli (1973)	297	2.8×10^{-11}	
	Igoshin, et al (1974)	195-296	$1.55 \times 10^{-10} \exp(-544/T)$	
	Kompa, Wanner (1972)	298	6.2×10^{-11}	
	Rabideau, et al (1972)	293	6.6×10^{-12}	
	Lam, et al (1974)	300	2.3×10^{-12}	

New entry. The value of k at ~298 K seems to be fairly well established with the results of Homann 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 ~2.8, 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.

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E. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
21,36	$N_2 + ClO \rightarrow$ products			
	NASA (1979) eval	200-300	$\leq 1 \times 10^{-12} \exp(-4800/T)$	
		298	$\leq 1 \times 10^{-19}$	

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 estimated from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this ~ 600 K data by choosing the "A factor".

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant k/cm^{3}molecule^{-1}s^{-1}	Uncert Factor at 298K, notes
22, 29	$H_2O + SO_3$ → products CODATA (1979) eval Castleman, et al (1975)	298	No recommendation $(9.1 \pm 2.9) \times 10^{-13}$	

This is the only reported study - no recommendation

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R. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
22.35F	$H_2C + F \rightarrow HF + HC$		$\Delta H (298) = -72$ kJ/mol	
	NASA (1979) eval	200-300	$2.2 \times 10^{-11} \exp(-(200\pm200)/T)$	5
	CODATA (1979) eval	240-360	$2.2 \times 10^{-11} \exp(-(200\pm200)/T)$	3
	Zetzsch (1971)	243-365	$2.2 \times 10^{-11} \exp(-201/T)$	

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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Zetzsch, C., 1971, Ph.D. dissertation, Georg-August University, Gottingen.

R. F. Simpson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
23, 35	$H_2O_2 + Cl \rightarrow HCl + HO_2$		ΔH (298) = - 75 kJ/mol	
	NASA (1979) eval	200-300	$1.1 \times 10^{-11} \exp(-(980 \pm 500)/T)$	1.5
	CODATA (1979) eval	265-424	$1.0 \times 10^{-11} \exp(-(980 \pm 500)/T)$	1.5
	Keyser (1979)	298-424	$(1.05 \pm 0.31) \times 10^{-11} \exp(-(982 \pm 102)/T)$	
	Michael, et al (1977)	265-400	$(1.24 \pm 0.74) \times 10^{-12} \exp(-(384 \pm 168)/T)$	
	Poulet, et al (1978)	298	$(4.0 \pm 0.4) \times 10^{-13}$	
	Leu, DeMore (1976)	295	$(6.2 \pm 1.5) \times 10^{-13}$	
	Watson, et al (1976)	298	5.2×10^{-13}	

This revised value is based on the Arrhenius expression reported by Keyser (1979). The A-factor reported by Michael et al (1977) is considerably lower than that expected from theoretical considerations and may possibly be attributed to decomposition of H_2O_2 at temperatures above 300K. The data of Michael et al at and below 300K are in good agreement with the Arrhenius expression reported by Keyser. More data are required before the Arrhenius parameters can be considered to be well-established.

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Keyser, L., Manuscript in preparation. Jet Propulsion Laboratory, Pasadena, CA. 91003 (1979)

Leu, M-T., and DeMore, W. B., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H_2O_2, HO_2, O_3, CH_4 and HNO_3," Chem Phys. Lett. 41, 121-124 (1976)

Michael, J. V., Whytock, D. A., Lee, J. H., Payne, W. A., and Stief, L. J., "Absolute Rate Constant for the Reaction of Atomic Chlorine with Hydrogen Peroxide Vapor over the Temperature Range 265-400 K," J. Chem. Phys. 67, 3533-3536 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA PP 1049 "The Stratosphere: Present and Future," W. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Warners Ferry Workshop).

Poulet, G., Le Bras, G., and Combourieu, J., "Kinetic Study of the Reactions of Cl Atoms with HNO_3, H_2O_2, and HO_2," J. Chem. Phys. 69, 767-773 (1978)

Watson, R., Machado, G., Fischer, S., and Davis, D. D., "A Temperature Dependence Kinetics Study of the Reaction of $Cl(^2P_{3/2})$ with O_3, CH_4 and H_2O_2," J. Chem. Phys. 65, 2126-2138 (1976)

R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
23, 35Br	$H_2O_2 + Br \rightarrow HBr + HO_2$		$\Delta H (298) = -10$ kJ/mol	
	NASA (1979) eval	200-300	$< 2 \times 10^{-12} \exp(-1400/T)$	2, 0.02
	CODATA (1979) eval	298	$< 2 \times 10^{-14}$	2, 0.02
	Leu, DeMore (1978)	298	$< 2 \times 10^{-14}$	

Changed from NASA 1010. Alternative selection of Arrhenius parameters consistent with unpublished upper limit reported for k (298 K) by Leu and DeMore (1978a). No temperature dependent data available

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Leu, M. T., and DeMore, W. B., 1978a, Provisional unpublished data. Jet Propulsion Laboratory.

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
24, 24	$HNO + HNO \rightarrow H_2O + N_2O$		$\Delta H (298) = -359$ kJ/mol	
	aBaulch, et al (1973) review	300	4×10^{-15}	2

This evaluation accepts the recommendation in the review of Baulch et al (1973)

REFERENCES

Baulch, D. L., Drysdale, D. D., and Horne, D. G., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 2: Homogeneous Gas Phase Reactions of the H_2-N_2-O_2 System," (Butterworths, London, 1973)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
26,35	$HNO_3 + Cl \rightarrow HCl + NO_3$		ΔH (298) = - 8 kJ/mol	
	NASA (1979) eval	200-300	$\leq 1 \times 10^{-11} \exp(-2170/T)$	2, 0.003
			$\Delta(E/R) = \pm 2500, -500$	
	CODATA (1979) eval	298	$\leq 7 \times 10^{-15}$	2, 0.003
	Leu, DeMore (1976)	295	$(6.8 \pm 3.4) \times 10^{-15}$	
	Poulet, et al (1978)	439-633	$1.5 \times 10^{-11} \exp(-4380/T)$	
		298	$< 2 \times 10^{-17}$	

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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Leu, M-T., and DeMore, W. B., "Rate Constants at 295 K for the Reactions of Atomic Chlorine with H_2O_2, HO_2, O_3, CH_4 and HNO_3," Chem Phys. Lett. 41, 121-124 (1976)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). "Recommendations of the NASA Panel for Data Evaluation, published in NASA PP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Poulet, G., Le Bras, G., and Combourieu, J., "Kinetic Study of the Reactions of Cl Atoms with HNO_3, H_2O_2, and HO_2," J. Chem. Phys. 69, 767-773 (1978)

P. F. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
26a,34b	$S + CS_2 \rightarrow S_2 + CS$		$\Delta H (298) = 6$ kJ/mol	
	*Baulch, et al (1976) review	298	6.5×10^{-13}	1.5

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
26a,34c	$S + CdS \rightarrow Cd + S_2$		$\Delta H (298) = -117$ kJ/mol	
	*Baulch, et al (1976) review	230-2600	$2.8 \times 10^{-12} \exp(-2050/T)$	3

This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
27,27	$SO + SO \rightarrow SO_2 + S$ or $(SO)_2$		$\Delta H(298) = -30$ kJ/mol	
	Schofield (1973) review	300	$< 3 \times 10^{-15}$	
		1000	$< 2 \times 10^{-13}$	
	Chung, Calvert, Bottenheim (1975)	300	$8.3 \pm 6.7 \times 10^{-16}$	

No recommendation

REFERENCES

Chung, K., Calvert, J. G., and Bottenheim, J. W., "The Photochemistry of Sulfur Dioxide Excited within its First Allowed Band (3130 Å) and the 'Forbidden' Band (3700-4000 Å)," Int. J. Chem. Kinet. 7, 161-182 (1975)

Schofield, K., "Evaluated Chemical Kinetic Rate Constants for Various Gas Phase Reactions," J. Phys. Chem. Ref. Data 2, 25-84 (1973)

W. F. Hampson
May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
27,29	$SO + SO_3 \rightarrow 2SO_2$		$\Delta H (298) = -203$ kJ/mol	
	Chung, Calvert, Bottenheim (1975)	300	$2 \pm 1.2 \times 10^{-15}$	

No recommendation

REFERENCES

Chung, K., Calvert, J. G., and Bottenheim, J. W., "The Photochemistry of Sulfur Dioxide Excited within its First Allowed Band (3130 Å) and the 'Forbidden' Band (3700-4000 Å)," Int. J. Chem. Kinet. 7, 161-182 (1975)

P. F. Wampson
May 1978

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
28.49M	$SO_2 + CH_3 (+M) \rightarrow CH_3SO_2 (+M)$ James, et al (1973)	300	3×10^{-13}	

This rate constant was found to be independent of pressure over the range 50 to 200 torr Ar and N_2

REFERENCES

James, F. C., Kerr, J. A., and Simons, J. P., "A Direct Measurement of the Rate of Reaction of the Methyl Radical with Sulphur Dioxide," J. Chem. Soc. Faraday Trans. I 69, 2124-2129 (1973)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
31, 31	$HS + HS \rightarrow H_2S + S$		$\Delta H (298) = -36$ kJ/mol	
	*Baulch, et al (1976) review	295	1.3×10^{-11}	1.5

