Chemical Kinetic Data Sheets for High-Temperature Reactions. Part II

N. Cohen, and K. R. Westberg

View Online

Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions
Journal of Physical and Chemical Reference Data **12**, 531 (1983); https://doi.org/10.1063/1.555692

Evaluated Kinetic Data for Combustion Modelling
Journal of Physical and Chemical Reference Data **21**, 411 (1992); https://doi.org/10.1063/1.555908

Chemical Kinetic Data Base for Propellant Combustion I. Reactions Involving NO, NO$_2$, HNO, HNO$_2$, HCN and N$_2$O
Journal of Physical and Chemical Reference Data **20**, 609 (1991); https://doi.org/10.1063/1.555890

Chemical Kinetic Data Sheets for High-Temperature Reactions. Part II

N. Cohen and K. R. Westberg

Space and Environment Technology Center, The Aerospace Corporation, P. O. Box 92957, Los Angeles, CA 90009

Rate coefficient measurements for over fifty gas-phase bimolecular reactions were critically evaluated and compared to theoretical calculations. The results of this work are summarized here in forty-nine Data Sheets, one sheet for each reaction or set of reactions of a single pair of reagents. The reactions chosen are of interest in propulsion, combustion, and atmospheric chemistry. Each Data Sheet consists of two pages that include a brief resumé of the important experimental measurements and theoretical calculations, a graphical presentation of the data, a recommended rate coefficient expressed as a function of temperature, $k(T) = AT^n\exp(-B/T)$, with probable uncertainty limits, a discussion of the basis for the recommendation, an equilibrium constant and a rate coefficient for the reverse reaction where applicable, and pertinent references.

Contents

1. Introduction

In a previous paper[1] we presented Chemical Kinetic Data Sheets for twenty-seven gas-phase reactions, together with a discussion of the procedures used in evaluating the data and arriving at the recommended rate expressions.

In this second compilation, we present an additional forty-nine Data Sheets for as many gas-phase bimolecular reactions (or sets of reactions of the same reagents leading to different products). The reactions fall into three categories: (1) reactions of O atoms with alkanes; (2) reactions of OH radicals with haloalkanes; and (3) reactions of importance in the O/NH$_3$ system. The process of evaluating these reactions and preparing the Data Sheets resulted in the generation of a good deal more material than could be fitted into the concisely formatted Data Sheets themselves, and consequently separate journal papers were prepared and published.[2,3,4,5,6] These studies are cited individually in the appropriate Data Sheets.

A detailed guide to the use of the Data Sheets was published in Ref. 1 and should be consulted. Here only the salient points are noted.

Reaction Title. Titles for elementary reactions are always written in the exothermic direction. A double arrow in the title indicates that an equilibrium constant and reverse rate coefficient are also recommended. A single arrow indicates that a reverse rate coefficient is not recommended. This can be for one of two reasons: (1) the reverse reaction is sufficiently endothermic that it will never be important; or (2) the forward rate coefficient is the sum of rate coefficients for more than one elementary reaction. In the latter case, the rate coefficient is identified as k_A; otherwise, forward rate coefficients are k_1, k_2, etc., and reverse rate coefficients (endothermic direction), k_{-1}, k_{-2}, etc.

Thermochemical Data. In most cases, enthalpy of formation and entropy data are taken from the JANAF Thermochemical Tables, 3rd edn.[7] An equilibrium constant has been calculated from those data for all reactions identified by a double arrow (see preceding paragraph). Following the identification of data sources, a statement is given describing how well this equilibrium constant expression fits the calculated data (typically within 5 to 10% over a temperature range of 298 to 3000 K). This statement of accuracy of fit has no relation to the accuracy of the calculated values of $K(T)$ themselves. The analytic expression of K in the form $K(T) = AT^n\exp(-B/T)$ is given above the graph of the experimental data, together with an estimate of the uncertainty in $\log K(T)$. This uncertainty is estimated from the uncertainties in ΔH°_{298} and in ΔS°_{298}. The uncertainty in $K(T)$ at low temperatures is due principally to the uncertainty in ΔH°_{298}; at high temperatures it is due to uncertainties in S and C_p.

Measurements/Graph. Each Data Sheet contains a graph on which either $\log k$ or $\log k_{-1}$ is plotted vs

$1000/T$. The graph includes the recommended value(s) and those experimental data thought to be the most accurate and precise. For a well-studied reaction, the standard for accuracy is higher than for a less well-studied reaction. In some cases, experimental data have been reanalyzed, and the reanalyzed data are plotted on the graph. The Measurements section of the Data Sheet gives the reasons for preferring some measurements to others, as well as the reasons why some of the data may have been reanalyzed. At the bottom of the graph is a date that indicates when the literature search was concluded.

Calculations. In the present state of chemical kinetics, a good measurement is superior to the best calculation. Calculations are valuable, nonetheless, for extrapolating experimental data to temperatures for which no measurements exist; for evaluating experiments of dubious validity; or for estimating rate coefficients for homologous, unmeasured reactions.

We routinely compare measured rate coefficients to our own transition-state theory (TST) calculations. TST is applicable to reactions that occur on a potential energy surface (PES) that has a single saddle point separating reactants from products. Among other things, use of TST requires information about the shape of the PES in the vicinity of the saddle point as well as the height of the saddle point, which is often termed the classical barrier to reaction. The equations of TST are given in Ref. 1; below we summarize the assumptions we routinely make in applying these equations to reactions for which there is little information about their PES.

As has been pointed out many times, TST is basically a classical theory, accurate only if all trajectories cross the saddle point only once and if quantum mechanical effects such as tunneling are unimportant. A correction factor, κ, called the transmission coefficient, is added to the theory to account for trajectories that cross the saddle more than once, for quantum mechanical tunneling, and for other quantum effects not accounted for by the substitution of quantum-mechanical partition functions for the classical ones in terms of which the theory is formulated.

One of the principal difficulties in using TST is a lack of a general procedure for calculating κ. We assume in our calculations that κ has the form $\kappa = \exp(C'/T)$, where C' is a constant. This assumption is equivalent to assuming that tunneling, barrier recrossing, and other nonidealities together lower the effective reaction barrier without changing the shape of the PES in the vicinity of the saddle point. This assumption appears to account accurately (i.e., with $\pm 25\%$ for $1000 < T/K < 200$) for tunneling and other quantum effects in the H + *para*-$H_2 \rightarrow$ *ortho*-H_2 + H reaction calculated on the surface of Porter and Karplus,[8] but it is unlikely to be valid for all reactions. For this reason, we usually use TST calculations to extrapolate data to high temperatures where quantum effects are less important, rather than to lower temperatures, where tunneling could be extensive. As is explained in Ref. 1, the effective barrier height is derived from measured values of the rate coefficient. (In our formulation of TST, the effective barrier = $\Delta H_0^{\ddagger} - RC'$,

where R is the gas constant and $\Delta H_0^{\ddagger}$ is the enthalpy of activation at zero kelvin.) The shape of the PES is estimated so as to be maximally consistent with experimental data and with *ab initio* calculations or sound chemical principles.

Occasionally, the experimental data suggest that the simple expression $\kappa = \exp(C'/T)$ may be inadequate at low temperatures. In such cases we used instead $\kappa = \Gamma\exp(C''/T)$, where C'' is a constant and Γ is an explicit tunneling correction. We have used either the Wigner or the Eckart correction, choosing the one that better explains the data.

In spite of its uncertainties, TST is useful in extrapolating and evaluating data because rate coefficients calculated with it often depend only weakly on the exact shape of the PES near the saddle point. An imperfect TST calculation will usually be more reliable than the simple two-parameter Arrhenius expression commonly used in the past.

Recommended Rate Coefficients and Uncertainties. Recommended rate coefficients are always expressed in the form $k = AT^n\exp(-B/T)$, where A, n, and B are constants. The quotient of forward and reverse rate coefficients is taken to be equal to the equilibrium constant for the reaction: $k_1/k_{-1} = K(T)$. The uncertainties assigned to the logarithms of the recommended rate coefficients are subjective, rather than statistically precise, because systematic errors in chemical kinetics are almost always larger than the statistically calculable random errors.

2. Acknowledgments

3. References

[1]N. Cohen and K. R. Westberg, J. Phys. Chem. Ref. Data 12, 531 (1983).

[2]N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).

[3]N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

[4]N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

[5]N. Cohen and S. W. Benson, J. Phys. Chem. 91, 171 (1987).

[6]N. Cohen, Int. J. Chem. Kinet. 19, 319 (1987).

[7]M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables, Third Edition," J. Phys. Chem. Ref. Data 14, Supplement No. 1 (1985).

[8]A. Kuppermann, J. Phys. Chem. 83, 171 (1979).

4. Data Sheets

4.1 List of Data Sheets

1.　　$OH + CH_3 \rightleftharpoons O + CH_4$
2.　　$O + C_2H_6 \rightarrow OH + C_2H_5$

3. $O + C_3H_8 \rightarrow OH + C_3H_7$
4. $O + C_4H_{10} \rightarrow OH + C_4H_9$
5. $O + C_5H_{12} \rightarrow OH + C_5H_{11}$
6. $O + C_6H_{14} \rightarrow OH + C_6H_{13}$
7. $O + C_7H_{16} \rightarrow OH + C_7H_{15}$
8. $O + C_8H_{18} \rightarrow OH + C_8H_{17}$
9. $O + i\text{-}C_4H_{10} \rightarrow OH + C_4H_9$
10. $O + (CH_3)_4C \rightarrow OH + C_5H_{11}$
11. $O + (CH_3)_2CHCH(CH_3)_2 \rightarrow OH + C_6H_{13}$
12. $O + (CH_3)_3CC(CH_3)_3 \rightarrow OH + C_8H_{17}$
13. $O + c\text{-}C_5H_{10} \rightarrow OH + C_5H_9$
14. $O + c\text{-}C_6H_{12} \rightarrow OH + C_6H_{11}$
15. $O + c\text{-}C_7H_{14} \rightarrow OH + C_7H_{13}$

16. $OH + CH_3F \rightarrow CH_2F + H_2O$
17. $OH + CH_2F_2 \rightarrow CHF_2 + H_2O$
18. $OH + CHF_3 \rightarrow CF_3 + H_2O$
19. $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$
20. $OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$
21. $OH + CHCl_3 \rightarrow CCl_3 + H_2O$
22. $OH + CH_3Br \rightarrow CH_2Br + H_2O$
23. $OH + CH_2ClF \rightarrow CHClF + H_2O$
24. $OH + CHClF_2 \rightarrow CClF_2 + H_2O$
25. $OH + CHCl_2F \rightarrow CCl_2F + H_2O$
26. $OH + CH_3CH_2F \rightarrow C_2H_4F + H_2O$

27. $OH + CH_3CH_2Cl \rightarrow C_2H_4Cl + H_2O$
28. $OH + CH_3CHF_2 \rightarrow C_2H_3F_2 + H_2O$
29. $OH + CH_3CHCl_2 \rightarrow C_2H_3Cl_2 + H_2O$
30. $OH + CH_2FCH_2F \rightarrow CH_2FCHF + H_2O$
31. $OH + CH_2BrCH_2Br \rightarrow CH_2BrCHBr + H_2O$
32. $OH + CH_2FCHF_2 \rightarrow C_2H_2F_3 + H_2O$
33. $OH + CH_2ClCHCl_2 \rightarrow C_2H_2Cl_3 + H_2O$
34. $OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$
35. $OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$
36. $OH + CH_2ClCF_2Cl \rightarrow CHClCF_2Cl + H_2O$
37. $OH + CHF_2CHF_2 \rightarrow CHF_2CF_2 + H_2O$
38. $OH + CHF_2CF_3 \rightarrow CF_2CF_3 + H_2O$
39. $OH + CHClFCF_3 \rightarrow CClFCF_3 + H_2O$
40. $OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$
41. $OH + CH_3CF_3 \rightarrow CH_2CF_3 + H_2O$
42. $OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$
43. $OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$

44. $OH + NH_3 \rightarrow NH_2 + H_2O$
45. $OH + NH_2 \rightarrow NH + H_2O$
46. $OH + NH \rightleftharpoons Products$
47. $OH + NH_2 \rightleftharpoons O + NH_3$
48. $O + NH_2 \rightleftharpoons Products$
49. $O + NH \rightarrow Products$

4.2. Data Sheets

$$OH + CH_3 \rightleftharpoons O + CH_4$$
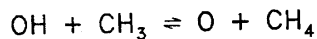
$\Delta H^o_{298} = -11.6 \pm 1.4$ kJ mol^{-1} (-2.8 kcal mol^{-1}) $\Delta S^o_{298} = -30.6 \pm 1.3$ J mol^{-1}K^{-1} (-7.3 cal mol^{-1}K^{-1})

$$K(T) = 1.43 \times 10^{-2} \exp(1580/T)$$

The uncertainty in log K is ±0.3 at 298 K, decreasing to ±0.1 at 2000 K.
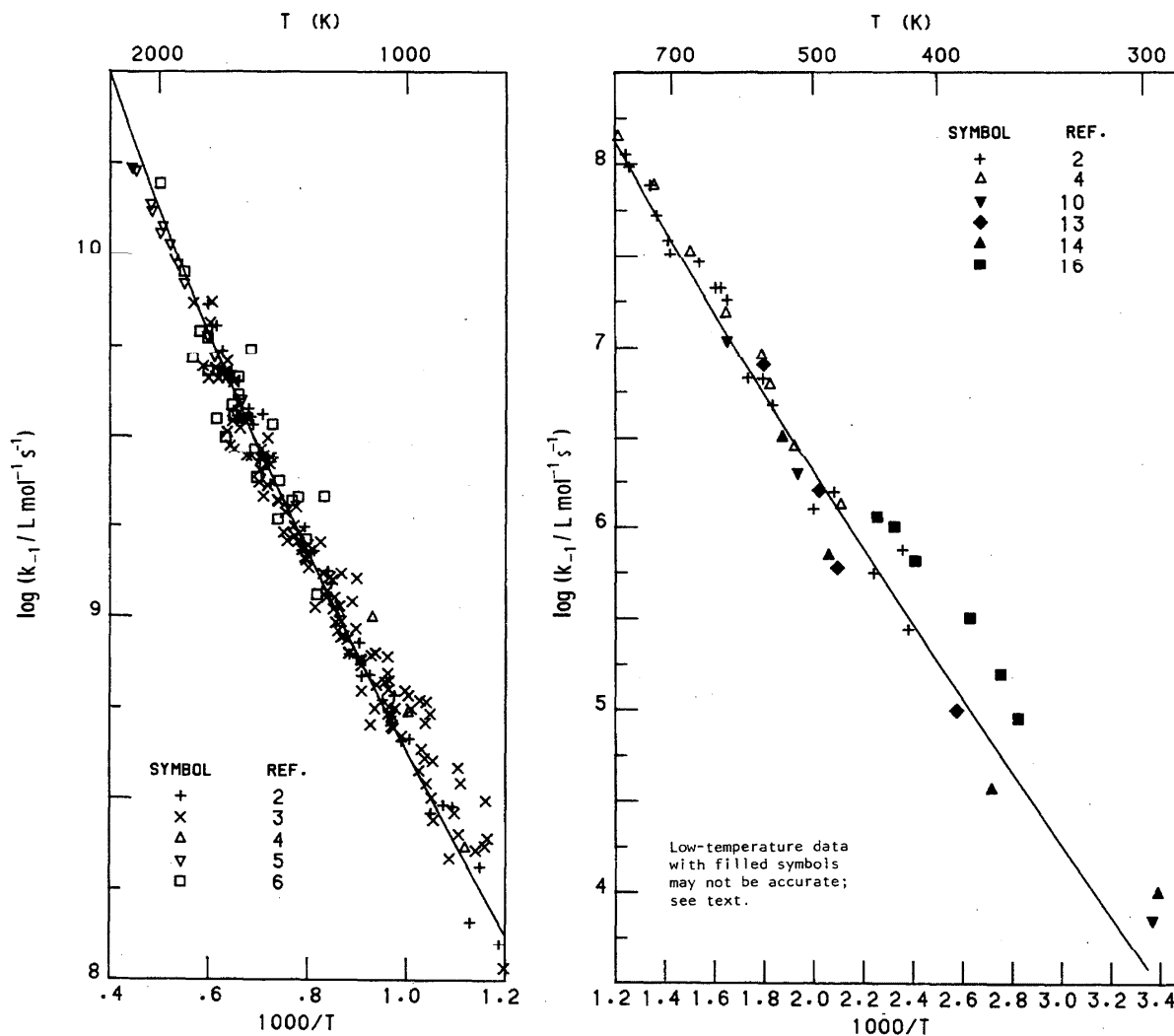
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	70 $T^{2.2}$ exp(-2240/T)	298 - 2500 K	1.1×10^4	L mol^{-1}s^{-1}
	1.16×10^{-19} $T^{2.2}$ exp(-2240/T)		1.8×10^{-17}	cm^3 molecule^{-1}s^{-1}
k_{-1}	4.9×10^3 $T^{2.2}$ exp(-3820/T)	298 - 2500 K	4×10^3	L mol^{-1}s^{-1}
	8.1×10^{-18} $T^{2.2}$ exp(-3820/T)		7×10^{-18}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 between 700 and 1500 K, increasing to ±0.6 at 298 K and ±0.3 at 2500 K. Uncertainty in log k_{-1}: ±0.15 between 600 and 1500 K, increasing to ±0.5 at 298 K and ±0.3 at 2500 K. The uncertainty in log k_1 reflects uncertainties in both log k_{-1} and log K(T).

November 1987

$OH + CH_3 \updownarrow O + CH_4$
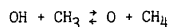
THERMOCHEMICAL DATA

Thermochemical data were taken from the JANAF Thermochemical Tables 3rd ed. (1985), except that the enthalpy of formation of CH_3 at 298 K was taken to be 146.9 ± 0.7 kJ mol^{-1}, in accordance with recent measurements[1]. The analytical expression chosen for $K(T)$ matches equilibrium constants calculated from the above data to within 7% between 298 and 2500 K.

MEASUREMENTS

There are no reported measurements of k_1, only of k_{-1}, the most direct and precise of which are the most recent.[2-4] Felder and Fontijn[2] used pulsed or flash photolysis at 420-1670 K with O atom detection by resonance fluorescence or O/NO chemiluminescence. Sutherland et al.[3] used a shock tube at 763-1755 K with O atoms produced by flash photolysis and detected by resonance absorption. Klemm et al.[4] used discharge flow/resonance fluorescence at 548-1156 K and flash photolysis/resonance fluorescence at 424 and 520 K. As the graph shows, the values of k_{-1} from these three studies are in accord. In two conventional shock tube studies[5,6] k_{-1} was determined from 1200 to 2250 K. These determinations are less direct than those of Refs. 2-4, but are included on the graph because they are the best measurements above 1755 K. Three other determinations[7-9] of k_{-1} are neither plotted nor used in this evaluation because the reported values depend on many uncertain assumptions about the rates of competitive reactions.

In five studies[10-14] O was mixed with CH_4, and the fractional decrease in [O] was measured after a set time, which was always longer than the mixing time. k_{-1} can be derived from such data if it is known what fraction of the atomic oxygen disappeared by reaction with methane and what fraction by other, secondary reactions. Cohen[15] recently formulated a chemical model for methane oxidation and determined the fraction (1/m) of atomic oxygen that reacted with methane in several of the experiments reported in Refs. 10, 13, and 14. These values of m were used to derive the values of k_{-1} that are plotted on the graph. In general, the lower the temperature, the larger the value for m. At the lowest temperature, 298 K, m is both large and uncertain, and the plotted values of k_{-1} are more likely to be too large than too small. Cohen did not reanalyze all the measurements of Ref. 10 nor any of the measurements of Refs. 11 and 12 primarily because too little information was given. Barassin and Combourieu[16] determined k_{-1} between 354 and 443 K; although they published too little information for us to assess the probable accuracy of their results their values for k_{-1} are plotted on the graph inasmuch as all determinations of k_{-1} in the vicinity of 354 K are only approximate.

CALCULATIONS

Several transition-state-theory (TST) calculations[17] were performed to extrapolate the reliable measured rate coefficients between 500 and 2250 K to higher and lower temperatures, where the data are either sparse or uncertain. The structure of the transition state was chosen, insofar as possible, to be in accord with ab initio calculations[18] and with the measured values of k_{-1} between 500 and 2250 K. A complete description of the TST calculations is given in Ref. 17. A calculation with the Wigner tunneling correction gave $k_{-1} = 4.9 \times 10^3 \, T^{2.2} \exp(-3820/T)$ L $mol^{-1}s^{-1}$ $250 \le T \le 2500$, which matches experimental data above 500 K and is in accord with the sparse, uncertain data at lower temperatures. Calculations with a one-dimensional Eckart potential gave larger values for k_{-1} below 500 K; at 298 K, the Wigner correction gives $k_{-1} \sim 4 \times 10^3$, while the Eckart correction gives 1.7×10^4. The Wigner tunneling correction, like all simple tunneling corrections, is imprecise, but the one-dimensional Eckart correction gives too large a correction and hence provides an upper limit to the true value of the rate coefficient.

DISCUSSION

The recommended expression for k_{-1}, $k_{-1} = 4.9 \times 10^3 \, T^{2.2} \exp(-3820/T)$ L $mol^{-1}s^{-1}$, $298 \le T \le 2500$ K, is the one calculated using TST with a Wigner tunneling correction. As can be seen from the graph, this recommendation gives values of k_{-1} that match the experimental data between 500 and 2250 K and are in accord with the sparse, uncertain data at lower temperatures. No recommendation is made for k_{-1} below 298 K because the tunneling correction becomes large and uncertain.

References
1. S. P. Heneghan, P. A. Knoot, and S. W. Benson, Int. J. Chem. Kinet. 13, 677 (1981).
2. W. Felder and A. Fontijn, private communications (1987); W. Felder and A. Fontijn, Chem. Phys. Lett. 67, 53 (1979); W. Felder, A. Fontijn, H. N. Volltrauer, and D. R. Voorhees, Rev. Sci. Instrum. 51, 195 (1980); W. Felder and S. Madronich, Combust. Sci. Tech. 50, 135 (1986).
3. J. W. Sutherland, J. V. Michael, and R. B. Klemm, J. Phys. Chem. 90, 5941 (1986).
4. R. B. Klemm, T. Tanzawa, E. G. Skolnik, and J. V. Michael, 18th Symp. (Int.) Combust. 785 (1981).
5. P. Roth and Th. Just, Ber. Bunsenges. Phys. Chem. 81, 572 (1977); NBS Spec. Pub. 561, 1339 (1979).
6. T. A. Brabbs and R. S. Brokaw, 15th Symp. (Int.) Combust. 893 (1975).
7. L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 620 (1963); L. I. Avramenko and R. V. Kolesnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2693 (1971) [Eng. Transl. Bull. Acad. Sci. USSR, Div. Chem. Sci. 20, 2556 (1971)].
8. V. V. Azatvan, A. B. Nalbandvan, and M. Y. Ts'ui, Kinet. Katal. 5, 201 (1964) [Eng. Transl. Kinet. Catal. 5, 177 (1964)].
9. A. M. Dean and G. B. Kistiakowsky, J. Chem. Phys. 54, 1718 (1971).
10. A. A. Westenberg and N. deHaas, J. Chem. Phys. 50, 2512 (1969).
11. F. W. Froben, Ber. Bunsenges. Phys. Chem. 72, 996 (1968).
12. J. M. Brown and B. A. Thrush, Trans. Faraday Soc. 63, 630 (1967).
13. E. L. Wong and A. E. Potter Jr., Can. J. Chem. 45, 367 (1967).
14. R. D. Cadle and E. R. Allen, J. Phys. Chem. 69, 1611 (1965).
15. N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).
16. J. Barassin and J. Combourieu, Bull. Soc. Chim. Fr., 1 (1974).
17. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
18. S. P. Walch and T. H. Dunning Jr., J. Chem. Phys. 72, 3221 (1980); private communication (1983).

$$O + C_2H_6 \rightarrow OH + C_2H_5$$

$\Delta H^O_{298} = -8.0 \pm 2$ kJ mol^{-1} (-1.9 kcal mol^{-1}) $\Delta S^O_{298} = 40.7 \pm 4$ J mol^{-1} K^{-1} (9.7 cal mol^{-1} K^{-1})

$$K(T) = 1.1 \times 10^9 \; T^{-2.3} \; \exp(110/T)$$

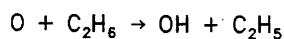The uncertainty in log K is ±0.6 at 300 K, decreasing to ±0.3 at 1500 K.
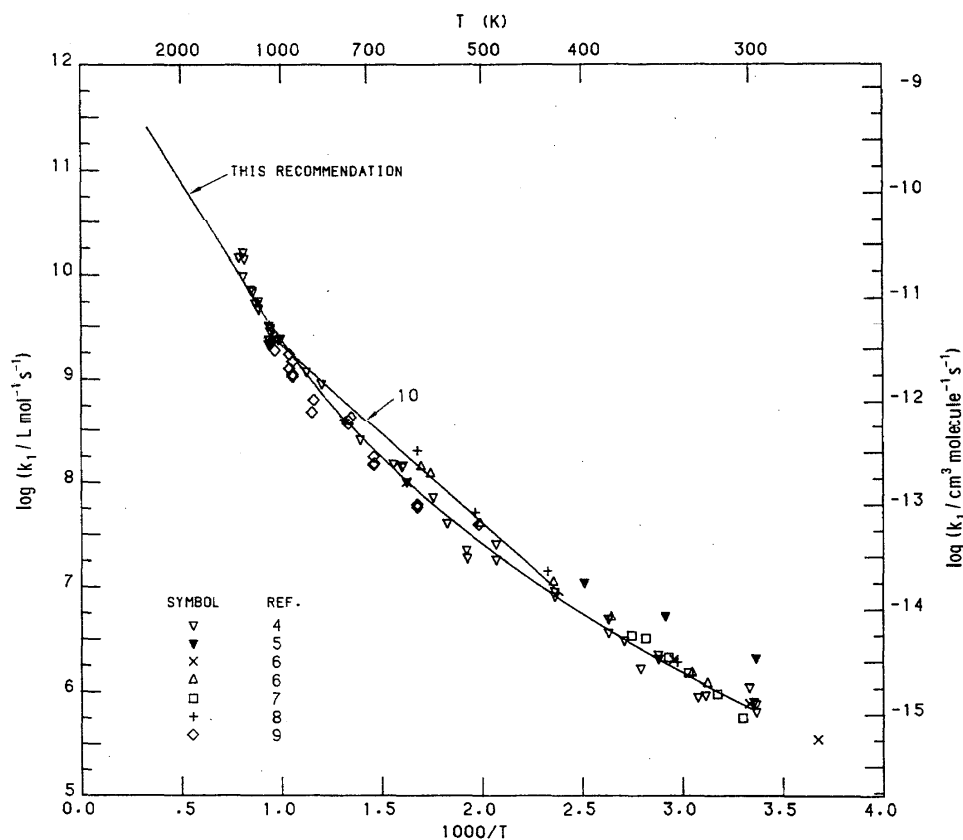
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.1 \times 10^{-10} \; T^{6.5} \exp(140/T)$	298-1300 K	6.6×10^5	L mol^{-1}s^{-1}
	$1.8 \times 10^{-31} \; T^{6.5} \exp(-140/T)$		1.1×10^{-15}	cm^3 molecule^{-1}s^{-1}
	$2.6 \times 10^{12} \exp(-7010/T)$	1300-3000 K		L mol^{-1} s^{-1}
	$4.3 \times 10^{-9} \exp(-7010/T)$			cm^3 molecule^{-1} s^{-1}
k_{-1}	$1.0 \times 10^{-19} \; T^{8.8} \exp(-250/T)$	298-1500 K	256	L mol^{-1}s^{-1}
	$1.7 \times 10^{-40} \; T^{8.8} \exp(-250/T)$		4.3×10^{-19}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.4 for 298 < T/K < 1300, increasing to ±0.5 at 3000 K. Uncertainty in log k_{-1}: ±0.7 at 298 K, decreasing to ±0.5 at 1500 K. This uncertainty reflects uncertainties in both log k_1 and log K(T).

May 1991

$O + C_2H_6 \rightarrow OH + C_2H_5$
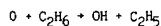
THERMOCHEMICAL DATA

Thermochemical data for C_2H_6 (ethane) were taken from Stull et al.[1] Data for O and OH were taken from JANAF Thermochemical Tables, 3rd edn. (1985). ΔHf^o_{298} for C_2H_5 (ethyl) was taken[2] to be 119 kJ mol^{-1}; S^o_{298} (247.5 J mol^{-1} K^{-1}) and Cp were calculated using vibrational frequencies given by Pacansky and Schrader[3] and assuming free internal rotation. The analytic expression chosen for K(T) matches equilibrium constants calculated from these data within 8% between 300 and 1500 K.

MEASUREMENTS

As in the case of the reaction of $O + CH_4$, the measurement of k_1 is complicated by the frequent presence of secondary reactions involving the products OH and C_2H_5 with one or both of the reagents; and by trace impurities, such as C_2H_4, in the C_2H_6. Except for the most recent study,[4] the room temperature measurements[5-7] provide insufficient information to assure the reader that these complications were avoided or accounted for. The reaction has been studied in three different regimes: (a) $[O]_o = [C_2H_6]_o$; (b) $[O]_o \ll [C_2H_6]_o$; or (c) $[O]_o \gg [C_2H_6]_o$. In case (a), the stoichiometry, which varies with $[O]:[C_2H_6]$, T, and extent of reaction, must be determined from product analysis in order to relate the experimentally measured disappearance of either reagent to the elementary rate coefficient k_1. In case (b), $[C_2H_6]/[O]$ must exceed 500 at 300 K for the reaction of OH with O to contribute less than 10% to the rate of O disappearance; under these conditions impurities become a prime concern. At higher temperatures secondary reactions are relatively slower and therefore less important. Ref. 5 used method (b) in a stationary cell with mercury-sensitized photodecomposition of N_2O as an O atom source and measured rates by competition with the O + C_3F_6 reaction; Ref. 6 used method (a) in a discharge flow system with EPR detection of O atoms; Ref. 7 used method (a) in a flow system with gas chromatographic analysis of products. Ref. 8 used method (c) at temperatures between 336 and 595 K for the analogous reaction $O + C_2H_5D \rightarrow OH (OD) + C_2H_4D (C_2H_5)$ in a flow sytem with mass spectrometric monitoring of the alkane; their precision is greatly limited by the small amount of alkane consumed during the reaction. Method (c) was also used by Caymax and Peeters[9] at 600-1030 K with a discharge-flow technique and their work seems to be free of unaccounted for complications. Tanzawa and Klemm[10] measured k_1 over 416-1048 K using a discharge flow technique with C_2H_6 in excess and obtained somewhat larger values (a factor of 2.5 at 600 K) than reported in Ref. 9; at the reported ratios of $[C_2H_6]:[O]$ greater than 1000 the technique should have been free from secondary reactions, but full experimental details have not been published. Mahmud, Marshall, and Fontijn[4] used method (b) in a high-temperature flow reactor at 300 < T/K < 1270, producing atoms by flash photolysis of either O_2 or CO_2 and atomic resonance fluorescence to monitor [O] decay. They fitted their data by $k_1 = 1.1 \times 10^{-10} T^{6.5} \exp(-138/T)$ L mol^{-1}, with log k_1(298) = 5.92 ± 0.12. Other work has been reviewed in Refs. 11 and 12.

CALCULATIONS

Transition-state-theory calculations assuming a Wigner tunneling correction, described in detail elsewhere[13] could not match the experimental data of Ref. 4: the problem is the $T^{6.5}$ preexponential temperature dependence, which produces a curvature in the plot of log k_1 vs. 1/T that is much larger than usual. The same TST calculations with an Eckart tunneling correction (ω = 1600i cm^{-1}; V_1 = 50.21 kJ/mol, V_2 = V_1 + ΔH^o_{298} = 58.21 kJ/mol) fit the experimental data within experimental error. The TST-Eckart results are described by $k_1 = 7.3 \times 10^{-9} T^{5.9} \exp(440/T)$ L mol^{-1} s^{-1} for 298 < T/K < 1000; and by 2.6 × 10^{12} $\exp(-7010/T)$ for 1000 < T/K < 3000. The calculations cannot be satisfactorily fitted by a three-parameter expression of the form $AT^n \exp(-B/T)$ over the entire temperature range of 298 < T/K < 3000.

DISCUSSION

The large extent of curvature in the log k vs. 1/T plot of the results of Ref. 4 is puzzling in that it is not consistent with the behavior of other O + alkane reactions, all of which we have been able to fit by a TST model with a Wigner tunneling correction. We recommend the empirical fit to the results of Ref. 4 for 298 < T/K < 1300: $k_1 = 1.1 \times 10^{-10} T^{6.5} \exp(-140/T)$ L mol^{-1} s^{-1}. If an analytic expression is required for higher temperatures, we recommend the fit to the TST/Eckart calculations described above: 2.6 × 10^{12} $\exp(-7010/T)$ L mol^{-1} s^{-1} for 1300 < T/K < 3000, with an uncertainty in log k_1 of ±0.5. The large degree of curvature in the log k vs. 1/T plot could be due to quantum mechanical tunneling, but other explanations are possible.[14] Clearly, further theoretical and experimental work are needed before the tunneling explanation and the low-temperature data can be accepted without reservation.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 244.
2. P. D. Pacey and J. H. Wimalasena, J. Phys. Chem. 88, 5657 (1984); M. Brouard, P. D. Lightfoot, and M. J. Pilling, J. Phys. Chem. 90, 445 (1986).
3. J. Pacansky and B. Schrader, J. Chem. Phys. 78, 1033 (1983).
4. K. Mahmud, P. Marshall, and A. Fontijn, J. Chem. Phys. 88, 2393 (1988).
5. D. Saunders and J. Heicklen, J. Phys. Chem. 70, 1950 (1966).
6. A. A. Westenberg and N. DeHaas, J. Chem. Phys. 46, 490 (1967); 50, 2512 (1969).
7. C. Papadopoulos, P. G. Ashmore, and B. J. Tyler, 13th Symp. (Int.) Combust., 281 (1971).
8. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
9. M. Caymax and J. Peeters, 19th Symp. (Int.) Combust., 51 (1982).
10. T. Tanzawa and R. B. Klemm, 179th Natl. ACS Mtg., Houston, March 1980; J. V. Michael, 19th Symp. (Int.) Combust., 59 (1982).
11. J. T. Herron, Int. J. Chem. Kinet. 1, 527 (1969).
12. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 2, 467 (1974).
13. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
14. N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).

$$O + C_3H_8 \rightarrow OH + C_3H_7$$

$O + C_3H_8 \xrightarrow{1} OH + n\text{-}C_3H_7$
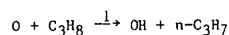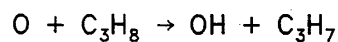
$\Delta H^{o}_{298} = -11.6 \pm 6 \text{ kJ mol}^{-1}(-2.8 \text{ kcal mol}^{-1})$

$\Delta S^{o}_{298} = 37.7 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (9.0 cal mol}^{-1} \text{ K}^{-1})$

$O + C_3H_8 \xrightarrow{2} OH + i\text{-}C_3H_7$
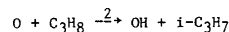
$\Delta H^{o}_{298} = -25.4 \pm 4 \text{ kJ mol}^{-1} \text{ (-6.1 kcal mol}^{-1})$

$\Delta S^{o}_{298} = 32.2 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (7.7 cal mol}^{-1} \text{ K}^{-1})$
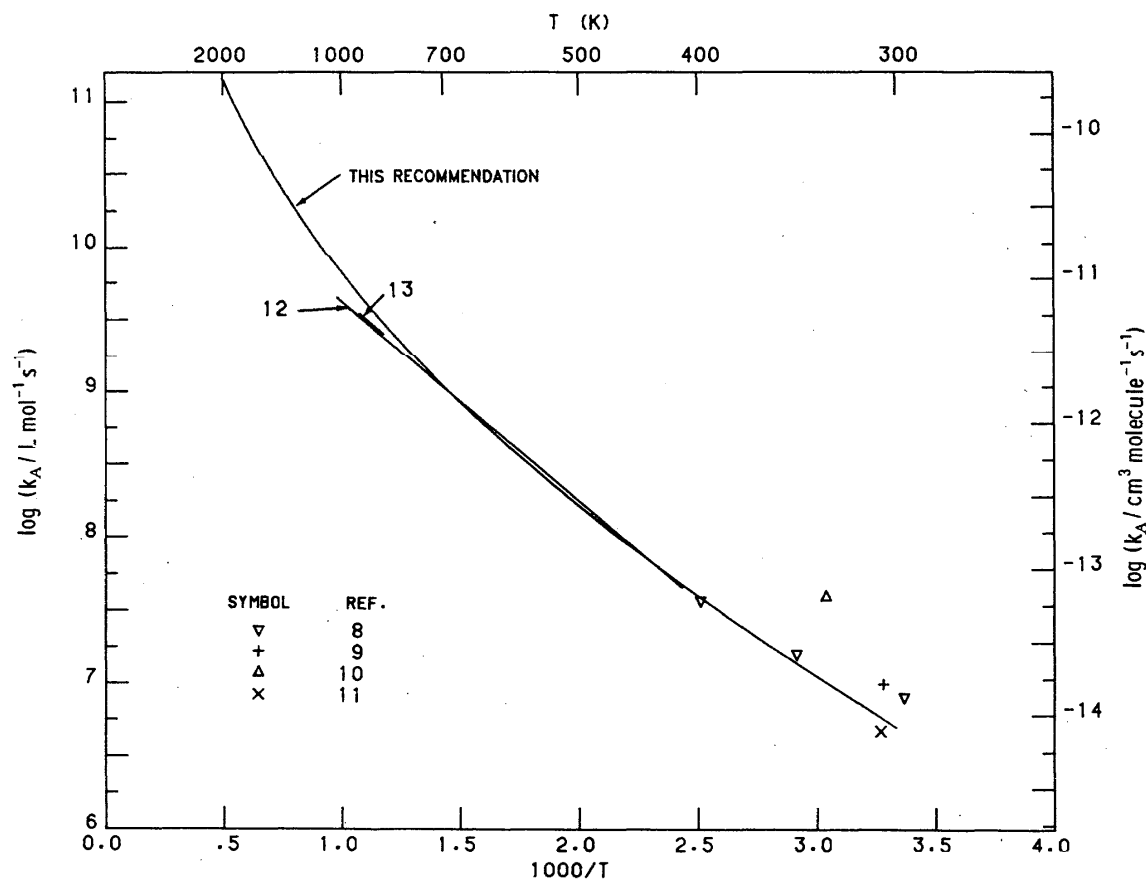
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$0.76 \ T^{3.5} \ \exp(-1280/T)$	298-2000 K	4.0×10^{6}	L mol^{-1}s^{-1}
	$1.3 \times 10^{-21} \ T^{3.5} \ \exp(-1280/T)$		6.6×10^{-15}	cm^3 molecule^{-1}s^{-1}
k_2/k_1	$0.15 \ T^{0.1} \ \exp(1170/T)$	298-2000 K	13	—

Uncertainty in log k_A: ±0.3 throughout temperature range. Uncertainty in log k_2/k_1: ±0.5. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + C_3H_8 \xrightarrow{A} C_3H_7 + OH$$

THERMOCHEMICAL DATA

The title reaction represents the sum of two elementary reactions:

$$O + C_3H_8 \xrightarrow{1} OH + \dot{C}H_2CH_2CH_3 \text{ [n-propyl]}$$
$$O + C_3H_8 \xrightarrow{2} OH + CH_3\dot{C}HCH_2 \text{ [i-propyl]}$$

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). $\Delta Hf^o_{298}(C_3H_8)$ and $S^o_{298}(C_3H_8)$ are taken to be[1,2] -5.93 kJ mol^{-1} and 15.42 J mol^{-1}K^{-1}, respectively. Thermochemical data for the two propyl radicals are subject to some uncertainty. We accept $\Delta Hf^o_{298}(n-C_3H_7)$ = 94.6[3] and $\Delta Hf^o_{298}(i-C_3H_7)$ = 80.8[4] kJ mol^{-1}. However, the former may be too low.[5] Entropies were calculated by group additivity, assuming no barrier to internal rotation about the α C-C bond in $n-C_3H_7$[6] and 8 kJ/mol in the $i-C_3H_7$ radical,[7] yielding $S^o_{298}(n-C_3H_7)$ = 282.4 and $S^o_{298}(i-C_3H_7)$ = 279.5 mol^{-1}K^{-1}. Analytic expressions for K(T) have not been calculated because the reverse reactions will, under all conditions of practical interest, be slower than the competing radical recombination reaction (OH + $C_3H_7 \rightarrow C_3H_7OH$).

MEASUREMENTS

There are no separate measurements of k_1 and k_2, only of their sum, k_A. Of the measurements of k_A at or near room temperature,[8-11] the most reliable is that of Ref. 11, carried out in a flow tube with O atoms produced by passing purified N_2 through a microwave discharge and then titrating the N atoms with NO. Measurements were made by two methods. With method 1, $[O]_0/[C_3H_8]_0 \approx 1$ and k_A was determined by measuring propane consumption gas chromatographically. This procedure required knowing the stoichiometry, which varied with the initial ratio of reactants. With method 2, $[O]_0/[C_3H_8]_0$ = 150 - 250, and k_A was determined by monitoring O atom consumption. This gave $k_A(303)$ = (4.0 ± 0.5) × 10^6 L mol^{-1}s^{-1}, compared to method 1, which gave $k_A(306)$ = (4.9 ± 0.4) × 10^6. Of these two techniques, method 2, and hence the smaller value for k_A, is preferred.

Of the higher temperature studies,[12,13] that by Azatyan et al. was obtained from ignition limits, a generally unreliable technique. That by Tanzawa et al., obtained by discharge flow-resonance fluorescence, has not been published in sufficient detail for full evaluation. However, in view of the acceptable results for O with other alkanes from the same laboratory (see data sheets for O + CH_4 and O + $(CH_3)_4C$) we consider the results of Ref. 13 to be provisionally reliable.

CALCULATIONS

Separate transition-state-theory (TST) calculations were carried out for the attack on the primary and on the secondary H atoms. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the best experimental value[11] for k_A at 298 K is 5 to 20 times larger than the rate coefficient at the same temperature for O + C_2H_6, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was calculated assuming an activation energy the average of the activation energies for the O + C_2H_6 and O + neo-C_5H_{12} reactions (see data sheets for those reactions). For additional details see Ref. 14. The resulting values of k_1 and k_2 calculated separately were added together to give $k_A(T)$, which could be expressed by k_A = 0.76 T$^{3.5}$ exp(-1280/T). According to this model, k_2/k_1 is approximately 13 at 298 K, decreasing to approximately 0.6 at 2000 K. Another TST calculation has been described by Michael et al.[15]

DISCUSSION

Because there are no measurements above 1000 K, we rely on the TST calculations for extrapolating k_A to higher temperatures. The calculations in turn depend sensitively on the choice of $k_A(298)$; consequently the spread of results near room temperatures is a matter of concern. Although the low temperature values of k_A are not sensitive to the contribution from k_1, the high temperature values are. Because the value assumed for k_1 depends on the choice of value for k(298) for the O + C_2H_6 reaction, it reflects uncertainty in that number. That the chosen model fits data for O abstraction from higher alkanes supports its validity, and consequently the accuracy of the high temperature extrapolation. We therefore recommend the expression obtained by TST calculation: k_A = 0.76 T$^{3.5}$ exp(-1280/T) L mol^{-1}s^{-1} between 300 and 2000 K, with an uncertainty in log k_A of ±0.3 throughout the temperature range.

