Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions

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A new program for the compilation and evaluation of chemical kinetic data is described. Rate coefficient measurements are assessed for probable accuracy and precision. Transition-state theory is often used to extrapolate measurements to higher temperatures. For every reaction reviewed, a recommended rate coefficient is given in the form $k = AT^n \times \exp(-B/T)$. Pertinent data and conclusions are summarized on a two-page Data Sheet, each sheet covering one reaction or occasionally two or three closely related reactions. Twenty-seven Data Sheets are presented for reactions important in modeling and understanding chemical lasers, hydrogen–oxygen combustion, hydrocarbon oxidation, and aluminum or boron propellant systems.

Key words: chemical kinetic data; data compilation and evaluation; rate coefficient; rate constant; reaction rate; review.

Contents

1. Introduction

Under the auspices of the National Bureau of Standards Office of Standard Reference Data, and with the support of the Air Force Office of Scientific Research, a program has been undertaken for the compilation and evaluation of chemical kinetic data. The program's aim is to prepare and publish, for selected gas-phase reactions, concise Data Sheets that provide, among other things, recommended rate coefficients. The adopted format, which is described in Sec. 2, is designed to meet the needs of both the kineticist and nonkineticist. It is also designed for easy updating. Considerable time was devoted to developing the format. A preliminary version of one Data Sheet was published in a special issue of the *Journal of Physical Chemistry*,[1] along with a request for comments; preliminary versions of several others were sent to a large group of potentials users. The comments received contributed to improving the style and usefulness of presentation. We encourage others who may find such a concise format useful to adopt it.

Of course, concise data sheets cannot be all-inclusive. Space limitations usually do not allow detailed critiques of individual experiments and techniques. Publication of these Data Sheets then does not obviate the need for more detailed, in-depth data reviews.

A feature that makes these Data Sheets different from most other chemical kinetics evaluations is the use of transition-state theory to extrapolate rate coefficient measurements to higher temperatures. Theoretical calculations have long been used to extrapolate thermochemical data, as, for example, in the preparation of the JANAF Thermochemical Tables.[2] The method used to extrapolate chemical kinetic data (described in Sec. 2.5) is similar to that used in extrapolating thermochemical data in that both methods require calculation of an entropy and an enthalpy change.

2. Guide to the Use of the Chemical Kinetic Data Sheets

2.1. Reaction Title

The title of the Data Sheet is the reaction or reactions being reviewed. Elementary reactions are always written in the exothermic direction. For example, in the Data Sheet

entitled "O + OH$\rightleftharpoons$H + O$_2$," reaction 1, O + OH$\rightarrow$H + O$_2$, is exothermic; its rate coefficient is k_1 and its equilibrium constant is $K(T) = ([H][O_2])/([O][OH])$, where here [X] is the equilibrium concentration of species X. Reaction -1, H + O$_2\rightarrow$O + OH, is endothermic and has the rate coefficient k_{-1}. The first reagent in the reaction is in general the more reactive one; that is, if the reaction involves a stable molecule and an atom or radical, the atom or radical appears first. If the reaction is between two molecules or between two radicals, the species with the simpler molecular structure appears first.

2.2. Thermochemical Data

Above the graph on the first page of each Data Sheet are $\Delta H°_{298}$ and $\Delta S°_{298}$, the enthalpy and entropy changes for the reaction at 298.15 K (25 °C), and an analytic expression for the equilibrium constant in the form $K(T) = AT^n\exp(B/T)$. Experimental uncertainties are also given. [Definitions of $\Delta H°_{298}$, $\Delta S°_{298}$, and $K(T)$ are given in Sec. 5, "Nomenclature."]

An exact analytic expression for the equilibrium constant for ideal gases is

$$K(T) = \left(\frac{101.325}{RT}\right)^{\Delta v}\exp(\Delta S°/R)\exp(-\Delta H°/RT),$$

(1)

where $R = 8.314\,41$ J mol^{-1}K^{-1} = 8.314 41 L kPa mol^{-1} K^{-1}. The exponent Δv denotes the sum of the stoichiometric coefficients in the reaction. For the reaction O + OH$\rightarrow$H + O$_2$, Δv is zero and the equilibrium constant is dimensionless; for the reaction H + H$\rightarrow$H$_2$, Δv is -1 and $K(T)$ has units of liter per mole. $\Delta S°$ and $\Delta H°$ are the changes in the standard entropy and enthalpy for the reaction at temperature T. $\Delta S°$ is computed assuming reactants and products are ideal gases, each having a partial pressure of 101.325 kPa (1 standard atmosphere). In general, since $\Delta S°$ and $\Delta H°$ are complex functions of temperature, $K(T)$ will not be precisely of the form $AT^n\exp(B/T)$, with A, n, and B constant. However, in virtually every case, A, n, and B can be chosen so that the expression $K(T) = AT^n\exp(B/T)$ will not differ from Eq. (1) by more than a few percent over a wide temperature range (e.g., 300–5000 K). This discrepancy, specified on the second page of the Data Sheet in the section entitled "Thermochemical Data," is usually small compared with the experimental uncertainty in $K(T)$.