*This evaluation accepts the recommendation in the review of Baulch et al (1976)

REFERENCES

Baulch, D. L., Dryadale, D. D., Duxbury, J., and Grant, S. J., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3: Homogeneous Gas Phase Reactions of the O_2-O_3 System, the CO-O_2-H_2 System, and of Sulphur-Containing Species," (Butterworths, London, 1976)

R. F. Hampson
May 1978

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,35W	$Cl + Cl + M \rightarrow Cl_2 + M$		ΔH (298) = -243 kJ/mol	
	*Watson (1977) review	195-514	$6.3 \times 10^{-34} \exp(900/T)$ $cm^6 molecule^{-2} s^{-1}$, M = Ar	1 3

*This evaluation accepts the recommendation in Watson's (1977) review

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35, 37	Cl + OClO → 2ClO		ΔH (298) = - 14 kJ/mol	
	NASA (1979) eval	200-300	$5.9 \times 10^{-11} \exp((0 \pm 250)/T)$	1.25
	Bemand, Clyne, Watson (1973)	298-588	$(5.9 \pm 0.9) \times 10^{-11}$	(a)
			(a) Recommended in Watson's (1977) review	

Unchanged from NASA 1010. Data reported by Bemand, Clyne and Watson (1973)

REFERENCES

Bemand, P. P., Clyne, M. A. A., and Watson, R. T., "Reactions of Chlorine Oxide Radicals. Part 4.-Rate Constants for the Reaction Cl + OClO, O + OClO, H + OClO, NO + OClO and F + ClO," J. Chem. Soc., Faraday Trans. I 69, 1356-1374 (1973)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

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Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

W. P. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,37	$Cl + ClOO \rightarrow Cl_2 + O_2$ (a) $\rightarrow 2ClO$ (b)		ΔH (298) = -210 kJ/mol = - 6 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 1 \times 10^{-10} \exp((0\pm250)/T)$	3
		200-300	$k_b = 5 \times 10^{-12} \exp((0\pm250)/T)$	3
	Cox, et al (1979)	297	$k_a = 9.8 \times 10^{-11}$ $k_b = 4.7 \times 10^{-12}$	
	Johnston, et al (1969)	298	$k_a = 1.56 \times 10^{-10}$ $k_a/k_b = 108$	
	Nicholas, Norrish (1968)	298	$k_a/k_b = 15$	

Changed from NASA 1010 due to new data. Cox et al (1979) reported values for k_a and k_b which result 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 ΔH_f° (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

REFERENCES

Cox, R. A., Derwent, R. G., Eggleton, A. E. J., and Reid, H. J., "Kinetics of Chlorine Oxide Radicals using Modulated Photolysis. Part 2. - ClO and ClOO Radical Kinetics in the Photolysis of $Cl_2 + O_2 + N_2$ Mixtures," J. Chem. Soc. Faraday Trans. I 75, 1648-1666 (1979)

Johnston, H. S., Morris, E. D., Jr., and Van den Bogaerde, J., "Molecular Modulation Kinetic Spectrometry. ClOO and ClO_2 Radicals in the Photolysis of Chlorine in Oxygen," J. Amer. Chem. Soc. 91, 7712-7727 (1969)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Nicholas, J. E., and Norrish, R. G. W., "Some Reactions in the Chlorine and Oxygen System Studied by Flash Photolysis," Proc. Roy. Soc. (London) A 307, 391-397 (1968)

R. F. Hampson

June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,44a	$Cl + Cl_2O \rightarrow Cl_2 + ClO$		ΔH (298) = -101 kJ/mol	
	*Watson (1977) review	300	6.8×10^{-13}	

This evaluation accepts the recommendation in Watson's (1977) review

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,42	$Cl + NOCl \rightarrow NO + Cl_2$		$\Delta H\ (298) = -83$ kJ/mol	
	NASA (1979) eval	200-300	3.0×10^{-11}	2
	Clyne, Cruse (1972)	298	$\Delta(E/R) = +500, -250$ $(3.0 \pm 0.5) \times 10^{-11}$ (a) Recommended in Watson's (1977) review	(a)

Unchanged from NASA 1010. Value based on the data of Clyne and Cruse (1972). No reliable data on the temperature dependence

REFERENCES

Clyne, M. A. A., and Cruse, H. W., "Atomic Resonance Fluorescence Spectrometry for Rate Constants of Rapid Bimolecular Reactions. Part 1. Reactions $H + NO_2$, $Cl + ClNO$, $Br + ClNO$," J. Chem. Soc., Faraday Trans. II 68, 1281-1299 (1972)

NASA PP-1010, "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979), Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
June 1979

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No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,43	$Cl + NO_2Cl \rightarrow NO_2 + Cl_2$		$\Delta H(298) = -100$ kJ/mol	
	Watson (1977) review	298	$k >> 3 \times 10^{-14}$	

No recommendation - entry based on provisional, unpublished data

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

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No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,43a	Cl + NO_3Cl → products			
	NASA (1979) eval	200-300	$1.7 \times 10^{-12} \exp(-(607 \pm 388)/T)$	2
	CODATA (1979) eval	224-273	$1.7 \times 10^{-12} \exp(-(610 \pm 400)/T)$	2
	Kurylo, Manning (1977)	224-273	$1.68 \times 10^{-12} \exp(-607/T)$	
	Ravishankara, et al (1976)	245	$\sim 8 \times 10^{-14}$	preliminary

Unchanged from NASA 1910. Considering the experimental difficulties associated with handling $ClNO_2$, and the low precision of the data of Ravishankara et al (1976), the results are in fair agreement at 245 K. 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

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Kurylo, M. J., and Manning, W. G., "Flash Photolysis Resonance Fluorescence Investigation of the Reaction of $Cl(^2P)$ Atoms with $ClNO_2$," Chem. Phys. Lett. 48, 279-283 (1977)

NASA RP-1010. "Chlorofluoromethanes and the Stratosphere" R. D. Hudson, Editor, August 1977 This reference contains the NASA (1977) rate constant recommendations.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Ravishankara, A. R., Smith, G., Tesi, G., and Davis, D. D., Presented at 12th Informal Conference on Photochemistry, National Bureau of Standards, Gaithersburg, MD June 1976

P. F. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
35.48	$Cl + CH_2O \rightarrow HCl + HCO$		$\Delta H (298) = -67$ kJ/mol	
	NASA (1979) eval	200-300	$9.2 \times 10^{-11} \exp(-(68 \pm 100)/T)$	1.15
	CODATA (1979) eval	200-500	$7.9 \times 10^{-11} \exp(-(34 \pm 100)/T)$	1.15
	Anderson, Kurylo (1979)	223-323	$1.09 \times 10^{-10} \exp(-(131 \pm 98)/T)$	
	Michael, et al (1979)	200-500	$(7.48 \pm 0.5) \times 10^{-11}$	

New entry. The results of the three studies (Michael et al (1979), Anderson and Kurylo (1979), Niki et al (1978)) 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 and Anderson and Kurylo (7.18×10^{-11}), with the value (7.4×10^{-11}) obtained by combining the ratio of $k(H_2CO)/k(C_2H_6)$ reported by Niki et al (1.34 ± 0.1) with the preferred value of $5.7 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$ for $k(C_2H_6)$ at 298 K. The value of E/R was based on averaging the values of Michael et al and Anderson and Kurylo.

REFERENCES

Anderson, P. C., and Kurylo, M. J., "Rate Constant Measurements for the Reaction $Cl + CH_2O \rightarrow HCl + CHO$: Implications Regarding the Removal of Stratospheric Chlorine," J. Phys. Chem. 83, 2055-2057 (1979)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Michael, J. V., Nava, D. F., Payne, W. A., and Stief, L. J., "Rate Constant for the Reaction of Atomic Chlorine with Formaldehyde from 200 to 500 K," J. Chem. Phys. 70, 1147-1150 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Niki, H., Maker, P. D., Breitenbach, L. P., and Savage, C. M., "FTIR Studies of the Kinetics and Mechanism for the Reaction of Cl Atom with Formaldehyde," Chem. Phys. Lett. 57, 596-599 (1978)

S. P. Sander
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,56	$Cl + CH_4 \rightarrow HCl + CH_3$		ΔH (298) = 7 kJ/mol	
	NASA (1979) eval	200-300	$9.9 \times 10^{-12} \exp(-(1359 \pm 150)/T)$	1.15
	CODATA (1979) eval	200-300	$9.9 \times 10^{-12} \exp(-(1360 \pm 150)/T)$	1.15
	Watson (1977) review	200-300	$7.3 \times 10^{-12} \exp(-1260/T)$	(a)
	Manning, Kurylo (1977)	218-322	$(7.93 \pm 1.53) \times 10^{-12} \exp(-1273 \pm 51/T)$	
	Watson, et al (1976)	218-401	$(7.94 \pm 0.7) \times 10^{-12} \exp(-1260 \pm 35/T)$	(b)
	Whytock, et al (1977)	200-500	$5.44 \times 10^{-19} T^{2.50} \exp(-608/T)$	
		200-299	$(6.51 \pm 0.79) \times 10^{-12} \exp(-1229 \pm 27/T)$	
	Zahniser, et al (1978)	200-500	$8.6 \times 10^{-18} T^{2.11} \exp(-795/T)$	
		200-300	$(8.2 \pm 0.6) \times 10^{-12} \exp(-1329 \pm 20/T)$	
	Lin, Leu, DeMore (1978)	268-423	$(1.07 \pm 0.4) \times 10^{-11} \exp(-(1410 \pm 120)/T)$	
	Keyser (1978)	220-298	$(7.4 \pm 2.0) \times 10^{-12} \exp(-(1291 \pm 68)/T)$	
		298-423	$(1.65 \pm 0.3) \times 10^{-11} \exp(-(1530 \pm 68)/T)$	
	Poulet, et al (1974)	295-490	$(1.84 \pm 0.14) \times 10^{-11} \exp(-(1410 \pm 100)/T)$	
	Michael, Lee (1977)	298	$(1.08 \pm 0.07) \times 10^{-13}$	
	Davis, et al (1970)	300	$1.5 \pm 0.1 \times 10^{-13}$	
	Fettis, Knox (1964)		$4 \times 10^{-11} \exp(-1930/T)$	
	Clyne, Walker (1973)	300-686	$5.1 \times 10^{-11} \exp(-1790/T)$	

(a) Based on four direct 1976, 1977 studies listed immediately below.