References

1. J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds (Academic Press, London, 1970), p. 141.
2. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 244.
3. H. E. O'Neal and S. W. Benson, in Free Radicals, Vol 2, J. K. Kochi ed. (Wiley, 1973), p. 275.
4. R. R. Baldwin, R. W. Walker, and R. W. Walker, J. Chem. Soc. Faraday Trans. I, 76, 825 (1980).
5. W. Tsang, Int. J. Chem. Kinet. 10, 821 (1978).
6. J. Pacansky and W. Schubert, J. Chem. Phys. 76, 1459 (1982).
7. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, 1976).
8. D. Saunders and J. Heicklen, J. Phys. Chem. 70, 1950 (1966).
9. L. Stockburger, III, and J. Heicklen, J. Am. Chem. Soc. 93, 3331 (1971).
10. A. B. Harker and C. S. Burton, Int. J. Chem. Kinet. 7, 907 (1975).
11. S. P. Jewell, K. A. Holbrook, and C. A. Oldershaw, Int. J. Chem. Kinet. 13, 69 (1981).
12. V. V. Azatyan, A. B. Nalbandyan, and M. Y. Ts'ui, Dokl. Akad. Nauk Arm. SSR 36, 23 (1963), as in Chem. Abst. 59, 2201e (1963).
13. T. Tanzawa, D. G. Keil, and R. B. Klemm, Amer. Chem. Soc. 2nd Chem. Congress, Las Vegas, Aug. 1980, abstract #280.
14. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
15. J. V. Michael, D. G. Keil, and R. B. Klemm, Int. J. Chem. Kinet. 15, 705 (1983).

$$O + C_4H_{10} \rightarrow OH + C_4H_9$$

$O + C_4H_{10} \xrightarrow{\ 1\ } OH + n\text{-}C_4H_9$

$O + C_4H_{10} \xrightarrow{\ 2\ } OH + s\text{-}C_4H_9$

$\Delta H^o_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1}$ $(-2.7 \text{ kcal mol}^{-1})$
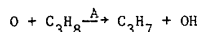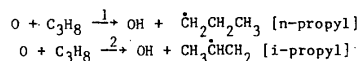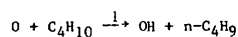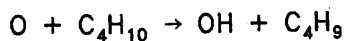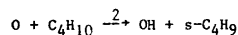$\Delta S^o_{298} = 43.6 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$ $(10.4 \text{ cal mol}^{-1}\text{K}^{-1})$

$\Delta H^o_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1}$ $(-6.9 \text{ kcal mol}^{-1})$
$\Delta S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$ $(9.4 \text{ cal mol}^{-1}\text{K}^{-1})$

SYMBOL	REF.
■	2
×	4
◆	5
+	6
◇	7
▽	8
△	9
▲	10
□	11
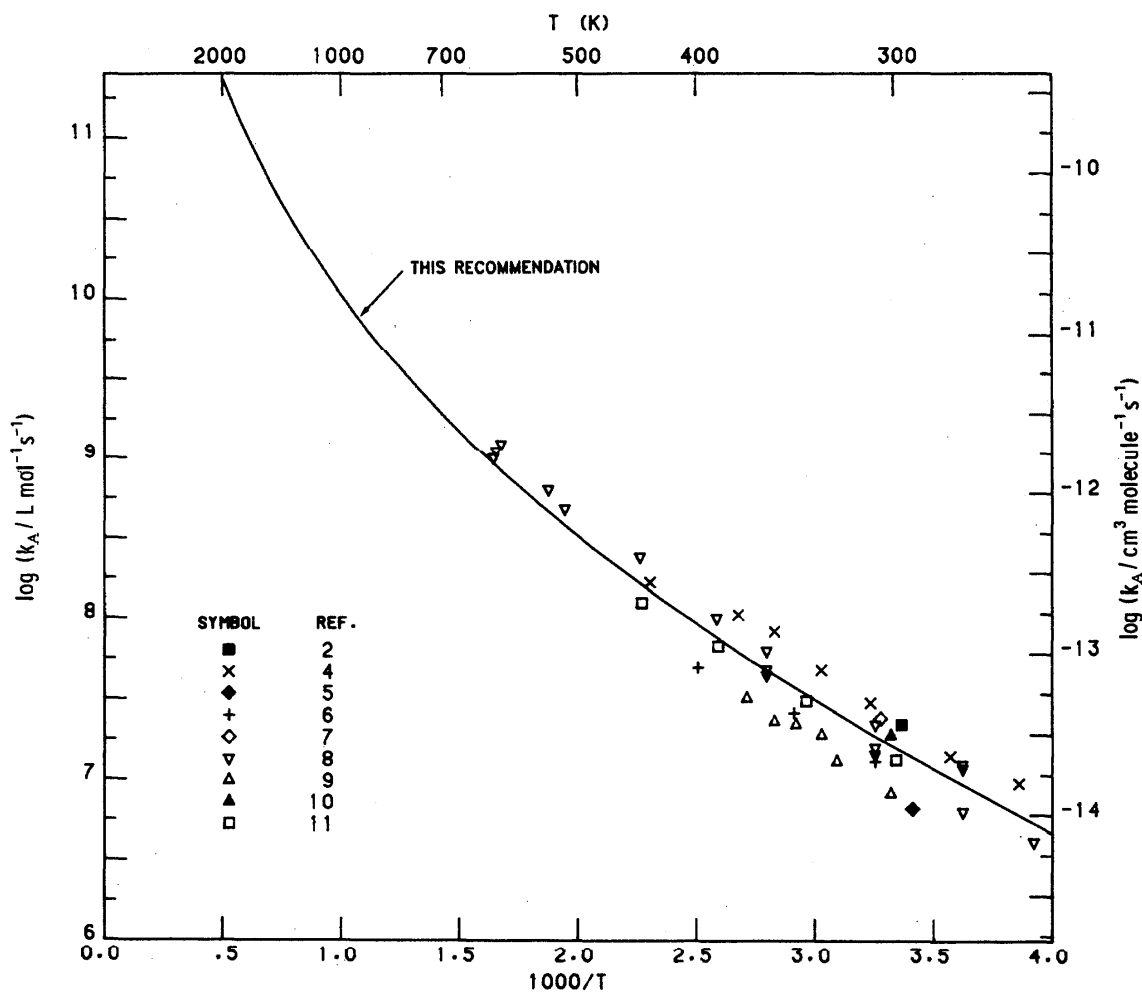
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$4.7 \times 10^{-2} \ T^{3.9} \ \exp(-780/T)$	250 - 2000 K	1.6×10^{7} K	L mol^{-1}s^{-1}
	$7.8 \times 10^{-23} \ T^{3.9} \ \exp(-780/T)$		2.6×10^{-14}	cm^3 molecule^{-1}s^{-1}
k_2/k_1	$8.7 \times 10^{-2} \ T^{0.2} \ \exp(1470/T)$	298 - 2000 K	35	

Uncertainty in log k_A: ±0.2 at 298 K, increasing to ±0.3 at 2000 K. Uncertainty in log k_2/k_1: ±0.3 near 298 K, increasing to ±0.5 at 2000 K. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + C_4H_{10} \xrightarrow{A} OH + C_4H_9$$
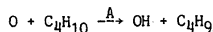
THERMOCHEMICAL DATA

The title reaction represents the sum of two different elementary reactions:

$$O + C_4H_{10} \xrightarrow{1} OH + n\text{-}C_4H_9 \quad (n\text{-}C_4H_9 \text{ is } \cdot CH_2CH_2CH_2CH_3)$$
$$\xrightarrow{2} OH + s\text{-}C_4H_9 \quad (s\text{-}C_4H_9 \text{ is } CH_3\dot{C}HCH_2CH_3)$$

Thermochemical data for O and OH are from JANAF Thermochemical Tables, 3rd ed. (1985). Differences between the enthalpies and entropies of the two C_4H_9 radicals and of the parent alkane were estimated by group additivity methods outlined by Benson et al.[1] Analytic expressions for K(T) have not been calculated because the reverse reactions will, under all conditions of interest, be slower than radical recombination (OH + $C_4H_9 \rightarrow C_4H_9OH$).

MEASUREMENTS

k_1 and k_2 have not been measured separately. Cvetanovic[2] reported $k_A/k_3 = 21 \pm 5$ where k_3 is the rate coefficient for O + C_2H_4. The value shown on the graph is calculated from the value of k_3 recommended by Herron and Huie.[3] Elias and Schiff[4] measured k_A in a fast-flow system; O atoms were produced by discharge through O_2 and reacted with excess alkane. It was assumed (incorrectly) that no secondary reactions consume or produce the n-butane. Wright[5] assumed (incorrectly) that the principal reaction is carbonyl formation; his results are not used in this evaluation. Marsh and Heicklen[6] measured k_A relative to O + C_3F_6; Stockburger and Heicklen,[7] relative to O + 1,3-C_4F_6. Herron and Huie[8] produced O atoms in large excess in a flow tube and monitored alkane consumption (C_4H_{10}-1-d_1 was used) by mass spectrometry. The principal shortcomings of the method are the uncertainty in the O + C_2H_4 titration used to measure [O] and the imprecision in the alkane analysis because small amounts of alkane were consumed (a 5% error in alkane assay means a 25-50% error in k_A). They obtained $k_A(307) = 1.8 \pm 0.4 \times 10^7$ L mol^{-1}s^{-1}. Papadopoulos et al.[9] produced O by the N + NO reaction in a flow tube with $[O]_0 = [C_4H_{10}]$ and analyzed products by gas chromatography. The value of k_A depends on the stoichiometry, which was reported as a function of $[O]_0/[RH]_0$, but not of T. They reported $k_A(301) = 8.2 \times 10^6$ L mol^{-1}s^{-1}. Atkinson and Pitts[10] produced O atoms at 301 K by Hg-photosentization of N_2O in the presence of excess alkane and monitored [O] loss by a phase modulation technique, watching emission from O + NO. Corrections for trace butenes in the butane were made later.[11] Atkinson, et al.[11] measured k_A at 298-439 K by flash photolysis-NO_2 chemiluminescence in excess butane. The correction for the 0.05% butenes amounted to almost 30% of the rate at 299 K, decreasing at higher temperatures. The corrected values (of both Refs. 10 and 11) differ negligibly from the results of Ref. 8 except at the highest temperature. The most reliable measurements should be those of Refs. 8 and 9; the former give rate coefficients approximately 50% faster than the latter over the overlapping temperature range. Thus we conclude that log $k_A(298) = 7.1 \pm 0.2$.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack of O atoms on the primary and the secondary H atoms. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the best experimental value for $k_A(298)$ is more than 20 times larger than the rate coefficient at the same temperature for O + C_2H_6, it was assumed that $k_A(298)$ is essentially $k_2(298)$. $k_1(298)$ was calculated assuming the activation energy at 300 K to be the average of those of O + C_2H_6 and O + neo-C_5H_{12} (see data sheets for those reactions). For additional details see Ref. 12. The resulting values of k_1 and k_2 were added to give $k_A(T)$, which could be expressed by $k_A = 4.7 \times 10^{-2} T^{3.9} \exp(-780/T)$ L mol^{-1}s^{-1}. The calculated ratio k_2/k_1 is approximately 35 at 298 K, decreasing to approximately unity at 2000 K.

DISCUSSION

The calculations indicate that there should be curvature on an Arrhenius plot (i.e., log k_A vs. 1/T), making $k_A(2000)$ about 3 times larger than a linear extrapolation would predict. Our recommendation is based on the calculations described above, which are in good agreement with the experimental data. The range in experimental values for k_A is a factor of 3 throughout the temperature range of 250-400 K. This uncertainty adds to the uncertainty inherent in the TST calculations. Thus, we recommend $k_A = 4.7 \times 10^{-2} T^{3.9} \exp(-780/T)$ over the temperature range of 250 - 2000 K, with an uncertainty in log k_A of ± 0.2 at 298 K, increasing to ± 0.3 at 2000 K. A reliable high-temperature measurement of k_A would be very useful, as would a determination of k_1/k_2 at any temperature.

References

1. (a) S. W. Benson, Thermochemical Kinetics, 2nd ed. (Wiley, N.Y., 1976); (b) H. E. O'Neal and S. W. Benson, Int. J. Chem. Kinet. 1, 221 (1969).
2. R. J. Cvetanovic, J. Chem. Phys. 23, 1375 (1955).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 2, 467 (1974).
4. L. Elias and H. I. Schiff, Can. J. Chem. 38, 1657 (1960).
5. F. J. Wright, 10th Symp. (Int.) Combust., 387 (1965).
6. G. Marsh and J. Heicklen, J. Phys. Chem. 71, 250 (1967).
7. L. Stockburger III and J. Heicklen, J. Am. Chem. Soc. 93, 3331 (1971).
8. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
9. C. Papadopoulos, P. G. Ashmore, and B. J. Tyler, 13th Symp. (Int.) Combust., 281 (1971). The data are presented only graphically; numerical values are taken from Herron and Huie (Ref. 4).
10. R. Atkinson and J. N. Pitts, Jr., J. Phys. Chem. 78, 1780 (1974).
11. R. Atkinson, R. A. Perry, and J. N. Pitts, Jr., Chem. Phys. Lett. 47, 197 (1977).
12. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + C_5H_{12} \rightarrow OH + C_5H_{11}$$

$O + C_5H_{12} \xrightarrow{1} OH + n\text{-}C_5H_{11}$

$\Delta H^o_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1}$ $(-2.7 \text{ kcal mol}^{-1})$

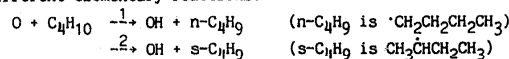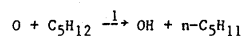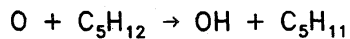$\Delta S^o_{298} = 43.6 \pm 8 \text{ J mol}^{-1}K^{-1}$ $(10.4 \text{ cal mol}^{-1}K^{-1})$

$O + C_5H_{12} \xrightarrow{2a} OH + CH_3CH(CH_2)_2CH_3$

$\Delta H^o_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1}$ $(-6.9 \text{ kcal mol}^{-1})$

$\Delta S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}K^{-1}$ $(9.4 \text{ cal mol}^{-1}K^{-1})$

$O + C_5H_2 \xrightarrow{2b} OH + CH_3CH_2CHCH_2CH_3$

$\Delta H^o_{298} = -32.2 \pm 11 \text{ kJ mol}^{-1}$ $(-7.7 \text{ kcal mol}^{-1})$

$\Delta S^o_{298} = 32.6 \pm 8 \text{ J mol}^{-1}K^{-1}$ $(7.8 \text{ cal mol}^{-1}K^{-1})$

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$38\ T^{3.0}\ \exp(-1010/T)$	250–2000 K	3.5×10^7	$L\ mol^{-1}s^{-1}$
	$6.3 \times 10^{-20}\ T^{3.0}\ \exp(-1010/T)$		5.9×10^{-14}	$cm^3\ molecule^{-1}s^{-1}$
k_2/k_1	$0.21\ T^{0.1}\ \exp(1650/T)$	298–2000 K	90	—

Uncertainty in log k_A: ±0.2 near 298 K, increasing to ±0.3 at 2000 K. Uncertainty in log k_2/k_1: ±0.5. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$O + C_5H_{12} \xrightarrow{A} OH + C_5H_{11}$

THERMOCHEMISTRY

The title reaction is the sum of three separate processes: attack on one of the six equivalent primary H atoms,

$$O + CH_3(CH_2)_3CH_3 \xrightarrow{1} OH + CH_3(CH_2)_3CH_2$$

attack on one of the four equivalent secondary H atoms on the number 2 carbons,

$$O + CH_3(CH_2)_3CH_3 \xrightarrow{2a} OH + CH_3(CH_2)_2CHCH_3$$

and attack on one of the two equivalent secondary H atoms on the number 3 carbon,

$$O + CH_3(CH_2)_3CH_3 \xrightarrow{2b} OH + CH_3CH_2CHCH_2CH_3$$

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules[1] were used to estimate the differences between ΔHf^o_{298} and S^o_{298} for the three pentyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between pentyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions ($OH + C_5H_{11} \rightarrow C_5H_{11}OH$).

MEASUREMENTS

Herron and Huie[2] measured k_A over the temperature range of 255-597 K in a flow system, with $[O]_0/[C_5H_{12}]_0 > 15$, by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, $k_A = 4.4 \pm 0.4 \times 10^7$ L mol^{-1}s^{-1}, and interpolated[3] k_A at 298 K to be 3.5×10^7.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. Trial calculations on the two different kinds of secondary H atoms suggested that the differences in the two calculations were too slight, and the respective uncertainties too large, to justify carrying out separate calculations. Consequently, k_{2a} and k_{2b} were grouped together and only their sum, k_2, was calculated. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for k_A at 298 K is approximately 50 times larger than the rate coefficient at the same temperature for $O + C_2H_6$, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was assumed to be 3.8×10^5 L mol^{-1}s^{-1}, a value obtained by calculating the entropy of activation by the usual method and assuming approximately the same activation energy at 300 K as for the reaction of $O + C_4H_{10}$. The vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of $O + C_4H_{10}$ (see data sheet for that reaction). For further details, see Ref. 4. The resulting values of k_1 and k_2 calculated separately were added together to give $k_A(T)$, which could be expressed by $k_A = 38$ $T^{3.0}$ exp(-1010/T) L mol^{-1}s^{-1} over the temperature range of 250-2000 K. The calculated ratio k_2/k_1 is approximately 90 at 298 K, decreasing to approximately 1 at 2000 K.

DISCUSSION

Although there is only one set of experimental data, its consistency with data for O atom reaction with higher alkanes (see data sheets for $O + C_6H_{14}$, $O + C_7H_{16}$, and $O + C_8H_{18}$), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthens the reliability of both the experiments and the calculations. Consequently, we recommend $k_A = 38$ $T^{3.0}$ exp(-1010/T) L mol^{-1}s^{-1} for 250-2000 K, with an uncertainty in log k_A of ± 0.2 at 298 K, increasing to ± 0.3 at 2000 K.

References

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York; 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + C_6H_{14} \rightarrow OH + C_6H_{13}$$

$O + C_6H_{14} \xrightarrow{1} OH + n\text{-}C_6H_{13}$

$H^o_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1}$ $(-2.7 \text{ kcal mol}^{-1})$
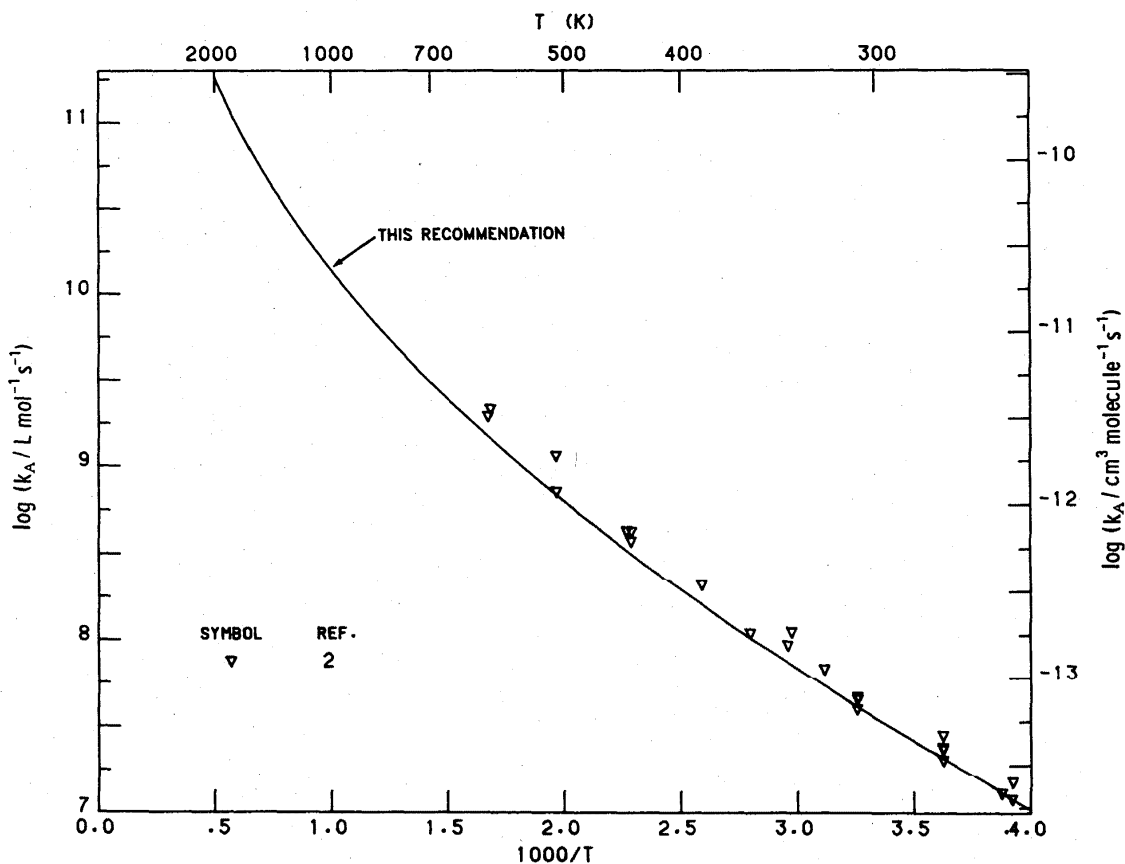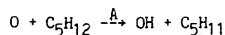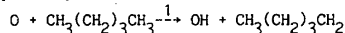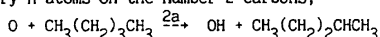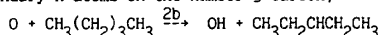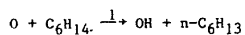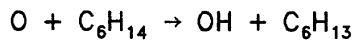$S^o_{298} = 43.6 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$ $(10.4 \text{ cal mol}^{-1}\text{K}^{-1})$

$O + C_6H_{14} \xrightarrow{2a} OH + CH_3CH(CH_2)_3CH_3$

$H^o_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1}$ $(-6.9 \text{ kcal mol}^{-1})$
$S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$ $(9.4 \text{ cal mol}^{-1}\text{K}^{-1})$

$O + C_6H_{14} \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_2CH_3$

$H^o_{298} = -32.2 \pm 11 \text{ kJ mol}^{-1}$ $(-7.7 \text{ kcal mol}^{-1})$
$S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}\text{K}^{-1}$ $(9.4 \text{ cal mol}^{-1}\text{K}^{-1})$

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$100 \ T^{2.9} \exp(-1000/T)$	250–2000 K	5.5×10^7	L mol^{-1}s^{-1}
	$1.7 \times 10^{-19} \ T^{2.9} \exp(-1000/T)$		9.1×10^{-14}	cm^3 molecule^{-1}s^{-1}
k_2/k_1	$0.19 \ T^{0.2} \exp(1610/T)$	298–2000 K	125	

Uncertainty in log k_A: ±0.2 near 298 K, increasing to ±0.3 at 2000 K. Uncertainty in log k_2/k_1: ±0.5. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$O + C_6H_{14} \xrightarrow{A} OH + C_6H_{13}$
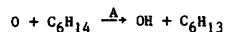
THERMOCHEMISTRY

The title reaction is the sum of three separate processes: attack on one of the six equivalent primary H atoms,

$$O + CH_3(CH_2)_4CH_3 \xrightarrow{1} OH + CH_3(CH_2)_4CH_2$$

attack on one of the four equivalent secondary H atoms on the number 2 carbons,

$$O + CH_3(CH_2)_4CH_3 \xrightarrow{2a} OH + CH_3(CH_2)_4CHCH_3$$

and attack on one of the equivalent secondary H atoms on the number 3 carbons,

$$O + CH_3(CH_2)_4CH_3 \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_2CH_3$$

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group contribution rules[1] were used to estimate the differences between ΔHf^o_{298} and S^o_{298} for the three hexyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between hexyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions ($OH + C_6H_{13} \rightarrow C_6H_{13}OH$).

MEASUREMENTS

Herron and Huie[2] measured k_A over the temperature range of 247 - 597 K in a flow system, with $[O]_o/[C_6H_{14}]_o > 15$, by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, $k_A = 6.8 \pm 0.7 \times 10^7$ L mol^{-1}s^{-1}, and interpolated[3] k_A at 298 K to be 5.6×10^7.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. As in the case of $O + n-C_5H_{12}$ (see data sheet for that reaction), k_{2a} and k_{2b} were grouped together and only their sum, k_2, was calculated. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for k_A at 298 K is approximately 100 times larger than the rate coefficent at the same temperature for $O + C_2H_6$, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was estimated by the same procedure used for the $O + n-C_4H_{10}$ reaction. Similarly, the vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of $O + n-C_4H_{10}$ (see data sheet for that reaction). For further details, see Ref. 4. The resulting values of k_1 and k_2 calculated separately were added together to give k_A (T), which could be expressed by $k_A = 100 \ T^{2.9}$ exp (-1000/T) L mol^{-1}s^{-1} over the temperature range of 250-2000 K. The calculated ratio k_2/k_1 is approximately 125 at 298 K, decreasing to approximately 2 at 2000 K.

DISCUSSION

Although there is only one set of experimental data, its consistency with data for O atom reaction with homologous alkanes (see data sheets for $O + C_5H_{12}$, $O + C_7H_{16}$, and $O + C_8H_{18}$), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthens the reliability of both the experiments and the calculations. Consequently, we recommend $k_A = 100 \ T^{2.9}$ exp(-1000/T) L mol^{-1}s^{-1} for 250-2000 K, with an uncertainty in log k_A of ± 0.2 at 298 K, increasing to ± 0.3 at 2000 K.

References

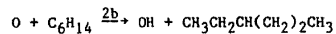1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York; 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

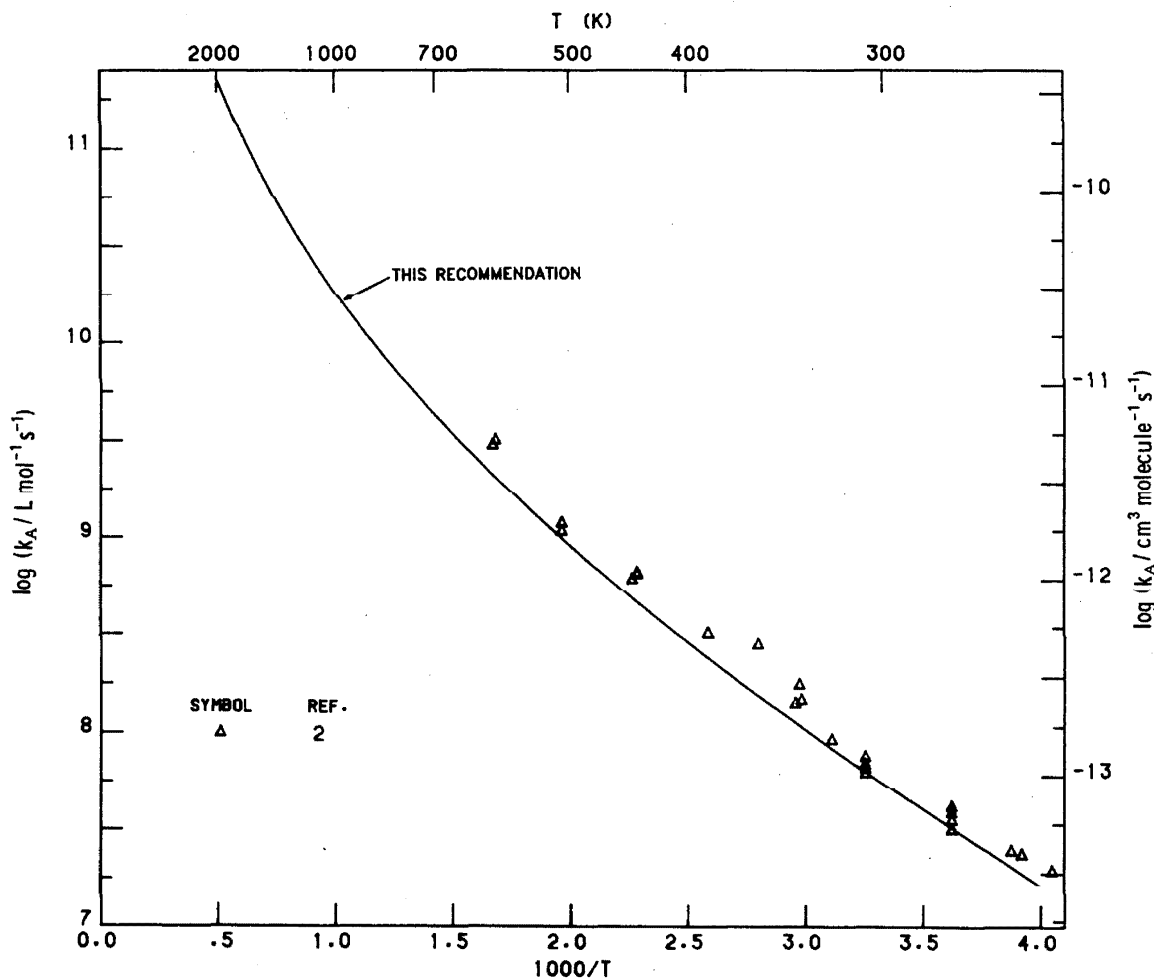$$O + C_7H_{16} \rightarrow OH + C_7H_{15}$$

$O + C_7H_{16} \xrightarrow{1} OH + n\text{-}C_7H_{15}$

$\Delta H^o_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1} \ (-2.7 \text{ kcal mol}^{-1})$
$\Delta S^o_{298} = 42.6 \pm 8 \text{ J mol}^{-1}K^{-1} \ (10.4 \text{ cal mol}^{-1}K^{-1})$

$O + C_7H_{16} \xrightarrow{2a} OH + CH_3CH(CH_2)_4CH_3$

$\Delta H^o_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1} \ (-6.9 \text{ kcal mol}^{-1})$
$\Delta S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}K^{-1} \ (9.4 \text{ cal mol}^{-1}K^{-1})$

$O + C_7H_{16} \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_3CH_3$

$\Delta H^o_{298} = -32.2 \pm 11 \text{ kJ mol}^{-1} \ (-7.7 \text{ kcal mol}^{-1})$
$\Delta S^o_{298} = 38.4 \pm 8 \text{ J mol}^{-1}K^{-1} \ (9.4 \text{ cal mol}^{-1}K^{-1})$

$O + C_7H_{16} \xrightarrow{2c} OH + CH_3(CH_2)_2CH(CH_2)_2CH_3$

$\Delta H^o_{298} = -32.2 \pm 11 \text{ kJ mol}^{-1} \ (-7.7 \text{ kcal mol}^{-1})$
$\Delta S^o_{298} = 32.6 \pm 8 \text{ J mol}^{-1}K^{-1} \ (7.8 \text{ cal mol}^{-1}K^{-1})$

SYMBOL	REF.
Δ	2
×	4

RECOMMENDED RATE COEFFICIENTS

k	$k(T)$	Range	$k(298)$	Units
k_A	$93 \ T^{2.9} \ \exp(-880/T)$	250–2000 K	7.6×10^7	$L \text{ mol}^{-1} \text{ s}^{-1}$
	$1.5 \times 10^{-19} \ T^{2.9} \ \exp(-880/T)$		1.3×10^{-13}	$cm^3 \text{ molecule}^{-1}s^{-1}$
k_2/k_1	$0.24 \ T^{0.2} \ \exp(1810/T)$	298–2000 K	300	

Uncertainty in log k_A: ± 0.2 near 298 K, increasing to ± 0.3 at 2000 K.   Uncertainty in log k_2/k_1: ± 0.5 from 300 to 2000 K. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + C_7H_{16} \xrightarrow{A} OH + C_7H_{15}$$

THERMOCHEMISTRY

The title reaction is the sum of four separate elementary processes: attack on one of the six equivalent primary H atoms,

$$O + CH_3(CH_2)_5CH_3 \xrightarrow{1} OH + CH_3(CH_2)_5CH_2$$

attack on one of the four equivalent secondary H atoms on the number 2 carbons,

$$O + CH_3(CH_2)_5CH_3 \xrightarrow{2a} OH + CH_3CH(CH_2)_4CH_3$$

attack on one of the four equivalent secondary H atoms on the number 3 carbons,

$$O + CH_3(CH_2)_5CH_3 \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_3CH_3$$

attack on one of the two equivalent secondary H atoms on the number 4 carbon,

$$O + CH_3(CH_2)_5CH_3 \xrightarrow{2c} OH + CH_3(CH_2)_2CH(CH_2)_2CH_3$$

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group contribution rules[1] were used to estimate the differences between enthalpies and entropies for the four heptyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between heptyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions ($OH + C_7H_{15} \rightarrow C_7H_{15}OH$).

MEASUREMENTS

Herron and Huie[2] measured k_A over the temperature range of 247 - 597 K in a flow system, with $[O]_0/[C_7H_{16}]_0 > 20$, by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, $k_A = (9.7 \pm 6) \times 10^7$ L $mol^{-1}s^{-1}$, and interpolated[3] k_A at 298 K to be 7.7×10^7. Marsh and Heicklen[4] generated O atoms from Hg-sensitized photodecomposition of N_2O in the presence of C_3F_6 and alkane at 307-398 K. k_A was determined relative to the rate coefficient k_3 for the $O + C_3F_6$ reaction by measuring the decrease in oxygenated fluorocarbon products gas chromatographically. k_3 had been determined previously[5]. Their room temperature result is close to that of Ref. 2 but their activation energy is noticeably smaller.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. As in the case of $O + n-C_5H_{12}$ (see data sheet for that reaction), k_{2a}, k_{2b}, and k_{2c} were grouped together and only their sum, k_2, was calculated. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for k_A at 298 K is more than 100 times larger than the rate coefficient at the same temperature for $O + C_2H_6$, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was assumed to be 2.5×10^5 L $mol^{-1}s^{-1}$, a value obtained by the same procedure as used for $O + n-C_4H_{10}$. Similarly, the vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of $O + n-C_4H_{10}$ (see data sheet for that reaction). For further details, see Ref. 6. The resulting values of k_1 and k_2 calculated separately were added together to give $k_A(T)$, which could be expressed by $k_A = 93$ $T^{2.9}$ $exp(-880/T)$ L $mol^{-1}s^{-1}$ over the temperature range of 250-2000 K. The calculated ratio k_2/k_1 is approximately 298 at 298 K, decreasing to approximately 3 at 2000 K.

DISCUSSION

The data of Ref. 2 are preferred because of the directness of the method. The consistency with data for O atom reaction with other alkanes (see data sheets for $O + C_5H_{14}$, $O + C_6H_{14}$, and $O + C_8H_{18}$), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthen the reliability of both the experiments and the calculations. Consequently, we recommend $k_A = 93$ $T^{2.9}$ $exp(-880/T)$ L $mol^{-1}s^{-1}$ for 250-2000 K, with an uncertainty in log k_A of ± 0.2 at 298 K, increasing to ± 0.3 at 2000 K.
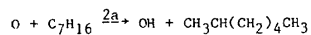
References:

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York; 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data, 2, 467 (1974).
4. G. Marsh and J. Heicklen, J. Phys. Chem. 71, 250 (1967).
5. D. Saunders and J. Heicklen, J. Phys. Chem. 70, 1950 (1966).
6. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O \; + \; C_8H_{18} \; \rightarrow \; OH \; + \; C_8H_{17}$$

$O + C_8H_{18} \xrightarrow{1} OH + n\text{-}C_8H_{17}$

$O + C_8H_{18} \xrightarrow{2a} OH + CH_3CH(CH_2)_5CH_3$

$O + C_8H_{18} \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_4CH_3$

$O + C_8H_{18} \xrightarrow{2c} OH + CH_3(CH_2)_2CH(CH_2)_3CH_3$

$\Delta H^o_{298} = -11.3 \pm 6$ kJ mol^{-1} (-2.7 kcal mol^{-1})
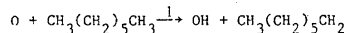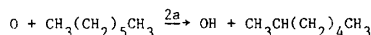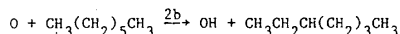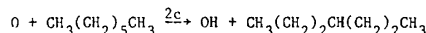$\Delta S^o_{298} = 43.6 \pm 8$ J mol^{-1} K^{-1} (10.4 cal mol^{-1} K^{-1})

$\Delta H^o_{298} = -28.9 \pm 7$ kJ mol^{-1} (-6.9 kcal mol^{-1})
$\Delta S^o_{298} = 38.4 \pm 8$ J mol^{-1} K^{-1} (9.4 cal mol^{-1} K^{-1})

$\Delta H^o_{298} = -32.2 \pm 11$ kJ mol^{-1} (-7.7 kcal mol^{-1})
$\Delta S^o_{298} = 38.4 \pm 8$ J mol^{-1} K^{-1} (9.4 cal mol^{-1} K^{-1})

$\Delta H^o_{298} = -32.2 \pm 11$ kJ mol^{-1} (-7.7 kcal mol^{-1})
$\Delta S^o_{298} = 38.4 \pm 8$ J mol^{-1} K^{-1} (9.4 cal mol^{-1} K^{-1})

THIS RECOMMENDATION

SYMBOL	REF.
Δ	2

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$1.9 \times 10^2 \; T^{2.8} \; \exp(-840/T)$	250-2000 K	1.0×10^8	L mol^{-1}s^{-1}
	$3.2 \times 10^{-19} \; T^{2.8} \; \exp(-840/T)$		1.7×10^{-13}	cm^3 molecule^{-1}s^{-1}
k_2/k_1	$0.28 \; T^{0.2} \; \exp(1880/T)$	298-2000 K	450	

Uncertainty in log k_A: ± 0.2 near 298 K, increasing to ± 0.3 at 2000 K.   Uncertainty in log k_2/k_1: ± 0.5 from 298 to 2000 K.
Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + C_8H_{18} \xrightarrow{A} OH + C_8H_{17}$$

THERMOCHEMISTRY

The title reaction is the sum of four separate elementary processes: Attack on one of the six equivalent primary H atoms,

$$O + CH_3(CH_2)_6CH_3 \xrightarrow{1} OH + CH_3(CH_2)_6CH_2$$

attack on one of the four equivalent secondary H atoms on the number 2 carbons,

$$O + CH_3(CH_2)_6CH_3 \xrightarrow{2a} OH + CH_3CH(CH_2)_5CH_3$$

attack on one of the four equivalent secondary H atoms on the number 3 carbons,

$$O + CH_3(CH_2)_6CH_3 \xrightarrow{2b} OH + CH_3CH_2CH(CH_2)_4CH_3$$

and attack on one of the four equivalent secondary H atoms on the number 4 carbons

$$O + CH_3(CH_2)_6CH_3 \xrightarrow{2c} OH + CH_3(CH_2)_2CH(CH_2)_3CH_3$$
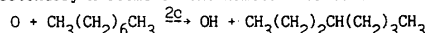
Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group contribution rules[1] were used to estimate differences between enthalpies and entropies for the four heptyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between octyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (OH + C_8H_{17} → $C_8H_{17}OH$).

MEASUREMENTS

Herron and Huie[2] measured k_A over the temperature range of 247 - 597 K in a flow system, with $[O]_0/[C_8H_{18}]_0 > 14$, by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, k_A = (1.23 ± 0.16) × 10^8 L $mol^{-1}s^{-1}$, and interpolated[3] k_A at 298 K to be 1.0 × 10^8. An earlier measurement[4] gave values of k_A in the temperature range of 353 to 473 K smaller by a factor of approximately 5 than those reported in Ref. 2. Because these values, and others from the same laboratory, are inconsistent with the majority of measurements for other homologous alkanes, they are not used in this evaluation.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. As in the case of O + C_5H_{12} (see data sheet for that reaction), k_{2a}, k_{2b} and k_{2c} were grouped together and only their sum, k_2, was calculated. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for k_A at 298 K is approximately 300 times larger than the rate coefficient at the same temperature for O + C_2H_6, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was estimated to be 2.2 × 10^5 L mol^{-1} s^{-1}, by the same procedure used for the O + C_4H_{10} reaction. Similarly, the vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of O + C_4H_{10} (see data sheet for that reaction). For further details, see Ref. 5. The resulting values of k_1 and k_2 calculated separately were added together to give $k_A(T)$, which could be expressed by k_A = 1.9 × 10^2 $T^{2.8}$ exp(-840/T) L $mol^{-1}s^{-1}$ over the temperature range of 250-2000 K. The calculated ratio k_2/k_1 is approximately 450 at 298 K, decreasing to approximately 3 at 2000 K.

DISCUSSION

The consistency of the data of Ref. 2 with data for O atom reactions with similar alkanes (see data sheets for O + C_5H_{12}, O + C_6H_{14}, and O + C_7H_{16}), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthens the reliability of both the experiments and the calculations. Consequently, we recommend k_A = 1.9 x 10^2 $T^{2.8}$ exp(-840/T) L $mol^{-1}s^{-1}$ for 250-2000 K, with an uncertainty in log k_A of ±0.2 at 298 K, increasing to ±0.3 at 2000 K.

References

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York; 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. L. I. Avramenko, R. B. Kolesnikova, and G. I. Savinova, Izvest. Akad. Nauk SSSR, Ser. Khim. 253 (1967), as reported in Ref. 4.
5. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + i\text{-}C_4H_{10} \rightarrow OH + C_4H_9$$

$O + i\text{-}C_4H_{10} \xrightarrow{\ 1\ } OH + i\text{-}C_4H_9$

$O + i\text{-}C_4H_{10} \xrightarrow{\ 2\ } OH + t\text{-}C_4H_9$
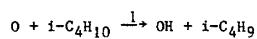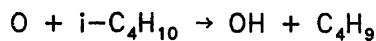
$\Delta H^o_{298} = -18.2 \pm 6 \ kJ \ mol^{-1} \ (-4.4 \ kcal \ mol^{-1})$

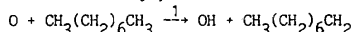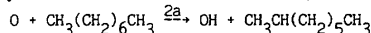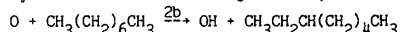$\Delta S^o_{298} = 38.5 \pm 8 \ J \ mol^{-1} \ K^{-1} \ (9.2 \ cal \ mol^{-1} \ K^{-1})$
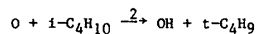
$\Delta H^o_{298} = -39.1 \pm 8 \ kJ \ mol^{-1} \ (-9.3 \ kcal \ mol^{-1})$

$\Delta S^o_{298} = 46.0 \pm 8 \ J \ mol^{-1} \ K^{-1} \ (11.0 \ cal \ mol^{-1} \ K^{-1})$

SYMBOL	REF.
▽	6
×	7
△	8
+	9
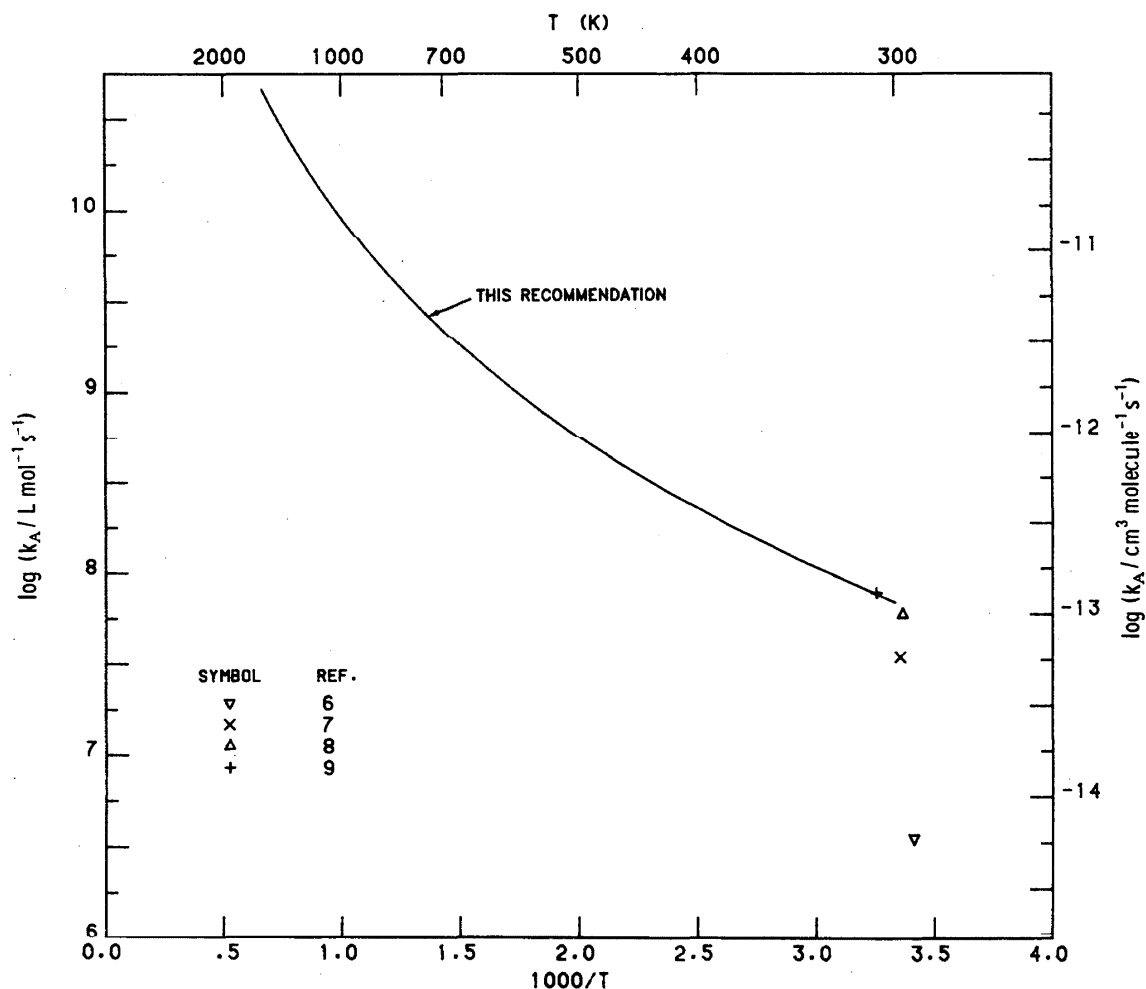
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$2.0 \times 10^{-2} \ T^{3.9} \ exp(-80/T)$	298-2000 K	7×10^7	$L \ mol^{-1}s^{-1}$
	$3.3 \times 10^{-23} \ T^{3.9} \ exp(-80/T)$		1.2×10^{-13}	$cm^3 \ molecule^{-1}s^{-1}$
k_2/k_1	$3.7 \times 10^{-2} \ T^{0.1} \ exp(2315/T)$	298-2000 K	150	

Uncertainty in log k_A: ±0.2 near 300 K, increasing to ±0.4 at 2000 K. Uncertainty in log k_2/k_1: ±0.3 near 300 K, increasing to ±0.5 at 2000 K. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + i\text{-}C_4H_{10} \xrightarrow{A} OH + C_4H_9$$
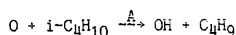
THERMOCHEMISTRY

The title reaction is the sum of two elementary reactions: removal of one of the nine equivalent primary H atoms to form isobutyl:

$$O + (CH_3)_3CH \xrightarrow{1} OH + (CH_3)_2CHCH_2$$
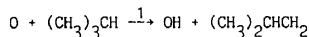
and removal of the single tertiary H to form t-butyl:
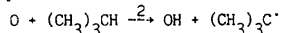
$$O + (CH_3)_3CH \xrightarrow{2} OH + (CH_3)_3C^{\cdot}$$

Thermochemical data for O and OH are taken from to JANAF Thermochemical Tables, 3rd edn. (1985). Data for isobutane are from Stull et al.[1] $\Delta Hf^O_{298}(i\text{-}C_4H_9) = 57.3$ kJ mol^{-1} is taken from Benson;[2] $\Delta Hf^O_{298}(t\text{-}C_4H_9)$ has been the subject of considerable disagreement, as reviewed by McMillen and Golden.[3] We use their recommended value of 36.4 kJ mol^{-1}, but the uncertainty is at least ±8 kJ mol^{-1}. $S^O_{298}(i\text{-}C_4H_9)$ was calculated to be 310.5 J mol^{-1} K^{-1} using group additivity methods and assuming that the barrier to rotation about the CC bond is 1.2 kJ mol^{-1}.[4] $S^G(t\text{-}C_4H_9)$ was taken to be 318 J $mol^{-1}K^{-1}$.[5]

MEASUREMENTS

Four measurements of k_A have been reported, all near room temperature.[6-9] Of these, the earliest[6] is discarded because it is based on an incorrect mechanism and furthermore the method is too indirect to be reliable. The second[7] was cited in a footnote of another study and has not been reported in detail; consequently it is not possible to evaluate it properly, although it does agree within a factor of 2 with the two remaining, and most reliable, measurements. Washida and Bayes[8] produced O atoms in a fast-flow reactor by passing O_2/He through a microwave discharge. Isobutane or isobutane-d $((CH_3)_3CD)$ at pressures comparable to the O atom pressure (approximately 0.1 - 0.3 mPa) was added to the flow. Alkyl radical concentrations were monitored by photoionization mass spectrometry. Based on the results with the deuteroalkane, those workers concluded that abstraction of the tertiary hydrogen was the dominant but not exclusive pathway. k_A at room temperatures was reported to be $(6 \pm 1.2) \times 10^7$ L $mol^{-1}s^{-1}$. Jewell et al.[9] produced O atoms by the N + NO reaction, N atoms being formed in a microwave discharge through N_2. Hydrocarbon was added downstream. Kinetic measurements were made by monitoring gas chromatographic consumption of isobutane in the presence of excess O atoms. They reported $k_A = (7.9 \pm 1.4) \times 10^7$ L $mol^{-1}s^{-1}$ at 307 K. There are no measurements at higher temperatures.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack of O atoms on the primary and on the tertiary H atoms. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because experimental evidence indicates that $k_A(298)$ is approximately 50 times larger than $k(298)$ for the $O + (CH_3)_4C$ reaction, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was assumed to be 5×10^5 L $mol^{-1}s^{-1}$, a value obtained by calculating the entropy of reaction by the usual methods and taking the activation energy at 298 K to be the same as for tertiary attack on 2,3-dimethylbutane (see data sheet for that reaction). The vibrational frequencies and effects of O adduct on the internal rotations of the two activated complexes were assumed to be the same as in the case of O + 2,3-dimethylbutane as well. For additional details, see Ref. 10. This model gave good agreement with experimental data in the case of the latter molecule. The resulting values of k_1 and k_2 were added together to give $k_A(T)$, which could be represented over the temperature range of 298-2000 K by the expression, $k_A(T) = 2 \times 10^{-2} T^{3.9} \exp(-80/T)$ L $mol^{-1}s^{-1}$. According to this model $k_2/k_1 \doteq 150$ at 298 K, decreasing to 0.3 at 2000 K.