(b) Value changed subsequent to publication to allow for effect of small C_2H_6 impurity see Watson's review (1977)

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 x 10^{-13} with a mean value of 1.16 x 10^{-13}. However, based upon the stated confidence limits reported in each study, the range of values far exceeds that to be expected. A preferred average value of 1.05 x 10^{-13} can be determined from the absolute rate coefficient studies for k at 298 K by giving equal weighting to the values reported in (Lin et al (1978a), Watson et al (1976), Manning and Kurylo (1977), Whytock et al (1977), Zahniser et al (1978), Michael and Lee (1977), and Keyser (1978)). The values derived for k at 298 K from the competitive chlorination studies (Lin et al (1978a), Knox and Nelson (1959), Knox (1955), and Pritchard et al (1955)) range from 0.95 - 1.13 x 10^{-13}, with an average value of 1.02 x 10^{-13}. The preferred value was obtained by taking a mean value from the most reliable absolute and relative rate coefficient studies

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 (1977), Zahniser et al (1978), 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) x 10^{-14}. The mean of

the two discharge flow (Zahniser et al (1978) 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 (1977) 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 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.

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
35,58	$Cl + C_2H_6 \rightarrow HCl + C_2H_5$		$\Delta H(298) = -22$ kJ/mol	
	CODATA (1979) eval	220-350	$7.7 \times 10^{-11} \exp(-(90 \pm 100)/T)$	1-15
	Manning, Kurylo (1977)	222-322	$(7.29 \pm 1.23) \times 10^{-11} \exp(-60 \pm 44/T)$	
	Lewis, et al (1979)	220-604	$8.3 \times 10^{-11} \exp(-130/T)$	

Recommended expression gives the best fit to the data between 220 and 350 K reported in these two studies

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R. F. Hampson

June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
38.64	$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$		$\Delta H (298) = -7$ kJ/mol	
	NASA (1979) eval	200-300	$3.4 \times 10^{-11} \exp(-(1256 \pm 200)/T)$	1.2
	CODATA (1979) eval	233-350	$3.4 \times 10^{-11} \exp(-(1260 \pm 200)/T)$	1.25
	Clyne, Walker (1973)	300-604	$2.1 \times 10^{-10} \exp(-(1787 \pm 70)/T)$	
	Watson, et al (1978)	245-350	$3.7 \times 10^{-11} \exp(-(1287 \pm 150)/T)$	
	Manning, Kurylo (1977)	233-322	$3.36 \times 10^{-11} \exp(-(1250 \pm 57)/T)$	

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

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R. P. Hampson
June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
3SP,86	$F + CH_4 \rightarrow HF + CH_3$		ΔH (298) = -139 kJ/mol	
	NASA (1979) eval	200-300	$3.6 \times 10^{-10} \exp(-(400\pm300)/T)$	2
	CODATA (1979) eval	250-450	$3.0 \times 10^{-10} \exp(-(400\pm150)/T)$	1.5
	Wagner, et al (1971)	298-450	$5.5 \times 10^{-10} \exp(-579/T)$	
	Clyne, et al (1973)	300	6×10^{-11}	
	Koppa, Wanner	298	7.2×10^{-11}	

New entry. The three absolute rate coefficients determined by Wagner et al (1971), Clyne et al (1973) and Koppa and Wanner (1972) at 298 K are in good agreement; however, this may be somewhat fortuitous as the ratios of $k(F + H_2)/k(F + CH_4)$ determined by these same groups can only be considered to be in fair agreement, 0.23, 0.42 and 0.88. The values determined for k (298) from the relative rate coefficient studies are also in good agreement with those determined in the absolute rate coefficient studies, and the value of 0.42 reported for $k(F + H_2)/k(F + CH_4)$ by Foon and Reid (1971) is in good agreement with that reported by Clyne et al. The preferred value of 8.0×10^{-11} for k (298) is a weighted mean of all the results. The magnitude of the temperature dependence is somewhat uncertain. The preferred Arrhenius parameters are based on the data reported by Wagner et al, and Foon and Reid, and the preferred Arrhenius parameters of the $F + H_2$ reaction. This reaction has recently been reviewed by both Foon and Kaufman (1975) and Jones and Skolnik (1976). A-factor may be too high

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,36	$ClO + ClO \rightarrow Cl + ClOO$ (a) $\rightarrow Cl_2 + O_2$ (b) $\rightarrow OClO + Cl$ (c) NASA (1979) eval		ΔH (298) = 6 kJ/mol = -204 kJ/mol = 14 kJ/mol no recommendation; see note	

No recommendation at present; however, if values are needed for modelling purposes, use those shown in NASA 1010, i.e., $k(ClO + ClO \rightarrow Cl + ClOO) = 1 \times 10^{-12} \exp(-1238/T)$; $k(ClO + ClO \rightarrow Cl_2 + O_2) = 5 \times 10^{-13} \exp(-1238/T)$. The data base used for this evaluation has been discussed in detail by Watson (1977). At present no recommendation is given for the $ClO + ClO$ reaction as the partitioning between the channels (expecially the temperature dependence of the partitioning) is not well established. Cox and Derwent (1979) have recently written a paper concerning the absolute values of the following channels: $ClO + ClO \rightarrow Cl + ClOO$; $ClO + ClO \rightarrow Cl_2 + O_2$; $ClO + ClO \rightarrow Cl + OClO$; $ClO + ClO + M \rightarrow Cl_2O_2 + M$. This data needs to be thoroughly evaluated before recommending any new values for these reaction pathways

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,36Br	$ClO + BrO \rightarrow Br + OClO$ (a) $\rightarrow Br + Cl + O_2$ (b)		ΔH (298) = - 14 kJ/mol = 5 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 6.7 \times 10^{-12} \exp((0\pm250)/T)$	1 5
			$k_b = 6.7 \times 10^{-12} \exp((0\pm250)/T)$	1.5
	CODATA (1979) eval	298	$k_a = 6.7 \times 10^{-12}$	2
			$k_b = 6.7 \times 10^{-12}$	2
	Clyne, Watson (1977)	298	$k_a = (6.7 \pm 1.7) \times 10^{-12}$	
			$k_b = (6.7 \pm 1.7) \times 10^{-12}$	
	Basco, Dogra (1971)	300	2.5×10^{-12} Products assumed to be $BrCl + O_2$	

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 BrO + BrO. Although the second reaction channel is shown proceeding directly to Br + Cl + O_2, it may proceed through Br + ClOO (ΔH° = -27.5 kJ mol^{-1}) or Cl + BrOO (ΔH° unknown).

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P. F. Hampson

June 1979

No.	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert. Factor at 298K, notes
36F,36F	$FO + FO \rightarrow 2F + O_2$		ΔH (298) = - 59 kJ/mol	
	NASA (1979) eval	200-300	$1.8 \times 10^{-11} \exp((0\pm250)/T)$	3
	CODATA (1979) eval	298	1.8×10^{-11}	2
	Clyne, Watson (1974)	298	$(8.5\pm2.8) \times 10^{-12}$	
	Wagner, et al (1972)	298	3.3×10^{-11}	

New entry. Although the value of k(FO + FO) reported by Clyne and Watson (1974) 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

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,45	$ClO + CO \rightarrow CO_2 + Cl$		$\Delta H (298) = -264$ kJ/mol	
	NASA (1979) eval	200-300	$\leq 1 \times 10^{-12} \exp(-3700/T)$	
		298	$\leq 4 \times 10^{-18}$	

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported by Clyne and Watson (1974a)) The upper limits shown for k (298) were estimated from data collected at either 587 K or 670 K. The Arrhenius expressions were estigated based on this ~ 600 K data by choosing the "A factor"

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,56	$ClO + CH_4 \rightarrow$ products			
	NASA (1979) eval	200-300	$\leq 1 \times 10^{-12} \exp(-3700/T)$	
		298	$\leq 4 \times 10^{-18}$	

Unchanged from NASA 1010. These upper limits are based on the data of Walker (reported by Clyne and Watson (1974a)) The upper limits shown for k (298) were estimated from data collected at either 587 K or 670 K. The Arrhenius expressions were estimated based on this ~ 600 K data by choosing the "A factor"

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions involving the $ClO\ X^2\Pi$ Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)

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R. F. Hampson
June 1979

No	Reaction/Reference	Temp-Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,57	$ClO + C_2H_4$ → products			
	Clyne, Watson (1974a)	670	$k \leq 1 \times 10^{-15}$	

Note that this is an upper limit - no reaction was observed

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions involving the ClO $X^2\Pi$ Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36,56a	$ClO + C_2H_2 \rightarrow$ products			
	Clyne, Watson (1974a)	670	$k \leq 1 \times 10^{-15}$	

Note that this is an upper limit - no reaction was observed

REFERENCES

Clyne, M. A. A., and Watson, R. T., "Kinetic Studies of Diatomic Free Radicals using Mass Spectrometry Part 2. Rapid Bimolecular Reactions involving the ClO $X^2\Pi$ Radical," J. Chem. Soc., Faraday Trans. I 70, 2250-2259 (1974a)

R. F. Hampson
May 1978

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
36Br,36Br	$BrO + BrO \rightarrow 2Br + O_2$ (a) $\rightarrow Br_2 + O_2$ (b)		ΔH (298) = - 28 kJ/mol = -256 kJ/mol	
	NASA (1979) eval	200-300	$k_a = 1.0 \times 10^{-12} \exp((244\pm150)/T)$	1.25 (a)
			$k_b = 1.8 \times 10^{-13} \exp((244\pm150)/T)$	1.25 (a)
	CODATA (1979) eval	220-440	$k = 2.8 \times 10^{-12} \exp((0\pm500)/T)$	1.25 (a)
	Sander, Watson (1979)	223-398	$k = 1.13 \times 10^{-12} \exp((244\pm100)/T)$	(a)
	Clyne, Watson (1975)	298	$k = 3.2 \times 10^{-12}$	(a)
	Basco, Dogra (1971)	298	$k = 1.1 \times 10^{-12}$	(a)
	Clyne, Cruse (1970)	293	$k = 2.6 \times 10^{-11} \exp(-450/T)$	(a)
	Clyne, Coxon (1968)	298	$k = 0.65 \times 10^{-12}$	(a)
			(a) $-d[BrO]/dt = 2\,k[BrO]^2$	

Changed from NASA 1010 due to new data. Four of the five studies (Clyne and Coxon (1968), Clyne and Cruse (1970), 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 technique (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.

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R. P. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
50,4	$CH_3O + O_2 \rightarrow CH_2O + HO_2$ (1)		ΔH (298) = -121 kJ/mol	
50,9	$CH_3O + NO \rightarrow CH_3ONO$ (2a)		= -170 kJ/mol	
	$\rightarrow CH_2O + HNO$ (2b)		= -114 kJ/mol	
50,10	$CH_3O + NO_2 \rightarrow CH_3ONO_2$ (3a)		= -167 kJ/mol	
	$\rightarrow CH_2O + HNO_2$ (3b)		= -236 kJ/mol	
50,45	$CH_3O + CO \rightarrow$ products (4)			
	NASA (1979) eval	200-300	$k_1 = 5 \times 10^{-13} \exp(-(2000 \pm 750)/T)$	2
	CODATA (1979) eval	300-450	$k_1 = 5 \times 10^{-13} \exp(-(2000 \pm 1000)/T)$	4
	Barker, et al (1977)	396-442	$k_1 = 5 \times 10^{-13} \exp(-2000/T)$	
	Batt, Robinson (1979)	383-433	$k_1 = 1.7 \times 10^{-12} \exp(-2400/T)$	
	Heicklen (1973)	298	$k_1 \sim 3 \times 10^{-18}$	
			$\sim 1.6 \times 10^{-13} \exp(-3300/T)$	
			$k_2 \sim 8 \times 10^{-14}$	
		298	$k_1/k_2 = 4.7 \times 10^{-5}$ ±20%	ratio probably is smaller at 220K
			$k_{2b}/k_2 = 0.145 \pm 0.015$	
			$k_2/k_3 = 1.2 \pm 0.1$	
		298	$k_{2a}/k_{3a} = 1.1$	
		363	= 1.8	
		403	= 2.7	
		298	$k_{3a}/k_3 = 0.9 \pm 0.1$	k_{3a}/k_{3b} probably constant 300-400K
		298	$k_{3b}/k_3 = 0.1 \pm 0.01$	
		298-423	$k_4/k_2 = 5 \times 10^{-4}$	
	Demerjian, et al (1974) review	300	$k_1 = 1.6 \times 10^{-17}$	
			$\sim 4.2 \times 10^{-13} \exp(-3000/T)$	
			adjusted to fit C_4H_{10}/NO_x simulation studies	
			$k_{2a} = 1.7 \times 10^{-13}$	
			$k_{2b}/k_{2a} = 0.17$	
			$k_{3a} = 3.3 \times 10^{-13}$	
			$k_{3b}/k_{3a} = 0.1$	
	Batt, McCulloch, Milne (1975)	393-473	$k_{2a} \sim 3 \times 10^{-11}$	
			$k_{2b} \sim 7 \times 10^{-12}$	

The recommended A-factor and E/R values for k_1 are those determined by Barker et al (1977), who measured the ratio $k(CH_3O + O_2)/k(CH_3O + NO_2 + M)$ from 396 to 424K. Recent results on this same system have been reported by Batt and Robinson (1979). Although these new results yield a higher A-factor and somewhat higher E/R, they are consistent with the results of Barker et al over the limited temperature range studied. The k(298) value is calculated from the recommended A-factor and E/R. Further work over a wider temperature range is needed

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R. F. Hampson
June 1979

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No	Reaction/Reference	Temp. Range/K	Reaction Rate Constant $k/cm^3 molecule^{-1} s^{-1}$	Uncert Factor at 298K, notes
51,51	$2CF_3O_2 \rightarrow 2CF_3O + O_2$ (a) $\rightarrow CF_3OH + CF_2O + O_2$ (b) $\rightarrow CF_3O_2CF_3 + O_2$ (c)		ΔH (298) = 15 kJ/mol = -324 kJ/mol = -179 kJ/mol	
	CODATA (1979) eval	298	$k = 4.6 \times 10^{-13}$ ($k_a + k_b + k_c$) $k_a/k = 0.33$	1.25
	Parkes (1977)	300	$k_a = 1.6 \pm 0.4 \times 10^{-13}$ $k_b + k_c = 3.0 \pm 0.8 \times 10^{-13}$	
	Anastasi, et al (1978)	298	$k = (4.4 \pm 1) \times 10^{-13}$	
	Wochanadel, et al (1977)	298	$k = (3.8 \pm 0.7) \times 10^{-13}$	
	Weaver, et al (1975)	300	$k_a/k = 0.43$ $k_b/k = 0.50$ $k_c/k = 0.07$	

The recommended value for the overall rate constant is taken from the work of Parkes (1977)

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W. F. Wampson

June 1976

No.	Reaction/Reference	Photochemical Data
4,hν	$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$ (1)	ΔH = 494 kJ/mol; $\lambda_{threshold}$ = 242 nm
	$\rightarrow O(^3P) + O(^1D)$ (2)	ΔH = 683 kJ/mol; $\lambda_{threshold}$ = 175 nm

NASA (1979) eval

The absorption spectrum of O_2 in the Schumann-Runge bands (175-200nm) has been re-examined recently by Frederick and Hudson (1979), who found some of the the line widths to be smaller than those reported earlier by Ackerman and Biaume (1970). The recommended values are the new results of Frederick and Hudson, which will affect the calulations 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. Uncertainty factor for photochemical rates is 1.4 for S-R bands and 1.15 for continua.

CODATA (1979) eval

$\phi_1 = 1$ $\quad 175 < \lambda < 200$ nm

$\phi_2 = 1$ $\quad 140 < \lambda < 175$ nm

Absorption cross sections

10^{-2} ν/cm^{-1}	$10^{19}\sigma$	10^{-2} ν/cm^{-1}	$10^{24}\sigma$
680-690	141	490-495	11.4
660-670	115	470-475	8.9
640-650	82.4	450-455	6.3
620-630	49.7	430-436	3.8
600-610	20.8	410-415	0.7
580-590	7.2		
570-575	2.7		

These values are taken from Ackerman (1971).

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
7,hν	$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$	$\Delta H = 385$ kJ/mol; $\lambda_{threshold} = 310$ nm

NASA (1979)eval

The recommended values for the $O(^1D)$ quantum yield ϕ 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). The results agree within 10% with the data recommended in NASA RP-1010, which is only for 235 K. The mathematical expression is the following:

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

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

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

$$A(\tau) = 0.369 + 2.85 \times 10^{-4}\tau + 1.28 \times 10^{-5}\tau^2 + 2.57 \times 10^{-8}\tau^3$$
$$B(\tau) = -0.575 + 5.59 \times 10^{-3}\tau - 1.439 \times 10^{-5}\tau^2 - 3.27 \times 10^{-8}\tau$$
$$\lambda_0(\tau) = 308.20 + 4.4871 \times 10^{-2}\tau + 6.9380 \times 10^{-5}\tau^2 - 2.5452 \times 10^{-6}\tau^3$$
$$C(\tau) = 0.518 + 9.87 \times 10^{-4}\tau - 3.94 \times 10^{-5}\tau^2 + 3.91 \times 10^{-7}\tau^3$$

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

The results of recent laser studies by Brock and Watson (private communication, 1979) are in good agreement with this recommendation. The recommended value for the quantum yield for $O(^1D)$ production at wavelength shorter than 300 nm is unity, as reported by Amimoto et al (1978) and Kajimoto and Cvetanovic (1979). The results of Fairchild et al (1978) as well as those of Sparks et al (1979) indicate, however, that the quantum yield at those wavelengths is about 0.9. This question requires further study. Uncertainty factor for photochemical rate is 1.4.