DISCUSSION

There is very good agreement between the two most reliable measurements of k_A near room temperature,[8,9] but no measurements at higher temperatures. Consequently we rely entirely on the calculations to extrapolate k_A to 2000 K. The reliability of the model used to do this depends on the success of the same model for the analogous reaction of O + 2,3-dimethylbutane. The model agrees well with experiments for that reaction, and there is no reason to doubt its accuracy in this case. Consequently, we recommend $k_A(T) = 2 \times 10^{-2} T^{3.9} \exp(-80/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_A of ±0.2 at 300 K, increasing to ±0.4 at 2000 K.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, New York: 1969), p. 245.
2. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York: 1976).
3. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982).
4. J. Pacansky and W. Schubert, J. Chem. Phys. 76, 1459 (1986).
5. J. Pacansky and J. S. Chang, J. Chem. Phys. 74, 5539 (1981).
6. F. J. Wright, 10th Symp. (Int.) Combust., 387 (1965).
7. R. J. Cvetanovic and L. C. Doyle, as cited in G. Paraskevopoulos and R. J. Cvetanovic, J. Am. Chem. Soc 91, 7572 (1969).
8. N. Washida and K. D. Bayes, J. Phys. Chem. 84, 1309 (1980).
9. S. P. Jewell, K. A. Holbrook, and G. A. Oldershaw, Int. J. Chem. Kinet. 14, 585 (1982).
10. N. Cohen, and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + (CH_3)_4C \rightarrow OH + C_5H_{11}$$
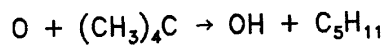
$\Delta H^o_{298} = -5.0 \pm 4.4 \text{ kJ mol}^{-1}$ ($-1.2 \text{ kcal mol}^{-1}$) $\Delta S^o_{298} = 48.6 \pm 8 \text{ J mol}^{-1}K^{-1}$ ($11.6 \text{ cal mol}^{-1}K^{-1}$)
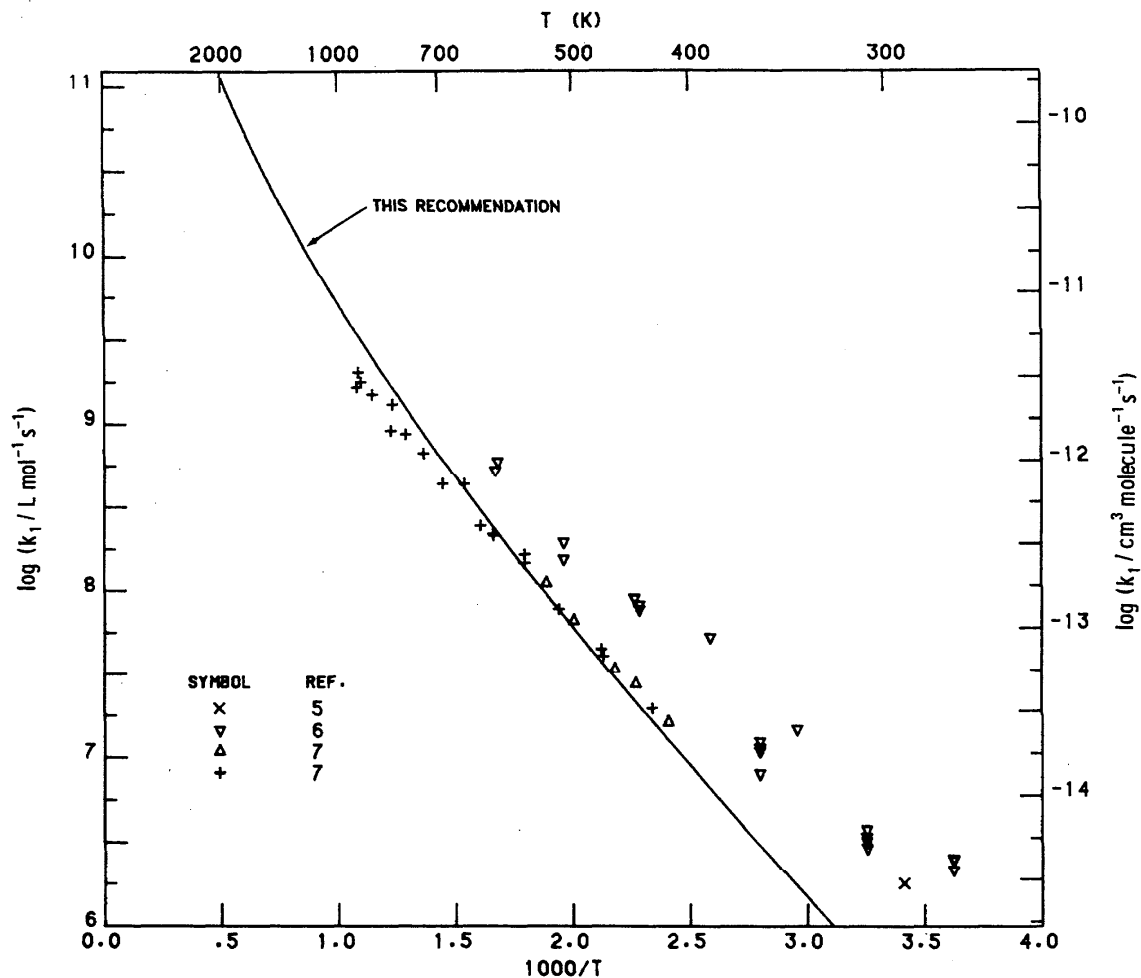

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.5 \times 10^3 \ T^{2.5} \exp(-2720/T)$	298-2000 K	4.5×10^5	$L \ mol^{-1}s^{-1}$
	$4.2 \times 10^{-18} \ T^{2.5} \exp(-2720/T)$		7.5×10^{-16}	$cm^3 \ molecule^{-1}s^{-1}$

Uncertainty in log k_1: ± 0.3 throughout range. Because the reverse reaction is unimportant at any temperature, values for k_{-1} and K(T) have not been recommended.

(October 1987)

$O + (CH_3)_4C \xrightarrow{1} OH + (CH_3)_3CCH_2$
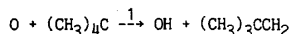
THERMOCHEMISTRY

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Data for $(CH_3)_4C$ (2,2-dimethylpropane, or neopentane) are taken from Stull et al.[1] The bond dissociation energy of $(CH_3)_4C$, D^O_{298} $((CH_3)_3CCH-H)$, was determined[2] relative to that of CH_4, from which ΔH^O_{298} can be calculated to be -5.0 kJ mol^{-1} for the reaction. The difference between the entropies of the radical and of the parent alkane was calculated[3] by group additivity methods to be 26.0 J mol^{-1} K^{-1}, assuming a near-zero barrier to internal rotation about the α-CC bond.[4] An analytic expression for K(T) has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the competing radical recombination reaction, $OH + (CH_3)_3CCH_2 \rightarrow (CH_3)_3CCH_2OH$.

MEASUREMENTS

Of the three measurements[5-7] of k_1, the most reliable is that of Michael et al.[7], made by both flash photolysis-resonance fluorescence (415-528 K) and discharge flow-resonance fluorescence (427-922 K). With $[(CH_3)_4C]/[O]$ always greater than 200, the contribution from secondary reactions should always have been less than 10%. The reported rate coefficients (calculated without taking secondary reactions into account) therefore require small if any, corrections. Herron and Huie[6] measured k_1 between 276 and 597 K in a flow system, with $[O]_0/[C_5H_{12}]_0 > 10$ (>200 at low temperatures), by monitoring alkane disappearance by mass spectrometry. Under their conditions the reaction should be free from secondary processes. Nevertheless, their rate coefficients are consistently larger than those of Ref. 7 by a factor of 2-3. There are no obvious flaws with their procedure, except possibly that the small change in alkane concentration (less than 10% at $T \leq 307$ K) means limited precision in measuring k_1 (a 5% error in $[RH]_0$ or $[RH]_t$ means a 40% error in k_1). The only likely source of systematic error is the ethylene titration technique needed to measure absolute [O]. If the stoichiometry is greater than the assumed value of 2 atoms O consumed per molecule of C_2H_4, then [O] will be larger than was assumed, and k_1 consequently smaller. The results of Wright[5] are not used in this evaluation because the method was too indirect and the conclusions are based on an incorrect mechanism.

CALCULATIONS

A transition-state-theory calculation (TST) was carried out assuming that $k(400) = 1.1 \times 10^7$ L $mol^{-1}s^{-1}$(7) and assuming linear geometry for the C·H·O structure. Further details are given in Ref. 8. With these assumptions, the resulting rate coefficients can be fitted by the expression $k = 2.5 \times 10^3$ $T^{2.5}$ $exp(-2720/T)$ L $mol^{-1}s^{-1}$. Another TST calculation has been described by Michael et al.[9]

DISCUSSION

Although it is difficult to pinpoint errors in the measurements of Ref. 6 we favor the more recent technique used in Ref. 7 which produced lower values for k_1. We recommend the expression for k_1 obtained by TST calculations, which also gives good agreement with the experimental data: $k_1 = 2.5 \times 10^3$ $T^{2.5}$ $exp(-2720/T)$ L $mol^{-1}s^{-1}$. The uncertainty in k_1 is a factor of 2 throughout the temperature range of 298-2000 K.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, New York, 1969), p. 247.
2. C. W. Larson, E. A. Hardwidge, and B. S. Rabinovitch, J. Chem. Phys. 50, 2769 (1969).
3. H. E. O'Neal and S. W. Benson, in Free Radicals, J. K. Kochi, ed. (Wiley, New York, 1973), p. 275.
4. J. Pacansky and W. Schubert, J. Chem Phys. 76, 1459 (1982).
5. F. J. Wright, 10th Symp. (Int.) Combust., 387 (1965).
6. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
7. J. V. Michael, D. G. Keil, and R. B. Klemm, 19th Symp. (Int.) Combust., 39 (1982).
8. N. Cohen and K. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
9. J. V. Michael, D. G. Keil, and R. B. Klemm, Int. J. Chem. Kinet. 15, 705 (1983).
10. N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).

$$O + (CH_3)_2CHCH(CH_3)_2 \rightarrow OH + C_6H_{13}$$

$O + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{1} OH + CH_2CH(CH_3)CH(CH_3)_2$
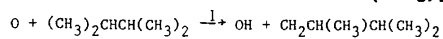
$\Delta H^o_{298} = -10.0 \pm 8$ kJ mol^{-1} $(-2.4$ kcal mol$^{-1})$

$\Delta S^o_{298} = 35.2 \pm 5$ J mol^{-1} K^{-1} $(8.4$ cal mol^{-1} K$^{-1})$

$O + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{2} OH + (CH_3)_2CCH(CH_3)_2$
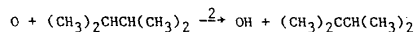
$\Delta H^o_{298} = -36.2 \pm 6$ kJ mol^{-1} $(-8.7$ kcal mol$^{-1})$

$\Delta S^o_{298} = 51.9 \pm 10$ J mol^{-1} K^{-1} $(12.4$ cal mol^{-1} K$^{-1})$
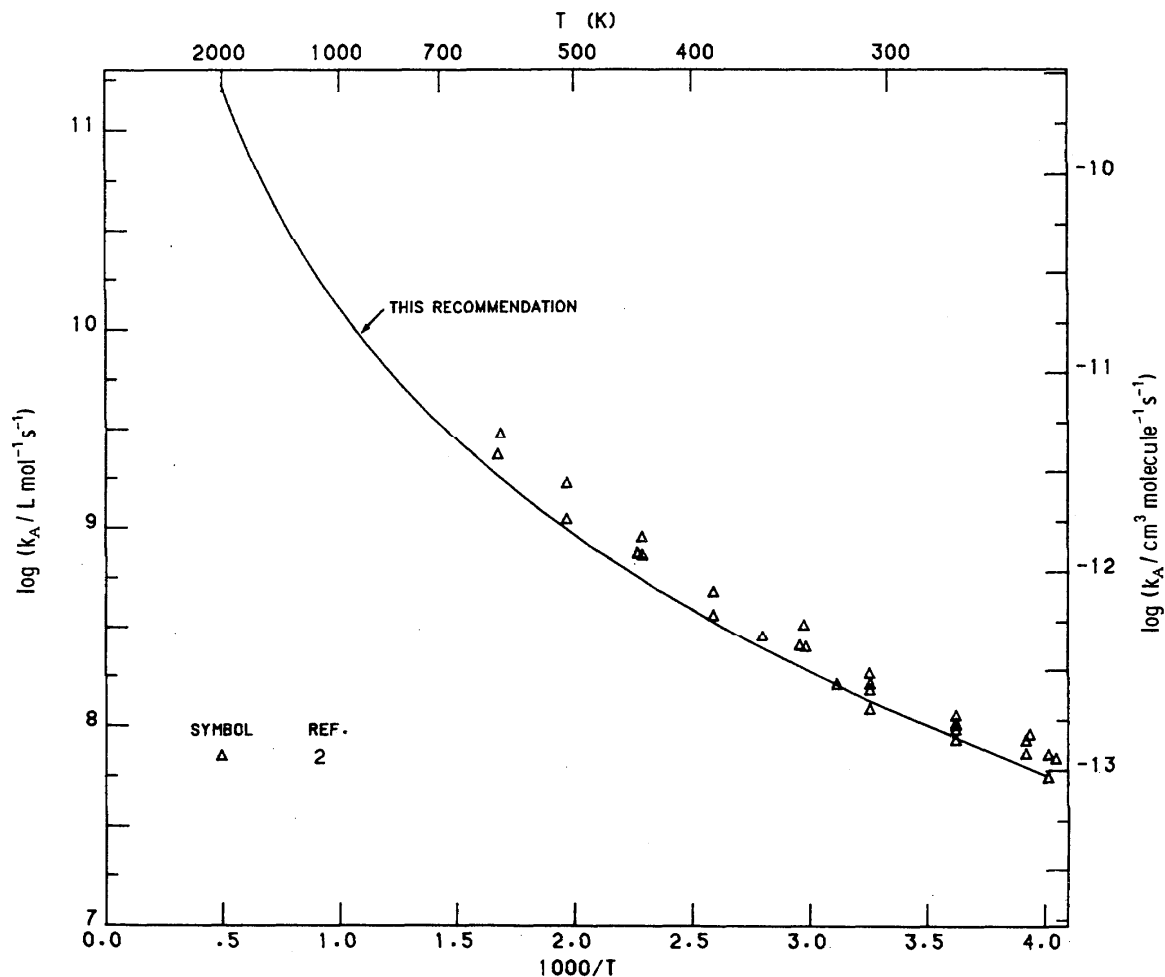
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	2.3×10^{-1} $T^{3.6}$ exp$(-140/T)$	250-2000 K	1.2×10^8	L mol^{-1} s^{-1}
	3.9×10^{-22} $T^{3.6}$ exp$(-140/T)$		2.0×10^{-13}	cm^3 molecule^{-1}s^{-1}
k_2/k_1	6.0×10^{-2} $T^{0.1}$ exp$(2330/T)$	298-2000 K	250	

Uncertainty in log k_A: ±0.2 near 300 K, increasing to ±0.4 at 2000 K. Uncertainty in log k_2/k_1: ±0.3 near 300 K, increasing to ±0.5 at 2000 K. Expressions for K, k_{-1} and k_{-2} are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

$$O + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{A} OH + \cdot C_6H_{13}$$
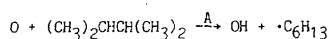
THERMOCHEMISTRY

The title reaction is the sum of two elementary reactions: removal of one of the twelve equivalent primary H atoms:

$$O + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{1} OH + \cdot CH_2CH(CH_3)CH(CH_3)_2$$
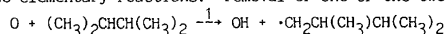
and removal of one of the two equivalent tertiary H atoms:
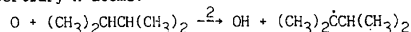
$$O + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{2} OH + (CH_3)_2\dot{C}CH(CH_3)_2$$

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). ΔHf^o_{298} and ΔS^o_{298} for both reactions are estimated by comparison with the analogous reactions of $i-C_4H_{10}$, with appropriate corrections for symmetry differences and for the effects of gauche interactions.[1]

Analytic expressions for $K(T)$ have not been calculated because the reverse reactions (between dimethylbutyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (OH + $C_6H_{13} \rightarrow C_6H_{13}OH$).

MEASUREMENTS

Herron and Huie[2] produced O atoms in large excess in a flow tube by the N + NO reaction and monitored alkane consumption by mass spectrometry. The principal shortcoming of the method is the uncertainty in the O + C_2H_4 titration used to measure [O]. They obtained values of k_A from 247 to 597 K; at 307 they found $k_A = 1.5 \pm 0.3 \times 10^8$ L mol^{-1}s^{-1}, and interpolated[3] $k_A(298)$ to be 1.2×10^8.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack of O atoms on the primary and on the tertiary H atoms. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and tertiary H atoms at 298 K, respectively. Because experimental evidence indicates that $k_A(298)$ is approximately 30 times larger than $k(298)$ for the O + $(CH_3)_4C$ reaction, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was assumed to be 5×10^5 L mol^{-1}s^{-1}, an estimation arrived at by calculating the entropy of reaction by the usual methods and taking the activation energy at 298 K to be the average of the activation energies of the reactions of O with C_2H_6 and with $(CH_3)_4C$. For additional details, see Ref. 4. The resulting values of k_1 and k_2 were added together to give $k_A(T)$, which could be represented over the temperature range of 250-2000 K by the expression, $k_A(T) = 0.23 \ T^{3.6} \ \exp(-140/T)$ L mol^{-1}s^{-1}. This expression agrees well with the experimental data. These calculations suggest k_2/k_1 to be = 250 at 298 K, rapidly decreasing with temperature.

DISCUSSION

There is only one set of experimental data for k_A. Because there is no other alkane for which tertiary attack by O atoms has been measured at temperatures above 300 K, there is no independent evidence to confirm the activated complex model that these data suggest. We recommend the calculated expression, which agrees with the experimental data: $k_A = 0.23 \ T^{3.6} \ \exp(-140/T)$ L mol^{-1}s^{-1}, over the temperature range of 250-2000 K. The uncertainty in log k_A is ±0.2 at 300 K, increasing to ±0.4 at 2000 K. The ratio k_2/k_1 is estimated to be 250 at 300 K, decreasing with increasing temperature. A confirmation of the high temperature values of k_A, or alternatively a high temperature measurement of the rate of O attack on isobutane, would be very useful.

References:

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York, 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + (CH_3)_3CC(CH_3)_3 \rightarrow OH + CH_2C(CH_3)_2C(CH_3)_3$$
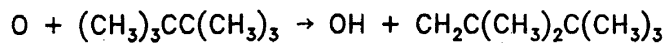
$\Delta H^o_{298} = -17.5 \pm 8$ kJ mol^{-1} (-4.2 kcal mol^{-1}) $\Delta S^o_{298} = 44.4 \pm 4$ J mol^{-1}K^{-1} (10.6 cal mol^{-1}K^{-1})
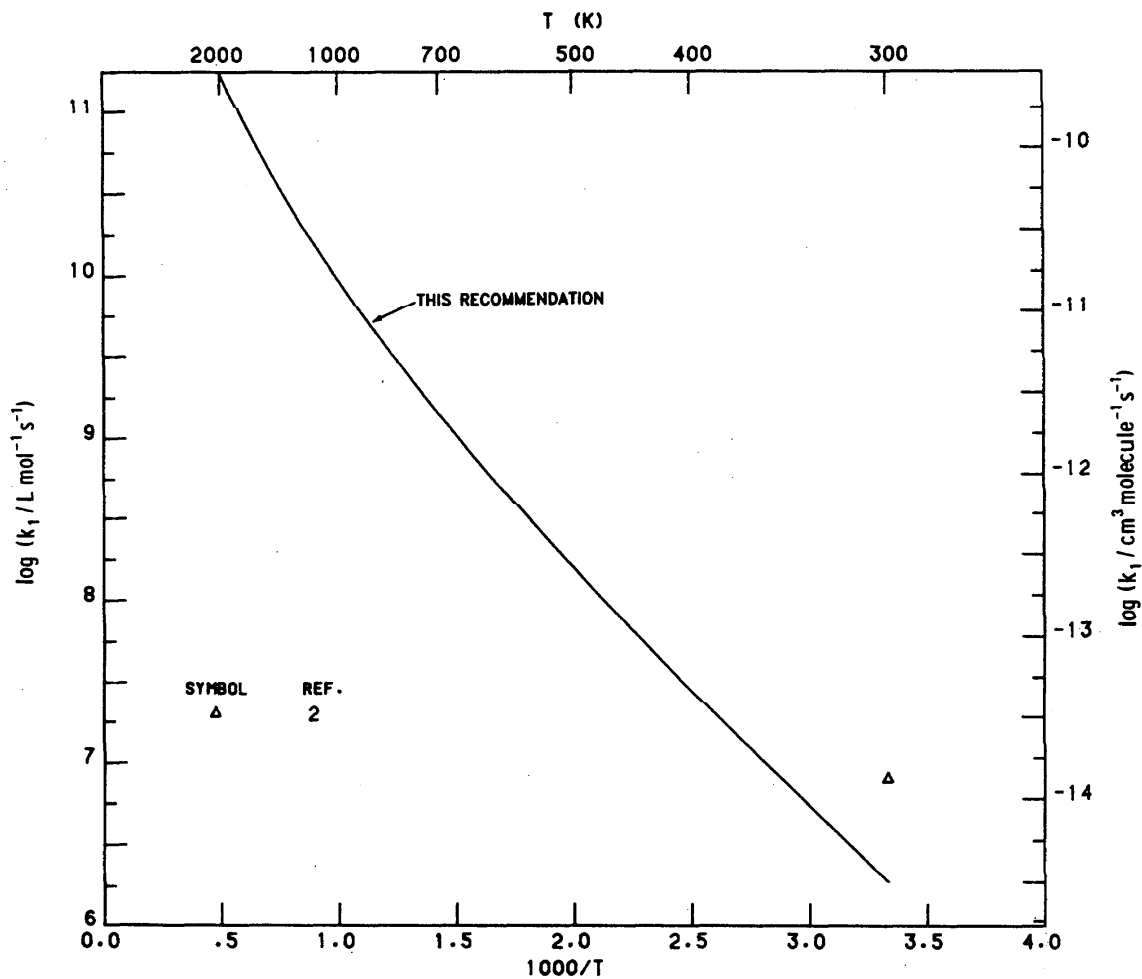
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	3.2×10^3 T$^{2.5}$ exp(-2360/T)	298–2000 K	2×10^6	L mol^{-1}s^{-1}
	5.3×10^{-18} T$^{2.5}$ exp(-2360/T)		3.4×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.4 throughout temperature range. Because the reverse reaction is unimportant at any temperature, values for k_{-1} and K(T) have not been recommended.

(October 1987)

$O + (CH_3)_3CC(CH_3)_3 \xrightarrow{1} OH + CH_2C(CH_3)_2C(CH_3)_3$
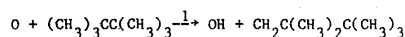
THERMOCHEMISTRY

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules[1] were used to estimate differences between the enthalpies and entropies of the neooctyl radical, and of the alkane itself, assuming a near-zero barrier to internal rotation about the α-CC bond. An analytic expression for K(T) has not been calculated because the reverse reaction, between OH and neooctyl radicals, will, under all conditions of practical interest, be slower than the competing radical combination process ($OH + C_8H_{17} \rightarrow C_8H_{17}OH$).

MEASUREMENTS

A single measurement of k_1 at 307 K has been reported.[2] The value obtained, 8×10^6 L mol^{-1}s^{-1}, is 2.4 times faster than the same workers reported for k_2, the rate coefficient for the analogous reaction of O + neopentane. The measurement was made in a flow system with O atoms in large excess; alkane disappearance was monitored by mass spectrometry, and [O] was determined by titration with ethylene.

CALCULATIONS

A transition-state-theory calculation was carried out assuming that $k(298) = 2 \times 10^6$ L mol^{-1}s^{-1} and using the same model for the activated complex that was used for the reaction of O + neopentane (see data sheet for that reaction). Details are given in Ref. 3 (except that there, $k(298)$ was assumed to be 1×10^6). With these assumptions, the resulting rate coefficients can be fitted by the expression, $k_1 = 3.2 \times 10^3 T^{2.5} \exp(-2360/T)$ L mol^{-1}s^{-1}.

DISCUSSION

At 298 K, the calculated entropy of activation for reaction 1 is only 0.5 cal mol^{-1}K^{-1} larger than that for reaction 2, O + neopentane. The C-H bond dissociation energy in neooctane has not been measured but is expected to be slightly lower (by 3-5 kJ/mole) than that of neopentane (423 kJ/mole), which should make the activation energy smaller by approximately 1-2 kJ/mol, and $k(298)$ larger by a factor of 1.3 - 2.7. The recommended value for $k_2(298)$ is 1×10^6. The measured value of $k_1(307)$ is 8×10^6, which seems too large because it implies that either the activation energy of reaction 1 is 5 kJ/mol less than that of reaction 2 or that one of the calculated entropies of activation is significantly in error. A more plausible explanation is that the measured value of k_1 is too high.[4] In Ref. 2, k_2 was also measured using the same technique. We concluded that their measurements of k_2 were also too high; see the data sheet for that reaction for a further discussion. We recommend $k_1(298) = 2 \times 10^6$ and the calculated expression for $k_1(T)$ based on this value, namely, $k_1 = 3.2 \times 10^3 T^{2.5} \exp(-2360/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.4 throughout the range of 298 K < T < 2000 K.

References

1   S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York; 1976).
2. J. T. Herron and R. E. Huie, J. Phys. Chem. 73, 3327 (1969).
3. N. Cohen, and K. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).
4. N. Cohen, Int. J. Chem. Kinet. 18, 59 (1986).

$$O + c-C_5H_{10} \rightarrow OH + c-C_5H_9$$
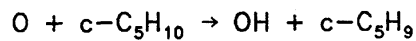
$\Delta H^o_{298} = -32.7 \pm 5$ kJ mol^{-1} (-7.8 kcal mol^{-1}) $\Delta S^o_{298} = 48.5 \pm 5$ J mol^{-1} K^{-1} (11.6 cal mol^{-1} K^{-1})
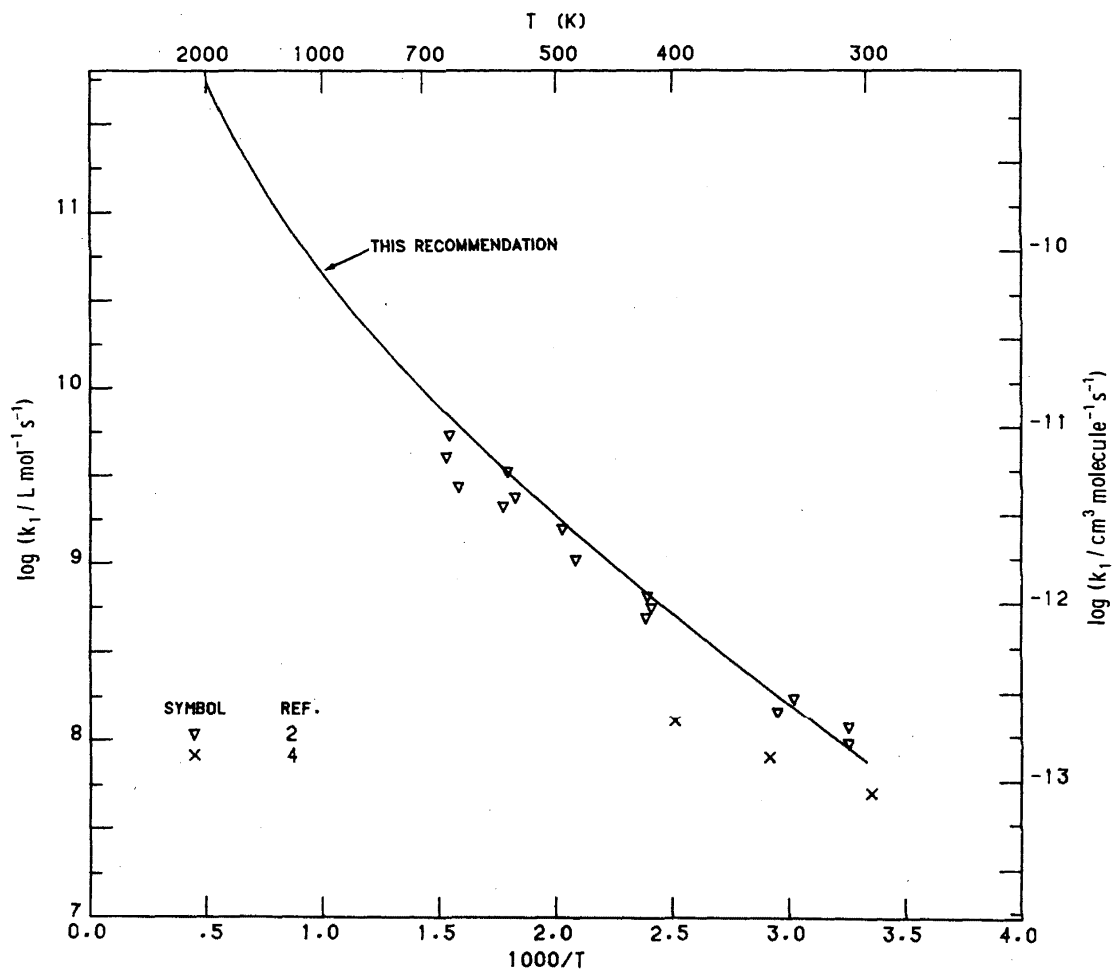
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.9 \times 10^3 \ T^{2.6} \ e^{-1390/T}$	298 - 2000 K	7.5×10^7	L mol^{-1}s^{-1}
	$4.8 \times 10^{-19} \ T^{2.6} \ e^{-1390/T})$		1.3×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1:   ±0.3 at 298 K, increasing to ±0.5 at 2000 K.   Expressions for K(T) and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

(October 1987)

$$O + c\text{-}C_5H_{10} \xrightarrow{1} OH + c\text{-}C_5H_9$$
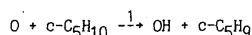
THERMOCHEMISTRY

Thermochemical data for O and OH are from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules[1] were used to estimate differences between ΔHf^o_{298} and S^o_{298} for the cyclopentyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction ($OH + c\text{-}C_5H_9 \rightarrow c\text{-}C_5H_9OH$).

MEASUREMENTS

The most reliable measurements are those of Huie and Herron,[2] who studied the reaction at 307-652 K in a flow tube, producing O atoms by passing a few percent of O_2 in Ar through a microwave discharge. O atoms were kept in considerable excess over alkane. Relative [O] was determined by mass spectrometry, put on an absolute basis by titration with NO_2. The alkane concentration was also measured by mass spectrometry. Because [O] was kept in excess and at most 10% of the alkane was consumed, the method was free of complications caused by secondary reactions. However, since k is proportional to $\ln([RH]_0/[RH]_t)$, a 5% error in measuring either $[RH]_0$ or $[RH]_t$ results in a 50% error in k. From their own data, they later[3] extrapolated a value of $k_1(300)$ of 7.5×10^7 L $mol^{-1}s^{-1}$. An earlier measurement[4] of k_1 relative to the rate of reaction of O atoms with C_3F_6, in turn measured relative to the rate of O with $1\text{-}C_4H_8$, is not used in this evaluation because of its indirectness.

CALCULATIONS

Transition-state theory calculations were carried out for k_1 in order to extrapolate the rate coefficients to higher temperatures. $S^{\ddagger}(298)$ was estimated by group additivity methods, using the parent cycloalkane as a model compound. The C·H·O was assumed to be linear -- an assumption supported by experiments of Dutton, et al.[5] Vibrational frequencies assumed for the activated complex are described in Ref. 6, along with other details. With an assumed value for $k_1(298)$ of 7.5×10^7 L $mol^{-1}s^{-1}$ based on Ref. 3, this model yields values for k_1 that are fitted by the expression, $k_1 = 2.9 \times 10^3$ $T^{2.6}$ exp(-1390) L $mol^{-1}s^{-1}$.

DISCUSSION

The calculations are in reasonable agreement with the data of Ref. 3, and also consistent with data and calculations for reactions of O with $c\text{-}C_6H_{12}$ and with $c\text{-}C_7H_{14}$ (see data sheets for those reactions). We therefore recommend $k_1 = 2.9 \times 10^3$ $T^{2.6}$ exp(-1390) L mol^{-1} s^{-1}, with an uncertainty in log k_1 of ±0.3 at 298 K, increasing to ±0.5 at 2000 K.

References

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, 1976).
2. R. E. Huie and J. T. Herron, J. Res. Nat. Bur. Stds. 76A, 77 (1972).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. W. K. Stuckey and J. Heicklen, J. Chem. Phys. 46, 4843 (1967).
5. N. J. Dutton, I. W. Fletcher, and J. C. Whitehead, Mol. Phys. 52, 475 (1984).
6. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet., 18, 99 (1986).

$$O + c-C_6H_{12} \rightarrow OH + c-C_6H_{11}$$

$$O + c-C_6H_{12} \rightarrow OH + c-C_6H_{11}$$
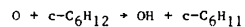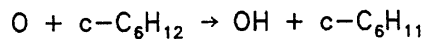
$\Delta H^o_{298} = -32.7 \pm 5 \text{ kJ mol}^{-1}$ (-7.8 kcal mol^{-1}) $\qquad\qquad$ $\Delta S^o_{298} = 53.0 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ (12.7 cal mol^{-1} K^{-1})

SYMBOL	REF.
▽	2
□	3
◇	4
△	6
×	8
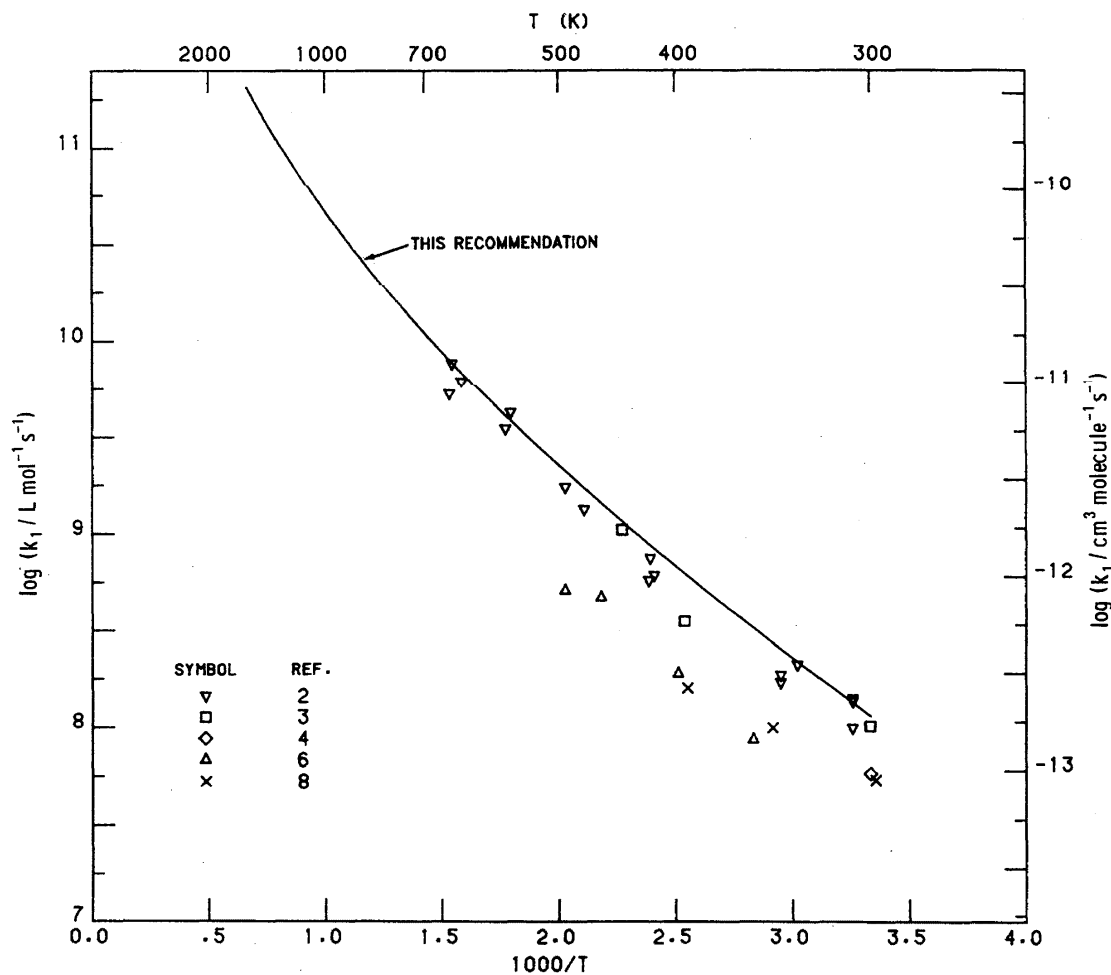
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.6 \times 10^3 \ T^{2.6} \ e^{-1240/T}$	298 - 2000 K	8.3×10^7	L mol^{-1}s^{-1}
	$4.3 \times 10^{-18} \ T^{2.6} \ e^{-1240/T}$		1.4×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.3 at 298 K, increasing to ±0.5 near 2000 K. Expressions for K(T) and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

(October 1987)

$$O + c\text{-}C_6H_{12} \xrightarrow{1} OH + c\text{-}C_6H_{11}$$
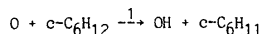
THERMOCHEMISTRY

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules[1] were used to estimate differences between ΔHf^o_{298} and S^o_{298} for the cyclohexyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction ($OH + c\text{-}C_6H_{11} \rightarrow c\text{-}C_6H_{11}OH$).

MEASUREMENTS

The most reliable measurements are those of Huie and Herron,[2] who studied the reaction at 307–652 K in a flow tube, producing O atoms by passing a few percent of O_2 in Ar through a microwave discharge. O atoms were kept in considerable excess over alkane. Relative [O] was determined by mass spectrometry, put on an absolute basis by titration with NO_2. Alkane concentration was also measured by mass spectrometry. Because [O] was kept in excess and at most 10% of the alkane was consumed, the method was free of complications caused by secondary reactions. However, since k is proportional to $\ln([RH]_o/[RH]_t)$, a 5% error in measuring either $[RH]_o$ or $[RH]_t$ results in a 50% error in k. At 307 K they obtained values between 1.0 and 1.4×10^8 L mol^{-1}s^{-1}.

Kim and Timmons[3] studied the reaction in a discharge flow facility, the O atoms being generated by the reaction between N and NO. Two procedures were used: in one, [O] was in excess and $[C_6H_{12}]$ was monitored mass spectrometrically; in the other, $[C_6H_{12}]$ was in excess and [O] was measured by epr. The epr results were not corrected for stoichiometry and hence are not useful as they stand. The mass spectrometric data, at 300–440 K, are in good agreement with the results of Huie and Herron: at 300 K they reported $k = 1.0 \times 10^8$. Washida and Takagi[4] used photoionization mass spectrometry to monitor $c\text{-}C_6H_{12}$ disappearance in the presence of excess O atoms and obtained a value for k_1 about 30% smaller than the 8.3×10^7 value recommended by Herron and Huie;[5] however, details of their data reduction are not given. Two earlier measurements are not used in this evaluation: that by Avramenko,[6] for reasons discussed by Kaufman;[7] and that by Stuckey and Heicklen[8] because k_1 was measured relative to the rate of reaction of $O + C_3F_6$, which in turn was measured relative to the rate of $O + 1\text{-}C_4H_8$.

CALCULATIONS

Transition-state theory calculations were carried out for k_1 in order to extrapolate the rate coefficients to higher temperatures. $S^{\ddagger}(298)$ was estimated by group additivity methods, using the parent cycloalkane as a model compound. The C·H·O geometry was assumed to be linear. Vibrational frequencies for the activated complex were taken to be the same as for the reaction of $O + c\text{-}C_5H_{10}$. For further details, see Ref. 9. With an assumed value for $k_1(298)$ of 8.3×10^7 L mol^{-1} s^{-1} from Ref. 5, this model gives values for k_1 that are fitted by the expression, $k_1 = 2.6 \times 10^3 T^{2.6} \exp(-1240/T)$ L mol^{-1} s^{-1}.

Although $c\text{-}C_6H_{12}$ in its most stable (chair) conformation has a symmetry number of 6, these calculations were carried out assuming all H atoms are equivalent. This assumption is questionable. If it is incorrect, and for example, the equatorial H atoms are significantly more reactive than the axial ones, the calculated rate coefficient will be slightly lower than given by the above expression.

DISCUSSION

The calculations, based on experimental values of $k_1(300)$ of Refs. 2 and 3, are in good agreement with higher temperature data of those studies. Apart from this, there is no reason to invalidate the result of Ref. 4. We recommend the calculated expression of $k_1 = 2.6 \times 10^3 T^{2.6} \exp(-1240/T)$ L mol^{-1} s^{-1}, with an uncertainty in log k_1 of ± 0.3 at 298 K, increasing to ± 0.5 at 2000 K.

References

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, 1976).
2. R. E. Huie and J. T. Herron, J. Res. Nat. Bur. Stds. 76A, 77 (1972).
3. P. Kim and R. B. Timmons, Int. J. Chem. Kinet. 7, 143 (1975).
4. N. Washida and H. Takagi, J. Am. Chem. Soc. 104, 168 (1982).
5. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
6. L. I. Avramenko, R. V. Kolesnikova, and G. I. Savinova, Izv. Akad. Nauk SSSR, Ser. Khim. 28 (1965), as reported in Ref. 5.
7. F. Kaufman, Prog. Reaction Kinet. 1, 1 (1961).
8. W. K. Stuckey and J. Heicklen, J. Chem. Phys. 46, 4843 (1967).
9. N. Cohen and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$O + c\text{-}C_7H_{14} \rightarrow OH + c\text{-}C_7H_{13}$$
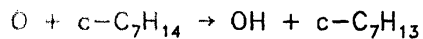
$\Delta H^o_{298} = -32.7 \pm 5 \text{ kJ mol}^{-1} \ (-7.8 \text{ kcal mol}^{-1})$ $\Delta S^o_{298} = 54.2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} \ (13.0 \text{ cal mol}^{-1} \text{ K}^{-1})$
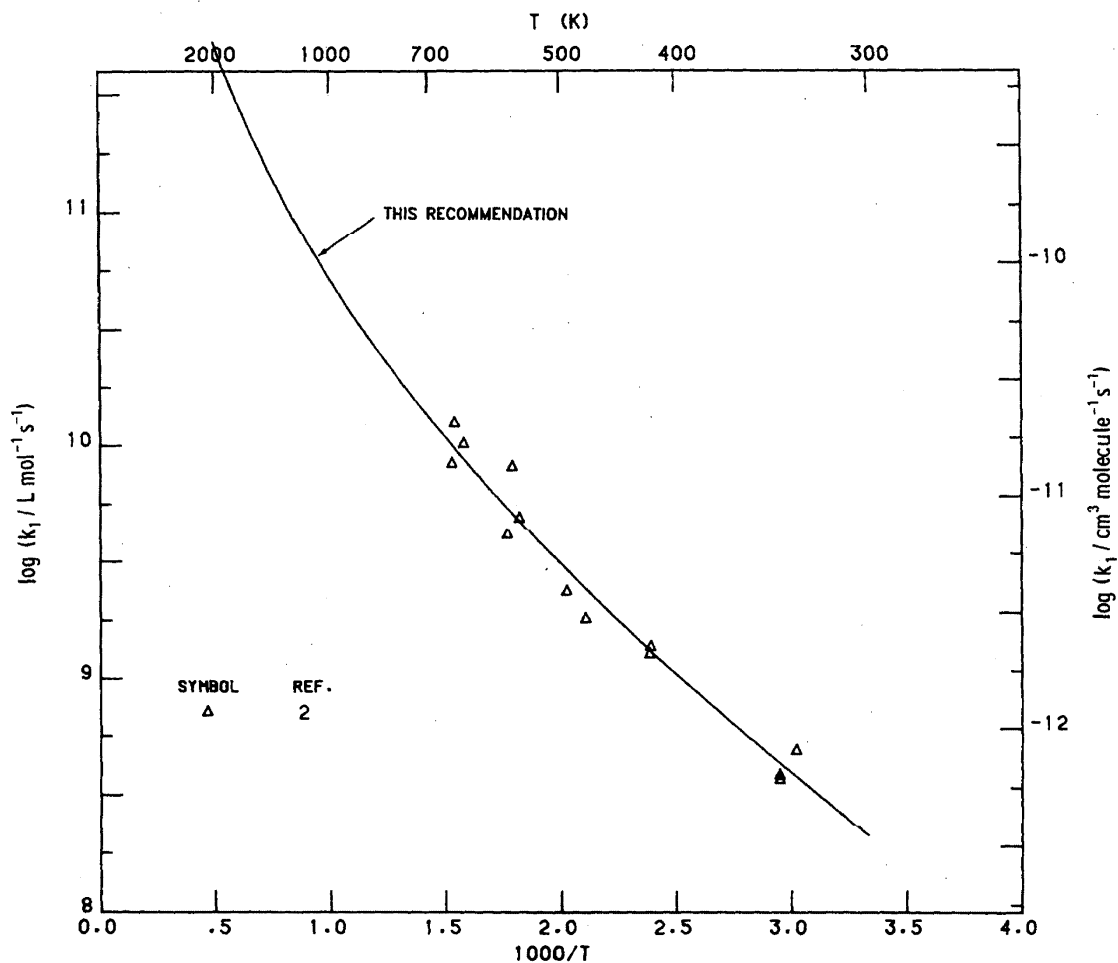

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.3 \times 10^3 \ T^{2.6} \ e^{-1020/T}$	298 - 2000 K	2.0×10^8	$\text{L mol}^{-1}\text{s}^{-1}$
	$3.8 \times 10^{-18} \ T^{2.6} \ e^{-1020/T}$		3.3×10^{-13}	$\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$

Uncertainty in log k_1: ± 0.3 at 298 K, increasing to ± 0.5 near 2000 K. Expressions for K(T) and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

(October 1987)

$$O + c\text{-}C_7H_{14} \xrightarrow{\;1\;} OH + c\text{-}C_7H_{13}$$
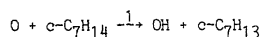
THERMOCHEMISTRY

Thermochemical data for O and OH are from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules[1] were used to estimate differences between ΔHf^o_{298} and S^o_{298} for the cycloheptyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction ($OH + c\text{-}C_7H_{13} \rightarrow c\text{-}C_7H_{13}OH$).

MEASUREMENTS

A single series of experimental measurements of k_1 has been reported. Huie and Herron[2] produced O atoms by passing a flow of argon with a few percent O_2 through a microwave discharge and added reagent gas downstream. O atoms were kept in considerable excess. Relative [O] was determined by mass spectrometry, put on an absolute basis by titration with NO_2. Alkane concentration was also measured by mass spectrometry. Measurements were made between 331 and 652 K. Because [O] was kept in excess and at most 10% of the alkane was consumed, the method was free of complications caused by secondary reactions. However, since k is proportional to $\ln([RH]_o/[RH]_t)$, a 5% error in measuring either $[RH]_o$ or $[RH]_t$ can mean a 50% error in k. The scatter in the data reflects this shortcoming. From their data, they[3] extrapolated a value of $k_1(298)$ of 1.6×10^8 L $mol^{-1}s^{-1}$, by assuming a linear Arrhenius plot.

CALCULATIONS

Transition-state theory calculations were carried out for k_1 in order to extrapolate the rate coefficients to higher temperatures. $S^+(298)$ was estimated by group additivity methods, using the parent cycloalkane as a model compound. The C·H·O structure was assumed to be linear. Vibrational frequencies for the activated complex were taken to be the same as reaction of $O + c\text{-}C_5H_{10}$. For further details, see Ref. 4. With an assumed value for $k_1(298)$ of 2.0×10^8 L mol^{-1} s^{-1}, this model gives values for k_1 that are fitted by the expression, $k_1 = 2.3 \times 10^3\ T^{2.6}\ \exp(-1020/T)$ L mol^{-1} s^{-1}. (This expression was obtained by treating the reaction as if there were a symmetry change of $14 \rightarrow 1$. Strictly speaking $c\text{-}C_7H_{14}$ has a symmetry of 1 and one should treat the problem as if there were 14 separate H atom abstraction reactions with (possibly) varying enthalpies and entropies of activation. The expected variations, though, are so slight that the calculation can effectively be carried out by assuming $\sigma(c\text{-}C_7H_{14}) = 14$.)

DISCUSSION

The calculations are in reasonable agreement with experiment, though the latter possibly suggest more curvature in the plot of log k vs 1/T than the former. Until there are more precise measurements available, we recommend an expression for k_1 derived from the calculations: $k_1 = 2.3 \times 10^3\ T^{2.6}\ \exp(-1020/T)$ L mol^{-1} s^{-1}, with an uncertainty in log k_1 of ± 0.3 at 298 K, increasing to ± 0.5 at 2000 K.

References

1. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, 1976).
2. R. E. Huie and J. T. Herron, J. Res. Nat. Bur. Stds. 76A, 77 (1972).
3. J. T. Herron and R. E. Huie, J. Phys. Chem. Ref. Data 2, 467 (1974).
4. N. Cohen, and K. R. Westberg, Int. J. Chem. Kinet. 18, 99 (1986).

$$OH + CH_3F \rightarrow CH_2F + H_2O$$
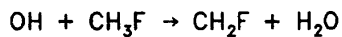
$\Delta H^O_{298} = -80.3 \pm 8 \text{ kJ mol}^{-1}$ (-19.2 kcal mol^{-1}) $\Delta S^O_{298} = 10.8 \pm 6 \text{ J mol}^{-1}K^{-1}$ (2.6 cal mol$^{-1}K^{-1}$)
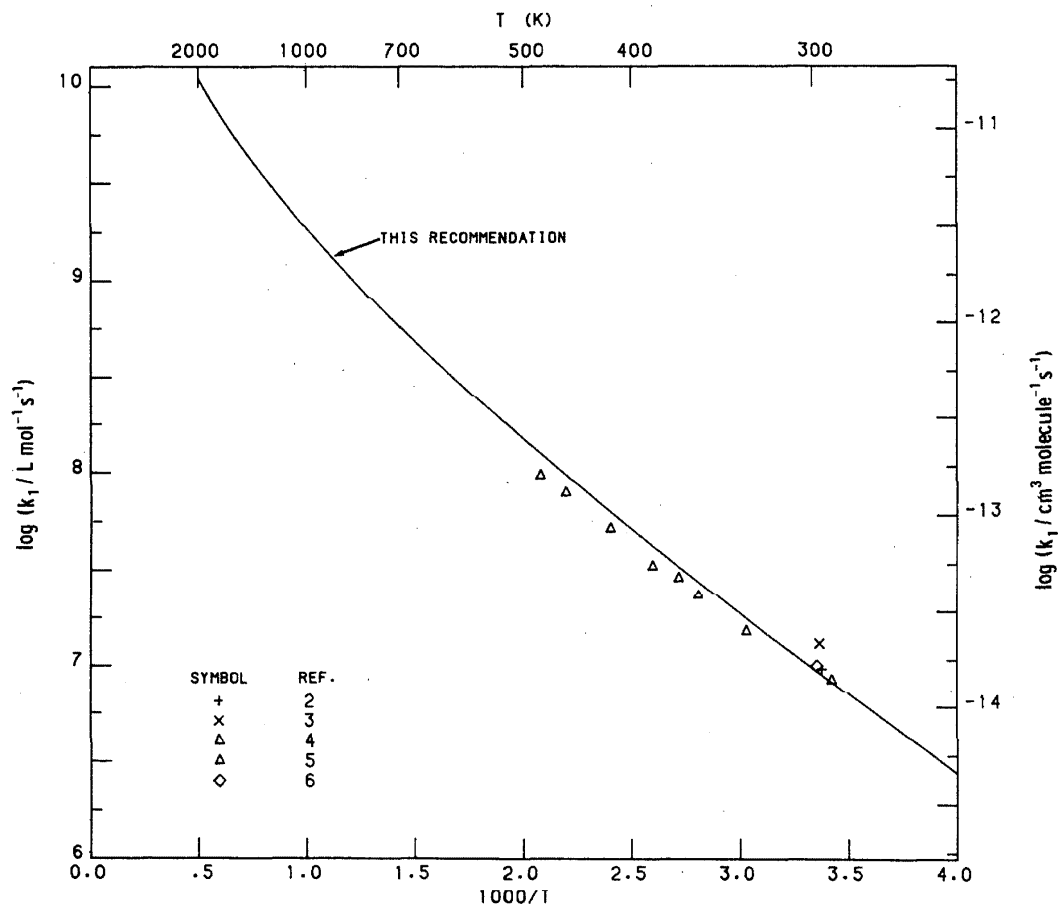
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.6 \times 10^5 \ T^{1.5} \exp(-1480/T)$	250-2000 K	9.3×10^6	L mol^{-1}s^{-1}
	$4.3 \times 10^{-16} \ T^{1.5} \exp(-1480/T)$		1.6×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_3F \rightarrow CH_2F + H_2O$
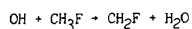
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CH_3F) = -233 \pm 8$ and $\Delta Hf^o_{298}(CH_2F) = -32.6 \pm 8$ kJ mol^{-1}. We estimate $S^o_{298}(CH_2F) = S^o_{298}(CH_3F) + R\ln g_e$, assuming that the radical is nonplanar and that $g_e = 2$. An analytic expression for $K(T)$ has not been calculated because the reverse reaction is unlikely ever to be important.

MEASUREMENTS

Howard and Evenson[2] measured k_1 at 296 K at 0.8 - 10 torr total pressure in a discharge flow system, using the $H + NO_2$ reaction to generate $10^9 - 10^{11}$ OH radicals/cm^3 and using laser magnetic resonance at 84.3 μm for radical detection. They obtained $(9.6 \pm 2.1) \times 10^6$ L mol^{-1}s^{-1}. Nip et al.[3] produced OH at 297 K by VUV flash photolysis of 0.3 torr H_2O and monitored OH decay by resonance absorption at 308.2 nm. They reported $k_1 = (1.3 \pm 0.1) \times 10^7$ L mol^{-1}s^{-1}. In the only temperature-dependent measurement, Jeong and Kaufman[4] studied the reaction between 292 and 480 K in the presence of excess fluorocarbon in a discharge flow apparatus, also using the $H + NO_2$ reaction as an OH radical source, and monitoring OH decay by resonance fluorescence. Their results are fitted by[5] $k_1 = (4.9 \pm 0.8) \times 10^9$ exp(-1890/T) L mol^{-1}s^{-1}, with a 292 K value of $(8.4 \pm 0.5) \times 10^6$. Bera and Hanrahan[6] measured k_1 at room temperature using pulse radiolysis--absorption spectroscopy, and reported $(1.0 \pm 0.16) \times 10^7$ L mol^{-1} s^{-1}. The spread among the room temperature values is thus approximately 0.2 units in log k_1, or 60% in k_1.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The value of $k(298)$ required for the calculation was taken from Ref. 4. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data within 25% for $T \geq 298$ K, could be described by the expression, $k_1 = 2.6 \times 10^5$ $T^{1.5}$ exp(-1480/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 7.

DISCUSSION

The calculations are in very good agreement with the data of Ref. 4 throughout the range of experiments. Hence, we rely on them to extrapolate k_1 to higher temperatures and recommend $k_1 = 2.6 \times 10^5$ $T^{1.5}$ exp(-1480/T) L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and higher.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
3. W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. 83, 2440 (1979).
4. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
5. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
6. R. K. Bera and R. J. Hanrahan, Radiat. Phys. Chem. 32, 579 (1988).
7. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$$
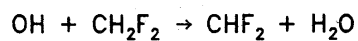
$\Delta H^{o}_{298} = -76.1 \pm 8 \text{ kJ mol}^{-1}$ (-18.2 kcal mol^{-1}) $\qquad\qquad$ $\Delta S^{o}_{298} = 10.8 \pm 6 \text{ J mol}^{-1}\text{K}^{-1}$ (2.6 cal mol^{-1}K^{-1})
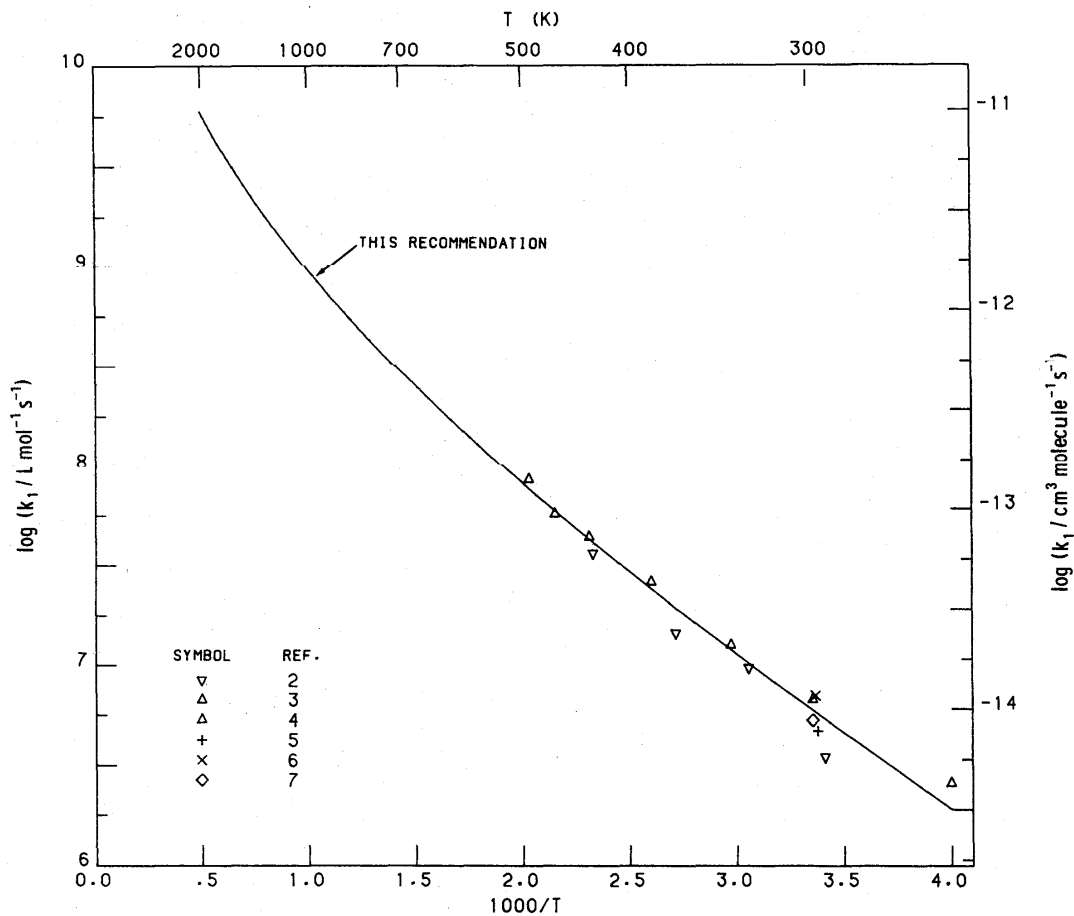
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.8 \times 10^4 \; T^{1.7} \exp(-1290/T)$	250-2000 K	5.9×10^6	L mol^{-1}s^{-1}
	$4.7 \times 10^{-17} \; T^{1.7} \exp(-1290/T)$		9.9×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K and higher. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$
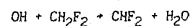
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CH_2F_2)$ = -452.2 and $\Delta Hf^o_{298}(CHF_2)$ = -247.6 kJ mol^{-1}. We estimate $S^o_{298}(CHF_2)$ = $S^o_{298}(CH_2F_2)$ + Rln g_e, assuming that the radical is nonplanar and that g_e = 2. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

| Reference	Temp. Range (K)	P(torr)	Method	log k(298) (L mol^{-1}s^{-1})	$k - A \exp(-B/T)$ Log A	B
2	293-429	1.5-2	discharge flow-resonance fluorescence	6.54	9.65	2100
3, 4	250-492	3	discharge flow-resonance fluorescence	6.83	9.41	1700
5	296	0.8-9.8	discharge flow-magnetic resonance	6.67	---	---
6	297	~ 50	flash photolysis-resonance absorption	6.85	---	---
7	(298)	600	pulse radiolysis-resonance absorption	6.72	---	---

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The room temperature value of k_1 used in the calculations was based on the results of Ref. 3. The results, in agreement with the data of Ref. 3 within 25%, could be described by the expression, k_1 = 2.8 × 10^4 $T^{1.7}$ exp(-1290/T) L mol^{-1}s^{-1}. For further details, see Ref. 8.

DISCUSSION

The calculations are used as a basis for extrapolating k_1 to temperatures above the range of experimental data. Thus we recommend k_1 = 2.8 × 10^4 $T^{1.7}$ exp(-1290/T) L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above. This expression differs from all the data (excepting the lowest-temperature value of Ref. 2) by no more than 25%.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
3. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
4. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
5. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
6. W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. 83, 2440 (1979).
7. R. K. Bera and R. J. Hanrahan, Radiat. Phys. Phys. Chem. 32, 579 (1988).
8. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CHF_3 \rightarrow CF_3 + H_2O$$
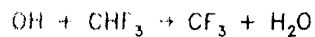
$\Delta H^O_{298} = -52.3 \pm 4$ kJ mol^{-1} (-12.5 kcal mol^{-1}) $\Delta S^O_{298} = 10.8 \pm 6$ J mol^{-1}K^{-1} (2.6 cal mol^{-1}K^{-1})

SYMBOL	REF.
∇	3
$\triangle$	4
$\triangle$	5
+	6
×	7
□	8
◇	9
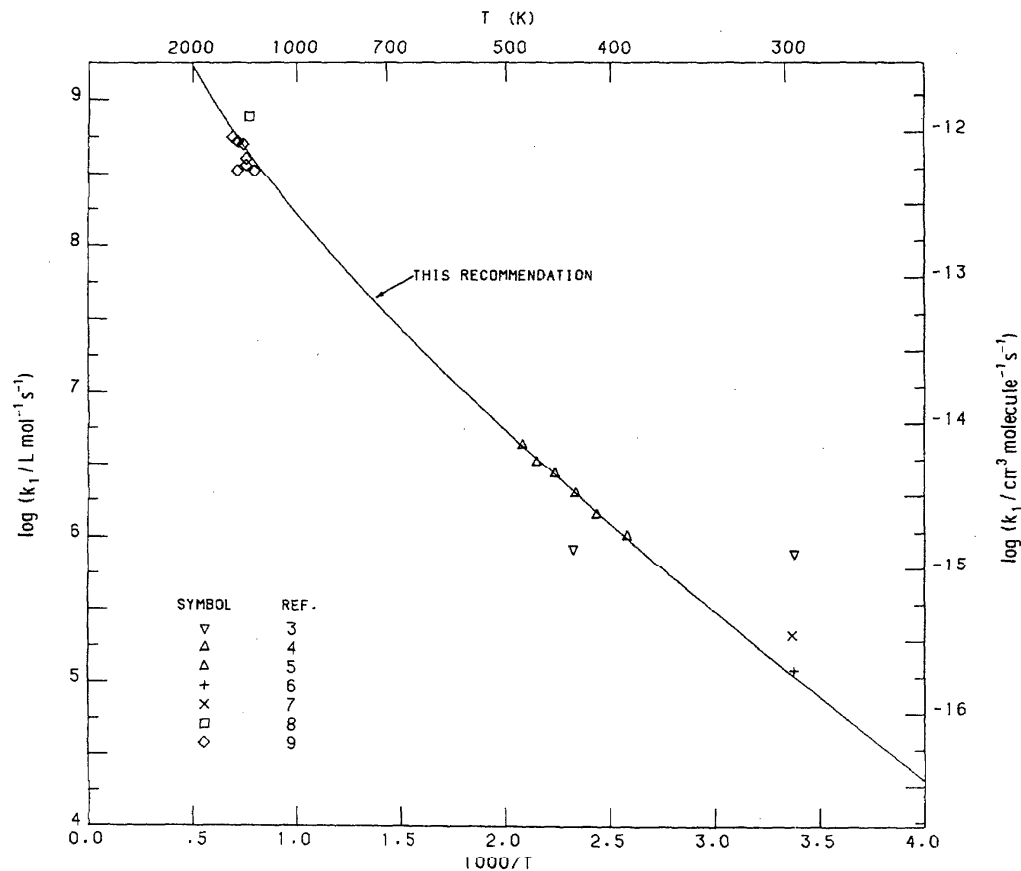
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$5.7 \times 10^3 \, T^{1.8} \exp(-2160/T0$	298-2000 K	1.2×10^5	L mol^{-1}s^{-1}
	$9.5 \times 10^{-18} \, T^{1.8} \exp(-2160/T)$		1.9×10^{-16}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 298 K, increasing to ±0.3 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CHF_3 \rightarrow CF_3 + H_2O$
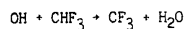
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CHF_3) = -695.6$ and $\Delta Hf^o_{298}(CHF_3) = -467.2$ kJ mol^{-1}. Rogers[2] recommends a slightly larger value of -464.8 ± 4 kJ/mol. We estimate $S^o_{298}(CF_3) = S^o_{298}(CHF_3) + R\ln g_e$, assuming that the radical is nonplanar and that $g_e = 2$. An analytic expression for $K(T)$ has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

Reference	Temp. Range (K)	P(torr)	Method	log k(298) (L mol^{-1}s^{-1})	K = A exp(-B/T) Log A	B
3	296-430	1.5-2	discharge flow-resonance fluorescence	5.89	see below	
4, 5	387-480	3	discharge flow-resonance fluorescence	---	9.26	2910
6	296	0.8-9.8	discharge flow-laser magnetic resonance	5.08	---	---
7	297	~ 50	flash photolysis-resonance absorption	5.32	---	---
8	~ 1300		shock tube	---	---	---
9	1255-1445	~ 760	flash photolysis-shock tube	---	---	---

A linear extrapolation on an Arrhenius plot through the data of Jeong and Kaufman passes very near to the result of Howard and Evenson of 1.2×10^5 L mol^{-1}s^{-1}. The data of Clyne and Holt, however, are inconsistent with the other workers; in fact, they observed practically no temperature variation between the two temperatures of their measurements. Bradley et al.[8] reported only relative rate coefficients for OH reacting with several compounds including CHF_3, H_2, CH_4, and C_2H_6. For these four species relative rate coefficients were 0.19:0.59:1.0:2.88. Using our own evaluated rate coefficients for $OH + H_2$, CH_4 and C_2H_6, the above ratios give values for k_1 between 6.4 and 8.1×10^8 L mol^{-1}s^{-1} at 1300 K, or log $k_1 = 8.85 \pm 0.05$, in reasonable agreement with an extrapolation based on the results of Jeong and Kaufman. Ernst et al.[9] used flash photolysis of H_2O to produce OH in shock-heated $Ar-CHF_3-H_2O$ mixtures and monitored [OH] disappearence. They reported $k_1 = (4.0 \pm 1.0) \times 18^8$ under their conditions.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 3 within 25% for $T \geq 298$ K, could be described by the expression, $k_1 = 5.7 \times 10^3 \, T^{1.8} \exp(-2160/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 10.

DISCUSSION

The calculations described above are in excellent agreement with all the data of Refs. 4 and 6 and in reasonable agreement with the high temperature datum of Refs. 8 and 9. The data of Ref. 3 are discounted, leaving only the room temperature value of Ref. 7 being unaccountably high by nearly a factor of 2. We rely on the expression obtained from the calculations and recommend $k_1 = 5.7 \times 10^3 \, T^{1.8} \exp(-2160/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.2 at 300 K, increasing to ± 0.3 at 2000 K.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. A. S. Rogers, "Thermochemistry of Fluorocarbon Radicals," in J. W. Root, ed., Fluorine-containing Free Radicals (ACS Symp. Ser. 66, 1978), p. 296.
3. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
4. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
5. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 00, 1222 (1984).
6. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
7. W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. 83, 2440 (1979).
8. J. N. Bradley, W. D. Capey, R. W. Fair, and D. K. Pritchard, Int. J. Chem. Kinet., 8, 549 (1976).
9. J. Ernst, H. Gg. Wagner, and R. Zellner, Ber. Bunsenges. Phys. Chem. 82, 409 (1978).
10. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$$
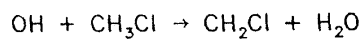
$\Delta H^o_{298} = -76.5 \pm 8 \text{ kJ mol}^{-1}$ (-18.3 kcal mol^{-1}) $\Delta S^o_{298} = 10.8 \pm 6 \text{ J mol}^{-1}\text{K}^{-1}$ (2.6 cal mol^{-1}K^{-1})
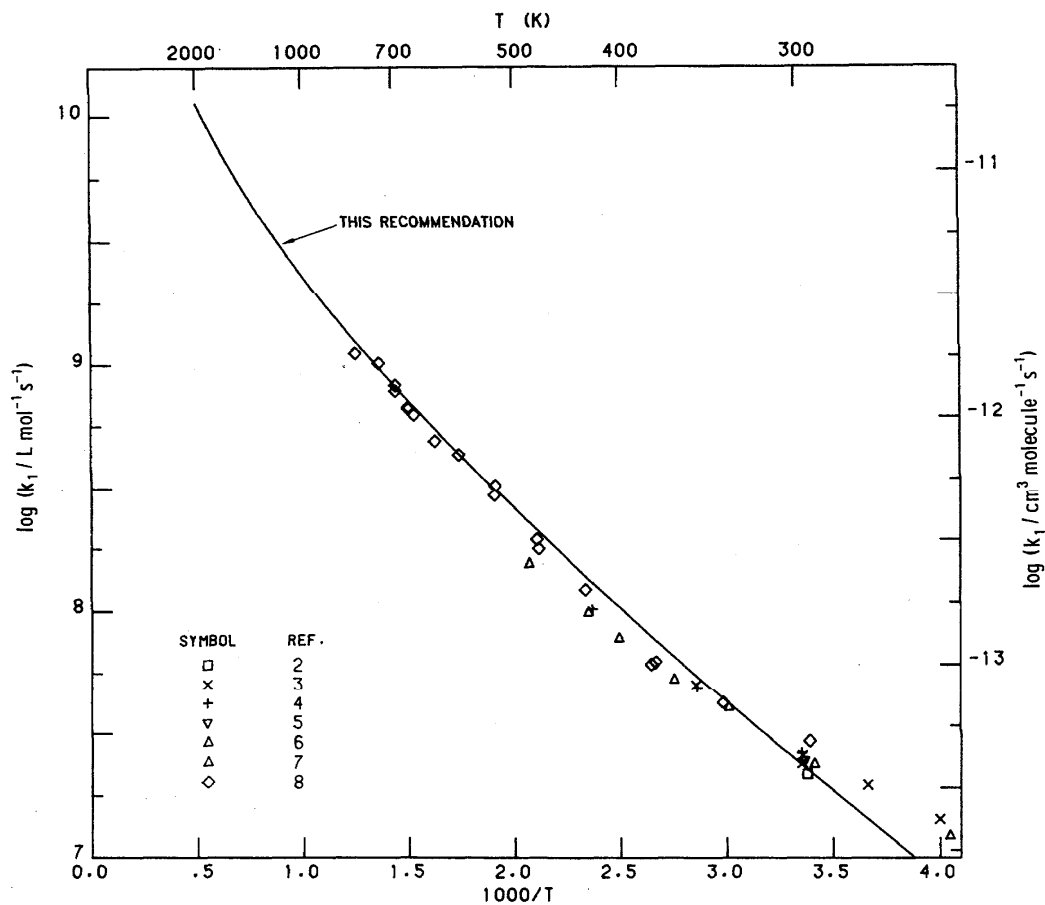
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$9.3 \times 10^4 \ T^{1.6} \exp(-1040/T)$	250-2000 K	2.6×10^7	L mol^{-1}s^{-1}
	$1.5 \times 10^{-16} \ T^{1.6} \exp(-1040/T)$		4.3×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$
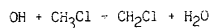
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^O_{298}(CH_3Cl) = -85.8$ and $\Delta Hf^O_{298}(CH_2Cl) = 118.4$ kJ mol^{-1}. We estimate $S^O_{298}(CH_2Cl) = S^O_{298}(CH_3Cl) + R\ln g_e$, assuming that the radical is nonplanar and that $g_e = 2$. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

| Reference	Temp. Range (K)	P(torr)	Method	log k(298) (L mol^{-1}s^{-1})	$k = AT^n \exp(-B/T)$ Log A	n	B
2	296	0.8-9.8	discharge flow-magnetic resonance	7.34	---	0	---
3	250-350	20-200	flash photolysis-resonance fluorescence	7.39	9.05	0	1100
4	298	25-50	flash photolysis-resonance fluorescence	7.42	---	---	---
5	297	[30-250?]	flash photolysis-resonance absorption	7.39	---	---	---
6, 7	247-483	3	discharge flow-resonance fluorescence	7.38 (293 K)	9.26	0	1260
8	295-800	760	laser photolysis-laser induced fluorescence	7.47 (295 K)	4.81	1.38	1200
9	1850-2100	38	flames	---	---	---	---

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. With an assumed value for log $k_1(298)$ of 7.37, the results could be described by the expression, $k_1 = 5.0 \times 10^5 T^{1.4} \exp(-1230/T)$ L mol^{-1} s^{-1}. This expression is in good agreement with results of Ref. 8 (except at their lowest temperature of 295 K), but overpredicts results of Refs. 3 and 6. The calculated value of log k_1 is proportional to $(298/T)$ log $k_1(298)$. For further computational details, see Ref. 10.

DISCUSSION

The flame study of Ref. 9 is considered too imprecise to be of use in this evaluation. Two other room temperature studies[11,12] disagree significantly with Refs. 2-8. The most recent results of Ref. 8 agree with earlier data near 335 K, but are systematically larger at other temperatures: at the highest temperature of Ref. 6, Ref. 8 is 40% larger; at 295 K, 23% larger. (Note that the analytic fit of Ref. 8--given in the table above--underpredicts their own datum at 295 K by 35%.) There is thus an unreconcilable systematic discrepancy in the experimental record at temperatures over ca. 400 K (increasing with temperature), notwithstanding the similarity in techniques. Inasmuch as the results of Ref. 8 cover the broadest temperature range and are in close agreement with the TST calculations, we tend to favor them. We recommend an expression very similar to both but with slightly more curvature, to decrease the discrepancy with Refs. 3 and 6 and 250 K: $k_1 = 9.3 \times 10^4 T^{1.6} \exp(-1040/T)$ L mol^{-1} s^{-1}. The uncertainty in log k_1 is ± 0.1 at 298 K, increasing to ± 0.3 at 1000 K and above. An additional experimental study to resolve the experimental discrepancies would be instructive.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982).
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
3. D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys. 65, 1268 (1976).
4. R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. 64, 1618 (1976).
5. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
6. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
7. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
8. P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Delinger, Int. J. Chem. Kinet. 21, 829 (1989).
9. W. E. Wilson, Jr., J. T. O'Donovan, and R. M. Fristrom, 12th Symp. (Int.) Combust. (1968), p. 929.
10. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).
11. R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
12. O. J. Niesen, P. Pagsberg, and A. Sillesen, Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 1984 (Riedel Publishing Co., Dordrecht, Holland, 1984), p. 283.

$$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$$
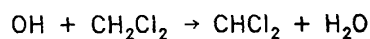
$H^o_{298} = -84.5 \pm 8.4$ kJ mol^{-1} (-20.2 kcal mol^{-1}) $\Delta S^o_{298} = 10.8 \pm 6$ J mol^{-1}K^{-1} (2.6 cal mol^{-1}K^{-1})
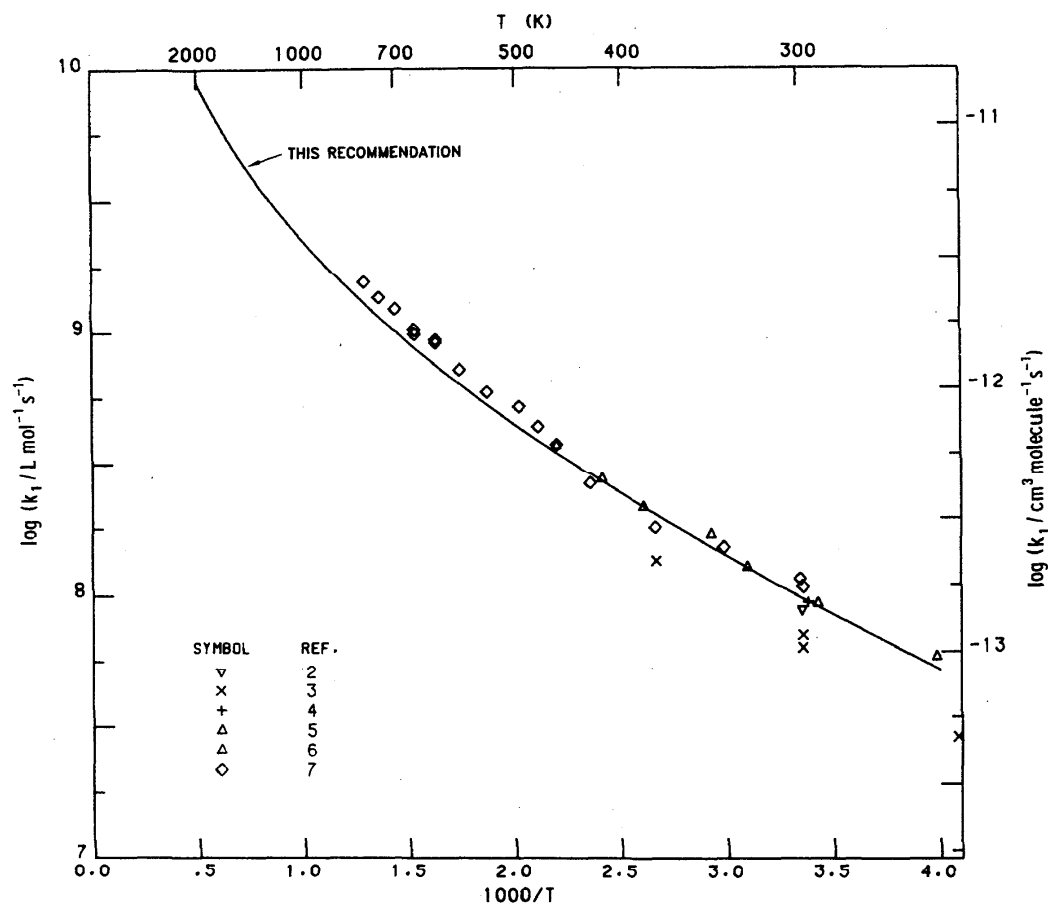
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	6.0×10^4 T$^{1.6}$ exp(-520/T)	250-2000 K	9.5×10^7	L mol^{-1}s^{-1}
	1.0×10^{-16} T$^{1.6}$ exp(-520/T)		1.6×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$
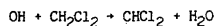
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CH_2Cl_2) = -95.4$ and $\Delta Hf^o_{298}(CHCl_2) = 100.8$ kJ mol^{-1}. We estimate $S^o_{298}(CHCl_2) = S^o_{298}(CH_2Cl_2) + Rln\ g_e$, assuming that the radical nonplanar and that $g_e = 2$. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

Reference	Temp. Range (K)	P(torr)	Method	log k(298) (L mol^{-1}s^{-1})	k = AT^n exp (-B/T) Log A	n	B
2	298	25-50	flash photolysis-resonance fluorescence	7.94	---	---	---
3	245-375	50-200	flash photolysis-resonance fluorescence	7.83	9.41	0	1090
4	296	0.8-9.8	discharge flow-magnetic resonance	7.97	---	---	---
5, 6	251-455	3	discharge flow-resonance fluorescence	7.96 (292 K)	9.52	0	1040
7	298-775	760	laser photolysis-laser induced fluorescence	8.03	4.96	1.58	622
8	298	760	HONO photolysis-NO yield	7.86	---	---	---
9	300-400	760	pulse radiolysis-absorption spectroscopy	7.94	9.61	0	1117

These results are in good agreement with each other except for those of Ref. 3, which are constantly lower by 40-60%. References 8 and 9 are omitted from the graph: the former is unreliable because of the indirectness of the method; the latter gives insufficient details.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with all the data (except those of Ref. 3) within 25% for T $\geq$ 298 K, could be described by the expression, $k_1 = 6.0 \times 10^4\ T^{1.6}\ exp(-520/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 10.

DISCUSSION

The data are all in good agreement with the exception of Ref. 3. The calculations, based on the room temperature value of Ref. 5, are also in good agreement at other temperatures with all the data excluding Ref. 3. Consequently, we rely on the calculations to extrapolate k_1 to higher temperatures than the range of experimental data: $k_1 = 6.0 \times 10^4\ T^{1.6}\ exp(-520/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and higher.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. 64, 1618 (1976).
3. D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys. 65, 1268 (1976).
4. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
5. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
6. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
7. P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, Int. J. Chem. Kinet. 21, 829 (1989).
8. R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
9. O. J. Nielsen, P. Pagsberg, and A. Sillesen, Proc. 3rd Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 1984 (Riedel Publishing Co., Dordrecht, Holland, 1984), p. 283.
10. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CHCl_3 \rightarrow CCl_3 + H_2O$$
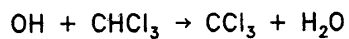
$\Delta H^O_{298} = -97.9 \pm 8.4 \text{ kJ mol}^{-1}$ ($-23.4 \text{ kcal mol}^{-1}$) $\Delta S^O_{298} = 10.8 \pm 6 \text{ J mol}^{-1}K^{-1}$ (2.6 cal $\text{mol}^{-1}K^{-1}$)
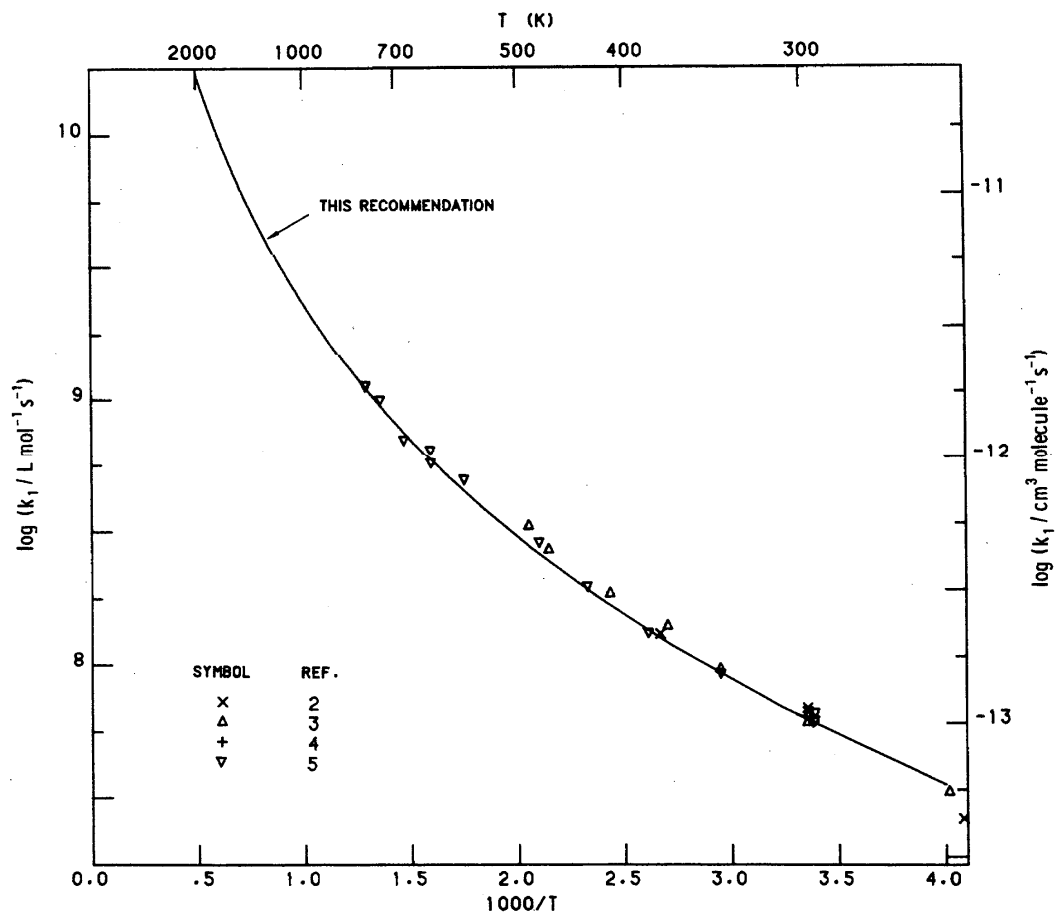
RECOMMENDED RATE COEFFICIENTS

k	$k(T)$	Range	$k(298)$	Units
k_1	$10.2 \; T^{2.8} \exp(-100/T)$	250-2000 K	6.2×10^7	$L \text{ mol}^{-1}s^{-1}$
	$1.7 \times 10^{-20} \; T^{2.8} \exp(-100/T)$		1.0×10^{-13}	$cm^3 \text{ molecule}^{-1}s^{-1}$

Uncertainty in log k_1: ± 0.3 from 250 to 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$$OH + CHCl_3 \rightarrow CCl_3 + H_2O$$
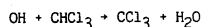
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CHCl_3) = -103.3$ and $\Delta Hf^o_{298}(CCl_3) = 79.5$ kJ mol^{-1}. We estimate $S^o_{298}(CCl_3) = S^o_{298}(CHCl_3) + R\ln g_e$, assuming that the radical is nonplanar and that $g_e = 2$. (JANAF Tables are based on the assumption that CCl_3 is planar.) An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

The reaction has been studied by Davis et al.[2] over the temperature range of 245 to 375 K by flash photolysis-resonance fluorescence, using H_2O as an OH radical source in the presence of a large excess of helium diluent; by Jeong and Kaufman[3] using discharge flow-resonance fluorescence at 249 - 487 K; by Howard and Evenson,[4] using discharge flow-laser magnetic resonance at 296 K; and by Taylor et al.[5] at 295 - 775 K using laser photolysis-laser induced fluorescence. All four studies are in excellent agreement. The room temperature values obtained in the four studies are (6.1 ± 0.9), (6.1 ± 0.8), (6.9 ± 0.4) and (6.4 ± 0.3) × 10^7 L mol^{-1}s^{-1}, respectively. Two relative room temperature measurements[6,7] disagree considerably with these results, and are not used in this evaluation.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results could be described by the expression, $k_1 = 6.6 \times 10^3 \ T^{1.7} \ \exp(-170/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 8. Unlike all the other halomethanes and haloethanes considered, the calculations were in poor agreement with experimental data, underpredicting k(T) more severely with increasing temperature, up to an error of a factor of approximately 2.5 at 775 K. There is no obvious reason why the model should fail in this one case.

DISCUSSION

Notwithstanding the very good agreement among the different experimental studies, the failure of the calculations to predict the same temperature dependence is disconcerting. (Failure of the model to give results in agreement with the data is so puzzling only because the same model gives good agreement in the cases of 18 other halomethanes and haloethanes.) Consequently, we recommend with caution the expression of Ref. 5: $k_1 = 10.2 \ T^{2.8} \ \exp(-100/T)$ L mol^{-1}s^{-1}, with an uncertainty of log $k_1 = \pm 0.3$ throughout the temperature range of 250 - 2000 K. This expression yields values that differ from the calculated values by no more than a factor of 2 throughout the temperature range.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys. 65, 1268 (1976).
3. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
4. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
5. P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, Int. J. Chem. Kinet. 21, 829 (1989).
6. R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
7. W. Klopffer, R. Frank, E.-G. Kohl, and F. Haag, Chemiker-Zeitung, 110, 57 (1986); "Methods of the Ecotoxicological Evaluation of Chemicals. Phytochemical Degradation in the Gas Phase," Vol. 6, OH Reaction Rate Constant and Tropospheric Lifetimes of Selected Environmental Chemicals. Report 1980-1093; K. H. Becker, H. M. Biehl, P. Bruckmann, E. H. Fink, F. Feuhr, W. Klöpffer, R. Zellner, and C. Zetsch, Editors, Kernforschungsanlage Jülich GmbH, November, 1984. (Cited by Atkinson, J. Phys. Chem. Ref. Data Monograph No. 1 (1989), p. 65.)
8. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3Br \rightarrow CH_2Br + H_2O$$
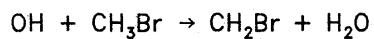
$\Delta H^O_{298} = -71.9 \pm 8.4$ kJ mol^{-1} (-17.2 kcal mol^{-1}) $\Delta S^O_{298} = 10.8 \pm 6$ J mol^{-1}K^{-1} (2.6 cal mol^{-1}K^{-1})
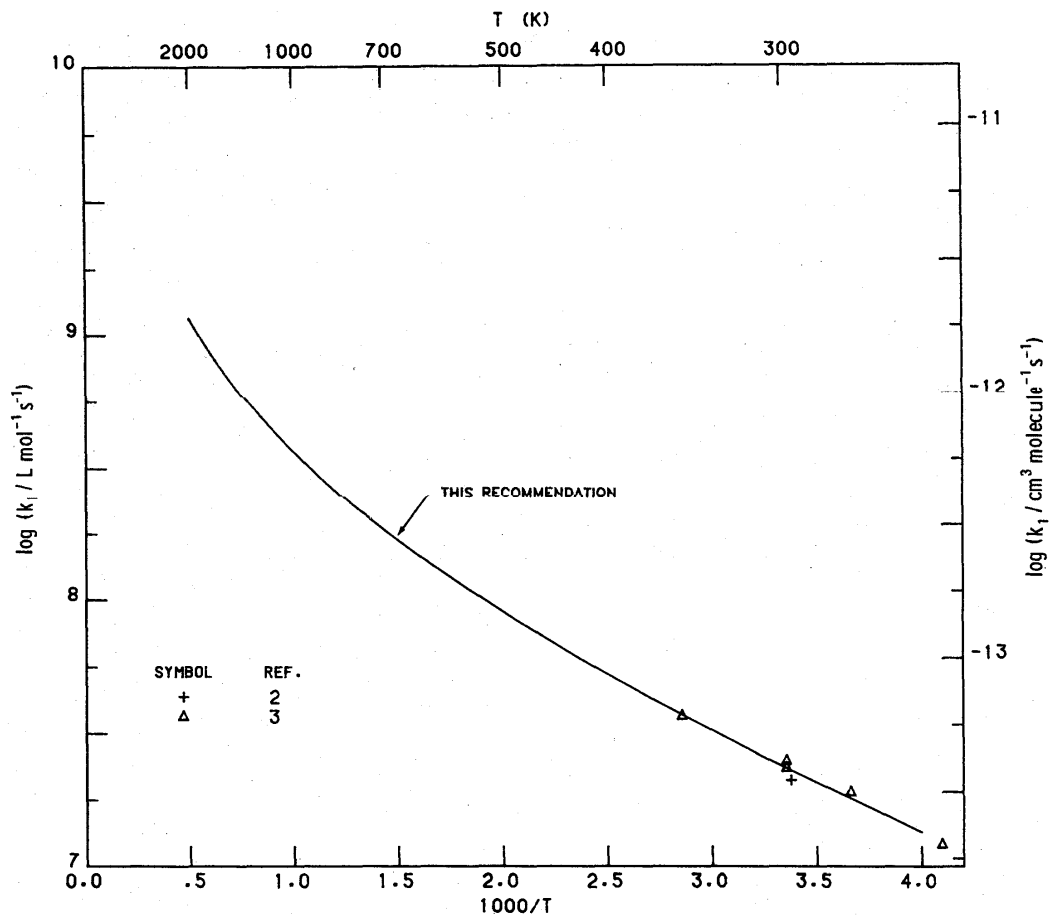
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	7.6×10^4 T$^{1.3}$ exp(-500/T)	250-2000 K	2.3×10^7	L mol^{-1}s^{-1}
	1.3×10^{-16} T$^{1.3}$ exp(-500/T)		3.9×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 at 298 K and below, increasing to ± 0.4 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_3Br \rightarrow CH_2Br + H_2O$
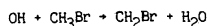
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CH_3Br) = -35.2$ and $\Delta Hf^o_{298}(CH_2Br) = 173.6$ kJ mol^{-1}. We estimate $S^o_{298}(CH_2Br) = S^o_{298}(CH_3Br) + Rln\ g_e$, assuming that the radical is nonplanar and that $g_e = 2$. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Howard and Evenson[2] reported a value for k_1 at 296 K of $(2.1 \pm 0.5) \times 10^7$ L mol^{-1}s^{-1} obtained in a discharge flow system with the H + NO$_2$ reaction as an OH radical source and laser magnetic resonance as the means of detecting OH disappearance. Davis et al.[3] studied the reaction at temperatures between 244 and 350 K in 20-200 torr Helium diluent. Flash photolysis of H_2O provided the OH radicals, whose disappearance was monitored by resonance fluorescence. They reported $k_1 = (4.8 \pm 0.5) \times 10^8$ exp$[-(890 \pm 58)/T]$ L mol^{-1}s^{-1}, with a room temperature value of 2.4×10^7. The flame studies of Wilson et al.[4,5] are subject to too many uncertainties to be useful in this evaluation.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data within 60% for T $\geq$ 298 K, could be described by the expression, $k_1 = 8.3 \times 10^5\ T^{1.3}$ exp(-1200/T) L mol^{-1}s^{-1}. For further details, see Ref. 6.