Absorption cross sections

10^{-2} w/cm^{-1}	$10^{19}\sigma$	10^{-2} w/cm^{-1}	$10^{19}\sigma$
500-505	3.30	370-375	82.3
475-480	4.84	360-365	53.1
450-455	19.7	350-355	28.4
425-430	57.9	340-345	11.4
400-405	107	330-335	3.7
390-395	112	320-325	1.0
380-385	103		

These values averaged over 500 cm^{-1} are taken from Ackerman (1971).

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
9.hν	$NO + h\nu \rightarrow N + O$	$\Delta H = 628$ kJ/mol; $\lambda_{threshold} = 190$ nm
	NASA (1979) eval	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 (1979). This problem is closely related to the question of penetration of solar radiation in the Schumann-Runge bands of O_2. Here again the reader is referred to the original publication of Frederick and Hudson.
	CODATA (1979) eval	Data sheet on photochemistry of NO

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
10, hν	$NO_2 + h\nu \rightarrow NO + O$	ΔH = 300 kJ/mol; $\lambda_{threshold}$ = 398 nm
	NASA (1979) eval	

Quantum yields

λ/nm	Φ	λ/nm	Φ
376	.75	396	.78
378	.74	398	.72
380	.81	400	.65
382	.65	402	.57
384	.66	404	.40
386	.74	406	.30
388	.76	408	.18
390	.74	410	.14
392	.73	415	.067
394	.83	420	.023

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	2.93	310	1.76
200	2.50	320	2.54
210	3.85	330	2.99
220	3.96	340	3.88
230	2.43	350	4.10
240	.67	360	4.51
250	.28	370	5.42
260	.19	380	5.99
270	.31	390	6.00
280	.55	400	6.76
290	.82	410	5.77
300	1.17		

CODATA (1979) eval

Detailed data sheet; tabulated values of Φ and σ

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 SP 513 and NASA RP-1010 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 quantum yield values tabulated here, are from Harker et al (1977). The recommended temperature dependent cross values, tabulated here for 298K, are from Base et al (1976). Davenport's results indicate that the quantum yields themselves are temperature dependent, although the effect of temperature on the cross sections is more pronounced. Uncertainty factor for photochemical rate is 1.25

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
11. $h\nu$	$NO_3 + h\nu \rightarrow NO_2 + O$ (1) $\rightarrow NO + O_2$ (2)	ΔH = 206 kJ/mol; $\lambda_{threshold}$ = 580 nm ΔH = 13 kJ/mol; $\lambda_{threshold}$ = 9000 nm

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
500	98	600	245
510	130	610	135
520	144	620	247
530	209	630	641
540	181	640	98
550	224	650	32
560	323	660	512
570	253	670	75
580	299	680	49
590	567		

CODATA (1979) eval

Detailed data sheet on photochemistry of NO_3

These cross section values at 10nm intervals are taken from the extensive table of preferred cross section values tabulated at 1 nm intervals in Graham and Johnston (1978). These are the values which were recommended in the original report (NASA RP 1010). The second evaluation (JPL 79-27, DeMore et al (1979) recommended instead the results of Wayne et al (1978), but these later results have now been withdrawn. However, Wayne (private communication, 1978) has now an absolute NO_3 cross section measurement at 662 nm which indicates that Graham and Johnson's (1978) values should be multiplied by approximately 0.7. The NO_3 spectrum requires further study. The corresponding photodissociation rates in the troposphere with overhead sun are $J_1 = 0.10\ sec^{-1}$ and $J_2 = 0.04 sec^{-1}$ with an uncertainty factor of 3.

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R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
13. hν	$N_2O + h\nu \rightarrow N_2 + O(^1D)$	ΔH = 351 kJ/mol; $\lambda_{threshold}$ = 341 nm

NASA (1979) eval

The recommended cross section values are those of Selwyn et al (1977), who measured the temperature *dependence of the absorption* cross sections in the atmospherically relevant wavelength region. They have fitted their data for λ = 173-240 nm and T = 194-302K 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 T: temperature, Kelvin λ: nm

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

ϕ = 1 185<λ<230nm

CODATA (1979) eval

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

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Selwyn, G., Podolske, J., and Johnston, H. S., "Nitrous Oxide Ultraviolet Absorption Spectrum at Stratospheric Temperatures," Geophys. Res. Lett. 4, 427-430 (1977)

W. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
14. hν	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$ $\rightarrow N_2O_4 + O$	$\Delta H = 89$ kJ/mol; $\lambda_{threshold} = 1340$ nm $\Delta H = 242$ kJ/mol; $\lambda_{threshold} = 495$ nm

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
210	520	300	3.2
220	206	310	1.5
230	93	320	.75
240	57	330	.40
250	35	340	.27
260	21.2	350	.18
270	15.2	360	.10
280	10.7	370	.05
290	6.3	380	.01

CODATA (1979) eval

Detailed data sheet on photochemistry of N_2O_5

The cross section values listed here are taken from Graham and Johnston (1978). They supersede the values given in Johnston and Graham (1974). The products and quantum yields are not known.

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Graham, R. A., and Johnston, H. S., "The Photochemistry of NO_3 and the Kinetics of the N_2O_5-O_3 System," J. Phys. Chem. 82, 254-268 (1978)

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

H. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
23, hν	$H_2O_2 + h\nu \rightarrow HO + HO$	ΔH = 207 kJ/mol; $\lambda_{threshold}$ = 578 nm

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
210	37.3	290	1.2
220	27.0	300	0.71
230	19.2	310	0.42
240	13.2	320	0.24
250	9.0	330	0.15
260	5.6	340	0.09
270	3.5	350	0.05
280	2.1		

CODATA (1979) eval ϕ = 1 200< λ < 350 nm

There are now two measurements of the absorption cross sections of H_2O_2 vapor in the 300 nm region (Molina et al (1977) and Lin et al (1978)). The recommended values are the mean of the two sets of data. Uncertainty factor for photochemical rate is 1.4

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
25. hν	$HNO_2 + h\nu \rightarrow HO + NO$	$\Delta H = 202$ kJ/mol; $\lambda_{threshold} = 590$ nm
	NASA (1979) eval	Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
310	0.0	355	24.6
315	0.4	360	6.8
320	2.1	365	13.3
325	4.0	370	11.9
330	7.3	375	2.7
335	6.4	380	7.8
340	10.5	385	19.0
345	8.5	390	1.2
350	6.8	395	0.0

CODATA (1979) eval — $\phi = 1$ $300 < \lambda < 400$ nm

Also tablulated values of σ averaged over 5 nm intervals

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 cross section values given here at 5 nm intervals are taken from the extensive table of preferred cross section values tabulated at 1nm intervals in that reference. No recommendation is given for the 200-300 nm range. Uncertainty factor for photochemical rate is 1.4

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

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Stockwell, W. R., and Calvert, J. G., "The Near Ultraviolet Absorption Spectrum of Gaseous HONO and N_2O_3." J. Photochem. 8, 193-203 (1978)

R. F. Hampson

June 1979

No.	Reaction/Reference	Photochemical Data
26. $h\nu$	$HNO_3 + h\nu \rightarrow HO + NO_2$	ΔH = 200 kJ/mol; $\lambda_{threshold}$ = 598 nm
	CODATA (1979) eval	Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	1320	260	1.90
200	550	270	1.63
210	97	280	1.14
220	14.4	290	0.63
230	5.6	300	0.28
240	2.6	310	0.09
250	1.9	320	0.02

$\phi = 1$ $\quad 190 < \lambda < 320$nm

The recommended cross section values are those of Johnston and Graham (1973).
The recommended quantum yield is based on result of Johnston et al (1974).
Uncertainty factor for photochemical rate is 1.2

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Johnston, H. S., Chang, S.-G., and Whitten, G., "Photolysis of Nitric Acid Vapor," J. Phys. Chem. 78, 1-7 (1974)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data

26a, hν $HC_2NC_2 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	1610	270	28
200	640	280	18
210	250	290	10.9
220	154	300	6.2
230	95	310	4.2
240	68	320	3.0
250	51	330	2.2
260	40		

CODATA (1979) eval — Detailed data sheet on photochemistry of HC_2NC_2

Two groups have investigated the UV spectrum of HC_2NC_2: Graham et al (1978) and Cox and Patrick (1979). Only the former reports cross section values in the critical wavelength region for atmospheric photodissociation beyond 290 nm. The results of Graham et al, which provides the basis of this recommendation, are listed here. The two sets of results are in reasonable agreement between 205 and 260 nm, but at 195 nm the cross-section value obtained by Graham et al is more than twice the value reported by Cox and Patrick. Additional studies of the HC_2NC_2 spectrum would be desirable.