DISCUSSION

The calculations suggest a weaker temperature dependence in k_1 than the results of Ref. 3 show, though the discrepancy in absolute values over the limited temperature range of the experiments is no more than 60%. There are no data for other brominated halomethanes for comparison. We recommend an expression for k_1 based on a fit through the experimental data but forced to have a $T^{1.3}$ dependence as suggested by the calculations. This yields $k_1 = 7.6 \times 10^4\ T^{1.3}$exp(-500/T) L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.2 at 298 K, increasing to ± 0.4 at 1000 K and above.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976)..
3. D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, J. Chem. Phys. 65, 1268 (1976).
4. W. E. Wilson, Jr., 10th Symp. (Int.) Combust. (1965), p. 47
5. W. E. Wilson, Jr., J. T. O'Donovan, and R. M. Fristrom, 12th Symp. (Int.) Combust. (1969), p. 929.
6. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

N. COHEN AND K. R. WESTBERG

$$OH + CH_2ClF \rightarrow CHClF + H_2O$$
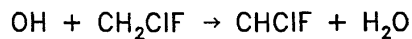
$\Delta H^o_{298} = -66.9 \pm 20$ kJ mol^{-1} (-16.0 kcal mol^{-1}) $\Delta S^o_{298} = 10.8 \pm 6$ J mol^{-1}K^{-1} (2.6 cal mol^{-1}K^{-1})
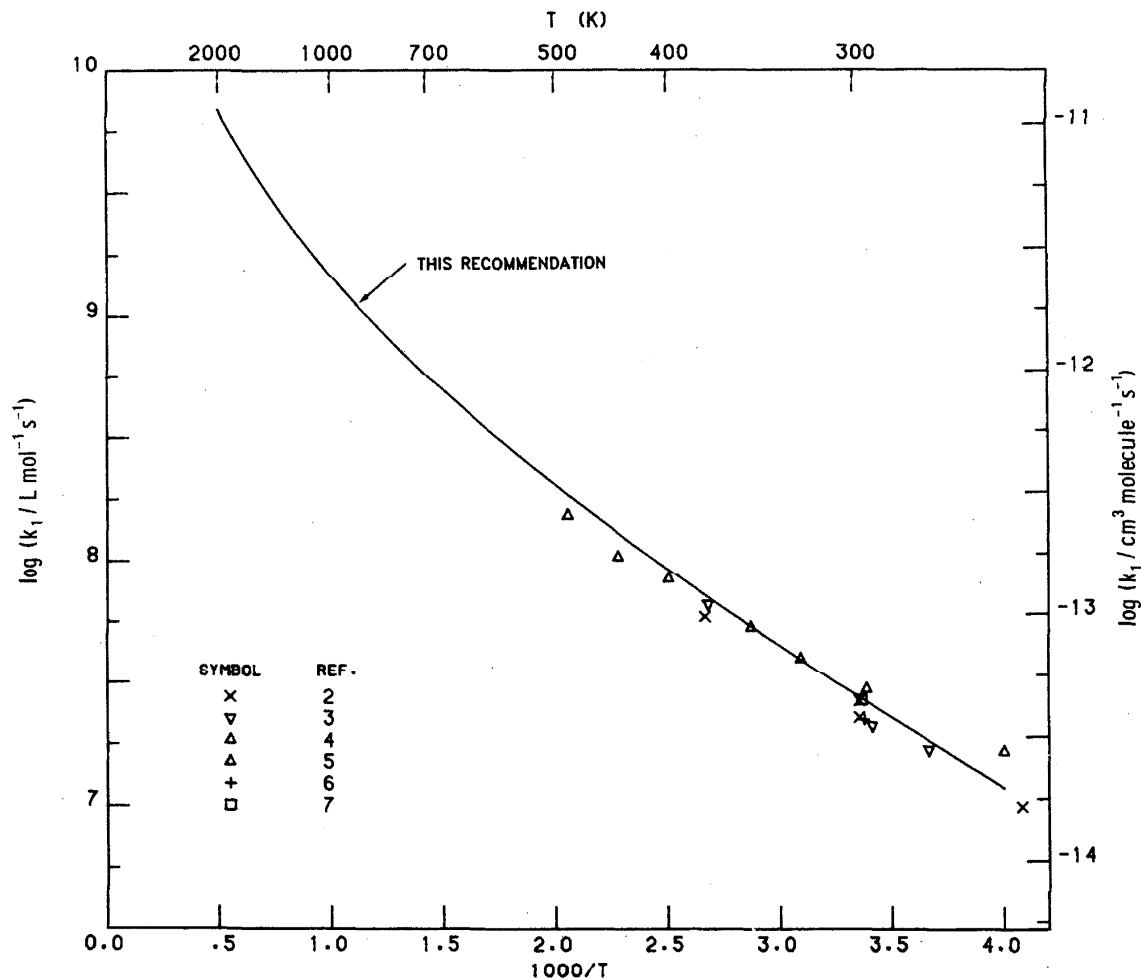
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	5.6×10^4 $T^{1.6}$ exp(-870/T)	250-2000 K	2.8×10^7	L mol^{-1}s^{-1}
	9.3×10^{-17} $T^{1.6}$ exp(-870/T)		4.6×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CH_2ClF \rightarrow CHClF + H_2O$
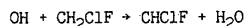
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). According to Chen et al.,[1] $\Delta Hf^o_{298}(CHClF) = -264$ kJ mol^{-1}. We estimate $\Delta Hf^o_{298}(CHClF)$ to be -50.2 ± 20 kJ mol^{-1}, and $S^o_{298}(CHClF) = S^o_{298}(CH_2ClF) + R\ln g_e$, assuming that the radical nonplanar and that $g_e = 2$. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

| Reference	Temp. Range (K)	P(torr)	Method	log k(298) ($L\ mol^{-1}s^{-1}$)	k = A exp(-B/T) Log A	B
2	245-375	40	flash photolysis-resonance fluorescence	7.42	9.23	1259
3	278-373	12-20	flash photolysis-resonance fluorescence	7.32	9.27	1320
4, 5	250-486	~ 3	discharge flow-resonance fluorescence	7.47	9.16	1140
6	296	0.8-9.8	discharge flow-magnetic resonance	7.34	---	---
7	297	[30-250?]	flash photolysis-resonance absorption	7.43	---	---

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 4 within 25% for $T \geq 298$ K, could be described by the expression, $k_1 = 5.6 \times 10^4\ T^{1.6}\ exp(-870/T)$ $L\ mol^{-1}s^{-1}$. For further computational details, see Ref. 8.

DISCUSSION

The experimental data are all in close agreement, except at the lowest temperatures, for which the data of Refs. 4 and 2, when the temperature dependence is taken into account, disagree by approximately 50%. The calculations described above are in good agreement with all the data, splitting the difference in the lowest temperature values. Consequently we rely on the calculated curve to extrapolate k to temperatures above those of the experiments and recommend $k_1 = 5.6 \times 10^4\ T^{1.6}\ exp(-870/T)$ $L\ mol^{-1}s^{-1}$. The uncertainty in log k_1 is ± 0.1 at 298 K, increasing to ± 0.3 at 1000 K and above.

References

1. S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data 5, 571 (1976).
2. R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Che. 81, 256 (1977).
3. V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem 82, 1161 (1978).
4. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982).
5. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
6. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
7. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
8. N. Cohen and S. W. Benson, Int. J. Phys. Chem. 91, 162 (1987).

$$OH + CHClF_2 \rightarrow CClF_2 + H_2O$$
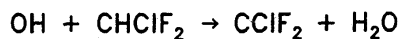
$\Delta H^{O}_{298} = -73.7 \pm 4 \text{ kJ mol}^{-1} \ (-17.6 \text{ kcal mol}^{-1})$ $\qquad\qquad$ $\Delta S^{O}_{298} = 10.8 \pm 6 \text{ J mol}^{-1}\text{K}^{-1} \ (2.6 \text{ cal mol}^{-1}\text{K}^{-1})$
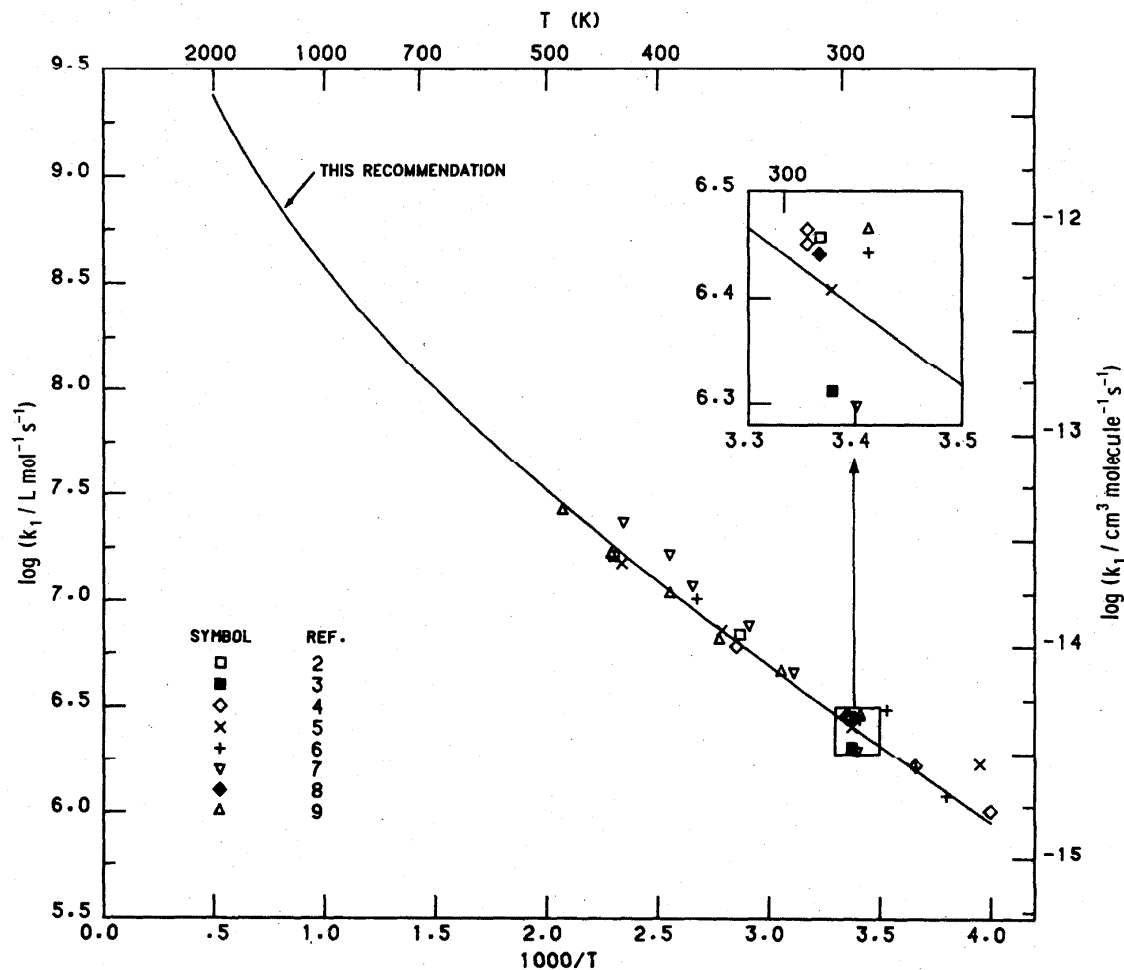

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$4.9 \times 10^3 \ T^{1.8} \exp(-1180/T)$	250-2000 K	2.7×10^6	L mol^{-1}s^{-1}
	$8.1 \times 10^{-18} \ T^{1.8} \exp(-1180/T)$		4.4×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CHClF_2 \rightarrow CClF_2 + H_2O$
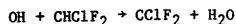
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,[1] $\Delta Hf^o_{298}(CHClF_2) = -476 \pm 8$ and $\Delta Hf^o_{298}(CClF_2) = -269 \pm 8$ kJ/mol. We estimate $S^o_{298}(CClF_2) = S^o_{298}(CHClF_2) + R \ln g_e$, assuming that the radical is nonplanar and that $g_e = 2$. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

Reference	Temp. Range (K)	P(torr)	Method	log k(298) ($L\ mol^{-1}s^{-1}$)	k = A exp(-B/T) Log A	B
2	297–434	15–25	flash photolysis-resonance fluorescence	6.46	8.86	1635
3	296	0.8–10	discharge flow-magnetic resonance	6.31	---	---
4	250–350	40–200	flash photolysis-resonance fluorescence	6.46	8.75	1575
5	253–427	2.3–5.8	discharge flow-resonance fluorescence	6.41	8.86	1657
6	263–373	10–30	flash photolysis-resonance absorption	(6.53)[a]	9.10	1780
7	294–426	1.5–2	discharge flow-resonance fluorescence	6.39	9.76	2300
8	297	[250?]	flash photolysis-resonance absorption	6.44	---	---
9	293–482	~3	discharge flow-resonance fluorescence	6.45	8.88	1660

[a] – interpolated value

For reasons that are not apparent, Clyne and Holt obtained a stronger temperature dependence than the other workers, recording larger values of k_1 at their higher temperatures and lower at 296 K than other measurements indicate. The lowest temperature results of Chang and Kaufman are also out of line with respect to other measurements.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 9 within 25% for $T \geq 298$ K, could be described by the expression, $k_1 = 4.9 \times 10^3\ T^{1.8}\ exp(-1180/T)\ L\ mol^{-1}s^{-1}$. For further computational details, see Ref. 10.

DISCUSSION

Except for the data of Ref. 7, the variations among the experimental data seem random. The calculated values, based on a room temperature value near the cluster of points from Refs. 2,, 4, 5, 6, 8, and 9, are in good agreement with the data at other temperatures. Thus, we rely on the calculations to extrapolate k_1 to temperatures above the range of the data and recommend $k_1 = 4.9 \times 10^3\ T^{1.8}\ exp(-1180/T)\ L\ mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ± 0.1 at 298 K, increasing to ± 0.3 at 1000 K and above.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982).
2. R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. 63, 1703 (1975).
3. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
4. R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. 81, 256 (1977).
5. J. S. Chang and F. Kaufman, J. Phys. Chem. 66, 4989 (1977).
6. V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. 82, 1161 (1978)
7. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
8. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
9. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86, 1808 (1982); see also K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
10. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CHCl_2F \rightarrow CCl_2F + H_2O$$
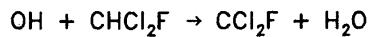
$\Delta H^O_{298} = -92.0 \pm 20 \text{ kJ mol}^{-1} \; (-22.0 \text{ kcal mol}^{-1})$

$\Delta S^O_{298} = 10.8 \pm 6 \text{ J mol}^{-1} K^{-1} \; (2.6 \text{ cal mol}^{-1} K^{-1})$
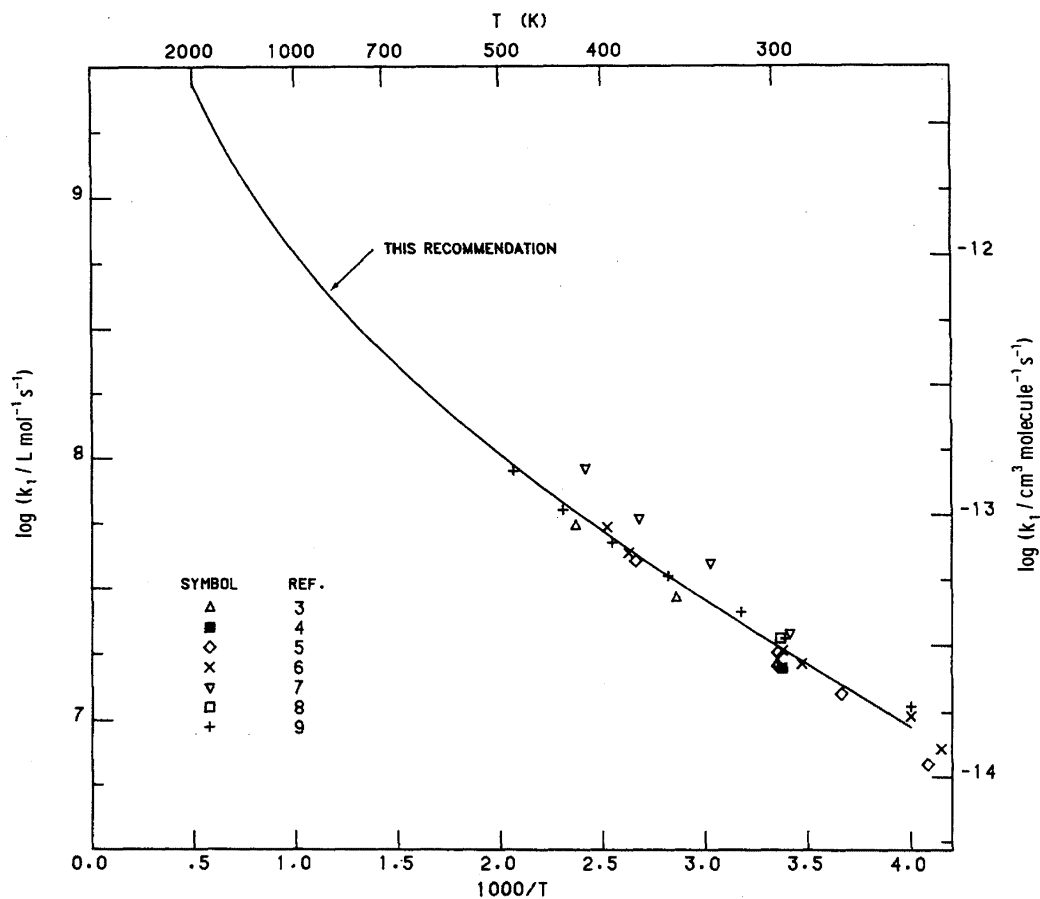
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$9.1 \times 10^3 \; T^{1.7} \exp(-610/T)$	250–2000 K	1.9×10^7	$L \; mol^{-1} s^{-1}$
	$1.5 \times 10^{-17} \; T^{1.7} \exp(-610/T)$		3.1×10^{-14}	$cm^3 \; molecule^{-1} s^{-1}$

Uncertainty in log k_1: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K and above. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CHCl_2F \rightarrow CCl_2F + H_2O$
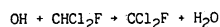
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the reviews of Chen et al.[1] and McMillen and Golden,[2] ΔHf^o_{298} ($CHCl_2F$) = -284.9 and ΔHf^o_{298}(CCl_2F) = -96.2 kJ mol^{-1}. We estimate S^o_{298}(CCl_2F) = S^o_{298}($CHCl_2F$) + Rln g_e, assuming that the radical is nonplanar and that g_e = 2. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

k_1 has been measured in eight separate experiments spanning the temperature range of 241 to 483 K. Except for Ref. 10, the discrepancy among the different results is less than a factor of 1.8 throughout the temperature range, and if the results of Ref. 7 are discounted, the spread in values is only 35% or less. Experimental conditions and results are tabulated below:

| Reference	Temp. Range (K)	P(torr)	Method	log k(298) ($L\ mol^{-1}s^{-1}$)	k = A exp(-E/RT) Log A	E/R
3	298-422	~ 50	flash photolysis-resonance fluorescence	7.21	9.02	1250
4	296	0.8 10	discharge flow-magnetic resonance	7.20	---	---
5	245-375	40-200	flash photolysis-resonance fluorescence	7.26	9.05	1245
6	241 396	2.2 5.9	discharge flow-resonance fluorescence	7.26 (296 K)	8.84	1073
7	293-413	1.5-2	discharge flow-resonance fluorescence	7.33 (293 K)	9.46	1400
8	297	[30-250?]	flash photolysis-resonance absorption	7.31	---	---
9	250-483	~ 3	discharge flow-resonance fluorescence	7.31	8.86	1050
10	300-400	760	pulse radiolysis-absorption spectroscopy	6.49	9.04	1787

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 9 within 25% for T $\geq$ 298 K, could be described by the expression, k_1 = 9.1 x 10^3 $T^{1.7}$ exp(-610/T) $L\ mol^{-1}s^{-1}$. For further computational details, see Ref. 11.

DISCUSSION

The calculated values are in very good agreement (within 35%) with all the data save those of Refs. 7 and 10 (not plotted). Thus, we rely on them for extrapolating k_1 to temperatures above those of the experimental range and recommend k_1 = 9.1 x 10^3 $T^{1.7}$ exp(-610/T) $L\ mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and higher.

References

1. S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data 5, 571 (1976).
2. D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. 33, 493 (1982).
3. R. A. Perry, R. Atkinson, and J. N. Pitts. Jr.. J. Chem. Phys. 64. 1618 (1976).
4. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 197 (1976).
5. R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. 81, 256 (1977).
6. J. S. Chang and F. Kaufman, J. Chem. Phys. 66, 4989 (1977).
7. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
8. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
9. K.-M. Jeong and F. Kaufman, J. Phys. Chem. 86. 1808 (1982): see also K.-M. Jeong. K.-J. Hsu. J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
10. O. J. Nielsen, P. Pagsberg, and A. Sillesen, Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 1984 (Riedel Publishing Co., Dordrecht, Holland, 1984), p. 283.
11. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3CH_2F \rightarrow C_2H_4F + H_2O$$

$OH + CH_3CH_2F \xrightarrow{1} CH_3CHF + H_2O$ $\Delta H^o_{298} = -82.4 \pm 8$ kJ mol^{-1} (-19.7 kcal mol^{-1}) $\Delta S^o_{298} = 16.7 \pm 4$ J mol^{-1} K^{-1} (4.0 cal mol^{-1} K^{-1})

$OH + CH_3CH_2F \xrightarrow{2} CH_2CH_2F + H_2O$ $\Delta H^o_{298} = -76.2 \pm 8$ kJ mol^{-1} (-18.2 kcal mol^{-1}) $\Delta S^o_{298} = 16.4 \pm 4$ J mol^{-1} K^{-1} (3.9 cal mol^{-1} K^{-1})
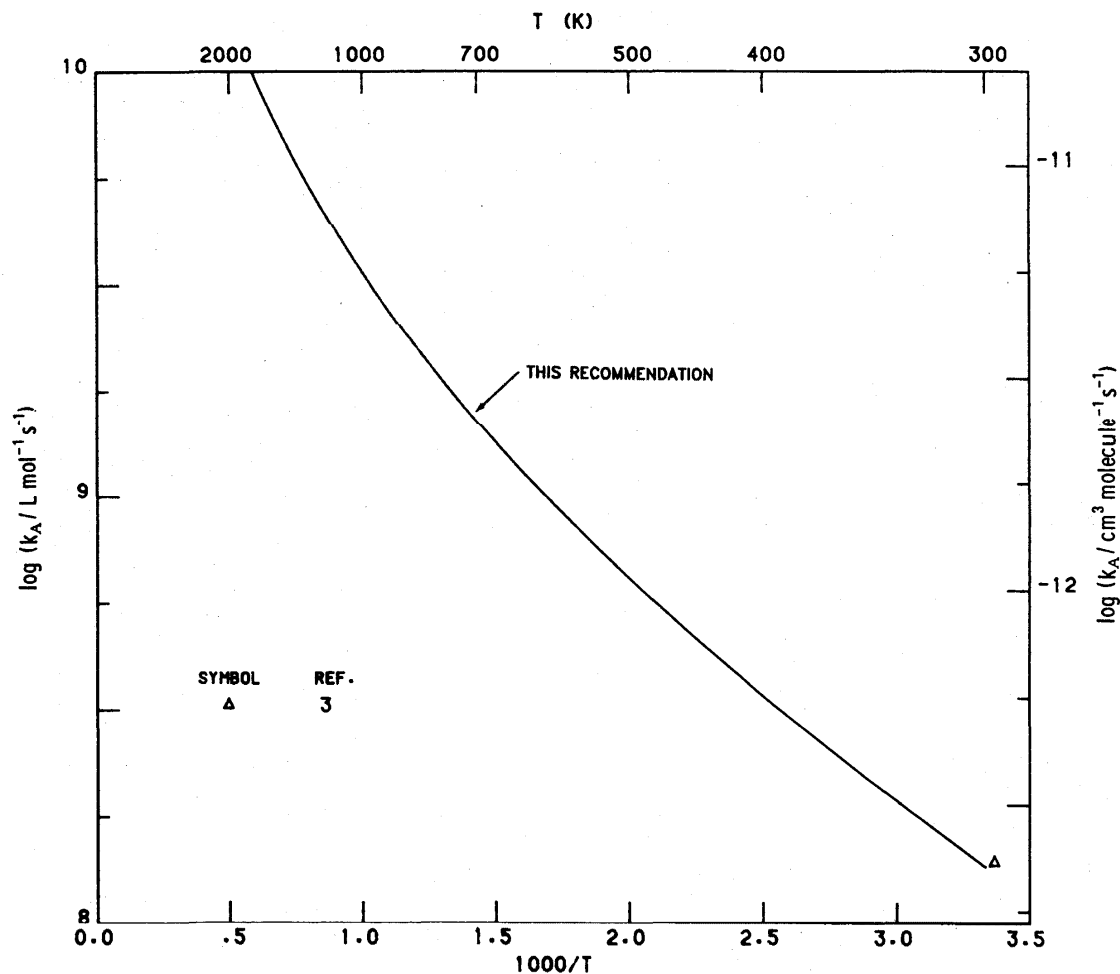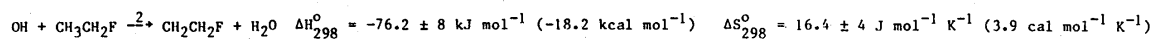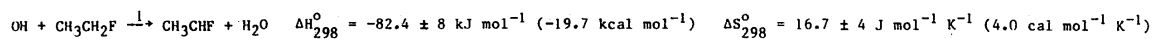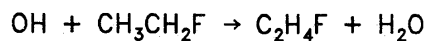
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$9.3 \times 10^4 \, T^{1.6}$ exp(-550/T)	298 – 2000 K	1.4×10^8	L mol^{-1}s^{-1}
	$1.5 \times 10^{-16} \, T^{1.6}$ exp(-550/T)		2.3×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_A: $\pm$ 0.3 at 298 K, increasing to $\pm$0.6 at 2000 K. k_A is the sum of $k_1 + k_2$; separate values for k_1 and k_2 are not recommended. Because the reverse reactions are unlikely to be important at any temperature, values for equilibrium constants and reverse rate coefficients are not recommended.

February 1987

$$OH + CH_3CH_2F \xrightarrow{1} CH_3CHF + H_2O$$
$$\xrightarrow{2} CH_2CH_2F + H_2O$$
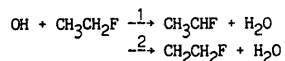
THERMOCHEMICAL DATA

The title reaction is the sum of two elementary processes: abstraction of the two α-hydrogen atoms (those attached to the same C atom as the fluorine):

$$OH + CH_3CH_2F \xrightarrow{1} CH_3CHF + H_2O$$

and abstraction of one of the three β-hydrogen atoms:

$$OH + CH_3CH_2F \xrightarrow{2} CH_2CH_2F + H_2O$$

The three β-H atoms are not exactly equivalent because there is a barrier to rotation about the C-C bond. Hence, the properties of the H atom trans to the F atom (opposite it, when viewed along the C-C axis) will differ slightly from those of other two β-H atoms. (Once one H atom is removed in reaction, there is practically free rotation about the C-C bond in the fluoroethyl radical, and the products are almost equivalent.) McKean et al.[1] predict the bond strengths of the trans and gauche β-H atoms to be 419.2 and 425.1 kJ mol^{-1}, respectively; and that of the α-H atoms to be 416.7 kJ mol^{-1}. These values have not been verified experimentally, and considering the usual uncertainties measuring bond strengths, the trans/gauche difference may be unmeasurable. We assume hereafter that the reactions involving the two different conformations are indistinguishable.

Thermochemical data for H_2O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for fluoroethane are from Stull et al.[2] Data for the fluoroethyl radicals are not available. Based on the predictions of Ref. 1, we estimate $\Delta Hf^{o}_{298}(CH_3CHF) = -62.8 \pm 12$ kJ mol^{-1} and $\Delta Hf^{o}_{298}(CH_2CH_2F) = -56.5 \pm 12$ kJ mol^{-1}. The entropies of the two radicals were estimated to be 276.6 $\pm$ 5 and 276.2 $\pm$ 5 J mol^{-1}K^{-1}, assuming barriers to internal rotation of 0 and 4 kJ mol^{-1}, respectively.

MEASUREMENTS

k_A has been measured at 297 K by Nip et al.[3] using VUV flash-photolysis of water vapor to produce OH radicals and resonance absorption to monitor their disappearance. From 18 separate measurements, a value of $k_A = (1.4 \pm 0.22) \times 10^8$ L mol^{-1}s^{-1} was determined. In a separate study, Singleton et al.[4] determined that 85 $\pm$ 3% of the abstraction occurs at the α positions, whence $k_1/k_2 = 5.7 \pm 1.6$.
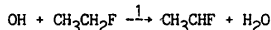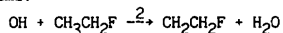
CALCULATIONS

Transition-state-theory (TST) calculations were carried out for k_1 and k_2 to extrapolate the room temperature results of Refs. 3 and 4 to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with halomethanes, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results for k_1 and k_2 were added together to give k_A, which could be described by the expression, $k_A = 9.3 \times 10^4$ T$^{1.6}$ exp(-550/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 5.

DISCUSSION

For want of more experimental data, we are forced to rely on the single experimental measurements of k_A and k_1/k_2, and the TST calculations based upon them. The experimental findng that $k_1/k_2 \cong 6$ requires an activation energy difference of $E_2 - E_1 \cong 6.5$ kJ mol^{-1}, since calculations suggest that the activation entropy for β-abstraction exceeds that for α-abstraction by -2.2 gibbs mol^{-1}. While such a large difference may seem questionable, it is consistent with the lower experimental values for rate coefficients for OH with haloethanes with only β-atoms. Hence, we recommend $k_A = 9.3 \times 10^4$ T$^{1.6}$ exp(-550/T) L mol^{-1}s^{-1}, with an uncertainty in log $k_A(298)$ of ± 0.3, increasing to ± 0.6 at 2000 K.

References

1. D. C. McKean, O. Saur, J. Travert, and J. C. Lavalley, Spectrochim. Acta, 31A, 1713 (1975).
2. D. R. Stull, E. F. Westrum, Jr., and C. G. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 497.
3. W. S. Nip, D. L. Singleton, R. Overend, and G. Paraskevopoulos, J. Phys. Chem. 83, 2440 (1979).
4. D. L. Singleton, G. Paraskovopoulos, and R. S. Irwin, J. Phys. Chem. 84, 2339 (1980).
5. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3CH_2Cl \rightarrow C_2H_4Cl + H_2O$$

$OH + CH_3CH_2Cl \xrightarrow{1} CH_3CHCl + H_2O$ $\Delta H^{O}_{298} = -78 \pm 12$ kJ mol^{-1} (-18.6 kcal mol^{-1}) $\Delta S^{O}_{298} = 17.6 \pm 5$ J mol^{-1} K^{-1} (4.2 cal mol^{-1} K^{-1})

$OH + CH_3CH_2Cl \xrightarrow{2} CH_2CH_2Cl + H_2O$ $\Delta H^{O}_{298} = -70 \pm 12$ kJ mol^{-1} (-16.8 kcal mol^{-1}) $\Delta S^{O}_{298} = 17.3 \pm 5$ J mol^{-1} K^{-1} (4.1 cal mol^{-1} K^{-1})
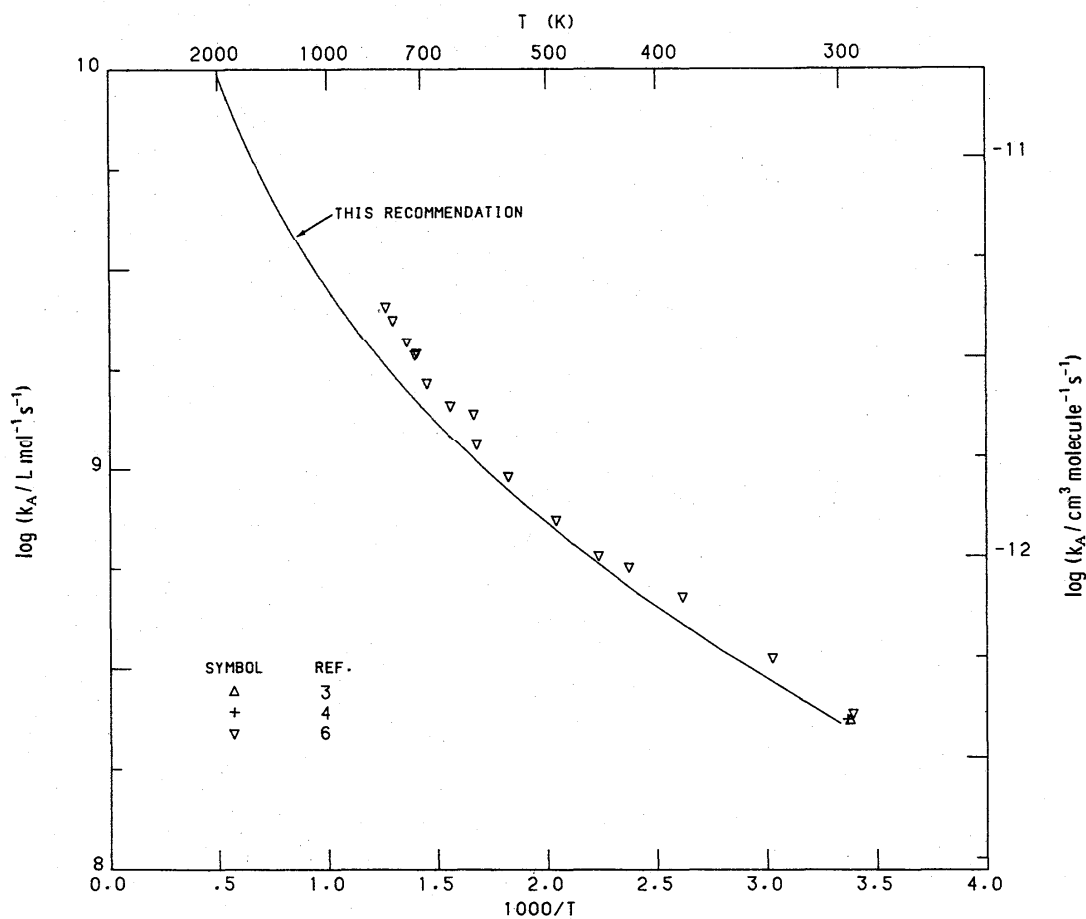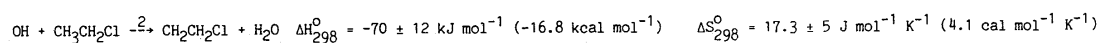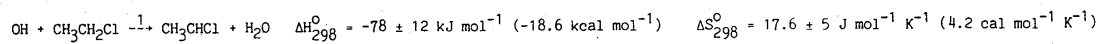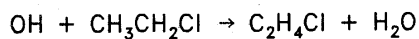
RECOMMENDED RATE COEFFICIENTS

k	$k(T)$	Range	$k(298)$	Units
k_A	$65\ T^{2.6}$ exp(110/T)	298 - 2000 K	2.3×10^8	L mol^{-1}s^{-1}
	$1.1 \times 10^{-19}\ T^{2.6}$ exp(110/T)		3.9×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_A: $\pm$ 0.2 at 298 K, increasing to $\pm$0.5 at 2000 K. k_A is the sum of $k_1 + k_2$; separate values for k_1 and k_2 are not recommended. Because the reverse reactions are unlikely to be important at any temperature, values for equilibrium constants and reverse rate coefficients are not recommended.

May 1991

$$OH + CH_3CH_2Cl \xrightarrow{1} CH_3CHCl + H_2O$$
$$\xrightarrow{2} CH_2CH_2Cl + H_2O$$

THERMOCHEMICAL DATA

The title reaction is the sum of two elementary processes: abstraction of one of the two α-hydrogen atoms (those attached to the same C atom as the chlorine):

$$OH + CH_3CH_2Cl \xrightarrow{1} CH_3CHCl + H_2O$$

and abstraction of one of the three β-hydrogen atoms:

$$OH + CH_3CH_2Cl \xrightarrow{2} CH_2CH_2Cl + H_2O$$

The three β-H atoms are not exactly equivalent because there is a barrier to rotation about the C-C bond. Hence, the properties of the H atom trans to the Cl atom (opposite it, when viewed along the C-C axis) will differ slightly from those of the two gauche β-H atoms. (Once one H atom is removed by reaction, there is practically free rotation about the C-C bond in the chloroethyl radical, and the products are almost equivalent.) McKean et al.[1] predict the bond strengths of the trans and gauche β-H atoms to be 415.0 and 424.7 kJ mol^{-1}, respectively; and that of the α-H atoms to be 428.9 kJ mol^{-1}. These values have not been verified experimentally, and considering the usual uncertainties measuring bond strengths, the trans/gauche difference may be unmeasurable. We assume hereafter that the reactions involving the two different conformations are indistinguishable.

Thermochemical data for H_2O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for chloroethane are from Stull et al.[2]. Data for the chloroethyl radicals are not available. Based on the predictions of Ref. 1, we estimate ΔHf°_{298} (CH$_3$CHCl) = 91.6 ± 12 kJ mol^{-1} and Hf°_{298} (CH$_2$CH$_2$Cl) = 99.2 ± 12 kJ mol^{-1}. The entropies of the two radicals were estimated to be 288.3 and 287.9 ± 5 J mol^{-1}K^{-1}, assuming barriers to internal rotation of 0 and 4 kJ mol^{-1}, respectively.

MEASUREMENTS

$k_A = k_1 + k_2$ was measured by Howard and Evenson[3] at 296 K in a discharge flow system using the H + NO$_2$ reaction as a source of OH radicals and laser magnetic resonance for monitoring OH consumption. From 9 separate measurements they determined k_A to be $(2.3 ± 0.4) \times 10^8$ L mol^{-1}s^{-1}. Paraskevopoulos et al.[4] used VUV flash photolysis of H$_2$O at 297 K and monitored OH disappearance by resonance absorption. They reported $k_A = (2.37 ± 0.32) \times 10^8$ L mol^{-1}s^{-1}, in excellent agreement with the earlier study. Neither group monitored the chloroethyl radicals produced and consequently could make no determination of k_1/k_2. Kasner et al.[6] used laser photolysis--laser-induced fluorescence to measure k_A at $294 \leq T/K \leq 789$ and 740 torr and reported $k_A = 68.4$ $T^{2.59}$ exp(115/T).

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other haloethanes. It was assumed that $k_1 \gg k_2$, so that the experimental measurement of k_A(298) is essentially a measure of k_1. This assumption is justified by (a) the much smaller rate coefficients for OH reactions with haloethanes having only β-hydrogen atoms (e.g., CH$_3$CF$_3$, CH$_3$CCl$_3$); and (b) the experimental determination that α-hydrogen abstraction from CH$_3$CH$_2$F accounts for approximately 85% of the total reaction.[5] The model for the activated complex was based on that used previously for the reaction of OH with CH$_4$, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results could be described by the expression. $k_1 = 5.8 \times 10^4$ $T^{1.6}$ exp(-250/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 7.

DISCUSSION

The transition state theory calculations described above underpredict results of Ref. 6 by up to 16% at their highest temperatures. Lacking a measurement of k_1/k_2 at any temperatures, we had to assume $k_1 \gg k_2$ at room temperature, and that $k_A = k_1$ throughout the temperature range. However, the neglect of contributions from k_2 means that the TST estimate of k_A will be a lower limit at temperatures above 296 K. We thus recommend the results of Ref. 6, namely $k_A = 65$ $T^{2.6}$ exp(110/T) L mol^{-1}s^{-1}, with an estimated uncertainty in log k_A of ±0.2 at 298 K, increasing to ±0.3 at 2000 K.

References

1. D. C. McKean, O. Saur, J. Travert, and J. C. Lavalley, Spectrochim. Acta, 31A, 1713 (1975).
2. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, New York; 1969), p. 512.
3. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
4. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
5. D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, J. Phys. Chem. 84, 2339 (1980).
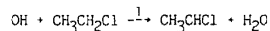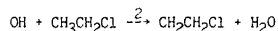6. J. H. Kasner, F. H. Taylor, and B. Dellinger, J. Phys. Chem. 94, 3250 (1990).
7. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_2BrCH_2Br \rightarrow CH_2BrCHBr + H_2O$$
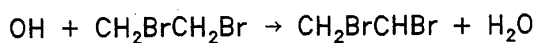
$\Delta H_{298}^{o} = -77 \pm 10$ kJ mol^{-1} (-18.4 kcal mol^{-1}) $\Delta S_{298}^{o} = 22.6 \pm 6$ J mol^{-1}K^{-1} (5.4 cal mol^{-1}K^{-1})
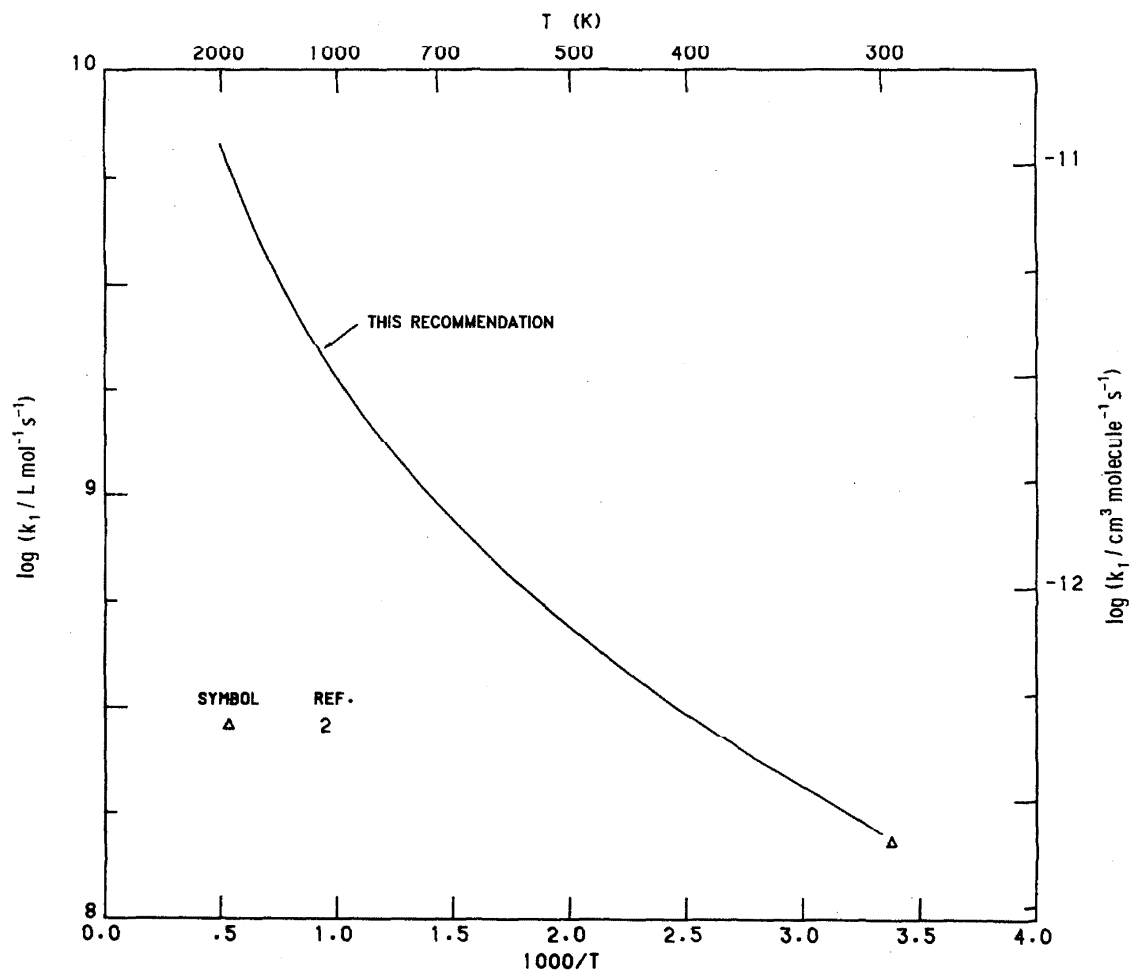
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	1.8×10^4 T$^{1.7}$ exp(-180/T)	298 - 2000 K	1.6×10^8	L mol^{-1}s^{-1}
	3.0×10^{-17} T$^{1.7}$ exp(-180/T)		2.6×10^{-13}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 298 K, increasing to ±0.5 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CH_2BrCH_2Br \rightarrow CHBrCH_2Br + H_2O$
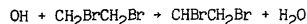
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from the third edition of JANAF Thermochemical Tables (1985). Data for 1,2-dibromoethane are given by Stull et al.[1] Data for the 1,2-dibromoethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1} whence ΔHf^o_{298} ($CHBrCH_2Br$) = 289 ± 10 kJ mol^{-1}; S^o_{298} ($CHBrCH_2Br$) is estimated to be 347 $\pm$ 6 J $mol^{-1}K^{-1}$.

MEASUREMENTS

k_1 has been measured at 296 K by Howard and Evenson[2] in a discharge flow system using the $H + NO_2$ reaction as a source of OH radicals and laser magnetic resonance to monitor OH consumption. From 19 separate measurements they determined k_1 to be $(1.5 \pm 0.3) \times 10^8$ L $mol^{-1}s^{-1}$.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k_1 to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results could be described by the expression, $k_1 = 1.8 \times 10^4$ $T^{1.7}exp(-180/T)$ L $mol^{-1}s^{-1}$. For further computational details, see Ref. 3.

DISCUSSION

In the absence of experimental data above room temperature, we rely on the TST calculations based on the single reliable measurement of Ref. 2. We recommend $k_1 = 1.8 \times 10^4$ $T^{1.7}$ $exp(-180/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ±0.2 at 298 K increasing to ±0.5 at 2000 K.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 539.
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
3. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_2FCHF_2 \rightarrow C_2H_2F_3 + H_2O$$
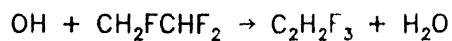
$OH + CH_2FCHF_2 \xrightarrow{1} CHFCHF_2 + H_2O$ $\Delta H^o_{298} = -77 \pm 10 \text{ kJ mol}^{-1}$ $(-18.4 \text{ kcal mol}^{-1})$ $\Delta S^o_{298} = 23.0 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ $(5.5 \text{ cal mol}^{-1} \text{ K}^{-1})$

$OH + CH_2FCHF_2 \xrightarrow{2} CH_2FCF_2 + H_2O$ $\Delta H^o_{298} = -77 \pm 10 \text{ kJ mol}^{-1}$ $(-18.4 \text{ kcal mol}^{-1})$ $\Delta S^o_{298} = 23.0 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ $(5.5 \text{ cal mol}^{-1} \text{ K}^{-1})$

SYMBOL	REF.
Δ	1
×	2

THIS RECOMMENDATION
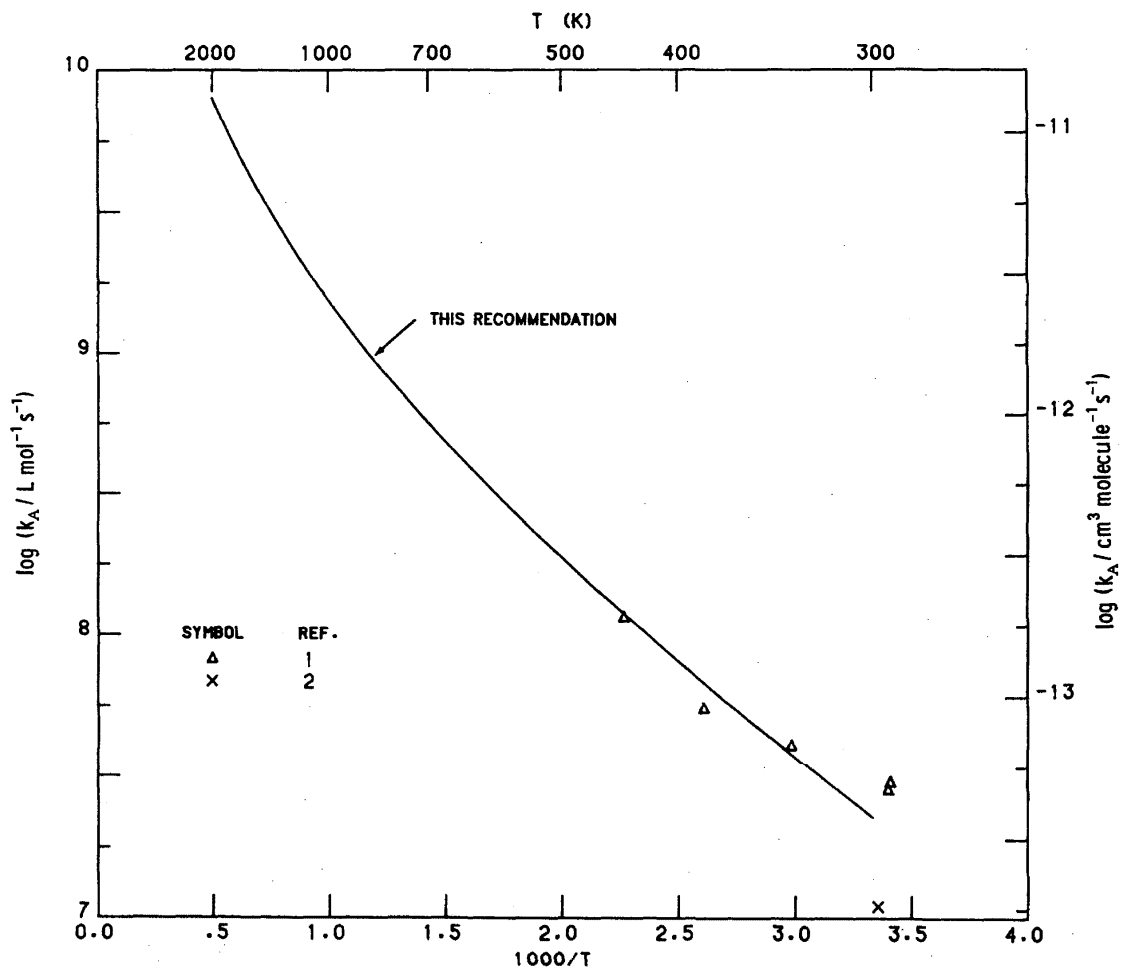
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$3.1 \times 10^4 \ T^{1.7} \exp(-930/T)$	298 – 2000 K	2.3×10^7	$L \ mol^{-1} s^{-1}$
	$5.2 \times 10^{-17} \ T^{1.7} \exp(-930/T)$		3.9×10^{-14}	$cm^3 \ molecule^{-1} s^{-1}$

Uncertainty in log k_A: ±0.3 at 298 K, increasing to ±0.5 at 2000 K. K_A is the sum of $k_1 + k_2$; separate values for k_1 and k_2 are not recommended. Because the reverse reactions are unlikely to be important at any temperature, values for equilibrium constants and reverse rate coefficients are not recommended.

February 1987

$$OH + CH_2FCHF_2 \xrightarrow{1} CHFCHF_2 + H_2O$$
$$\xrightarrow{2} CH_2FCF_2 + H_2O$$
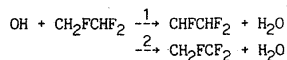
THERMOCHEMICAL DATA

The title reaction is the sum of two elementary processes: abstraction of one of the two equivalent H atoms to form 1,2,2-trifluoroethyl:

$$OH + CH_2FCHF_2 \xrightarrow{1} CHFCHF_2 + H_2O$$
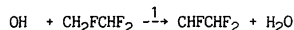
and abstraction of the single H-atom to form 1,1,2-trifluoroethyl:
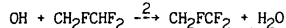
$$OH + CH_2FCHF_2 \xrightarrow{2} CH_2FCF_2 + H_2O$$

Thermochemical data for H_2O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for 1,2,2-trifluoroethane and for the radicals are not available. In the absence of such data we assume both C-H bond dissociation energies to be 423 ± 10 kJ mol^{-1}, whence $\Delta H^{o}_{298} = -77 \pm 10$ kJ/mol for both reactions. ΔS^{o}_{298} for each reaction is estimated to be 23 ± 6 J $mol^{-1}K^{-1}$.

MEASUREMENTS

Clyne and Holt[1] produced OH in a discharge-flow system by the reaction of H atoms with NO_2, and monitored OH consumption by resonance fluorescence. Because products were not monitored, their measurements gives only k_A, the sum of $k_1 + k_2$. Over the temperature range of 293 - 441 K, they reported log $k_A = (8.95 \pm 0.14) - (430 \pm 43)/T$; however, their data suggest considerable curvature on an Arrhenius plot of log k vs 1/T.

Martin and Parskevopoulos[2] studied the reaction at 298 K, generating OH radicals by VUV flash photolysis of H_2O vapor and monitoring OH disappearance by resonance absorption. They obtained log $k_A(298) = 7.04$, about a factor of 3 lower than Clyne and Holt's value of 7.47 at the same temperature. Both groups claim experimental uncertainties of $\pm 10\%$ in k_A.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_A to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_A(298)$ was assumed to be 7.37. k_1 and k_2 were calculated separately, assuming $k_1(298) = 2k_2(298)$, and the results added together to give k_A. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 25%, could be described by the expression, $k_A = 3.1 \times 10^4 \, T^{1.7} \exp(-930/T)$ L $mol^{-1}s^{-1}$. For further computational details, see Ref. 3; however, a slightly larger value of $k_1(298)$ was assumed there.

DISCUSSION

Although Clyne and Holt obtained log $k_A = 7.47$ at 298 K, in view of the scatter of the data at other temperatures, a value of 7.37 is consistent with their results. However, Ref. 2 suggests that k_A is smaller by as much as a factor of 3 at room temperature. We base our recommendation on the TST calculations described above, recognizing that this may be subject to revision when another, decisive measurement of $k_A(298)$ is made. An additional contribution to the uncertainty comes from having to apportion $k_A(298)$ arbitrarily between k_1 and k_2; we assumed an equal reaction rate coefficient for each of the 3 H atoms. Thus we recommend $k_A = 3.1 \times 10^4 \, T^{1.7} \exp(-930/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_A of ± 0.3 at 298 K, increasing to ± 0.5 at 2000 K. A negative error is more probable than a positive one.

References

1. M. A. A. Clyne and P. M. Holt. J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
2. J.-P. Martin and G. Paraskevopoulos, Canad. J. Chem. 61, 861 (1983).
3. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

N. COHEN AND K. R. WESTBERG

$OH + CH_2ClCHCl_2 \rightarrow C_2H_2Cl_3 + H_2O$

$OH + CH_2ClCHCl_2 \xrightarrow{1} CHClCHCl_2 + H_2O \quad \Delta H^O_{298} = -77 \pm 10 \text{ kJ mol}^{-1} \ (-18.4 \text{ kcal mol}^{-1}) \quad \Delta S^O_{298} = 19.2 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (4.6 \text{ cal mol}^{-1} \text{ K}^{-1})$

$OH + CH_2ClCHCl_2 \xrightarrow{2} CH_2ClCCl_2 + H_2O \quad \Delta H^O_{298} = -77 \pm 10 \text{ kJ mol}^{-1} \ (-18.4 \text{ kcal mol}^{-1}) \quad \Delta S^O_{298} = 19.2 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (4.6 \text{ cal mol}^{-1} \text{ K}^{-1})$

SYMBOL	REF.
$\triangle$	2

THIS RECOMMENDATION
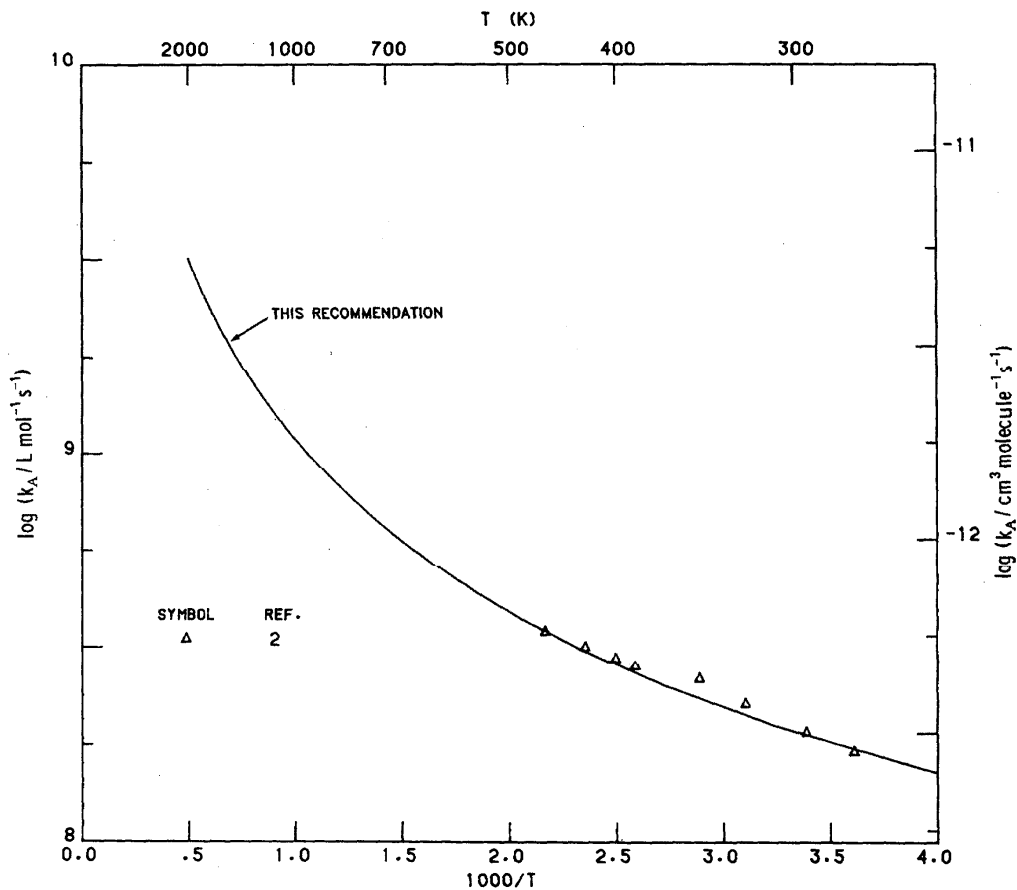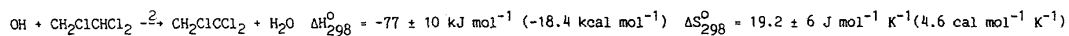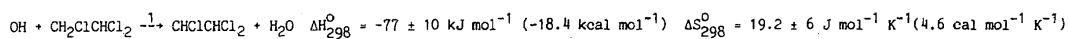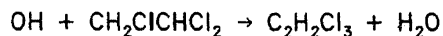
RECOMMENDED RATE COEFFICIENTS

k	$k(T)$	Range	$k(298)$	Units
k_A	$1.6 \times 10^4 \ T^{1.6} \ \exp(80/T)$	250 - 2000 K	1.9×10^8	$L \text{ mol}^{-1} s^{-1}$
	$2.7 \times 10^{-17} \ T^{1.6} \ \exp(80/T)$		3.2×10^{-13}	$cm^3 \text{ molecule}^{-1} s^{-1}$

Uncertainty in log k_A: ± 0.2 at 298 K, increasing to ± 0.4 at 2000 K and ± 0.3 at 250 K. k_A is the sum of $k_1 + k_2$; separate values for k_1 and k_2 are not recommended. Because the reverse reactions are unlikely to be important at any temperature, values for equilibrium constants and reverse rate coefficients are not recommended.

May 1991

$$OH + CH_2ClCHCl_2 \xrightarrow{1} CHClCHCl_2 + H_2O$$
$$\xrightarrow{2} CH_2ClCCl_2 + H_2O$$
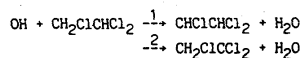
THERMOCHEMICAL DATA

The title reaction is the sum of two elementary processes: abstraction of one of the two equivalent H-atoms to form 1,2,2-trichloroethyl:

$$OH + CH_2ClCHCl_2 \xrightarrow{1} CHClCHCl_2 + H_2O$$
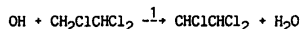
and abstraction of the single H-atom to form 1,1,2-trichloroethyl:
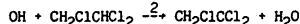
$$OH + CH_2ClCHCl_2 \xrightarrow{2} CH_2ClCCl_2 + H_2O$$

Thermochemical data for H_2O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for 1,1,2-trichloroethane are from Stull et al.[1]; data for the radicals are not available. In the absence of such data we assume both C-H bond dissociation energies to be 423 ± 10 kJ mol^{-1}, whence $\Delta H_{298}^{0} = -77 \pm 10$ kJ mol^{-1} for each reaction.

MEASUREMENTS

The only published study of this reaction is that of Jeong and Kaufman,[2] who produced OH in a discharge flow system by the reaction of H with NO_2, and monitored its consumption by resonance fluorescence. Over the temperature range of 277 to 461 K, they reported[3] $k_A = (9.9 \pm 1.6) \times 10^8 \exp[-(960 \pm 110)/T]$ L mol^{-1}s^{-1}, an expression only slightly different from that given in the earlier paper. Since products were not monitored, this represents the sum of $k_1 + k_2$.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_A to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Separate calculations were carried out for the two kinds of H atoms assuming $k_1(298) = 2k_2(298)$, and the resulting values of k_1 and k_2 were added together to give k_A. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 25%, could be described by the expression, $k_A = 1.6 \times 10^4 T^{1.7} \exp(-100/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 4.

DISCUSSION

The TST calculations described above are in good agreement with the lower four temperature measurements of Refs. 2 and 3, but overpredict k_A increasingly, albeit slightly, at the higher temperatures. Consequently, we rely on a least-squares fit through the experimental data to extrapolate k_A to higher temperatures, and recommend $k_A = 1.6 \times 10^4 T^{1.6} \exp(80/T)$ L mol^{-1}s^{-1}. This expression predicts a value of $k_A(2000)$ smaller by a factor of 2 than the TST calculation does. The estimated uncertainty in log k_A is ± 0.2 at 298 K, increasing to ± 0.4 at 2000 K and ± 0.3 at 250 K.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, New York; 1969), p. 514.
2. K.-M. Jeong and F. Kaufman, Geophys. Res. Lett. 6, 757 (1979).
3. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
4. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

N. COHEN AND K. R. WESTBERG

$$OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$$
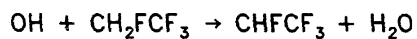
$\Delta H^o_{298} = -77 \pm 10 \text{ kJ mol}^{-1}$ (-18.4 kcal mol^{-1}) $\Delta S^-_{298} = 19.2 \pm 4 \text{ J mol}^{-1}K^{-1}$ (4.6 cal mol$^{-1}K^{-1}$)
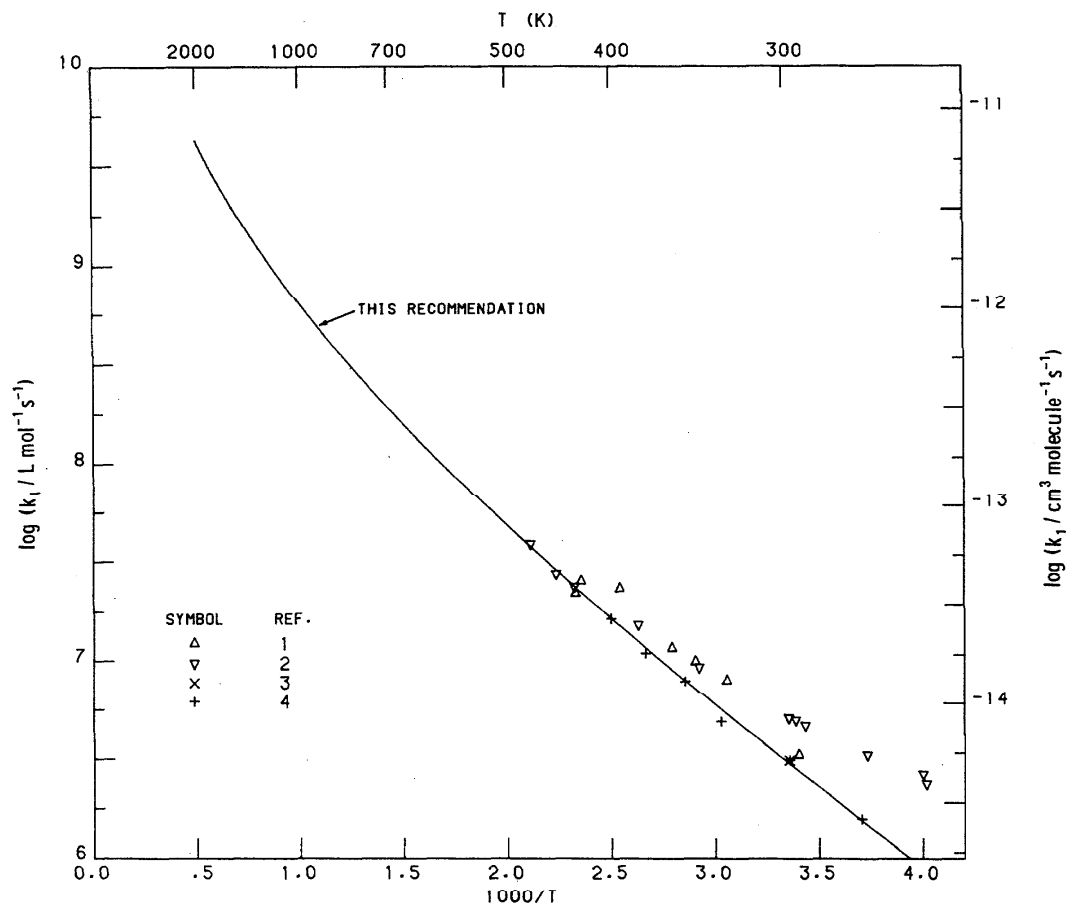
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.1 \times 10^4 \ T^{1.7} \exp(-1410/T)$	250 - 2000 K	3.0×10^6	L mol^{-1}s^{-1}
	$3.5 \times 10^{-19} \ T^{1.7} \exp(-1410/T)$		5.0×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 from 250 to 300 K, increasing to ±0.3 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_2FCF_3 \rightarrow CHFCF_3 + H_2O$
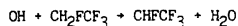
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1,2-tetrafluoroethane and for the 1,2,2,2-tetrafluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1}, whence ΔH_{298}^{o} for the reaction is -77 ± 10 kJ mol^{-1}. ΔS_{298}^{o} for the reaction is estimated to be 19.2 ± 4 J mol^{-1}K^{-1}.

MEASUREMENTS

There are two temperature-dependent measurements of k_1, both by the same method: in a discharge flow sytem, OH was generated by the reaction of H atoms with NO_2, and its disappearance monitored by resonance fluorescence. Clyne and Holt[1] made measurements at temperatures from 294 to 429; Jeong et al.,[2] from 249 to 493 K. Except at room temperature, the results are in fair agreement, but the two groups reported different Arrhenius parameters. Clyne and Holt gave log k_1 = (9.29 ± 0.23) - (780 ± 87)/T in L mol^{-1}s^{-1} units; Jeong et al. reported log k_1 = (8.82 ± 0.88) - (620 ± 15)/T. Martin and Paraskevopoulos[3] measured k_1 at 298 K using VUV flash photolysis of H_2O and resonance absorption detection and obtained (3.10 ± 0.35) × 10^6 L mol^{-1}s^{-1}, in near agreement with Clyne and Holt's value of (3.31 ± 0.42) × 10^6 (at 294 K) and smaller than Jeong et al.'s value of (5.08 ± 0.42) × 10^6. Liu et al.[4] measured by flash photolysis-resonance fluorescence at 270 < T/K < 400. Their values for k_1 agree with the other measurements at their highest temperature but diverge increasingly as temperatures decreases, giving 3.1 × 10^6 at 290 K.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures above the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k_1(298) was assumed to be 6.48. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 35%, except at the lowest temperature, could be described by the expression, k_1 = 2.1 × 10^4 $T^{1.7}$exp(-1270/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 5, where a different value for k(298) was used.

DISCUSSION

The TST calculations are in good agreement with Ref. 4, which should be the most reliable measurements. Consequently, we recommend k_1 = 2.1 × 10^4 $T^{1.7}$ exp (-1410/T) L mol^{-1} s^{-1} for 250 < T/K < 2000, with an uncertainty in log k_1 of ±0.1 at 300 K, increasing to ±0.2 at 250 K and to ±0.3 at 2000 K.

References

1. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
2. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
3. J.-P. Martin and G. Paraskevopoulos, Canad. J. Chem. 61, 861 (1983).
4. R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. 94, 3247 (1990).
5. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$$
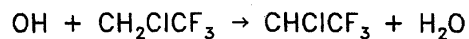
$\Delta H^o_{298} = -77 \pm 10$ kJ mol^{-1} (-18.4 kcal mol^{-1}) $\qquad\qquad$ $\Delta S^o_{298} = 20.5 \pm 4$ J mol^{-1}K^{-1} (4.9 cal mol^{-1}K^{-1})

SYMBOL	REF.
$\triangle$	2
$\triangledown$	3
+	4
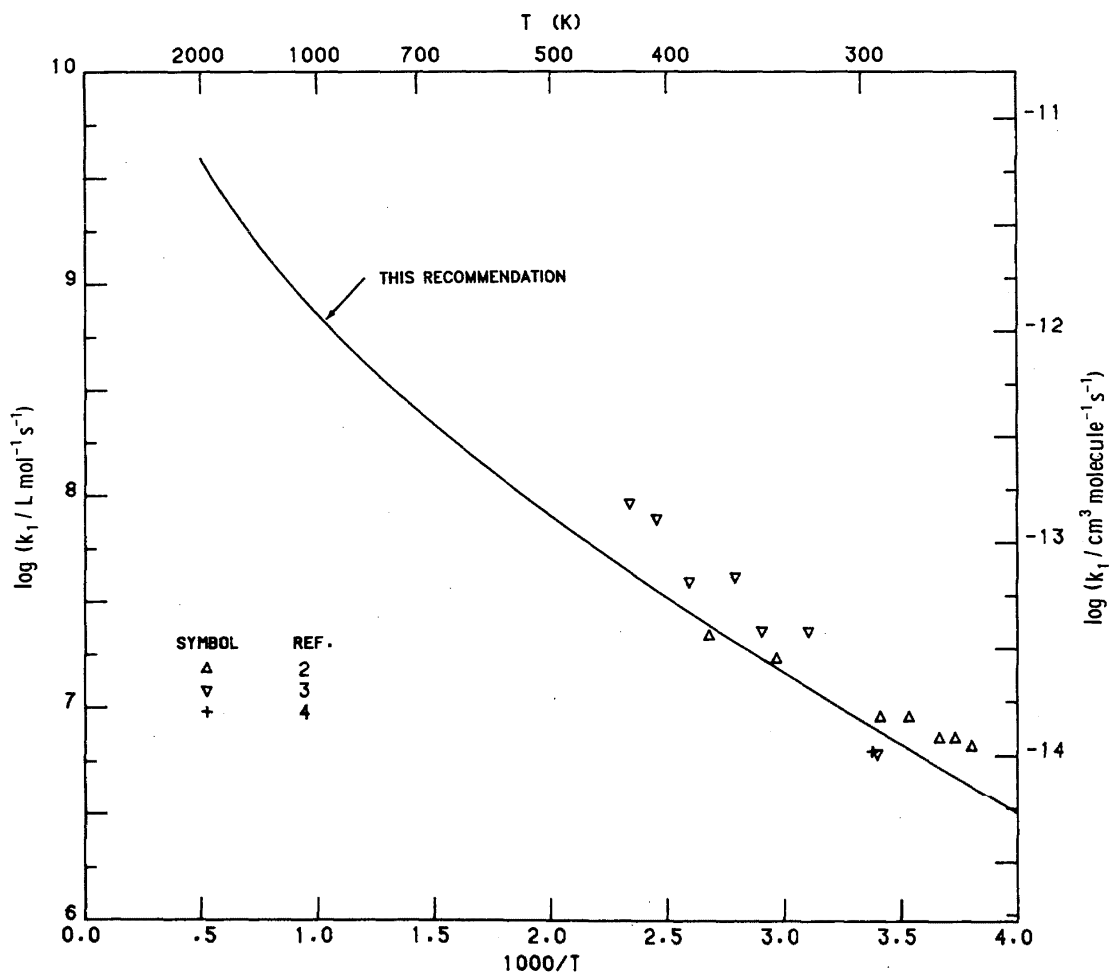
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.6 \times 10^4\ T^{1.7}\ \exp(-1020/T)$	250 – 2000 K	8.4×10^6	L mol^{-1}s^{-1}
	$2.7 \times 10^{-17}\ T^{1.7}\ \exp(-1020/T)$		1.4×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 at 298 K, increasing to ± 0.5 at 2000 K and to ± 0.3 at 250 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$

THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for the 1-chloro,2,2,2-trifluoroethyl radical and enthalpy data for 2-chloro,1,1,1-trifluoroethane are not available. The $H-CHClCF_3$ bond dissociation energy is given by McMillen and Golden.[1] From these data ΔH^o_{298} for the reaction is calculated to be -73 ± 10 kJ/mol. ΔS^o_{298} for the reaction is estimated to be 20.5 ± 4 J $mol^{-1}K^{-1}$, assuming that the three ligands on the unsaturated C atom of the radical are nonplanar.

MEASUREMENTS

Handwerk and Zellner[2] studied the reaction at temperatures between 263 and 373 K in a static system, using flash photolysis of H_2O to generate OH radicals and monitoring their disappearance by resonance absorption. They reported $k_1 = (6.62 \pm 1.8) \times 10^8$ $\exp[-(1260 \pm 60)/T]$ L $mol^{-1}s^{-1}$. Clyne and Holt[3] made measurements between 294 and 427 K in a discharge flow system, using the reaction between H and NO_2 to produce OH and monitoring its consumption by resonance fluorescence. They reported $\log k_1 = (10.37 \pm 0.34) - (1000 \pm 130)/T$ in L $mol^{-1}s^{-1}$ units. Howard and Evenson[4] reported a measurement near 296 K made in a discharge flow system also using the $H + NO_2$ reaction as an OH source but with laser magnetic resonance as a means of monitoring OH consumption. They reported $k_1 = (6.32 \pm 1.38) \times 10^6$ L $mol^{-1}s^{-1}$, in close agreement with the value of Clyne and Holt, but much smaller than Handwerk and Zellner's result of $(9.03 \pm 1.81) \times 10^6$ at 293 K.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. $\log k_1(298)$ was assumed to be 6.95. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data generally within a factor of 2, could be described by the expression, $k_1 = 1.6 \times 10^4 T^{1.7}\exp(-1020/T)$ L $mol^{-1}s^{-1}$. For further computational details, see Ref. 5.

DISCUSSION

The results of Ref. 3 exhibit a much stronger temperature dependence than do those of Ref. 2; however, the scatter in the data is so much greater that we are inclined to give more weight to Ref. 2. The TST calculations predict a slightly larger temperature dependence than the results of Ref. 1. Until another, definitive measurement of k_1 is made, we recommend the results of the TST calculation: $k_1 = 1.6 \times 10^4 T^{1.7} \exp(-1020/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in $\log k_1$ of ±0.2 at 298 K, increasing to ±0.5 at 2000 K and to ±0.3 at 250 K.

References

1. D. F. McMillen and D. M. Golden, Ann. Rev. Phys Chem. 33, 493 (1982).
2. V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. 82, 1161 (1978).
3. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
4. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
5. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).
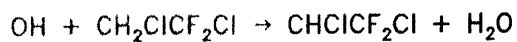
$$OH + CH_2ClCF_2Cl \rightarrow CHClCF_2Cl + H_2O$$

$\Delta H^o_{298} = -77 \pm 10$ kJ mol^{-1} (-18.4 kcal mol^{-1}) $\Delta S^o_{298} = 19.2 \pm 6$ J mol^{-1}K^{-1} (4.6 cal mol^{-1}K^{-1})
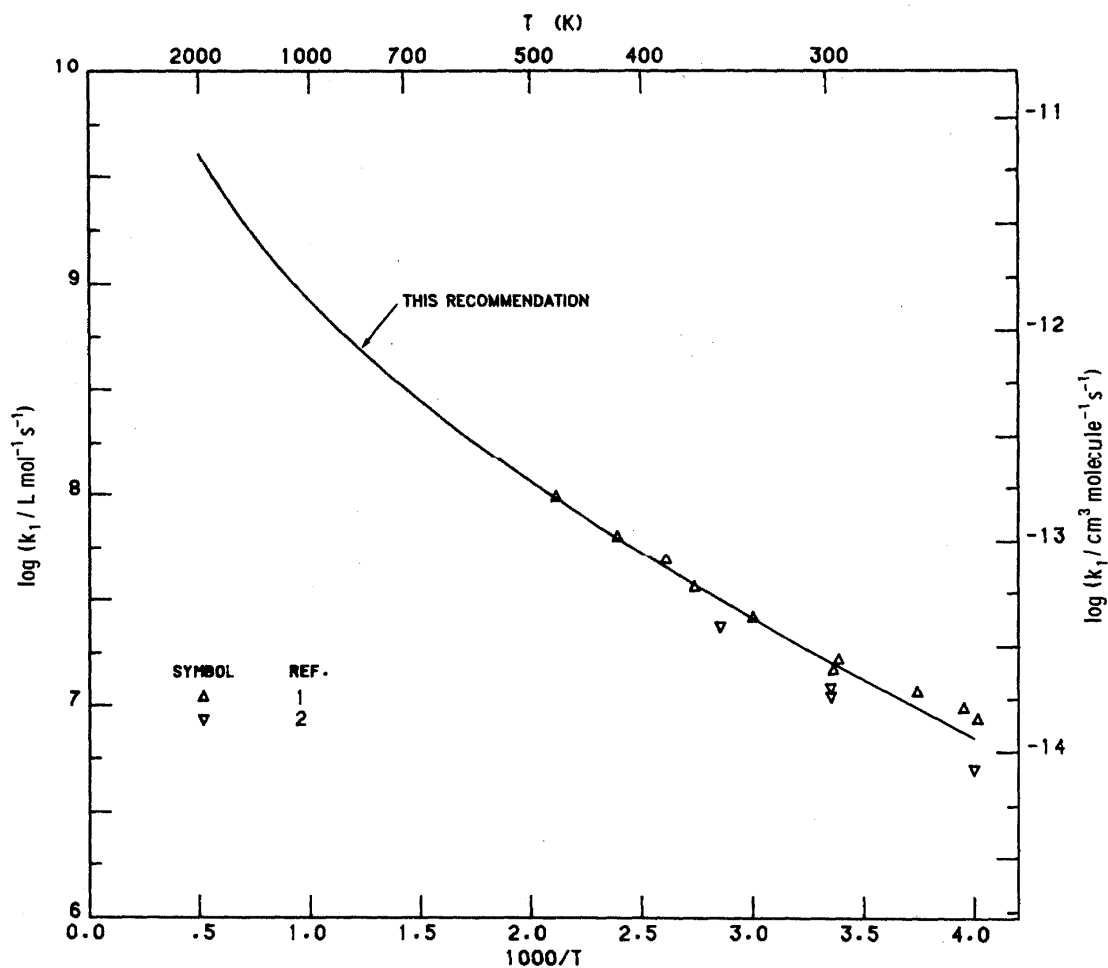
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	1.5×10^4 $T^{1.7}$ exp(-810/T)	250 –2000 K	1.6×10^7	L mol^{-1}s^{-1}
	2.5×10^{-17} $T^{1.7}$ exp(-810/T)		2.6×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 298 K, increasing to ±0.3 at 250 K and to ±0.4 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

(February 1987)

$OH + CH_2ClCF_2Cl \longrightarrow CHClCF_2Cl + H_2O$
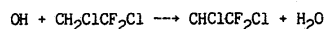
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,2-dichloro,1,1-difluoroethane and for the 1,2-dichloro,2,2-difluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1}, whence ΔH^o_{298} for the reaction is -77 ± 10 kJ mol^{-1}. ΔS^o_{298} for the reaction is estimated to be 19.2 ± 6 J mol^{-1}K^{-1}.

MEASUREMENTS

Jeong et al.[1] measured k_1 in a discharge-flow apparatus, using the H + NO_2 reaction to produce OH radicals and monitoring their disappearance by resonance fluorescence. Over the temperature range of 249 - 473 K they could express k_1 by $(1.22 \pm 0.12) \times 10^9$ exp$[-(1260 \pm 35)/T]$ L mol^{-1}s^{-1}, but noted that their data suggested considerable curvature on an Arrhenius plot.

Watson et al.[2] used flash photolysis-resonance fluorescence at 250, 298, and 350 K, with the source of OH radicals being 50 - 400 mtorr of H_2O. They reported $k = (1.8 \, ^{+3.6}_{-0.6}) \times 10^9$ exp$[-1580 \, ^{+400}_{-230})/T]$ L mol^{-1}s^{-1}, with an estimated correction made for the presence of 450 ppm of halogenated C_2 alkenes. Their approximate room temperature value of $(1 \pm 0.1) \times 10^7$ is about 2/3 of the value obtained by Jeong et al.[1]

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. A value of log $k_1(298) = 7.2$ was assumed. The results, in agreement with all the data within 40%, could be described by the expression, $k_1 = 1.5 \times 10^4$ $T^{1.7}$exp$(-810/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 3.

DISCUSSION

The results of Ref. 2 are consistently lower than those of Ref. 1, especially at the lowest temperature of both studies (250 K), where the discrepancy is a factor of 1.8. We see no compelling reason for preferring one set of results over the other, though we have made our TST calculations based on a value of $k_1(298)$ consistent with the results of Ref. 1. Until a third, decisive measure of k_1 is made, we recommend the results of the TST calculation: $k_1 = 1.5 \times 10^4$ $T^{1.7}$ exp$(-810/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.2 at 298 K, increasing to ± 0.4 at 2000 K and to ± 0.3 at 250 K.

References

1. K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
2. R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. 11, 187 (1979).
3. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH \ + \ CHF_2CHF_2 \ \rightarrow \ CHF_2CF_2 \ + \ H_2O$$
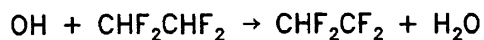
$\Delta H^o_{298} = -77 \pm 10 \ kJ \ mol^{-1} \ (-18.4 \ kcal \ mol^{-1})$ $\Delta S^o_{298} = 20.5 \pm 6 \ J \ mol^{-1}K^{-1} \ (4.9 \ cal \ mol^{-1}K^{-1})$
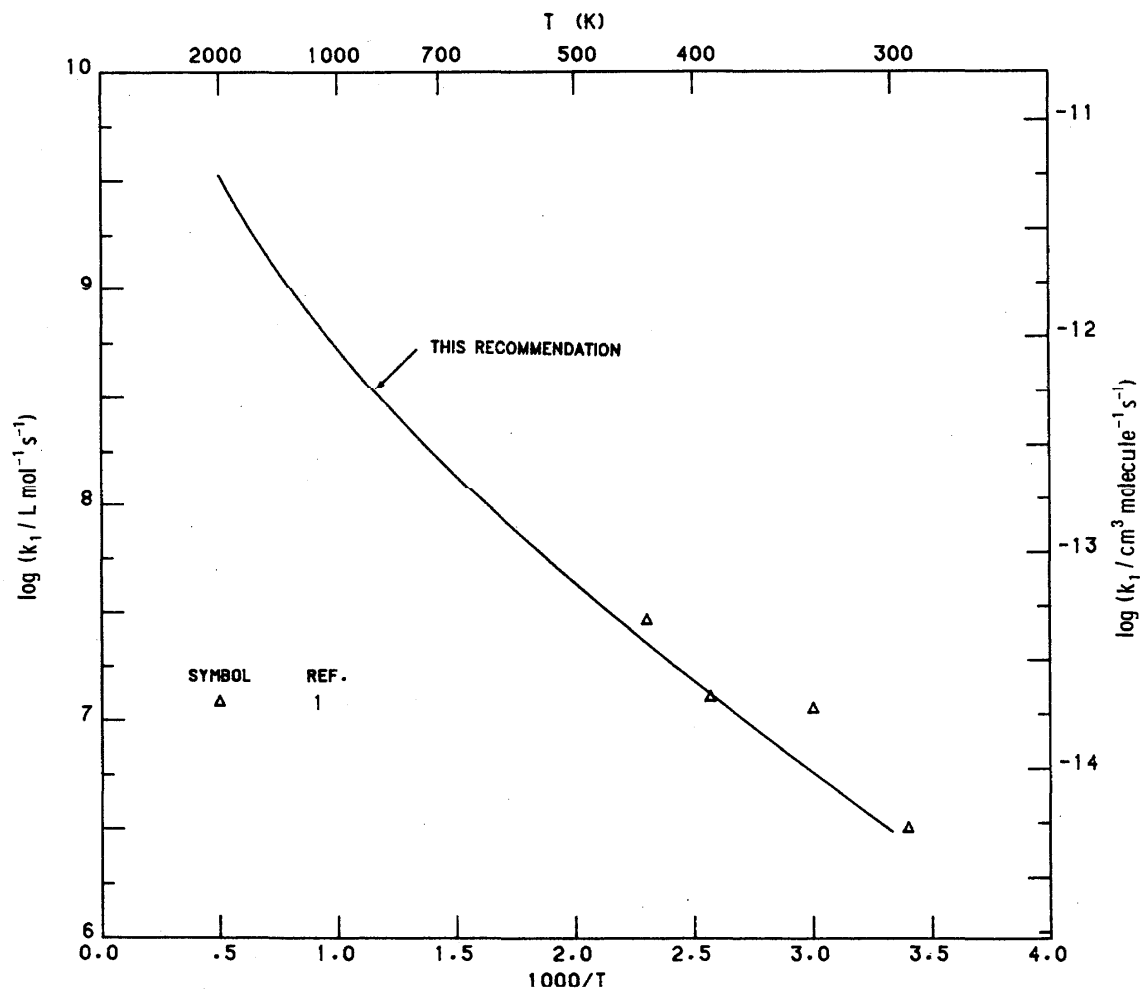
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.6 \times 10^4 \ T^{1.7} \ exp(-1330/T)$	298 - 2000 K	3.0×10^6	$L \ mol^{-1}s^{-1}$
	$2.7 \times 10^{-17} \ T^{1.7} \ exp(1330/T)$		4.9×10^{-15}	$cm^3 \ molecule^{-1}s^{-1}$

Uncertainty in log k_1: ± 0.3 at 298 K, increasing to ± 0.6 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CHF_2CHF_2 \rightarrow CF_2CHF_2 + H_2O$
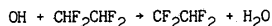
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,2,2-tetrafluoroethane and for the 1,1,2,2-tetrafluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ/mol, whence ΔH^O_{298} for the reaction is -77 ± 10 kJ/mol. ΔS^O_{298} for the reaction is estimated to be 20.5 ± 6 J mol^{-1}K^{-1}..

MEASUREMENTS

The single published study of this reaction to date is by Clyne and Holt,[1] who used a discharge flow system in which OH was generated by the reaction between H atoms and NO_2 and its consumption monitored by resonance fluorescence. For 4 temperatures between 294 and 434 K they reported $\log k_1 = (9.22 \pm 0.53) - (780 \pm 170)/T$ in L mol^{-1}s^{-1} units, with considerable deviation from linearity on an Arrhenius plot.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k_1(298) was assumed to be 6.50. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results in reasonable agreement with the data considering the scatter, could be described by the expression, $k_1 = 1.6 \times 10^4 T^{1.7} \exp(-1330)/T$ L mol^{-1}s^{-1}. For further computational details, see Ref. 2.

DISCUSSION

As the graph shows, the four data points of Ref. 1 exhibit considerable uncertainty in temperature dependence. Log k_1 at room temperature could easily be in error by ±0.25 units. The "universal" rate coefficient expression derived in Ref. 3 predicts a value of log k_1(298) of over 7.35. On the other hand, in the case of several other haloethanes the results of Ref. 1 are significantly larger than those of other workers. With some hesitancy, therefore, we rely on the TST calculations based on room temperature value of k_1 determined in Ref. 1, recognizing that another measurement is badly needed. We recommend $k_1 = 1.6 \times 10^4 T^{1.7} \exp(-1330/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.3 at 298 K, increasing to ±0.6 at 2000 K.

References

1. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
2. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).
3. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 171 (1987).

N. COHEN AND K. R. WESTBERG

$$OH + CHF_2CF_3 \rightarrow CF_2CF_3 + H_2O$$
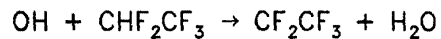
$\Delta H^O_{298} = -68 \pm 8 \text{ kJ mol}^{-1}$ (-16.2 kcal mol^{-1})

$\Delta S^O_{298} = 12.6 \pm 4 \text{ J mol}^{-1}\text{K}^{-1}$ (3.0 cal mol^{-1}K^{-1})
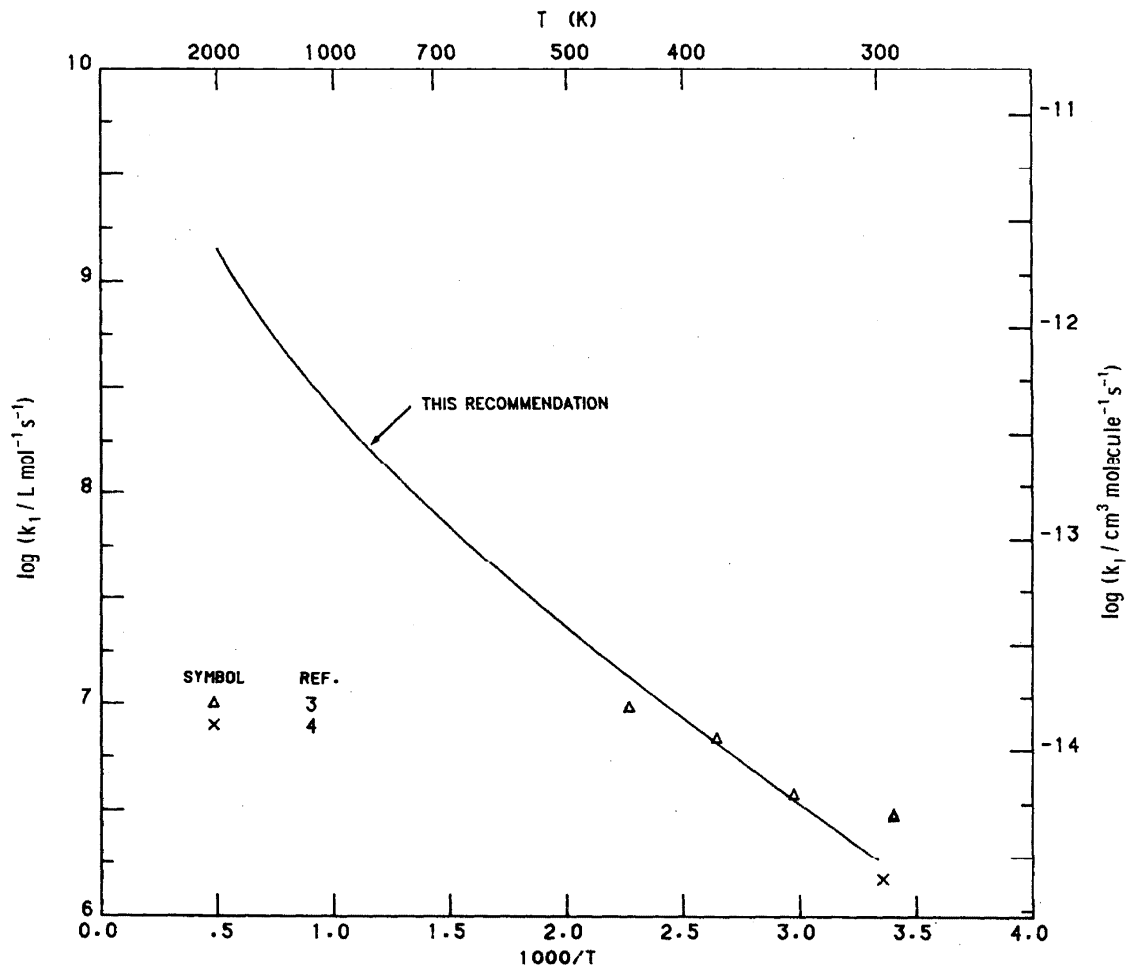
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.4 \times 10^4 \, T^{1.6} \exp(-1270/T)$	298 - 2000 K	3.2×10^6	L mol^{-1}s^{-1}
	$2.3 \times 10^{-17} \, T^{1.6} \exp(-1270/T)$		5.2×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.3 at 298 K, increasing to ± 0.6 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CHF_2CF_3 \rightarrow CF_2CF_3 + H_2O$
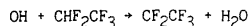
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for pentaflouroethane are from Chen et al.[1]. Data for the pentafluoroethyl radical are from Rogers,[2] who cites $\Delta Hf^o_{298} = -891 \pm 4$ kJ mol^{-1} and $S^o_{298} = 341.2$ J mol^{-1}K^{-1}. The uncertainty in ΔS^o_{298} for the reaction results primarily from the uncertainties in the barriers to internal rotation in both the haloalkane and the radical.

MEASUREMENTS

The only temperature-dependent study of this reaction to date is by Clyne and Holt[3], who used a discharge flow system in which OH was generated by the reaction between H atoms and NO_2 and its consumption monitored by resonance fluorescence. For 4 temperatures between 294 and 441 K they reported log $k_1 = (8.01 \pm 0.20) - (478 \pm 43)/T$ in L mol^{-1}s^{-1} units. Their room temperature value (294 K) was $(3.0 \pm 1.1) \times 10^6$. A much smaller value of $(1.5 \pm 0.17) \times 10^6$ L mol^{-1}s^{-1} at 298 K was reported by Martin and Paraskevopoulos[4], who used flash photolysis of H_2O vapor as an OH source and monitored the disappearance of OH radicals by resonance absorption.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_1(298)$ was assumed to be 6.28. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data though suggesting stronger temperature dependence, could be described by the expression, $k_1 = 1.4 \times 10^4$ $T^{1.6}$exp(-1270/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 5; however, a slightly larger value of $k_1(298)$ was assumed there.