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Cox, R. A., and Patrick, K., "Kinetics of the Reaction of HC_2 + $NC_2(+M)$ + HC_2NC_2 using Molecular Modulation Spectrometry. Int. J. Chem. Kinet., 11, 635-648 (1979)

Graham, R. A., Winer, A. M., and Pitts, J. N. Jr., "Ultraviolet and Infrared Absorption Cross Sections of Gas Phase HC_2NC_2." Geophys. Res. Lett. 11, 909-911 (1978)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
28, hν	$SO_2 + h\nu \rightarrow$ products NASA (1979) eval	The photodissociation of SO_2 in the atmosphere as well as the potential role of excited states of SO_2 in atmospheric chemistry has been rviewed recently by Calvert et al (1978) and will not be repeated here

REFERENCES

Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, O. P., "Mechanism of the Homogeneous Oxidation of Sulfur Dioxide in the Troposphere," Atmos. Environ. 12, 197 (1978)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
34c,hν	$CdS + h\nu \rightarrow Cd + S$	$\Delta H = 303$ kJ/mol; $\lambda_{threshold} = 395$ nm
	NASA (1979) eval	

Absorption cross sections

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

The recommended cross section values, listed here 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 arcund 200 nm, although they are likely to be unity. The results of Klemm et al (1975) indicate that oxygen atoms are not formed in the photodissociation of CdS; Cd and S are the only products. The uncertainty factor for the photochemical rate is 1.25

REFERENCES

Breckenridge, W. H., and Taube, H., "Ultraviolet Absorption Spectrum of Carbonyl Sulfide," J. Chem. Phys. 52, 1713-1715 (1970)

Chou, C. C., Ruiz, R. V., and Rowland, F. S., to be published in Geophys. Res. Lett. (1979)

Klemm, R. B., Glicker, S., and Stief, L. J., "Relative Quantum Yield for the Production of C-Atom and S-Atom from the Photodissociation of CCS in the Vacuum UV," Chem. Phys. Lett. 33, 512-517 (1975)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1975 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
36, hν	$ClO + h\nu \rightarrow Cl + O$	$\Delta H = 264$ kJ/mol; $\lambda_{threshold} = 453$ nm
	NASA (1979) eval	There are new measurements of ClO absorption cross sections in the 270-312 nm region, by Jourdain, et al (1978). Earlier absorption cross section data have been reviewed by Watson (1977). 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

REFERENCES

Coxon, J. A., Jones, W. E., and Ramsey, D. A., 12th International Symposium on Free Radicals, Laguna Beach, California. (1976)

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Langhoff, S. R., Jaffe, R. L., and Arnold, J. O., "Effective Cross Sections and Rate Constants for Predissociation of ClO in the Earth's Atmosphere," J. Quant. Spectrosc. Radiat. Transfer 18, 227-235 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
37, hν	$ClClO + h\nu \rightarrow Cl + ClO(^3P)$	$\Delta H = 252$ kJ/mol; $\lambda_{threshold} = 464$ nm
	$\rightarrow Cl + ClO(^1D)$	$\Delta H = 448$ kJ/mol; $\lambda_{threshold} = 267$ nm
	Watson (1977) review	

Absorption cross sections

λ/nm	$10^{18}\sigma$
225	2.6
235	7.8
245	12.7
255	12.4
265	7.3
275	3.4

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
37, hν	$ClClO + h\nu \rightarrow Cl + ClO(^3P)$	$\Delta H = 249$ kJ/mol; $\lambda_{threshold} = 480$ nm
	$\rightarrow Cl + ClO(^1D)$	$\Delta H = 439$ kJ/mol; $\lambda_{threshold} = 272$ nm
	Watson (1977) review	Absorption cross section data

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
476	0.54	183	360
469	0.80	163	1420
460	0.74	160	1160
454	5.8	153	1150
446	34.0	152	1110
440	26.5	151	1070
351	1140	150	688

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

No. Reaction/Reference — Photochemical Data

38, hν ClO_3 + hν → products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{18}\sigma$	λ/nm	$10^{18}\sigma$
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

These absorption cross sections of chlorine trioxide, ClO_3, for the 200-350 nm range have been 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.

REFERENCES

Goodeve, C. F., and Richardson, F. D., "The Absorption Spectrum of Chlorine Trioxide and Chlorine Hexoxide," Trans. Faraday Soc. 33, 453-457 (1937)

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R. F. Hampson

June 1979

No.	Reaction/Reference	Photochemical Data
39, hν	HCl + hν → H + Cl	ΔH = 428 kJ/mol; $\lambda_{threshold}$ = 280 nm
	Watson (1977) review	Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
140	211	185	31.3
145	281	190	14.5
150	345	195	6.18
155	382	200	2.56
160	332	205	0.98
165	248	210	0.39
170	163	215	0.14
175	105	220	0.05
180	58.8		

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

No.	Reaction/Reference	Photochemical Data
39P,hν	BF + hν → B + F	ΔH = 567 kJ/mol; $\lambda_{threshold}$ = 210 nm
	NASA (1979) eval	The ultraviolet absorption spectrum of BF has been studied by Safary et al (1951). The onset of absorption occurs beyond 170 nm, so that photodissociation of BF will be unimportant in the stratosphere

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the *June 1979 Harpers Ferry Workshop*).

Safary, E., Romand, J., and Vodar, B., "Ultraviolet Absorption Spectrum of Gaseous Hydrogen Fluoride," J. Chem. Phys. 19, 379-380 (1951)

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data
40, hν	HOCl + hν → HO + Cl	ΔH° = 233 kJ/mol; $\lambda_{threshold}$ = 513 nm

NASA (1979) eval

Absorption cross sections

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

CODATA (1979) eval

Detailed data sheet on photochemistry of HOCl

Knauth et al (1979) have recently measured absorption cross sections of HOCL using essentially the same technique as Molina and Molina (1978) except for a higher temperature, which allowed them to obtain a more accurate value for the equilibrium constant K_{eq} for the H_2O-Cl_2O-HOCl system. The cross section values from Molina and Molina's measurements, recalculated using the new K_{eq}, are in excellent agreement with the results of Knauth et al. The recommended values, taken from this later work, are given here. Molina et al (1979a), by monitoring directly OH radicals produced by laser photolysis of HOCl, obtain an absorption cross section value of ~6 x 10^{-20} cm^2 around 310 nm, again in excellent agreement with the data of Knauth et al (1979). In contrast, the theoretical predictions of Jaffe and Langhoff (1978) indicate negligible absorption at those wavelengths. The reason is not known, although it should be pointed out that no precedent exists to validate the theoretical approach for this particular type of problem.

REFERENCES

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Jaffe, R. L., and Langhoff, S. R., "Theoretical Study of the Photodissociation of HOCl," J. Chem. Phys. 68, 1638-1648 (1978)

Knauth, H.-D., Alberti, H., and Clausen, H., "Equilibrium Constant of the Gas Reaction $Cl_2O + H_2O = 2HOCl$ and the Ultraviolet Spectrum of HOCl, J. Phys. Chem. 83, 1604-1612 (1979)

Molina, L. T., and Molina, M. J., "Ultraviolet Spectrum of HOCl," J. Phys. Chem. 82, 2410-2414 (1978)

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R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data

41a,hν $HClO_4 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	405	240	1.4
195	230	245	0.78
200	130	250	0.40
205	78	255	0.21
210	45	260	0.12
215	25	265	0.06
220	14	270	0.03
225	8.0	275	0.02
230	4.4	280	0.01
235	2.5		

The results tabulated here are from the study of Molina et al (1979b)

REFERENCES

Molina, L. T., Beaman, L., Cook, J., and Molina, M. J., "Ultraviolet Absorption Spectrum of $HClO_4$ Vapor, submitted to J. Photochem. 1979b.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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Photochemical Data

No.	Reaction/Reference
42, hv	NOCl + hv → Cl + NO
	NASA (1979) eval

ΔH = 156 kJ/mol; $\lambda_{threshold}$ = 768 nm

Absorption cross sections

λ/nm	10^{19} σ	λ/nm	10^{19} σ
180	527	280	0.10
200	657	300	0.95
210	318	320	1.21
220	117	340	1.37
230	37.7	360	1.22
240	13.4	380	0.83
260	1.8	400	0.51

Nitrosy 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) 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 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.

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D. F. Hampson
June 1979

No. Reaction/Reference — Photochemical Data

43. hν $ClNO_2 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	2690	300	15.4
200	455	310	13.2
210	339	320	10.2
220	342	330	7.11
230	236	340	4.81
240	140	350	3.06
250	98.5	360	1.82
260	63.7	370	1.07
270	37.3	380	0.63
280	23.1	390	0.38
290	18.0	400	0.21

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. The recommended cross sections are 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.

REFERENCES

Illies, A. J., and Takacs, G. A., "Gas Phase Ultra-Violet Photoabsorption Cross-Sections for Nitrosyl Chloride and Nitryl Chloride," J. Photochem. 6, 35-42 (1976)

Martin, H., and Gareis, H., "Die Kinetik der Reaktion von ClO_2 mit NO_2 in der Loesungsphase," Z. Elektrochem. 60, 959-964 (1956)

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R. F. Hampson
June 1979

No. Reaction/Reference — Photochemical Data

43. hν $ClONO + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections at 231 K

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
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

Measurements in the near-ultraviolet of the cross sections at 231 K of chlorine nitrite ($ClONO$) have been made by Molina and Molina (1977). Their results are given here. 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 80 kJ so that chlorine atoms are likely photolysis products.