DISCUSSION

The room temperature value of k_1 reported in Ref. 4 is smaller by more than a factor of 2 than the value of Ref. 3; but it is consistent with higher temperature data of the latter study if the temperature dependence is as detemined by the TST calculations described above. In view of the unsatisfactory agreement between the experimental studies, we rely on the TST calculations until another, definitive experiment is published. We recommend $k_1 = 1.4 \times 10^4$ $T^{1.6}$ exp(-1270/T) L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.3 at 298 K, increasing to ± 0.6 at 2000 K.

References

1. S. S. Chen, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data 4, 441 (1975).
2. A. S. Rogers, "Thermochemistry of Fluorocarbon Radicals," in Fluorine-Containing Free Radicals: Kinetics and Dynamics of Reactions, J. W. Root, Ed. (ACS SS 66, 1978), 296.
3. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
4. J.-P. Martin and G. Paraskevopoulos, Canad. J. Chem. 61, 861 (1983).
5. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CHClFCF_3 \rightarrow CClFCF_3 + H_2O$$
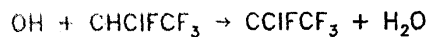
$\Delta H^O_{298} = -77 \pm 10$ kJ mol^{-1} (-18.4 kcal mol^{-1}) $\Delta S^O_{298} = 15.5 \pm 6$ J mol^{-1}K^{-1} (3.7 cal mol^{-1}K^{-1})
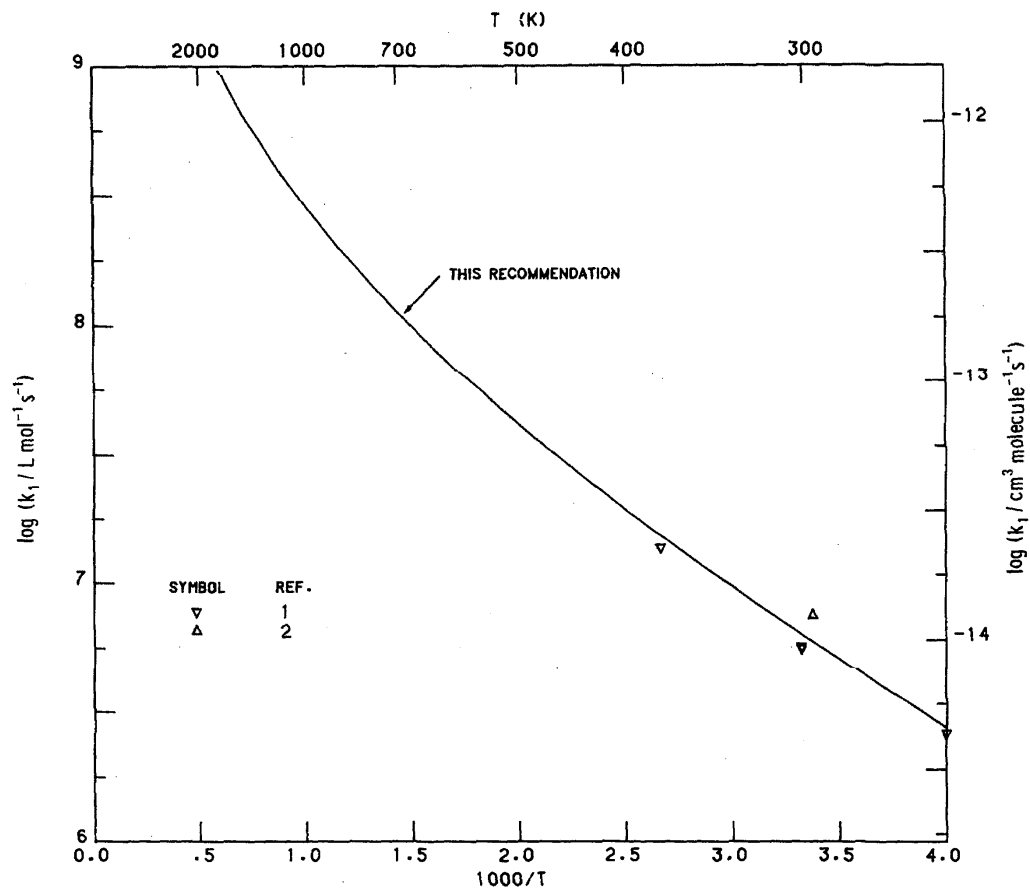
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	5.0×10^3 T$^{1.7}$ exp(-770/T)	250 - 2000 K	6.3×10^6	L mol^{-1}s^{-1}
	8.3×10^{-18} T$^{1.7}$ exp(-770/T)		1.0×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 298 K, increasing to ±0.5 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CHClFCF_3 \rightarrow CClFCF_3 + H_2O$
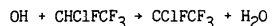
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1,2-tetraflouro,-2-chloroethane and for the 1,2,2,2-tetraflouro,1-chloroethane radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1}, whence ΔH^o_{298} for the reaction is estimated to be -77 ± 10 kJ mol^{-1}. ΔS^o_{298} for the reaction is estimated to be 15.5 ± 6 J mol^{-1}K^{-1}.

MEASUREMENTS

Watson et al.[1] measured k_1 at 250, 301, and 375 K using flash photolysis of 50 - 200 mtorr H_2O as an OH source and resonance fluorescence to monitor its disappearance. They reported $k_1 = (3.69 \pm 0.24) \times 10^8 \exp[-(1244 \pm 90)/T]$ L mol^{-1}s^{-1}, with a value at 301 K of $(5.7 \pm 0.2) \times 10^6$. Howard and Evenson[2] obtained a slightly higher room temperature value of $(7.5 \pm 1.1) \times 10^6$ (296 K) using the $H + NO_2$ reaction in a discharge flow to generate OH radicals and laser magnetic resonance to detect their disappearance.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_1(298)$ was assumed to be 6.80. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data considering the scatter, could be described by the expression, $k_1 = 5.0 \times 10^3$ $T^{1.7}\exp(-770/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 3; however, a slightly larger value of $k_1(298)$ was assumed there.

DISCUSSION

The experimental data are within approximately 25% of the values of k_1 calculated by TST; hence we recommend the TST expression of $k_1 = 5.0 \times 10^3$ $T^{1.7} \exp(-770/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.2 at 298 K, increasing to ± 0.5 at 2000 K.

References

1. R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. 11, 187 (1979).
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
3. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

N. COHEN AND K. R. WESTBERG

$$OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$$
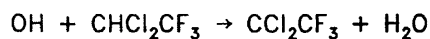
$\Delta H^O_{298} = -77 \pm 10 \text{ kJ mol}^{-1} \ (-18.4 \text{ kcal mol}^{-1})$

$\Delta S^O_{298} = 17.2 \pm 6 \text{ J mol}^{-1}\text{K}^{-1} \ (4.1 \text{ cal mol}^{-1}\text{K}^{-1})$
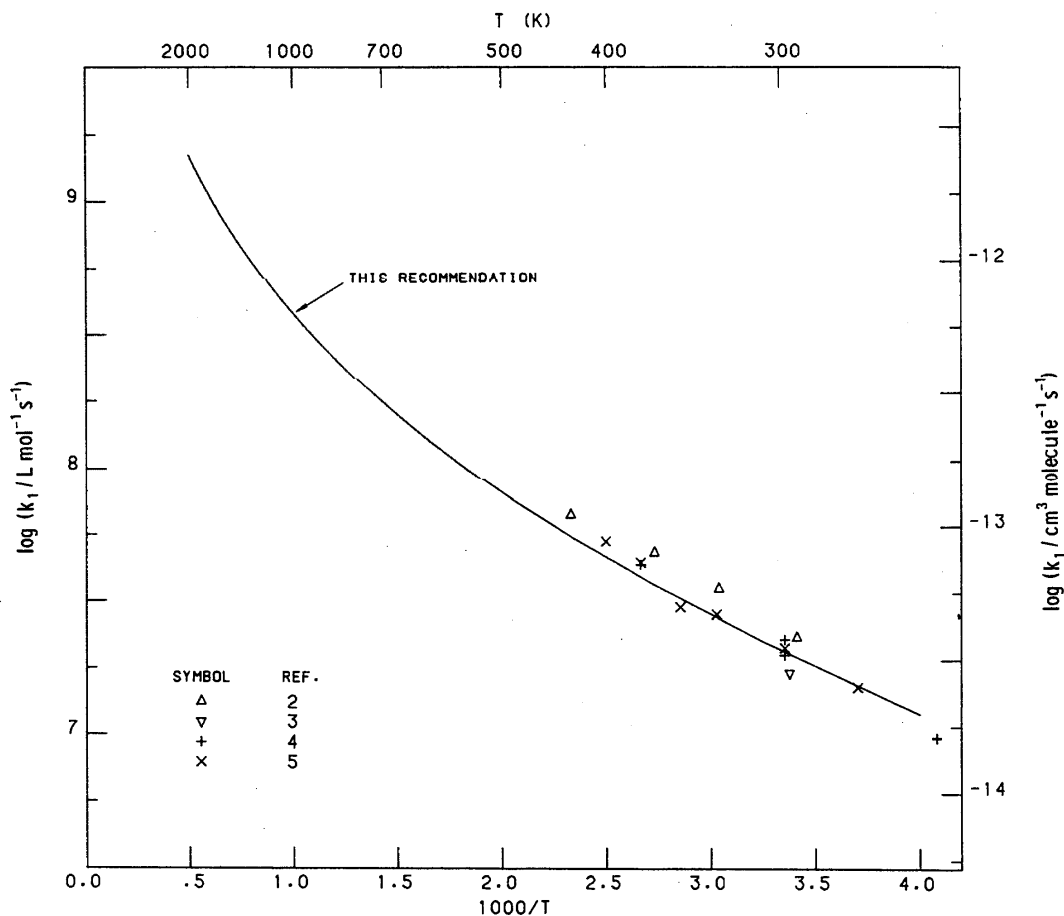
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$4.4 \times 10^3 \ T^{1.7} \exp(-370/T)$	250 - 2000 K	2.0×10^7	L mol^{-1}s^{-1}
	$7.3 \times 10^{-18} \ T^{1.7} \exp(-370/T)$		3.4×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 250 to 300 K, increasing to ±0.4 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CHCl_2CF_3 \rightarrow CCl_2CF_3 + H_2O$
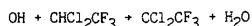
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1-trifluoro-2,2-dichloroethane (except for ΔS^o_{298} -- see Ref. 1) and for the 2,2,2-trifluoro-1,1-dichloroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 20 kJ mol^{-1}, whence ΔH^o_{298} for the reaction is -77 ± 10 kJ mol^{-1}. ΔS^o_{298} for the reaction is estimated to be 17.2 ± 6 J mol^{-1}K^{-1}.

MEASUREMENTS

Clyne and Holt[2] used a discharge flow system to measure k_1 at 4 temperatures between 293 and 429 K. OH was generated by the reaction between H atoms and NO_2, and its consumption monitored by resonance fluorescence. They reported log $k_1 = (8.83 \pm 0.02) - (435 \pm 44)/T$ in L mol^{-1}s^{-1} units. At 293 K they obtained $k_1 = (2.32 \pm 0.11) \times 10^7$ L mol^{-1}s^{-1}. Howard and Evenson[3] obtained a smaller room temperature value of $(1.71 \pm 0.26) \times 10^7$ in a similar experiment except that the OH was monitored by laser magnetic resonance. Watson et al.[4] used flash photolysis resonance fluorescence at 245, 298, and 375 K and reported a rate coefficient of $(8.4 \pm 0.24) \times 10^8$ exp[$(-1102 ^{+157}_{-106})/T$] L mol^{-1}s^{-1}. Their room temperature result of $(2.2 \pm 0.2) \times 10^7$ agrees with that of Ref. 1. (The higher and lower values shown for Ref. 4 on the graph represent experiments at 40 and 300 torr diluent, respectively.) Liu et al.[5] measured k_1 by flash photolysis-resonance fluorescence at $270 < T/K < 400$. Their values for k_1 agree with the other measurements.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. Log $k_1(298)$ was assumed to be 7.3. The results, in agreement with the data generally within 25%, could be described by the expression. $k_1 = 4.4 \times 10^3$ $T^{1.7}$exp$(-370/T)$ L mol^{-1}s^{-1}. For further computational details, see Ref. 5; however, a slightly larger value of $k_1(298)$ was assumed there.

DISCUSSION

The TST calculations are in satisfactory agreement with all the experimental data; hence we rely on them to extrapolate k_1 beyond the temperature range of the experiments and recommend $k_1 = 4.4 \times 10^3$ $T^{1.7}$ exp$(-370/T)$ L mol^{1}s^{-1}, with an uncertainty in log k_1 between 250 and 300 K of ±0.2, increasing to ±0.4 at 2000 K.

References

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 640.
2. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
3. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
4. R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, Int. J. Chem. Kinet. 11, 187 (1979).
5. R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. 94, 3247 (1990).
6. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3CF_3 \rightarrow CH_2CF_3 + H_2O$$
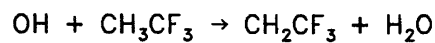
$\Delta H^0_{298} = -53 \pm 8$ kJ mol^{-1} (-12.6 kcal mol^{-1}) $\Delta S^0_{298} = 20.1 \pm 4$ J mol^{-1}K^{-1} (4.8 cal mol^{-1}K^{-1})

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	4.1×10^6 T$^{1.1}$ exp(-2380/T)	298 - 2000 K	7.3×10^5	L mol^{-1}s^{-1}
	6.8×10^{-15} T$^{1.1}$ exp(-2380/T)		1.2×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.3 at 298 K, increasing to ±0.5 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

February 1987

$OH + CH_3CF_3 \rightarrow CH_2CF_3 + H_2O$
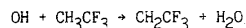
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1-trifluoroethane are from Stull et al.[1] Data for the 2,2,2-trifluoroethyl radical are from Rogers,[2] who cites ΔHf^{o}_{298} = -517 ± 8 kJ mol^{-1} and S^{o}_{298} = 299.4 J mol^{-1}K^{-1}. The uncertainty in ΔS^{o}_{298} for the reaction results primarily from the uncertainties in the barriers to internal rotation in both the haloalkane and the radical.

EXPERIMENTAL DATA

Clyne and Holt[3] studied the reaction at 4 temperatures between 293 and 425 K in a discharge-flow system. The OH was produced by the reaction of H atoms with NO_2, and its disappearance monitored by resonance fluorescence. They expressed their results by $\log k_1$ = (10.62 ± 0.40) - (1390 ± 220)/T in L mol^{-1}s^{-1} units. At 293 K they obtained only an upper limit to k_1 of 6.0 × 10^5. Martin and Paraskevopoulos[4] obtained a larger value for k_1 at 298 K of (1.03 ± 0.26) × 10^6. This result was obtained by flash photolysis of H_2O in the VUV to produce OH radicals, whose disappearance was then monitored by resonance absorption. Their fluorocarbon was of measured purity 99.6%, with 0.4% $CFClCH_2$ impurity. Assuming a reactivity of the latter compound characteristic of olefins with OH, there is sufficient impurity present to contribute significantly to the measured rate coefficient at room temperature. Clyne and Holt's reagent was stated to be 99.9% pure or better.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k_1 was assumed to be 5.9. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within a factor of 2, could be described by the expression, k_1 = 4.1 × 10^6 T$^{1.1}$exp(-2380/T) L mol^{-1}s^{-1}. For further computational details, see Ref. 5; however, a slightly larger value of k_1(298) was assumed there.

DISCUSSION

Both room temperature measurements of k_1 leave something to be desired: that of Ref. 4 may be too large because of possible impurities; the lower value of Ref. 3 is given as only an upper limit. A value of log k_1(298) - 5.9 is consistent with both measurements, but may still be too large. The TST calculation based on this value for k_1(298) predicts values at higher temperatures consistently lower than the other results of Ref. 3. However, values for the rate coefficient for the analogous reaction of OH with CH_3CCl_3 obtained in Ref. 3 are consistently higher than results of other workers (see Data Sheet for that reaction). The TST calculation for that reaction is in good agreement with the most reliable experimental data. Hence, we chose to rely on the TST calculations in this case, not withstanding the disagreement with Ref. 3. We recommend k_1 = 4.1 × 10^6 T$^{1.1}$exp(-2380/T) L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ±0.3 at 300 K, increasing to ±0.5 at 2000 K.
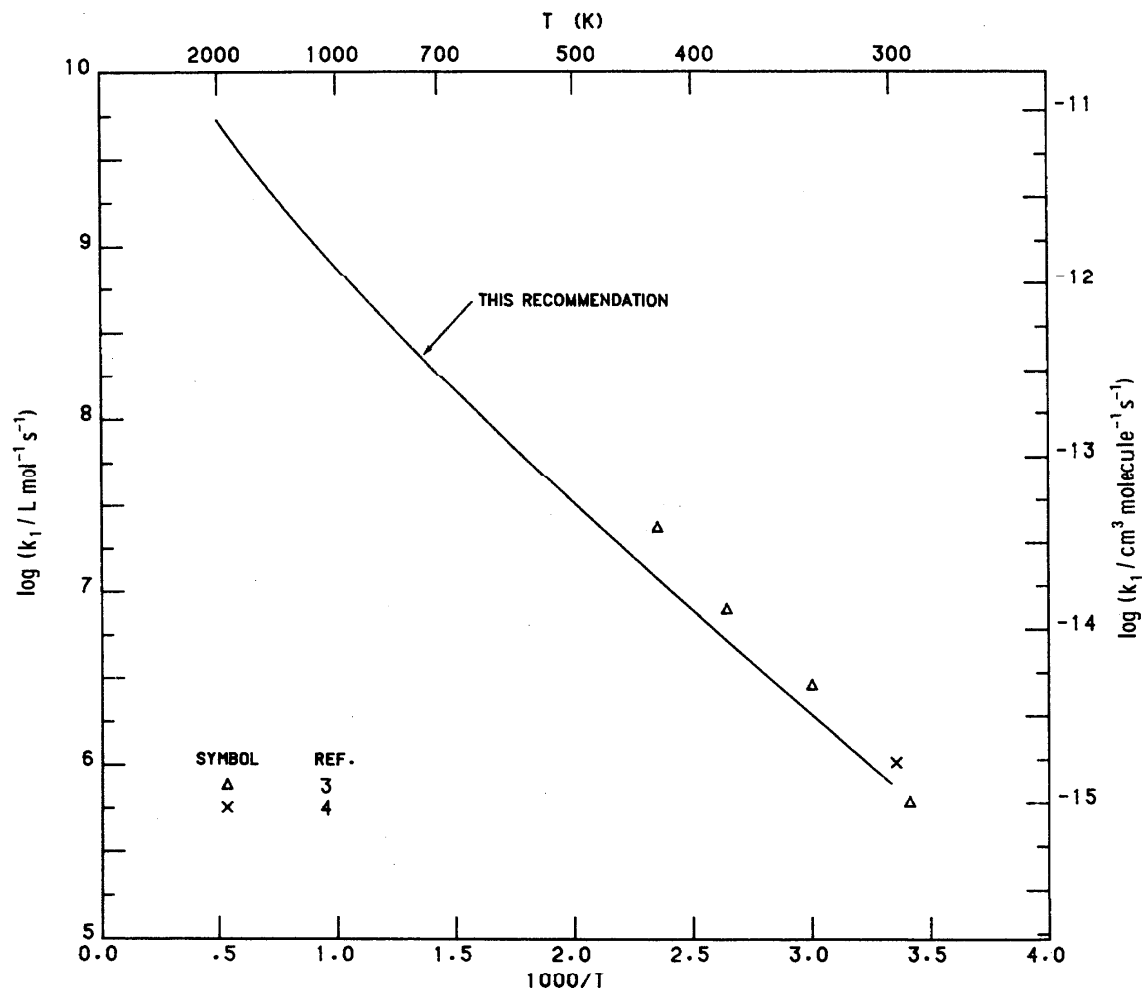
References

1.   D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, 1969), p. 639.
2.   A. S. Rogers, "Thermochemistry of Fluorocarbon Radicals," in Fluorine-Containing Free Radicals: Kinetic and Dynamics of Reactions, J. W. Root, Ed. (ACS SS 66, 1978), 296.
3.   M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582)1979).
4.   J.-P. Martin ande G. Paraskevopoulos, Canad. J. Chem. 61, 861 (1983).
5.   N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$$

$\Delta H^o_{298} = -77 \pm 10 \text{ kJ mol}^{-1} \text{ (-18.4 kcal mol}^{-1}\text{)}$ $\Delta S^o_{298} = 17.7 \pm 5 \text{ J mol}^{-1}\text{K}^{-1} \text{ (4.2 cal mol}^{-1}\text{K}^{-1}\text{)}$
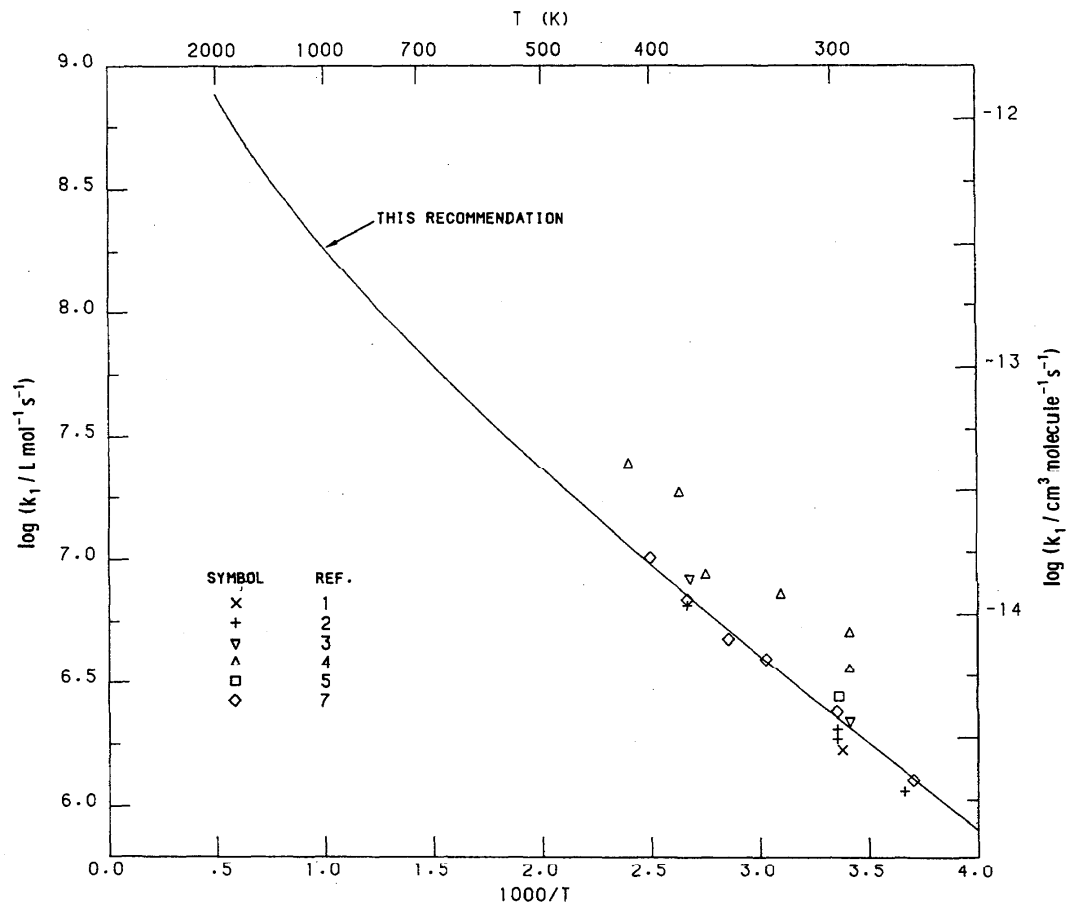
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$3.4 \times 10^5 \text{ T}^{1.1} \exp(-1300/T)$	250 - 2000 K	2.3×10^6	L mol^{-1}s^{-1}
	$5.7 \times 10^{-16} \text{ T}^{1.1} \exp(-1300/T)$		3.8×10^{-15}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 at 298 K and below increasing to ± 0.3 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$
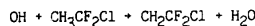
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1-chloro,1,1-difluorethane and the 2-chloro,2,2-difluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1}, whence ΔH_{298}^O for the reaction is -77 ± 10 kJ mol^{-1}. ΔS_{298}^O for the reaction is estimated to be 17.7 ± 5 J mol^{-1}K^{-1}.

MEASUREMENTS

The reported measurements[1-7] of k_1 show considerable scatter, much of which can probably be attributed to impurities. (Paraskevopoulos et al.[5] estimate that the 0.054% $C_2F_2Cl_2$ impurity could increase the apparent rate coefficient by 35% at room temperature.) Howard and Evenson[1] measured k_1 at 296 K, using a discharge-flow system to produce the OH radicals by the reaction of $H + NO_2$, and laser magnetic resonance for OH detection. Their haloethane was of greater than 99.99% analyzed purity. They obtained the lowest reported room temperature value for k_1 of $(1.7 \pm 0.25) \times 10^6$ L mol^{-1}s^{-1}. Watson et al.[2] used photolysis of H_2O by an N_2 spark discharge lamp as an OH source and resonance fluorescence for OH detection. Their halocarbon was of stated purity >99.8%. They fitted their data at 273, 298, and 375 K by $k_1 = (6.9 \pm 0.9) \times 10^8$ exp[-(1748 $\pm$ 30)/T] L mol^{-1}s^{-1}. Handwerk and Zellner[3] produced OH by flash photolysis of H_2O and used resonance absorption to monitor its disappearance. After purification the CH_3CF_2Cl contained 0.02-0.1% of other saturated fluorocarbons and unstated amounts of unsaturated fluorocarbons. They reported $k_1 = (1.08 \pm 0.3) \times 10^8$ exp[-(1790 $\pm$ 150)/T] based on measurements at 293 and 373 K. Clyne and Holt[5] studied the reaction at 5 temperatures between 293 and 417 K, using the $H + NO_2$ reaction in a discharge flow system to produce OH and resonance fluorescence to monitor its disappearance. The halocarbon was stated to be more than 99.8% pure. They reported log $k_1 = (9.3 \pm 0.36) - (780 \pm 130)/T$ in L mol^{-1}s^{-1} units, and $k(293) = (4.3 \pm 0.8) \times 10^6$. Paraskevopoulos et al.[5] measured k_1 at 297 K by flash photolysis-resonance absorption and reported $(2.79 \pm 1.04) \times 10^6$ L mol^{-1}s^{-1}. Their reagent was 99.9% pure. Cox et al.[6] reported the same result, but their method requires some unproven assumptions about the reaction mechanism. Liu et al.[7] measured k_1 by flash photolysis-resonance fluorescence at 270 < T/K < 400.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures above 300 K and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_1(298)$ was assumed to be 6.4. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in fair agreement with the data considering the scatter, could be described by the expression, $k_1 = 3.0 \times 10^6 \ T^{1.1} exp(-1940/T)$ L mol^{-1}s^{-1}. For further details, see Ref. 8; however, a slightly larger value of $k_1(298)$ was assumed there.

DISCUSSION

The TST calculations predict a slightly larger temperature dependence than the results of Ref. 7, which should be the most reliable experiments. We rely on the latter, but assume a preexponential factor of $T^{1.1}$, as the calculations predict, and recommend $k_1 = 3.4 \times 10^5 \ T^{1.1} \ exp(-1300/T)$ for 270 < T/K < 2000. This agrees with the data of Ref. 7 within 10%.

References

1. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
2. R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. 81, 156 (1977).
3. V. Handwerk and R. Zellner, Ber. Bunsenges. Phys. Chem. 82, 1161 (1978).
4. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 582 (1979).
5. G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. 85, 561 (1981).
6. R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
7. R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. 94, 3247 (1990).
8. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$$
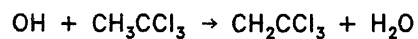
$\Delta H^O_{298} = -77 \pm 10$ kJ mol^{-1} (-18.4 kcal mol^{-1}) $\Delta S^O_{298} = 20.2 \pm 5$ J mol^{-1}K^{-1} (4.8 cal mol^{-1}K^{-1})
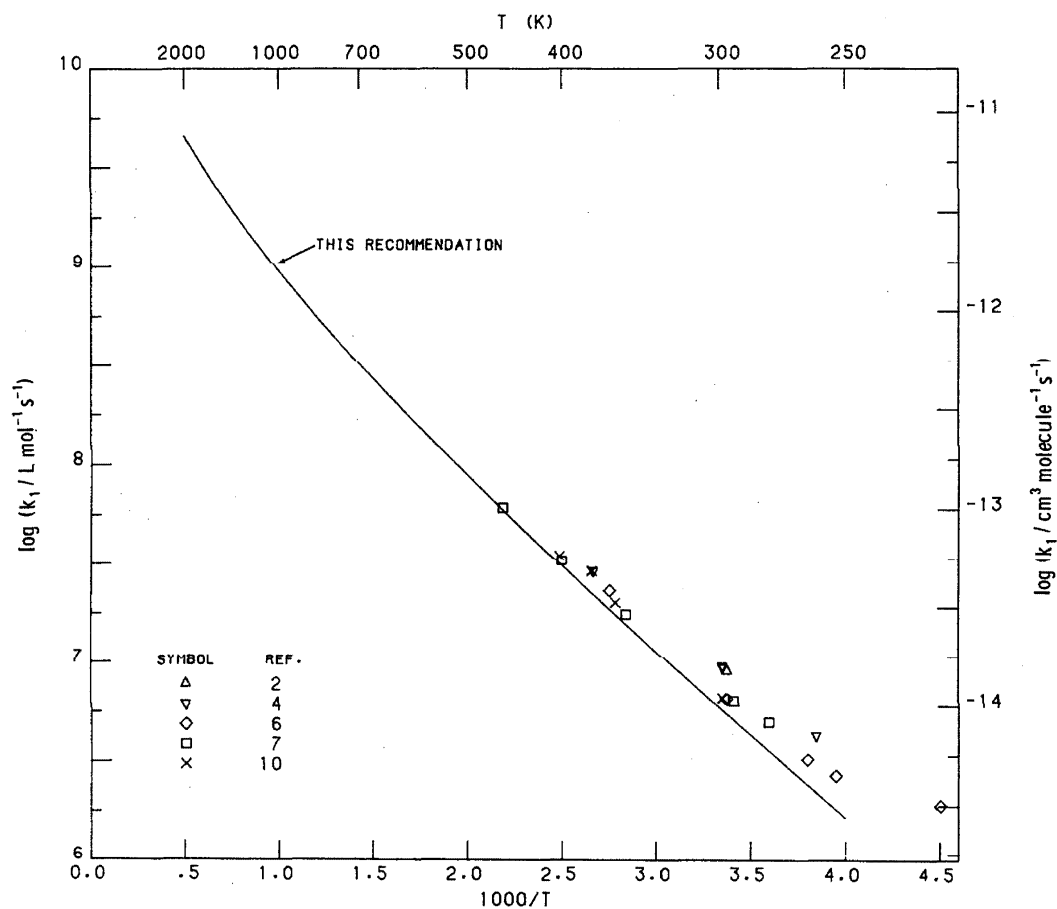
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	2.4×10^6 T$^{1.1}$ exp(-1610/T)	250 - 2000 K	6.3×10^6	L mol^{-1}s^{-1}
	4.0×10^{-15} T$^{1.1}$ exp(-1610/T)		1.0×10^{-14}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 250 - 300 K, increasing to ±0.4 at 2000 K. Expressions for K and k_{-1} are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$
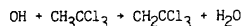
THERMOCHEMICAL DATA

Thermochemical data for H_2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 2,2,2-trichloroethane are from Chao et al.[1] Data for the 2,2,2-trichloroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol^{-1}, whence ΔHf^o_{298} for the reaction is -77 ± 10 kJ mol^{-1}. ΔS^o_{298} for the reaction is estimated to be 20.2 ± 5 J mol^{-1}K^{-1}.

MEASUREMENTS

Of the published studies of this reaction,[2-10] the first four have been invalidated on the grounds that the methyl chloroform contained significant levels (-0.1%) of CH_2CCl_2, which reacts two to three orders of magnitude more rapidly with OH and therefore gives spuriously large results for k_1 if not taken into account. This problem has been discussed in Refs. 6 and 7. Kurylo et al.[6] measured k_1 at 253-363 K by flash photolysis-resonance fluorescence, using $HONO_2$ photolyzed at 165 nm as the OH source. Jeong and Kaufman[7] studied the reaction in a discharge flow system over the temperature range of 278 to 460 K, using the H + NO_2 reaction as an OH source and with resonance fluorescence as a means of OH detection. The two studies are in excellent agreement, the former giving $k_1 = (3.25 \pm 1.1) \times 10^9 \exp[-(1810 \pm 100)/T]$ L mol^{-1}s^{-1} and the latter, $k_1 = (3.3 \pm 0.8) \times 10^9 \exp[-1832 \pm 98)/T]$. Both reported a room temperature value very close to 6.4×10^6 L mol^{-1}s^{-1}. Reference 8 is unreliable because of the indirectness of the method. Nelson et al.[9,10] measured k_1 by two separate techniques: at 298 K OH was produced by photolysis of CH_3ONO/O_2 mixtures and the rate was measured relative to that for OH + CH_3Cl by monitoring the relative disappearance of CH_3CCl_3 and CH_3Cl.[9,10] At 359, 376, and 402 K OH was produced by pulse radiolysis of H_2O/Ar mixtures and its absorption monitored by kinetic absorption spectroscopy at 309 nm.[10] The points plotted are from Ref. 10. Though both methods are somewhat indirect, the results are in good agreement with other studies.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k_1 to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_1(298)$ was assumed to be 6.8. The model for the activated complex was based on that used previously for the reaction of OH with CH_4, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data considering the scatter, could be described by the expression, $k_1 = 2.4 \times 10^6$ $T^{1.1}\exp(-1610/T)$ L mol^{-1}s^{-1}. For further details, see Ref. 11.

DISCUSSION

After discarding the results of Ref. 3, which were superseded by Ref. 7, those of Ref. 5, which have proven less reliable in the cases of other OH + haloalkane reactions, and Ref. 8, we are left with five presumably reliable measurements of log $k_1(298)$, three near 6.8 and two near 6.95. We accept the lower value because of possible reagent impurities in the other studies. The TST calculations based on this room temperature value are in good agreement with the other data of Refs. 6 and 7 at other temperatures, and we rely on them for our recommended expression. We recommend $k_1 = 2.4 \times 10^6$ $T^{1.1}$ $\exp(-1610/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of ± 0.2 at 250 - 300 K, increasing to ± 0.4 at 2000 K.

References

1. J. Chao, A. S. Rodgers, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data 3, 141 (1974).
2. C. J. Howard and K. M. Evenson, J. Chem. Phys. 64, 4303 (1976).
3. J. S. Chang and F. Kaufman, J. Chem. Phys. 66, 4989 (1977).
4. R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. 81, 256 (1977).
5. M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. II, 75, 569 (1979).
6. M. J. Kurylo, P. C. Anderson and O. Klais, Geophys. Res. Lett. 6, 760 (1979).
7. K.-M. Jeong and F. Kaufman, Geophys. Res. Lett. 6, 757 (1979); see also K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, J. Phys. Chem. 88, 1222 (1984).
8. R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
9. L. Nelson, J. J. Treacy, and H. W. Sidebottom, Proc. 3rd European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, 1984 (Riedel Publishing Co., Dordrecht, Holland, 1984), p. 258.
10. L. Nelson, I. Shanahan, H. W. Sidebottom, J. J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. 22, 577 (1990).
11. N. Cohen and S. W. Benson, J. Phys. Chem. 91, 162 (1987).

$$OH + NH_3 \rightarrow NH_2 + H_2O$$

$\Delta H^O_{258} = -44.56 \pm 6 \text{ kJ mol}^{-1}$ ($-10.65 \text{ kcal mol}^{-1}$) $\Delta S^O_{298} = 7.1 \pm 0.4 \text{ J mol}^{-1}\text{K}^{-1}$ ($1.7 \text{ cal mol}^{-1}\text{K}^{-1}$)

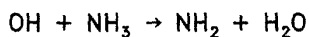$$K(T) = 19.8 \ T^{-0.3} \exp(5240/T)$$

The uncertainty in log K(T) is ±1.7 at 200 K, decreasing to ±1.1 at 298 K and ±0.1 at 3000 K.
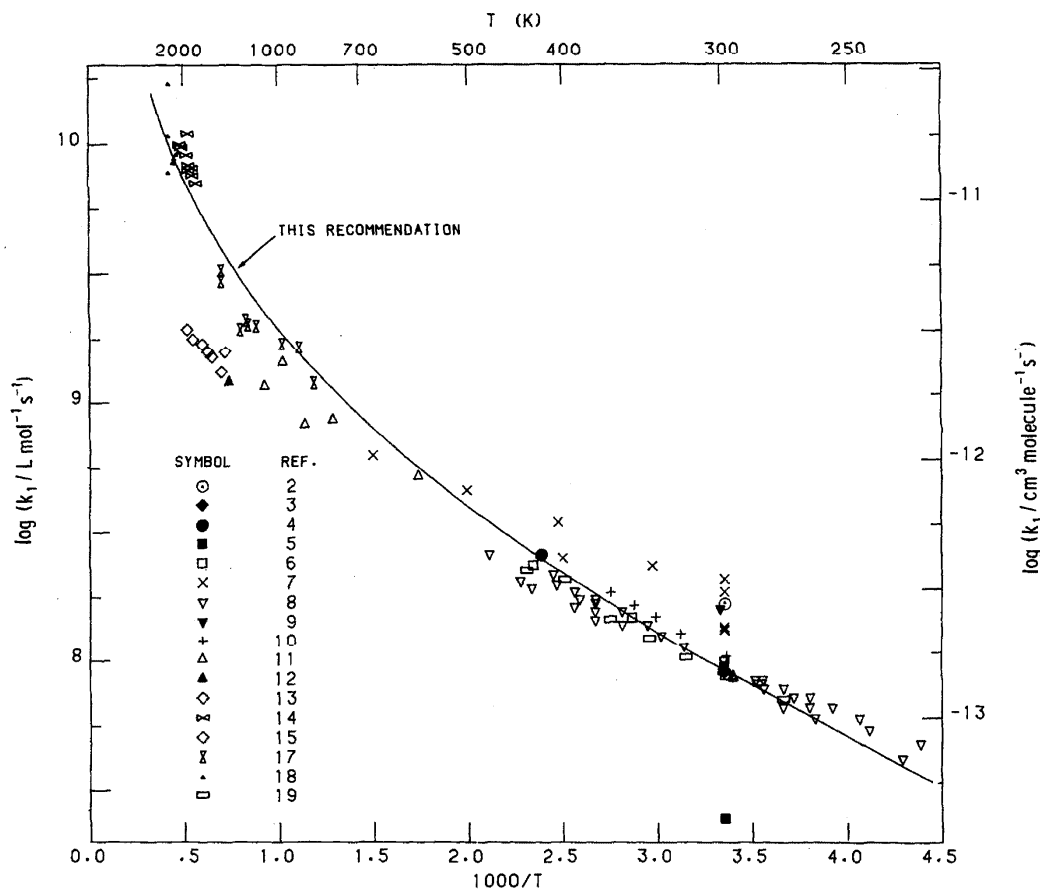
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$5.0 \times 10^4 \ T^{1.6} \exp(-480/T)$	225-3000 K	9.1×10^7	$L \ mol^{-1}s^{-1}$
	$2.3 \times 10^{-17} \ T^{1.6} \exp(-480/T)$		1.5×10^{-13}	$cm^3 \ molecule^{-1}s^{-1}$
k_{-1}	$2.5 \times 10^3 \ T^{1.9} \exp(-5720/T)$	300-3000 K	0.6	$L \ mol^{-1}s^{-1}$
	$4.2 \times 10^{-18} \ T^{1.9} \exp(-5720/T)$		9.6×10^{-22}	$cm^3 \ molecule^{-1}s^{-1}$

Uncertainty in log k_1: ±0.1 at 300 K increasing to ±0.3 at 225 and 2000 K, and ±0.4 at 3000 K. Uncertainty in log k_{-1}: ±1.1 at 300, decreasing to ±0.4 at 3000 K. This uncertainty reflects those of both log k_{-1} and of log K(T).
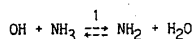
May 1991

$$OH + NH_3 \overset{1}{\rightleftharpoons} NH_2 + H_2O$$

THERMOCHEMICAL DATA

Thermochemical data are taken from the JANAF Thermochemical Tables, 3rd ed. (1985), according to which $\Delta Hf^\circ_{298}(NH_2)$ = 190.4 ± 6.3 kJ mol^{-1}. The analytic expression chosen for K(T) matches equilibrium constants calculated from those data to within 5% between 200 and 6000 K.

MEASUREMENTS

Since the 1972 review by Baulch et al.,[1] the following studies have been published. At low temperatures (<700 K), k_1 has been measured by discharge flow-mass spectrometry at 298 K[2], VUV photolysis-resonance fluorescence (298 K)[3], pulsed radiolysis-resonance absorption (418 K)[4], flash photolysis-resonance fluorescence (298 K[5], 297-447 K[6]), discharge flow-ESR (298-669 K[7]), flash photolysis resonance absorption (228-472 K[8]), pulsed radiolysis-computer modeling (300 K[9]), and discharge flow-resonance fluorescence (297-364 K[10] and 294-1075 K[11]). There have been 5 shock tube studies: a combined flash photolysis-shock tube experiment (1080-1695 K[12]); an induction time measurement (1390-1920 K[13]); a shock tube-laser absorption study[14] (1750-2060 K); a similar study but using resonance absorption[15] (1600-2000 K); and one[16] that obtained only an upper limit to the value of k_1 (not shown on the graph). More recently a laser pyrolysis-laser induced fluorescence study (840-1425 K),[17] a flame study (2080-2360 K),[18] and a flash photolysis laser-induced fluorescence study (273-433 K)[19] have appeared.

CALCULATIONS

Transition-state theory (TST) calculations were carried out for several activated complex configurations to test which of the high-temperature measurements could be consistent with the low-temperature results. The N·H·O and H·O·H bond angles were assumed to be 165 and 110° respectively; the N·H and H·O bond lengths were assumed only slightly lengthened from their normal lengths. The N·H·O symmetric stretching and the two H-N·H bending frequencies were assumed to be 2300 and 1000 cm^{-1}, respectively. The N·H·O and H·O·H bending frequencies were varied between 600 and 900 cm^{-1}. The two internal rotations were assumed either free or with low barriers of 4.2 and 8.4 kJ/mol. With the varied vibrational frequencies taken to be 900 cm^{-1} and free internal rotation, the calculations agreed with the data of Refs. 3, 6, 8, 10, and 17, and could be fitted over the temperature range of 250 to 3000 K by k_1 = 5.0 × 10^4 T$^{1.6}$ exp(-480/T). None of the models allowed the data of Ref. 13 to be consistent with a room temperature value of k_1 of 9 × 10^7 L mol^{-1}s^{-1}, which all the reliable room temperature data suggest. The calculations also imply that the results of Ref. 12 are too low by a factor of 3-5. The calculations suggest values of log k_1 at 2000 K of 9.7 - 10.0. Another TST calculation[17] gave nearly identical results at T > 400 K, but slightly larger at lower temperatures (50% at 250 K).

DISCUSSION

The shock tube study of Fujii et al.[13] has been criticized[14] for the oversimplified data analysis and the indirect dependence of k_1 on the induction time. Ref. 15, which corroborated the results of Ref. 13, may have been misled by the erroneous choice for the rate coefficient for the O + NH$_3$ reaction. The value of k_1 deduced in Ref. 12 depends on computer modeling and may be sensitive to assumed values for some other rate coefficients. The much larger values of k_1 deduced in Ref. 14 were obtained by a more direct experimental procedure; the flame study results of Ref. 17 agree with these. The recently reported larger values for the rate coefficient for the H + NH$_3$ reaction will lower the deduced value of k_1 in both of these studies -- possibly by 50%. Refs. 3, 6, 8, 10, and 11 all agree on a value for log k_1 of 7.95 ± 0.10 at 295-300 K. Between 500 and 1500 K there is at least a factor of 2 uncertainty in the data. We recommend the expression for k_1 based on the TST calculation described above: k_1 = 5.0 × 10^4 T$^{1.6}$ exp(-480/T) L mol^{-1} s^{-1}. This gives agreement with the lowest temperature experimental data[3,6,8,10,11,19] and the highest[14,18], within experimental error (taking into account the necessary lowering of k_1, because of the revised value for the H + NH$_3$ rate coefficient). The uncertainty in log k_1 is ±0.1 at 300 K, increasing to ±0.3 at 2000 K.

References

1. D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions, Vol. 2 (Butterworths, 1973), pp. 491-6.
2. M. Gehring, K. Hoyermann, H. Schacke, and J. Wolfrum, 14th Symp. (Int.) Combust. 99 (1973).
3. F. Stuhl, J. Chem. Phys. 59, 635 (1973).
4. S. Gordon and W. A. Mulac, Int. J. Chem. Kinet. Symp. No. 1, 289 (1975).
5. M. J. Kurylo, Chem. Phys. Lett. 23, 467 (1973).
6. R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. 64, 3237 (1976).
7. W. Hack, K. Hoyermann, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. 78, 386 (1974).
8. I. W. M. Smith and R. Zellner, Int. J. Chem. Kinet. Symp. No. 1, 341 (1975); R. Zellner and I. W. M. Smith, Chem. Phys. Lett. 26, 72 (1974).
9. P. B. Pagsberg, J. Eriksen, and H. C. Christensen, J. Phys. Chem. 83, 582 (1979).
10. R. D. Stephens, J. Phys. Chem. 88, 3308 (1984).
11. J. A. Silver and C. E. Kolb, Chem. Phys. Lett. 75, 191 (1980).
12. K. J. Niemitz, H. Gg. Wagner, and R. Zellner, Z. Phys. Chem. N.F. 124, 155 (1981).
13. N. Fujii, H. Miyama, M. Koshi, and T. Asaba, 18th Symp. (Int.) Combust. 873 (1981).
14. S. Salimian, R. K. Hanson, and C. H. Kruger, Int. J. Chem. Kinet. 16, 725 (1984).
15. N. Fujii, K. Chiba, S. Uchida, and H. Miyama, Chem. Phys. Lett. 127, 141 (1986); N. Fujii, S. Uchida, H. Sato, S. Fujimoto and H. Miyama, Bull. Chem. Soc. Japan 59, 3431 (1986).
16. J. E. Dove and W. S. Nip, Can. J. Chem. 52, 1171 (1974).
17. J. B. Jeffries and G. P. Smith, J. Phys. Chem. 90, 487 (1986).
18. M. F. Zabielski and D. J. Seery, Int. J. Chem. Kinet. 17, 1191 (1985).
19. E. W.-G. Diau, T.-L. Tso, and Y.-P. Lee, J. Phys. Chem. 94, 5261 (1990).

$$OH + NH_2 \rightleftharpoons NH + H_2O$$

$\Delta H^O_{298} = -119.3 \pm 12$ kJ mol^{-1} (-28.5 kcal mol^{-1}) $\Delta S^O_{298} = -8.3 \pm 0.4$ J mol^{-1}K^{-1} (-2.0 cal mol^{-1}K^{-1})

$K(T) = 0.73 \ T^{-0.1} \exp(14320/T)$

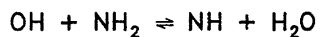The uncertainty in log K(T) is ±3.1 at 200 K, decreasing to ±2.1 at 298 K and ±0.24 at 3000 K.
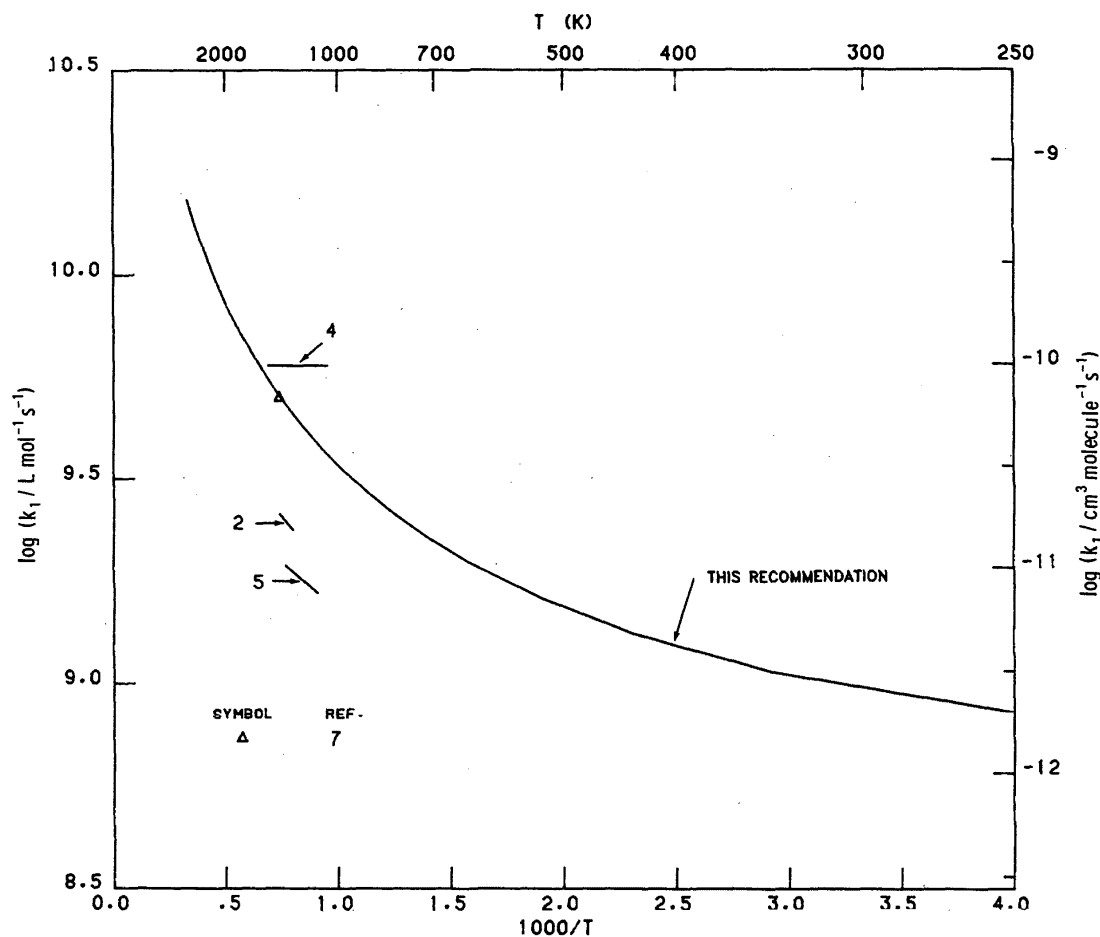
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$9.0 \times 10^4 \ T^{1.5} \exp(230/T)$	250-3000 K	1.0×10^9	L mol^{-1}s^{-1}
	$1.5 \times 10^{-16} \ T^{1.5} \exp(230/T)$		1.7×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.2 \times 10^5 \ T^{1.6} \exp(-14090/T)$	600-3000 K		L mol^{-1}s^{-1}
	$2.0 \times 10^{-16} \ T^{1.6} \exp(-14090/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.7 throughout range of 250-3000 K. Uncertainty in log k_{-1}: ±1.3 at 600 K, decreasing to ±0.8 at 3000 K. k_{-1} has not been studied directly. Its uncertainty reflects those of both k_1 and K(T).

(August 1987)

$OH + NH_2 \rightarrow NH + H_2O$
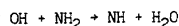
THERMOCHEMICAL DATA

Thermochemical data (except for $\Delta Hf^o_{298}(NH)$) are taken from the JANAF Thermochemical Tables, 3rd ed., according to which $\Delta Hf^o_{298}(NH_2) = 190.3 \pm 6.3$ kJ mol^{-1}; $\Delta Hf^o_{298}(NH) = 376.6 \pm 16$ kJ mol^{-1}. More recently, Piper[1] reanalyzed experimental data for $\Delta Hf^o_0(NH)$ and recommended 352 ± 10 kJ mol^{-1}; we use this value. The analytic expression chosen for K(T) matches equilibrium constants calculated from those data to within 3% between 200 and 6000 K.

MEASUREMENTS

There are no direct measurements of this reaction. Dean et al.[2] found the kinetics of NH_3 oxidation at 1279 to 1323 K to be sensitive to k_1, and that their model was consistent with experiments if they assumed $k_1 = 3 \times 10^7 \ T^{0.68} \exp(-600/T)$ L mol^{-1}s^{-1}, an expression taken from Tunder et al.[3]; this gives values of approximately 2.5×10^9 in their temperature range. Kimball-Linne and Hanson[4] modeled experiments in a combustion-driven flow reactor in which NO and NH_3 were reacted at 1050 - 1450 K. They optimized fits to data when k_1 was taken to be 6×10^9. Branch, Kee and Miller[5] modeled NH_3 reduction by NO near 1200 K and found they needed to have $k_1 = 4.5 \times 10^9 \exp(-1100/T)$ to predict NO behavior correctly. This gives $k_1 = 1.8 \times 10^9$ at 1200 K and is slightly smaller than the value they earlier assumed[6] because of the revised value for the NH_2 + NO reaction rate coefficient. Niemitz et al.[7] required a value of 5×10^9 at 1350 K to model their experiments on the OH + NH_3 reaction studied by flash photolysis of shock heated mixtures of NH_3, H_2O and Ar.

CALCULATIONS

We have used transition-state theory to calculate values of k_1, assuming a model for the transition state very similar to that used in a successful TST calculation for the OH + NH_3 rate coefficient (see data sheet for that reaction). (This model implicitly assumes the reactor proceeds directly by H atom abstraction, rather than by formation of an OH$\cdots$NH$_2$ complex that subsequently rearranges.) The principal differences in the transition state properties for the OH - NH_2 reaction are in the electronic degeneracies (NH_2OH^* is assumed to be a triplet state, whereas NH_3OH^* was assumed to be a doublet) and in the symmetry changes. With an assumed value of $k_1(298)$ of 1×10^9, the calculated values could be fitted by the expression, $k_1 = 9.0 \times 10^4 \ T^{1.5} \exp(230/T)$, which gives $k_1(1300) = 5 \times 10^9$, in reasonable agreement with the modeling requirements.

DISCUSSION

In the absence of direct measurements we recommend the above TST calculated values for k_1: $8.6 \times 10^4 \ T^{1.5} \exp(230/T)$, with an uncertainty of a factor of 5 throughout the range of 250 to 3000 K. This large uncertainty allows for the possibility that the reaction proceeds via two parallel pathways: direct abstraction (modeled by the TST calculations) and addition followed by rearrangement of an OH$\cdots$NH$_2$ complex.

References

1. L. G. Piper, J. Chem. Phys. 70, 3417 (1979).
2. A. M. Dean, J. E. Hardy, and R. K. Lyon, 19th Symp (Int.) Combust., 97 (1982).
3. R. Tunder, S. Mayer, E. Cook, and L. Schieler, Aerospace Report No. TR-10001(9210-02)-1 (1967).
4. M. Kimball-Linne and R. Hanson, Comb. Flame 64, 337 (1986).
5. M. C. Branch, R. J. Kee and J. A. Miller, Comb. Sci. Tech. 29, 147 (1982).
6. J. A. Miller, M. C. Branch, and R. J. Kee, Comb. Flame 43, 81 (1981).
7. K. J. Niemitz, H. Gg. Wagner, and R. Zellner, Z. Phys. Chem. (N.F.) 124, 155 (1981).
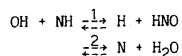
$$OH + NH \underset{-1}{\overset{1}{\rightleftharpoons}} H + HNO$$
$$\underset{-2}{\overset{2}{\rightleftharpoons}} N + H_2O$$

THERMOCHEMICAL DATA

Thermochemical data are taken from the JANAF Thermochemical Tables, 3rd ed. More recently, Piper[1] reanalyzed experimental data for $\Delta Hf_0^o(NH)$ and recommended 352 ± 10 kJ mol^{-1}; we use this value. The analytic expressions chosen for $K_1(T)$ and $K_2(T)$ match equilibrium constants calculated from those data to within 10% from 200 to 6000 K.

MEASUREMENTS

There are no direct measurements of either k_1 or k_2 or their sum. Dean and coworkers[2] used $k_1 = k_2 = 5 \times 10^8 \, T^{0.5}$ exp(-1000/T) L mol^{-1} s^{-1} in their mechanism for NH_3 oxidation near 2000 K, but provided no comment on the sensitivity of the modeling results to these values.

CALCULATIONS

k_2 can be estimated using the analogous reaction of $2OH = H_2O + O$ as a guide. The rate coefficient for that reaction is well-described by $k = 2.1 \times 10^5 \, T^{1.4}$ exp(200/T) L mol^{-1} s^{-1}. If we use this expression, augmented by a factor of 16/9 because of the different electronic degeneracies (assuming the activated complex is a quartet state), and converted to a two-parameter expression (a third seems unnecessary considering the approximations involved), the resulting expression is $k_2 = 2 \times 10^6 \, T^{1.2}$ L mol^{-1} s^{-1}.

k_1 can be estimated by comparison with k_4, the rate coefficient for the reaction $2OH \leftrightarrow H + HO_2$. The reverse reaction rate coefficient is 4.4×10^{10} L mol^{-1}s^{-1}, with formation of $2OH$ occurring 87% of the time.[3] This implies an intrinsic activation energy barrier of approximately 4 kJ mol^{-1} if the $g^{\ddagger} = 1$ and approximately 1 kJ mol^{-1} if $g^{\ddagger} = 3$. Assuming the transition state is a ^2A state, then $g^{\ddagger}$ for Reaction (1) is 2, and the maximum value k_1 can have (if there is no activation energy) is approximately 5×10^{10} L mol^{-1}s^{-1}. If the activation energy is as large as 4 kJ mol^{-1}, then k_1 will be only 1×10^{10}. Since both reactions 2 and 4 pass through addition complexes, we would expect very small, if any, activation barriers. We estimate $k_1(298) = 2 \times 10^{10}$, with an uncertainty of a factor of 2.5.

DISCUSSION

In the absence of experimental data, we choose the estimation described in the preceding section, namely, $k_2 = 2 \times 10^{10} \, T^{1.2}$ L mol^{-1} s^{-1}. k_1 should have little--or possibly negative--temperature dependence, and a large room temperature value, as is often the case for reactions that proceed through an addition complex. We assume the value estimated above, namely, 2×10^{10} and assume further that k_1 is essentially temperature-independent. Both of these rate coefficients have considerable uncertainty--at least a factor of 4 throughout the temperature range.

Two other reactions between OH and NH can be written:

$$OH + NH \rightarrow H_2 + NO$$
$$OH + NH \rightarrow NH_2 + O$$
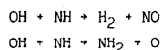
The first of these, though exothermic, is a four-center reaction and, like the analogous reaction of $2OH \rightarrow H_2 + O_2$, would be expected to have a large activation energy. It would therefore not compete with reactions (1) and (2), even at fairly high temperatures. The second reaction is slightly endothermic, and is discussed in the reverse direction in the data sheet for $O + NH_2$ reactions.

References

1. L. G. Piper, J. Chem. Phys. 70, 3417 (1979).
2. A. M. Dean, M.-S. Chou, and D. Stern, "Nitrogen Chemistry in Flames," in The Chemistry of Combustion Processes, T. M. Sloane, ed., ACS Symp. Ser. 249 (1984), p. 71.
3. See D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data 13, 1259 (1984) for a review of this reaction.

$$OH + NH_2 \rightleftharpoons O + NH_3$$
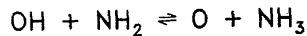
$\Delta H^o_{298} = -26.1 \pm 6 \text{ kJ mol}^{-1}$ (-6.2 kcal mol^{-1}) $\Delta S^o_{298} = -24.6 \pm 0.4 \text{ J mol}^{-1}\text{K}^{-1}$ (-5.9 cal mol^{-1}K^{-1})

$$K(T) = 1 \times 10^{-3} \ T^{0.5} \ \exp(3490/T)$$

The uncertainty in log K(T) is ±1.1 at 298 K, decreasing to ±0.1 at 3000 K.
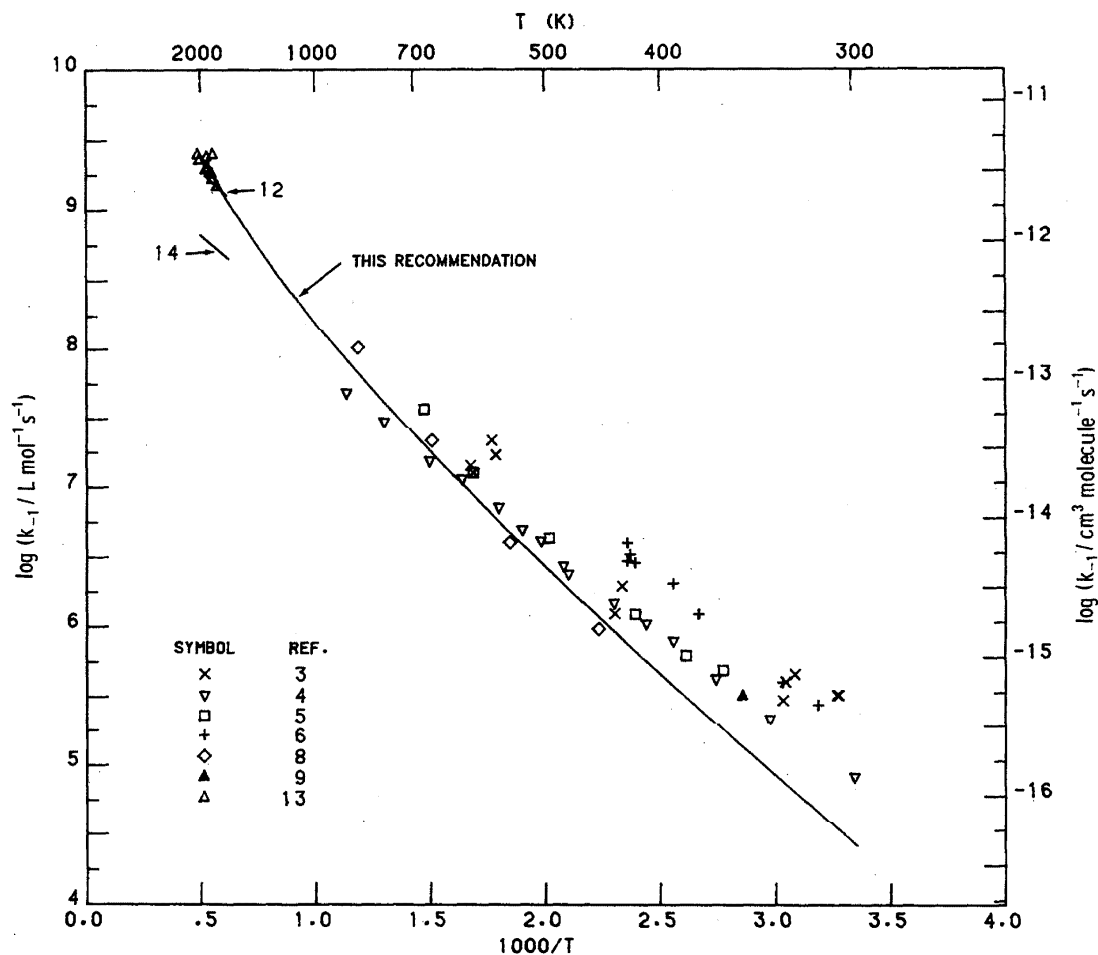
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.1 \ T^{2.6} \ \exp(870/T)$	298-2000 K	5.5×10^7	L mol^{-1}s^{-1}
	$1.8 \times 10^{-21} \ T^{2.6} \ \exp(870/T)$		9.2×10^{-14}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.1 \times 10^3 \ T^{2.1} \ \exp(-2620/T)$	298-2000 K	2.6×10^4	L mol^{-1}s^{-1}
	$1.8 \times 10^{-18} \ T^{2.1} \ \exp(-2620/T)$		4.3×10^{-17}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_{-1}: ±0.3 from 298 to 2000 K. Uncertainty in log k_1: ±1.2 at 298 K, decreasing to ±0.4 at 2000 K. k_1 is calculated from k_{-1} and K(T); its uncertainty reflects the uncertainties in both of those quantities.

(August 1987)

$$OH + NH_2 \xrightarrow{1} O + NH_3$$
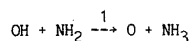
THERMOCHEMICAL DATA

Thermochemical data are taken from JANAF Thermochemical Tables, 3rd ed., according to which $\Delta Hf^0_{298}(NH_2)$ = 190.4 ± 6.3 kJ/mol. The analytic expression chosen for K(T) matches equilibrium constants calculated from these data to within 8% from 298 to 6000 K.

MEASUREMENTS

There are no direct measurements of k_1. k_{-1} has been measured at moderate temperatures (300-850 K) in flowing[1-9] and static[10] systems and at high (>1000 K) temperatures in flames[11] and in shock tubes.[12-15] The most precise study is that of Perry,[8] who used laser photolysis/NO_2 chemiluminescence to follow the reaction at 448 - 841 K. By maintaining a very large excess of NH_3, he minimized the effects of secondary reactions. He obtained log k_{-1} = 5.98 and 8.01 (L mol^{-1} s^{-1} units) at 448 and 841 K, respectively. The most reliable high-temperature study is that of Salimian et al.,[13] who shock heated mixtures of NH_3 and N_2O to 1750-2060 K and monitored OH absorption in the UV with a ring dye laser, obtaining log k_{-1} = 9.37 ± 0.3 at 2000 K. Earlier studies near 300 K[2-4] indicated values of log k_{-1} of 4.8 - 5.5. Baulch et al.[9] studied the reverse reaction at 350 K in a discharge-flow diffusion-stirred reactor. By measuring the NO yields with and without added NO reagent, they concluded that the experimental results were not consistent with a computer simulation in which the initial step produced NH_2, deciding therefore that O + NH_3 must form an NH_3O addition complex.

CALCULATIONS

Transition-state theory (TST) calculations of k_{-1} have been described by Salimian et al.[13] and by Cohen.[16] The latter obtained good agreement with the data of Refs. 8 and 13 by assuming log k_{-1}(300) = 4.5, which is a factor of 2 or more lower than the experiments near that temperature indicate.[2-4] These calculations are fitted by the expression k_{-1} = 1.1 × 10^3 T$^{2.1}$ exp(-2620/T) L mol^{-1}s^{-1} for 298 < T < 3000 K. Calculations by Hart[17] and Melius[18] indicate than an NH_3O addition complex would not be stable.

DISCUSSION

The literature through 1969 was reviewed by Cohen and Heicklen[19] and by Baulch et al.,[20] both of whom concluded that most of the early studies were unreliable. Detailed computer calculations[16] carried out to simulate the experimental conditions of Refs. 3, 4, and 9 showed that, notwithstanding the results of Ref. 9, the H-abstraction mechanism could not be unambiguously ruled out. However, a satisfactory explanation for values of k_{-1} factors of 2-3 larger than the TST calculations obtained in some experimental studies at 298 - 350 K could not be found. Accordingly, we regard the mechanism and the rate coefficient at low temperatures, to be uncertain at present. Provisionally, we recommend the results of the TST calculations of Ref. 16, which are in good agreement with the data of Refs. 8 and 13, but a factor of 2 lower than the lowest experimental results at 298-350 K: k_{-1} = 1.1 × 10^3 T$^{2.1}$ exp(-2620/T) L mol^{-1} s^{-1}, with an uncertainty in log k_{-1} of ±0.3 throughout the temperature range of 298 - 2000 K. The uncertainty in log k_1(298) is considerably larger, reflecting the uncertainty in $\Delta Hf^0_{298}(NH_2)$ and, thereby, in K(T).

References

1. L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznitsova, Izvest. Akad. Nauk. SSSR, Otd. Khim. Nauk, 983 (1962).
2. E. L. Wong and A. E. Potter, J. Chem. Phys. 39, 2211 (1963).
3. E. L. Wong and A. E. Potter, J. Chem. Phys. 43, 3371 (1965).
4. E. A. Albers, K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, 12th Symp. (Int.) Combust., 313 (1969).
5. M. J. Kurylo, G. A. Hollinden, H. F. LeFevre, and R. B. Timmons, J. Chem. Phys. 51, 4497 (1969).
6. K. Kirschner, N. Merget, and C. Schmidt, Chemie Ingenieur Technik 46, 661 (1974).
7. C. Lalo and C. Vermeil, J. Chim. Phys. 77, 131 (1980).
8. R. A. Perry, Chem. Phys. Lett. 106, 223 (1984).
9. D. L. Baulch, I. M. Campbell, and R. Hainsworth, J. Chem. Soc., Faraday Trans. I, 80, 2525 (1984).
10. K. T. Aganesyan and A. B. Nalbandyan, Dokl. Akad. Nauk. SSSR 160, 162 (1965) [Engl. transl. Dokl. Phys. Chem. 193, 18 (1965)].
11. C. P. Fenimore and G. W. Jones, J. Phys. Chem. 65, 298 (1961).
12. J. E. Dove and W. S. Nip, Can. J. Chem. 52, 1171 (1974).
13. S. Salimian, R. K. Hanson, and C. H. Kruger, Int. J. Chem. Kinet. 16, 725 (1984).
14. N. Fujii, H. Sato, S. Fujimoto, and H. Miyama, Bull. Chem. Soc. Japan 57, 277 (1984).
15. N. Fujii, K. Chiba, S. Uchida, and H. Miyama, Chem. Phys. Lett. 127, 141 (1986).
16. N. Cohen, Int. J. Chem. Kinet. 19, 319 (1987).
17. B. T. Hart, Aust. J. Chem. 29, 231 (1976).
18. C. F. Melius, unpublished calculations.
19. N. Cohen and J. Heicklen, Comp. Chem. Kinet. 6, C. H. Bamford and C. F. H. Tipper, eds. (Elsevier, 1972), p. 1.
20. D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, Evaluated Kinetic Data for High Temperature Reactions, Vol. 2 (Butterworths, 1973), p. 483.

$$O + NH_2 \rightleftharpoons NH + OH \quad \& \quad O + NH_2 \rightleftharpoons H + HNO \quad \& \quad O + NH_2 \rightarrow H_2 + NO$$

$O + NH_2 \overset{1}{\rightleftharpoons} NH + OH$

$$K_1(T) = 6.9 \ T^{-0.1} \exp(5800/T)$$
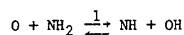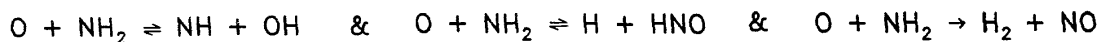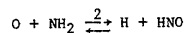
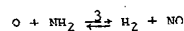$\Delta H^o_{298} = -48.5 \pm 12 \text{ kJ mol}^{-1} \ (-11.6 \text{ kcal mol}^{-1})$

$\Delta S^o_{298} = 9.2 \pm 0.4 \text{ J mol}^{-1}\text{K}^{-1} \ (2.2 \text{ cal mol}^{-1}\text{K}^{-1})$

$O + NH_2 \overset{2}{\rightleftharpoons} H + HNO$

$$K_2(T) = 1.3 \times 10^{-2} \ T^{0.3} \exp(14730/T)$$

$\Delta H^o_{298} = -122 \pm 7 \text{ kJ mol}^{-1} \ (-29.1 \text{ kcal mol}^{-1})$

$\Delta S^o_{298} = -20.5 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1} \ (-4.9 \text{ cal mol}^{-1} \text{ K}^{-1})$

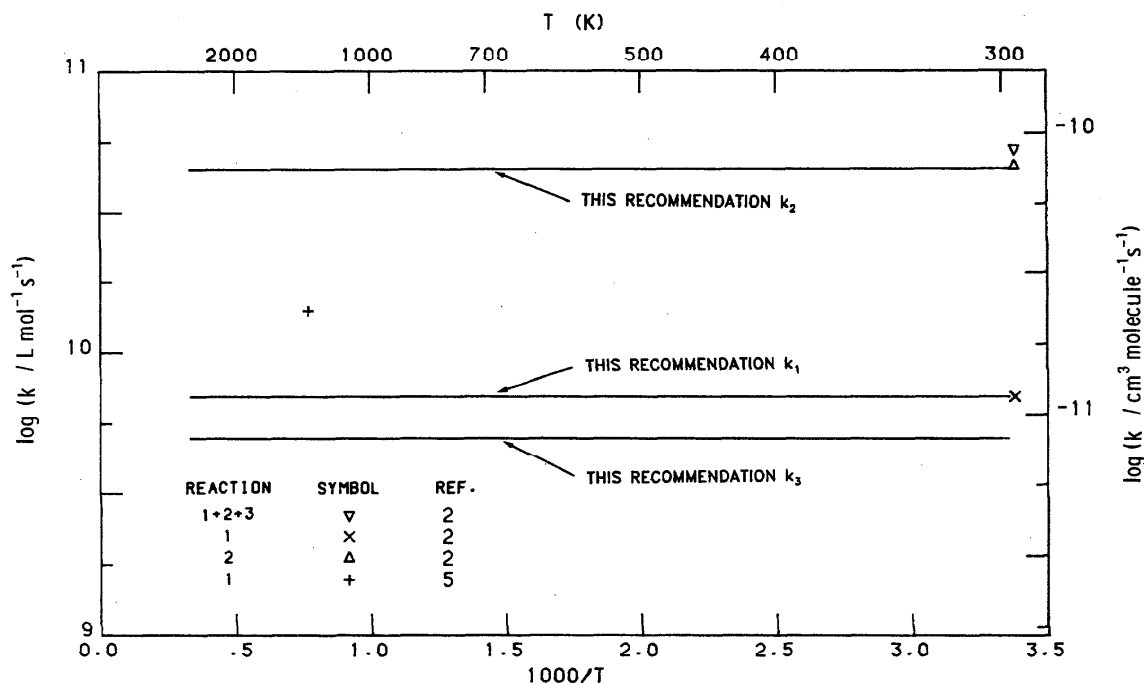$O + NH_2 \overset{3}{\rightleftharpoons} H_2 + NO$

$$K_3(T) = 2.2 \times 10^{-1} \exp(41960/T)$$

$\Delta H^o_{298} = -349.4 \pm 6 \text{ kJ mol}^{-1} \ (-83.5 \text{ kcal mol}^{-1})$

$\Delta S^o_{298} = -14.3 \pm 0.4 \text{ J mol}^{-1} \text{ K}^{-1} \ (-3.4 \text{ cal mol}^{-1} \text{ K}^{-1})$

The uncertainty in log $K_1(T)$ is ±3.1 at 200 K, decreasing to ±2.1 at 298 K and ±0.3 at 3000 K. The corresponding uncertainties in log $K_2(T)$ are ±1.8, ±1.2, and ±0.25, respectively. Those for log $K_3(T)$ are ±1.5, ±1.0, and ±0.2, respectively.


REACTION	SYMBOL	REF.
1+2+3	▽	2
1	×	2
2	△	2
1	+	5

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	5.3×10^{10}	298-3000	5.3×10^{10}	L mol^{-1}s^{-1}
	8.8×10^{-11}		8.8×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_1	7×10^{9}	298-3000	7×10^{9}	L mol^{-1}s^{-1}
	1.2×10^{-11}		1.2×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.0 \times 10^{9} \ T^{0.1} \exp(-5800/T)$	298-3000	7.1	L mol^{-1}s^{-1}
	$1.7 \times 10^{-12} \ T^{0.1} \exp(-5800/T)$		1.2×10^{-20}	cm^3 molecule^{-1}s^{-1}
k_2	4.5×10^{10}	298-3000	4.5×10^{10}	L mol^{-1}s^{-1}
	7.5×10^{-11}		7.5×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-2}	$3.5 \times 10^{12} \ T^{-0.3} \exp(-14730/T)$	550-3000		L mol^{-1}s^{-1}
	$5.8 \times 10^{-9} \ T^{-0.3} \exp(-14730/T)$			cm^3 molecule^{-1}s^{-1}
k_3	5×10^{9}	298-3000	5×10^{9}	L mol^{-1}s^{-1}
	8.3×10^{-12}		8.3×10^{-12}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_A: ±0.2 at 298 K, increasing to ±0.5 at 3000 K. Uncertainties in log k_1, log k_2, and log k_3: ±0.3, ±0.3, and ±0.7 throughout temperature range.

(August 1987)

$O + NH_2 \xrightarrow{1} NH + OH$

$O + NH_2 \xrightarrow{2} H + HNO$

$O + NH_2 \xrightarrow{3} H_2 + NO$
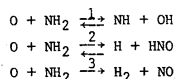
THERMOCHEMICAL DATA

Thermochemical data for HNO are taken from the JANAF Thermochemical Tables, 3rd ed., according which $\Delta Hf^o_{298}(NH_2) = 190.4 \pm 6$; $\Delta Hf^o_{298}(HNO) = 99.6$; $\Delta Hf^o_{298}(NH) = 376.6 \pm 16$ kJ/mol. More recently, Piper[1] reanalyzed experimental data for $\Delta Hf^o_0(NH)$ and recommended 352 ± 10 kJ/mol; we use this value. The analytic expressions chosen for $K_1(T)$, $K_2(T)$, and $K_3(T)$ match equilibrium constants calculated from those data to within 7%, 10%, and 10%, respectively, between 200 and 5000 K.

MEASUREMENTS

Dransfeld et al.,[2] studied these and other reactions of NH_2 radicals in a discharge-flow system at 296 K. NH_2 radicals were produced by the reaction between F atoms (produced by a microwave discharge through F_2) and NH_3 and were detected by either laser-induced fluorescence (LIF) or laser magnetic resonance (LMR). O atoms (at 7.1×10^{-10} to 1×10^{-8} mol/L) were generated in excess relative to NH_2 by microwave discharge through O_2-He mixtures. Time-dependent concentration profiles were determined by electron spin resonance, and absolute concentrations were determined by $O + NH_2$ chemiluminescence. The products NH and OH were detected by LMR; HNO, by LIF. A value of $(5.3 \pm 1.5) \times 10^{10}$ L $mol^{-1}s^{-1}$ (25 times larger than earlier reported by Gehring et al.[3]) was obtained for $k_A = k_1 + k_2 + k_3$ by monitoring NH_2 disappearance. Separate values for $k_1 = (7 \pm 3) \times 10^9$ and $k_2 = (4.6 \pm 1.2) \times 10^{10}$ L $mol^{-1}s^{-1}$ were determined by computer fits to [OH] and [NH] profiles. Reaction 3 was eliminated on the basis of results of Albers et al.,[3] who did not observe simultaneous appearance of NO and H_2 in $O + NH_3$ discharge flow experiments. Other possible reaction channels (yielding NO + 2H, or N + H_2O) could be eliminated in both experiments, either on thermochemical grounds or on the basis of product concentration profiles. In their high temperature mechanism, Dean et al.[5] assumed that reaction (1) dominates, obtaining agreement with experiment with $k_1(1300) = 1.4 \times 10^{10}$, but could not rule out reaction (2).

CALCULATIONS

Melius and Binkley[6] used fourth-order Møller-Plesset perturbation theory with bond additivity corrections to investigate the reaction. Their calculations indicate two possible paths to form NH + OH, one via two successive complexes:

$$O + NH_2 \longrightarrow H_2NO \longrightarrow HNOH \longrightarrow NH + OH \tag{1a}$$

and the other via direct H atom abstraction, with very little activation energy (approximately 20 kJ mol^{-1})

$$O + NH_2 \longrightarrow NH + OH \tag{1b}$$

They also found two separate paths for reaction (2) and one for reaction (3):

$$O + NH_2 \longrightarrow H_2NO \longrightarrow HNO + H \tag{2a}$$

$$O + NH_2 \longrightarrow H_2NO \longrightarrow HNOH \longrightarrow HNO + H \tag{2b}$$

$$O + NH_2 \longrightarrow H_2NO \longrightarrow NO + H_2 \tag{3}$$

They concluded that reaction 2 would dominate, with a smaller contribution from 1, and even less from reaction 3. We have carried out transition-state theory (TST) calculations for k_{1b} using a model for the transition state very similar to that used for the $O + NH_3$ reaction (see data sheet for that reaction) but assuming that $g_e^{\ddagger} = 4$. For different assumed values of $k_{1b}(298)$, the calculations can be fitted by $k_{1b} = 1.4 \times 10^{-5} T^{1.4} [k(298)]^{298/T} \exp(+780/T)$.

DISCUSSION

The experimental results of Ref. 2 for k_A, k_1, and k_2 are reasonable, but provide only room temperature values. The sensitivities of the separate values for k_1 and k_2 to details of the computational model assumed were not discussed. The TST calculations described above indicate that if $k_{1b}(298)$ is as large as 7×10^9 L $mol^{-1}s^{-1}$ (see Ref. 2), then the barrier height is less than 1 kJ/mol, which seems too small (cf. Ref. 6). Consequently, a considerable contribution to k_1 must come from k_{1a} if the experimental results are correct. The TST calculations indicate that k_{1b} varies by less than a factor of 2 from 200 to 3000 K. The association process (k_{1a}) should have little—or even negative—temperature dependence. Thus, in any case k_1 should have a very weak temperature dependence. The same is true for k_2. If the relative enthalpies of the intermediates H_2NO and HNOH calculated in Ref. 6 are correct (though we don't expect both the barriers to form HNO + H to be so large), then $[H_2NO]_{eq.} > [HNOH]_{eq.}$ except at the highest temperatures. Simple unimolecular reaction theory suggests $k_3 > k_{2a}$ and $k_{2b} > k_{1a}$, whence $k_3 > k_{2a} \gg k_{2b} > k_{1a}$. The entropy of activation for reaction 1b is 13-17 J $mol^{-1}k^{-1}$ larger than for the other four reaction paths. If it has an activation energy — even as small as 10 kJ/mol (Ref. 6 calculates 20), k_{1b} will not dominate until $T \gtrsim 1000$ K. Thus, we would expect $k_3 > k_2 > k_1$ at moderate and low temperatures and $k_1 > k_3 > k_2$ at high temperatures. The experimental evidence suggests $k_3 < k_2$ and k_1, which means the relative barrier heights are incorrect. But even so, k_3 may not be negligible.

We rely on Ref. 2, noting that the total value k_A is more reliable than the individual values of k_1 and k_2. We recommend $k_1 = 7 \times 10^9$ and $k_2 = 4.5 \times 10^{10}$ for 298 to 3000 K, with a factor of 2 uncertainty in each. We estimate, on theoretical grounds, that k_3 should not be less than 5×10^9, although there is no supporting experimental evidence at present.

References
1. L. G. Piper, J. Chem. Phys. 70, 3417 (1979).
2. P. Dransfeld, W. Hack, H. Kurzke, F. Temps, and H. Gg. Wagner, 20th Symp. (Int.) Combust., 655 (1985).
3. M. Gehring, K. Hoyermann, H. Schacke, and J. Wolfrum, 14th Symp. (Int.) Combust., 99 (1972).
4. E. A. Albers, K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, 12th Symp. (Int.) Combust., 313 (1969).
5. A. M. Dean, J. E. Hardy, and R. K. Lyon, 19th Symp. (Int.) Combust., 99 (1982).
6. C. F. Melius and J. S. Binkley, "Reactions of NH and NH_2 with O and O_2 in The Chemistry of Combustion Processes, T. M. Sloane, ed., ACS Symp. Ser. 249 (1984), p. 103.
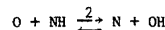
$$O + NH \rightleftharpoons H + NO \qquad \& \qquad O + NH \rightleftharpoons N + OH$$

$O + NH \overset{1}{\underset{}{\rightleftharpoons}} H + NO$
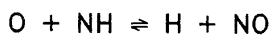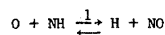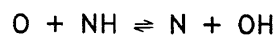
$\Delta H^{o}_{298} = -292.8 \pm 10 \text{ kJ mol}^{-1}$ (-70.0 kcal mol^{-1})

$\Delta S^{o}_{298} = -16.8 \pm 0.1 \text{ J mol}^{-1}\text{K}^{-1}$ (-4.0 cal mol^{-1}K^{-1})

$$K_1(T) = 7.1 \times 10^{-2} \, T^{0.1} \exp(35220/T)$$

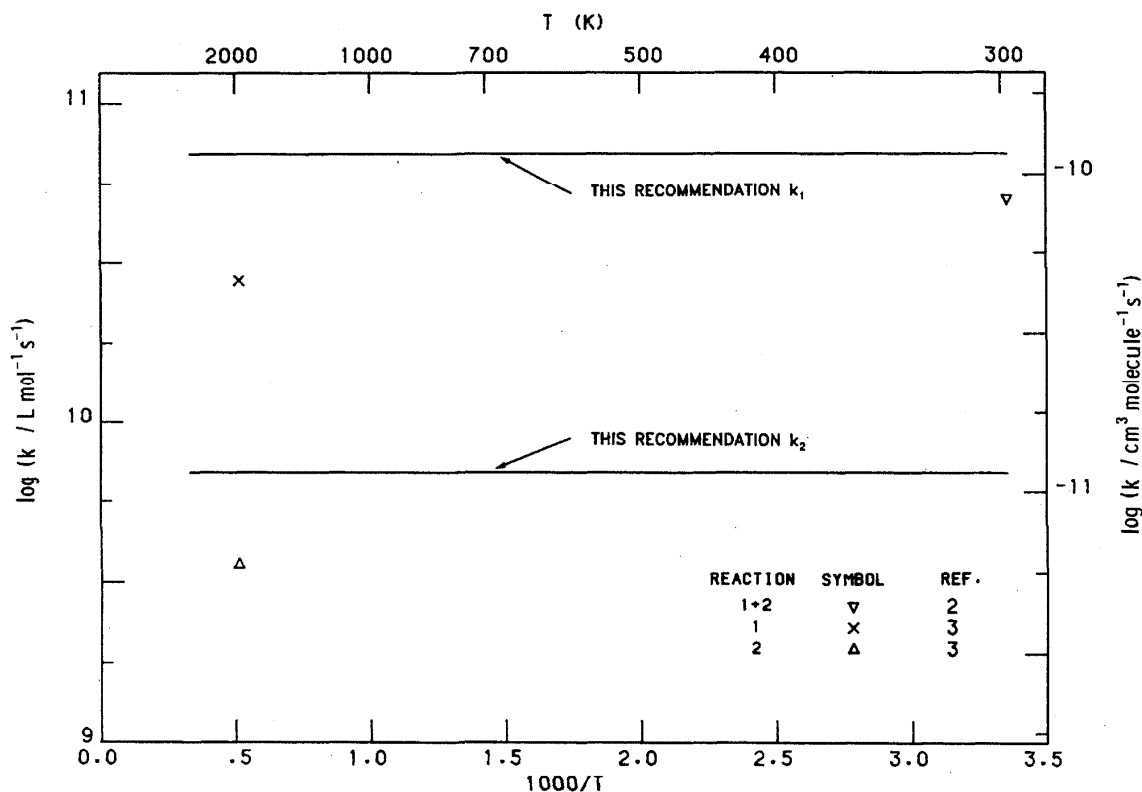$O + NH \overset{2}{\underset{}{\rightleftharpoons}} N + OH$

$\Delta H^{o}_{298} = -89.4 \pm 10 \text{ kJ mol}^{-1}$ (-21.4 kcal mol^{-1})

$\Delta S^{o}_{298} = -5.3 \pm 0.1 \text{ J mol}^{-1} \text{ K}^{-1}$ (-1.3 cal mol^{-1}K^{-1})

$$K_2(T) = 1.1 \, T^{-0.1} \exp(10700/T)$$

The uncertainties in log $K_1(T)$ and log $K_2(T)$ are ± 2.6 at 200 K, decreasing to ± 1.7 at 300 K and ± 0.3 at 3000 K.


RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	7×10^{10}	250–3000	1×10^{11}	L mol^{-1}s^{-1}
	1.2×10^{-10}		1.7×10^{-10}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$9.9 \times 10^{11} \, T^{-0.1} \exp(-35220/T)$	1300–3000		L mol^{-1}s^{-1}
	$1.6 \times 10^{-9} \, T^{-0.1} \exp(-35220/T)$			cm^3 molecule^{-1}s^{-1}
k_2	7×10^9	250–3000	3×10^9	L mol^{-1}s^{-1}
	1.6×10^{-11}		5×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-2}	$6.4 \times 10^9 \, T^{0.1} \exp(-10700/T)$	500–3000		L mol^{-1}s^{-1}
	$1.1 \times 10^{-11} \, T^{0.1} \exp(-10700/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1 and log k_2: ± 0.3 and ± 0.7, respectively, throughout range of 250–3000 K. Uncertainty in log k_{-1}: ± 0.5 at 1300 K, decreasing to ± 0.4 at 3000 K. Uncertainty in log k_{-2}: ± 1.2 at 500 K, decreasing to ± 0.8 at 3000 K. The uncertainties in log k_{-1} and log k_{-2} reflect those of both the respective forward rate coefficients and equilibrium constants.

(August 1987)

$$O + NH \xrightarrow{1} H + NO$$
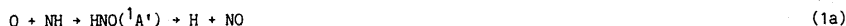$$\xrightarrow{2} N + OH$$
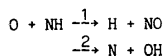
THERMOCHEMICAL DATA

Thermochemical data taken from the JANAF Thermochemical Tables, 3rd edition. More recently, Piper reanalyzed experimental data for $\Delta Hf^o_0(NH)$ and recommended 352 ± 10 kJ mol^{-1}; we use this value. The analytical expressions chosen for $K_1(T)$ and $K_2(T)$ match equilibrium constant calculated from those data to within 5% and 3%, respectively, between 200 to 6000 K.

EXPERIMENTAL DATA

There are no direct measurements of either k_1, k_2, or $k_A = k_1 + k_2$. Dransfeld et al.[2] best fitted their room temperature flow tube data on the $O + NH_2$ reaction system by assuming $k_A = (5 \pm 2) \times 10^{10}$ L mol^{-1}s^{-1}. Dean et al.[3] assumed $k_1 = 6.3 \times 10^8$ $T^{0.5}$ and $k_2 = 6.8 \times 10^8$ $T^{0.5}$exp(-4000/T) in their modeling of NH_3 flames near 2000 K. Neither gave any indication of the sensitivity of their model to these assumed values. Cohen[4] found much better agreement with experimental data on the $O + NH_3$ reaction by assuming $k_1 \gg k_2$.

CALCULATIONS

Melius and Binkley[5] carried out fourth-order Moller-Plesset perturbation theory calculations with bond additivity corrections. They found three pathways leading to H + NO, and two leading to N + OH:

$O + NH \rightarrow HNO(^1A') \rightarrow H + NO$	(1a)
$O + NH \rightarrow HNO(^3A'') \rightarrow H + NO$	(1b)
$\rightarrow HON \rightarrow H + NO$	(1c)
$\rightarrow HON \rightarrow N + OH$	(2a)
$O + NH \rightarrow [^5\pi] \quad \rightarrow N + OH$	(2b)

The addition paths, (1a), (1b), (1c), and (2a), were found[5] to have no activation barrier; the metathesis reaction (2b) was found to have a very small (~ 4 kJ/mol) activation energy.

An approximate lower limit for k_1 can be calculated by assuming that reaction (1) occurs only via path (1a); that the only energy barrier is the so-called centrifugal barrier imposed by conservation of angular momentum; and that all trajectories that cross this barrier lead to reaction. The average position of the barrier as a function of T can be calculated from data given by Chase et al.[6] and a formula given by Benson.[7] The collison frequency thus calculated must be corrected for electronic degeneracies by multiplying by $Q^\#/Q_0Q_{NH}$, where $Q^\#$ and Q_{NH} are assumed to be 1 and 3, respectively. k_{1a} thus obtained is $(1.4 \pm 0.2) \times 10^{10}$ L mol^{-1}s^{-1} for $200 < T/K < 2000$. Above 2000 K, the calculated centrifugal barrier lies inside the sum of Van der Waals radii for the reagents, and consequently there may be some steric restrictions, leading to a decrease in k_{1a}. An upper limit for k_1 can be calculated by assuming that all reactions on the $^3A''$ surface also lead to H + NO (via 1b and 1c), so that $k_{2a} = 0$. Using the same procedure, $(k_{1b} + k_{1c})$ is calculated to be $\leq 4.1 \times 10^{10}$, so that $k_1 = (3 \pm 2) \times 10^{10}$ for $200 < T/K < 2000$. A similar procedure was used[5] to calculate the rate coefficient for the analogous reaction between O and OH, and gave good agreement with the experimental value of 2.4×10^{10} at 298 K.

Because reaction 2b has a small potential energy barrier, k_{2b} cannot be calculated accurately; $k_{2a} < 4.1 \times 10^{10}$ but cannot be fixed more precisely.

DISCUSSION

The calculations are considered sufficiently reliable to recommend $k_1 = (3 \pm 2) \times 10^{10}$ L mol^{-1}s^{-1} for $200 < T/K < 2000$. Reaction (2) can proceed either by a temperature-independent addition mechanism or an abstraction mechanism, which should have a small activation energy. To keep $k_2 \ll k_1$ we recommend $k_2 = 3 \times 10^9$ L mol^{-1}s^{-1} over the same temperature range, with an uncertainty of a factor of 5.

References
1. L. G. Piper, J. Chem. Phys. 70, 3417 (1979).
2. P. Dransfeld, W. Hack, H. Kurzke, F. Temps, and H. Gg. Wagner, 20th Symp. (Int.) Combust., 655 (1984).
3. A. M. Dearn, M.-S. Chou, and D. Stern, in The Chemistry of Combustion Processes, T. M. Sloane, ed., ACD Symposium Series 249, p. 71 (1984).
4. N. Cohen, Int. J. Chem. Kinetics, to be published.
5. C. F. Melius and J. S. Binkley, in The Chemistry of Combustion Processes, T. M. Sloane, ed., ACD Symposium Series 249, p. 193 (1984); C. F. Melius, private communication.
6. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, JANAF Thermochemical Tables, 3rd Edn. (J. Phys. Chem. Ref. Data 14, Suppl. No. 1 [1985]).
7. S. W. Benson, Thermochemical Kinetics, 2nd Edn. (New York; Wiley, 1976), p. 89.
8. N. Cohen and K. R. Westberg, J. Phys. Chem. Ref. Data 12, 531 (1983).