REFERENCES

Molina, L. T., and Molina, M. J., "Ultraviolet Absorption Spectrum of Chlorine Nitrite, $ClONO$," Geophys. Res. Lett. 4, 83-86 (1977)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No. Reaction/Reference — Photochemical Data

43a. $NO_3Cl + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$ 227K	$10^{20}\sigma$ 296K	λ/nm	$10^{20}\sigma$ 227K	$10^{20}\sigma$ 296K
190	555	589	330	0.353	0.514
200	293	307	340	0.246	0.323
210	330	329	350	0.198	0.246
220	348	344	360	0.170	0.208
230	206	210	370	0.142	0.162
240	98.5	106	380	0.113	0.122
250	52.6	57.7	390	0.090	0.090
260	30.7	34.6	400	0.056	0.064
270	18.3	21.5	410	-	0.044
280	10.4	11.9	420	-	0.027
290	5.45	6.36	430	-	0.016
300	2.51	3.30	440	-	0.009
310	1.28	1.69	450	-	0.005
320	0.630	0.895			

CODATA (1979) eval — Detailed data sheet on photochemistry of $ClONO_2$

The cross sections recommended in NASA RP 1010 were based on measurements by Rowland, Spencer and Molina (1976). Molina and Molina (1979) 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 ~ 15% lower than the earlier measurements. The recommended values listed here are taken from the newer study. 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 (1979), 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. Uncertainty factor for photochemical rate is 1.25.

REFERENCES

Chang, J. S., Barker, J. R., Davenport, J. E., and Golden, D. M. "Chlorine Nitrate Photolysis by a new Technique: Very Low Pressure Photolysis," Chem. Phys. Lett. 60, 385-390 (1979)

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

Molina, L. T., and Molina, M. J., "Chlorine Nitrate Ultraviolet Absorption Spectrum at Stratospheric Temperatures," J. Photochem. 11, 139-144 (1979)

Rowland, F. S., Spencer, J. E., and Molina, M. J., "Stratospheric Formation and Photolysis of Chlorine Nitrate," J. Phys. Chem. 80, 2711-2713 (1976)

Smith, W. S., Chou, C. C., and Rowland, F. S., "The Mechanism for Ultraviolet Photolysis of Gaseous Chlorine Nitrate at 302.5 nm," Geophys. Res. Lett. 4, 517-519 (1977)

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data

43aBr,hν $BrClNO_2 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
190	1300	300	19
200	720	310	15
210	320	320	12
220	240	330	10
230	190	340	8.7
240	130	350	7.7
250	78	360	6.2
260	48	370	4.9
270	34	380	4.0
280	29	390	2.8
290	24		

CODATA (1979) eval — Detailed data sheet on photochemistry of $BrClNO_2$

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 here. By analogy with $ClClNO_2$, some temperature dependence may be expected. The photolysis products are not known. The uncertainty factor for the photochemical rate is 1.4

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Spencer, J. E., and Rowland, F. S., "Bromine Nitrate and its Stratospheric Significance," J. Phys. Chem. 82, 7-10 (1978)

R. F. Hampson

June 1979

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data
44, hν	$Cl_2 + h\nu \rightarrow Cl + Cl$	$\Delta H = 240$ kJ/mol; $\lambda_{threshold} = 500$ nm
	Watson (1977) review	Absorption cross sections

λ/nm	$10^{21}\sigma$
240	0.8
260	2.3
280	27
300	120
320	236
340	236
360	131
380	49
400	19
420	9.9
440	5.3

REFERENCES

Watson, R. T., "Rate Constants for Reactions of ClO_x of Atmospheric Interest," J. Phys. Chem. Ref. Data 6, 871-918 (1977)

R. F. Hampson
May 1978

CHEMICAL KINETICS DATA SURVEY

PREPARED AT CHEMICAL KINETICS DATA CENTER, NATIONAL BUREAU OF STANDARDS

No.	Reaction/Reference	Photochemical Data

48. $h\nu$ $CH_2O + h\nu \rightarrow H + HCO$ (1)
$\rightarrow H_2 + CO$ (2)

CODATA (1979) eval

$\Delta H = 358$ kJ/mol; $\lambda_{threshold} = 334$ nm
$\Delta H = -9$ kJ/mol

Absorption cross sections and quantum yields for 300K, 1 atm air

λ/nm	$10^{20}\sigma$	Φ_1	Φ_2
280	2.4	0.63	0.37
290	3.2	0.73	0.27
300	3.3	0.77	0.23
310	3.1	0.76	0.24
320	2.4	0.63	0.37
330	2.4	0.31	0.64
340	2.0	0	0.67
350	0.8	0	0.40
360	0.2	0	0.14

These recommendations accepted for NASA (1979) evaluation

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

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No. Reaction/Reference — Photochemical Data

53. hν $CH_3OOH + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	10^{20} σ	λ/nm	10^{20} σ
210	37.5	290	0.90
220	22.0	300	0.58
230	13.8	310	0.34
240	8.8	320	0.19
250	5.8	330	0.11
260	3.8	340	0.06
270	2.5	350	0.04
280	1.5		

Molina and Arguello (1979) have measured the absorption cross sections of CH_3OOH. Their results are given here. The uncertainty factor for the photochemical rate is 1.4

REFERENCES

Molina, M. J., and Arguello, G., "Ultraviolet Absorption Spectrum of Methylhydroperoxide Vapor," Geophys. Res. Lett. 6, 953-955 (1979)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

CHEMICAL KINETICS DATA SURVEY

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No.	Reaction/Reference		Photochemical Data
S4, hν	$CH_3ONO + h\nu \rightarrow CH_3O^* + NO$ (a) $\rightarrow$ isomer (b) $\rightarrow CH_2O + HNO$ (c) $\rightarrow CH_2O + H + NO$ (d)		
	*Heicklen (1973) review	298	$k_a/k = 0.76 \pm 0.02$, $\lambda = 366$nm
		298	$k_b/k = 0.24 \pm 0.04$, $\lambda = 366$nm
		298	$(k_c + k_d)/k < 0.02$, $\lambda = 366$nm
			$k = k_a + k_b + k_c + k_d$

REFERENCES

Heicklen, J., "Photochemical and Rate Data for Methyl Nitrite, Methoxy and *Methylperoxy*," *Chemical Kinetics Data Survey V.* Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions, NBSIR 73-206, D. Garvin, Ed., National Bureau of Standards, Washington, D.C. (1973) pages 43-48

R. F. Hampson
May 1978

No.	Reaction/Reference	Photochemical Data
60b,hν	$CF_3Cl + h\nu \rightarrow$ products NASA (1979) eval	Absorption cross sections

λ/nm	$10^{20}\sigma$
184.6	0.36
186.0	0.31
187.8	0.23
189.6	0.168
191.4	0.126
193.2	0.090
195.1	0.064
197.0	0.041
199.0	0.026
201.0	0.017
203.0	0.012

The cross section values given here are taken from the work of Chou et al (1978)

REFERENCES

Chou, C. C., Milstein, R. J., Smith, W. S., Vera-Ruiz, H. V., Molina, M. J., and Rowland, F. S., "Stratospheric Photodissociation of Several Saturated Perhalo Chlorofluorocarbon Compounds in Current Technological Use (Fluorocarbons-12,-113,-114, and -115)," J. Phys. Chem. 82, 1-7 (1978)

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data

61, hν $CF_2Cl_2 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections at 296K

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
186.0	106.0	205.1	2.59
187.8	85.4	207.3	1.50
189.6	64.6	209.4	0.85
191.4	48.7	211.6	0.51
193.2	35.3	213.9	0.29
195.1	24.5	216.2	0.17
197.0	16.6	218.6	0.095
195.0	10.8	221.0	0.05
201.0	6.87	223.5	<0.05
203.0	4.36	226.0	<0.05

$$\sigma_T = \sigma_{296}\exp[3.6 \times 10^{-4}(\lambda-184.9)(T-296)]$$

Where: σ_{296} : cross section at 296 K
λ : nm
T : temperature, Kelvin

CODATA (1979) eval

Detailed data sheet on photochemistry of CF_2Cl_2

The recommended values remain unchanged from NASA RP-1010. They are the mean of the values reported by Chou et al (1977), Robbins and Stolarski (1976) and Bass and Ledford (1978). The formula for temperature dependence is from Chou et al (1977). Vanlaethem-Meuree et al (1978) measured 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 (1978) and Chou et al (1977); they are, however, in agreement with the values at 214 nm reported by Rehbert and Ausloos (1975).

REFERENCES

Bass, A. M., and Ledford, A. E. Jr., "Ultraviolet Photoabsorption Cross Sections of CF_2Cl_2 and $CFCl_3$ as a Function of Temperature," pages 282-284 in "12th Informal Conference on Photochemistry," M. J. Kurylo and W. Braun, Eds., Nat. Bur. Stand. (U.S.), Spec. Publ. 526 (1978)

Chou, C. C., Smith, W. S., Vera Ruiz, H., Moe, K., Crescentini, G., Molina, M. J., and Rowland, F. S., "The Temperature Dependences of the Ultraviolet Absorption Cross Sections of CCl_2F_2 and CCl_3F, and their Stratospheric Significance," J. Phys. Chem. 81, 286-290 (1977)

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Rebbert, R. E., and Ausloos, P. J., "Photodecomposition of $CFCl_3$ and CF_2Cl_2." J. Photochem. 4, 419-434 (1975)

Robbins, D. E., and Stolarski, R. S., "Comparison of Stratospheric Ozone Destruction by Fluorocarbons 11, 12, 21 and 22," Geophys. Res. Lett. 3, 603-606 (1976)

Vanlaethem-Meuree, N., Wisemberg, J., and Simon, P. C., "Influence de la Température sur les Sections Efficaces D'absorption des Chlorofluorométhanes dans l'ultraviolet," Bull. Acad. Roy. Belgique, Cl. Sci. 64, 42-51 (1978)

R. F. Hampson
June 1979

AD-A091 631 NATIONAL BUREAU OF STANDARDS WASHINGTON DC CHEMICAL --ETC F/G 4/1
CHEMICAL KINETIC AND PHOTOCHEMICAL DATA SHEETS FOR ATMOSPHERIC --ETC(U)
APR 80 R F HAMPSON DOT-FA79WAI-005

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6 OF 6
AD A091631

No.	Reaction/Reference	Photochemical Data

62, hν $CFCl_3 + h\nu \rightarrow$ products

NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$			
	213K	232K	252K	298K
186.0	-	-	-	243.0
187.8	-	-	-	217.0
189.6	-	-	-	186.0
191.4	161.0	161.0	164.0	159.0
193.2	137.0	137.0	141.0	133.0
195.1	110.0	110.0	114.0	111.0
197.0	88.5	88.5	91.3	90.3
199.0	69.1	69.1	72.1	73.0
201.0	53.1	54.3	56.6	57.3
203.0	40.2	41.1	43.0	45.2
205.1	28.6	30.0	31.7	33.3
207.3	19.8	21.1	22.6	23.9
209.4	13.3	14.2	15.2	16.8
211.6	8.5	9.1	9.9	11.5
213.9	-	5.7	6.4	7.6
216.2	-	3.4	3.9	5.0
218.6	-	2.0	2.3	3.1
221.0	-	-	-	2.0
223.5	-	-	-	1.2
226.0	-	-	-	0.8

CODATA (1979) eval

Detailed data sheet on photochemistry of $CFCl_3$

The recommended values remain unchanged from NASA RP-1010. The 298 K values are the mean of the values reported by Chou et al (1977), Robbins and Stolarski (1976) and Bass and Ledford (1978). The low temperature data of Chou et al (1977) are given here. The low temperature results of Bass and Ledford (1978) and of Vanlaethem-Meuree et al (1978) are in good agreement. The temperature effect at stratospherically important wavelengths is much smaller than for CF_2Cl_2, but no such simple expression exists for $CFCl_3$.

REFERENCES

Basco, A. M., and Ledford, A. E. Jr., "Ultraviolet Photoabsorption Cross Sections of CF_2Cl_2 and $CFCl_3$ as a Function of Temperature," pages 282-284 in "12th Informal Conference on Photochemistry," M. J. Kurylo and W. Braun, Eds., Nat. Bur. Stand. (U.S.), Spec. Publ. 526 (1978)

Chou, C. C., Smith, W. S., Vera Ruiz, H., Moe, K., Crescentini, G., Molina, M. J., and Rowland, F. S., "The Temperature Dependences of the Ultraviolet Absorption Cross Sections of CCl_2F_2 and CCl_3F, and their Stratospheric Significance," J. Phys. Chem. 81, 286-289 (1977)

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NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Robbins, D. E., and Stolarski, R. S., "Comparison of Stratospheric Ozone Destruction by Fluorocarbons 11, 12, 21 and 22," Geophys. Res. Lett. 3, 603-606 (1976)

Vanlaethem-Meuree, M., Wisemberg, J., and Simon, P. C., "Influence de la Température sur les Sections Efficaces D'absorption des Chlorofluorométhanes dans l'ultraviolet," Bull. Acad. Roy. Belgique, Cl. Sci. 64, 42-51 (1978)

R. F. Hampson
June 1979

No. Reaction/Reference — Photochemical Data

63. hν $CCl_4 + h\nu \rightarrow$ products

CODATA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$	λ/nm	$10^{20}\sigma$
176	1007	208	52.0
180	772	212	39.7
184	450	216	27.2
188	218	220	17.0
192	98.9	224	9.6
196	68.2	228	5.5
200	64.8	232	3.0
204	60.4	236	1.5

REFERENCES

CODATA(1979). Recommendations of the CODATA Task Group on Chemical Kinetics. To be published in the Journal of Physical and Chemical Reference Data.

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June 1979

No.	Reaction/Reference	Photochemical Data

68.hν CH_3CCl_3 + hν → products

This survey

Absorption cross sections

λ/nm	$10^{20}\sigma$ (a)	$10^{20}\sigma$ (b)
186.0	325.0	305.0
187.8	284.0	225.0
189.6	246.0	200.0
191.4	215.0	175.0
193.2	189.0	152.0
195.1	166.0	129.0
197.0	146.0	108.0
199.0	128.0	88.0
201.0	111.0	72.5
203.0	95.4	59.0
205.1	80.5	46.0
207.3	67.9	35.5
209.4	51.1	25.8
211.6	39.4	19.0
213.9	28.1	12.8
216.2	19.6	8.4
218.6	12.5	5.4
221.0	8.3	3.6
223.5	5.1	2.3
226.0	2.9	1.5

(a) NASA (1979)

(b) Vanlaethem-Meuree et al (1979)

No recommendation is given here. Two sets of cross section data are tabulated. The values in column(a) are the NASA (1979) values which are taken from F. S. Rowland (private communication, 1976). The values in column(b) are taken from the very recent study by Vanlaethem-Meuree et al (1979). These latter values are significantly lower than the NASA (1979) values and yield a calculated photodissociation rate which is nearly a factor of two smaller

REFERENCES

NASA (1979). Recommendations of the NASA Panel for Data Evaluation, published in NASA RP 1049 "The Stratosphere: Present and Future," R. D. Hudson and E. I. Reed, Editors, Dec. 1979 (report of the June 1979 Harpers Ferry Workshop).

Vanlaethem-Meurée, N., Wisemberg, J., and Simon, P. C., "Ultraviolet Absorption Spectrum of Methylchloroform in the Vapor Phase," Geophys. Res. Lett. 6, 451-454 (1979)

R. F. Hampson
June 1979

No.	Reaction/Reference	Photochemical Data

68.hν CF_2O + hν → products
$CFClO$ + hν → products
CCl_2O + hν → products
NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$		
	CCl_2O	$CFClO$	CF_2O
184.9	204.0		4.7
186.0	189.0	15.6	5.5
187.8	137.0	14.0	5.2
189.6	117.0	13.4	4.5
191.4	93.7	12.9	4.0
193.2	69.7	12.7	3.3
195.1	52.8	12.5	2.8
197.0	41.0	12.4	2.3
199.0	31.8	12.3	1.9
201.0	25.0	12.0	1.4
203.0	20.4	11.7	1.1
205.1	16.9	11.2	0.86
207.3	15.1	10.5	0.65
209.4	13.4	9.7	0.48
211.6	12.2	9.0	0.36
213.9	11.7	7.9	0.26
216.2	11.6	6.9	0.21
218.6	11.9	5.8	0.15
221.0	12.3	4.8	0.12
223.5	12.8	4.0	0.10
226.0	13.2	3.1	0.08

CODATA (1979) Detailed data sheets on photochemistry of these species

The absorption cross sections of CCl_2O (phosgene), $CFClO$, and CF_2O are taken from the work of Chou et al (1977a). The spectrum of CF_2O shows considerable structure. The values listed here 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 $CFClO$ shows less structure, and the CCl_2O spectrum is a continuum; its photodissociation quantum yield is unity (Calvert and Pitts, 1967)

REFERENCES

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No. Reaction/Reference — Photochemical Data

68.hν $CClF_2CF_3 + h\nu \rightarrow$ products
$CClF_2CClF_2 + h\nu \rightarrow$ products
$CClF_2CCl_2F + h\nu \rightarrow$ products
NASA (1979) eval

Absorption cross sections

λ/nm	$10^{20}\sigma$		
	$CClF_2CF_3$	$CClF_2CClF_2$	$CClF_2CCl_2F$
186.0	0.61	10.0	105.0
187.8	0.49	7.91	85.0
189.6	0.36	5.97	68.9
191.4	0.27	4.44	53.8
193.2	0.20	3.13	41.0
195.1	0.14	2.52	30.0
197.0	0.093	1.54	21.3
199.0	0.066	1.00	14.9
201.0	-	0.67	10.4
203.0	-	0.44	7.0
205.1	-	0.30	4.7
207.3	-	0.18	3.2
209.4	-	0.11	2.05
211.6	-	0.063	1.26
213.9	-	0.043	0.78
216.2	-	-	0.47
218.6	-	-	0.29

The cross section values given here for $CClF_2CF_3$ (fluorocarbon 115) and for $CClF_2CClF_2$ (fluorocarbon 114) are the mean of the results reported by Chou et al (1978) and by D. E. Robbins, private communication (1976). The values given here for $CClF_2CCl_2F$ (fluorocarbon 113) are those reported by Chou et al (1978)

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