The section entitled "Thermochemical Data" outlines how $\Delta H°$ and $\Delta S°$ were computed. If no method is explicitly stated, $\Delta H°$ and $\Delta S°$ were computed, by their definitions, from thermochemical data of the individual reactants and products, that is, from the standard enthalpies of formation and the standard entropies of those species. The JANAF Thermochemical Tables[2] are the preferred source of such data. The equilibrium constant is always computed from Eq. (1), rather than from tabulated Gibbs energies of formation.

2.3. Measurements/Graph

Each Data Sheet contains a graph of log k_1 (or log k_{-1}) versus 1000/T (or, in rare cases, T). The graph is computer

drawn to minimize plotting errors and facilitate updating. On it are the recommended rate coefficient and the experimental data thought to be the most accurate and precise. Accuracy and precision are relative terms: for a well-studied reaction, the standard is high; for a less well-studied reaction with sparse experimental data, the standard is necessarily much lower.

Only one graph is presented even when both k_1 (the rate coefficient in the exothermic direction) and k_{-1} (the rate coefficient in the endothermic direction) have been measured. When the ordinate of the graph is log k_1, experimental data for k_{-1} are plotted as log[$k_{-1}K(T)$].

In general, each experimental measurement (or the result of a set of related measurements) is plotted on the graph as a single point. Symbols that overlap may be slightly separated to improve clarity. If there are more experimental measurements than can be plotted conveniently on the graph, only representative results are shown or a least-squares fit is plotted, and a statement to that effect is included in the "Measurements" section of the Data Sheet.

Usually all the points plotted within a small temperature range are believed to represent experimental measurements of comparable accuracy, so their scatter indicates the experimental uncertainties (either systematic or statistical). Sometimes, error bars are used to indicate uncertainty.

The original experimental data are sometimes reanalyzed. Examples of situations requiring reanalysis are those in which (1) there are more modern and accurate rate coefficients for competing reactions, (2) the thermochemistry of the reaction system has become better known, (3) an incomplete reaction mechanism was originally used in the analysis, (4) there is a more accurate value for an absorption coefficient or an f number, (5) the original analysis was only approximate because of the lack of computing facilities, or (6) the effects of experimental nonidealities were neglected. The Measurements section of the Data Sheet outlines how the data were reanalyzed.

As already mentioned, the graph contains only the data considered most accurate and precise. If space permits, the Measurements section also presents the reasons for judging certain rate coefficient determinations unreliable or inaccurate, and thus for excluding them from the graph. The principal reasons for rejecting a measurement are:

1. Reanalysis of the experimental data appears necessary; however, no raw data were given, making reanalysis impossible.

2. The measurements were not sensitive to the value of the rate coefficient purportedly being determined.

3. The experiments appear to suffer excessively from systematic errors due to nonidealities in the experimental setup or design. Some of the nonidealities that occur in chemical kinetics studies are (a) wall reactions, (b) impurities, (c) secondary reactions whose effects on the experimental results cannot be quantitatively assessed, (d) molecular diffusion, especially in flames and in flash-photolysis experiments, (e) excess boundary-layer buildup in shock-tube experiments, and (f) nonplug flow in flow-tube experiments.

4. Not enough information is reported about the experimental conditions and procedures to judge whether the experiment can reasonably be considered free of major syste-

matic errors, or whether the measurements are sensitive to the value of the rate coefficient of the reaction being studied. The results of such papers are generally discarded; to accept them would require an act of faith rather than rational judgment.

5. The rate coefficient determination is a byproduct, or even an afterthought, of an experiment designed to measure something else. In such cases, it is often impossible to deduce from the experiment a precise value for the rate coefficient.

Measurements are rarely, if ever, rejected solely because they disagree with other measurements or with the recommended values for the rate coefficient. Actually, it often happens that a measurement rejected as imprecise agrees with the recommended value more closely than some of the measurements considered accurate and reliable.

Persons making rate coefficient measurements usually categorize them as accurate to within some stated percentage, or as approximate, or occasionally as a crude estimate. The Data Sheets contain references to all measurements in the first two categories, whereas measurements in the last category are ignored. Original papers are cited except when the number is large, in which case, for older data not included in the graph, a review article is cited. Frequently, when an approximate measurement is reported, the authors' real interest was in measuring something else, and a precise determination was not attempted or may be impossible to obtain. So, even though a paper may be referred to as containing a rate coefficient measurement not good enough to be included on the graph and in the evaluation, it does not mean its authors are guilty of poor work.

2.4. Calculations

In 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 or for evaluating experiments of dubious validity.

We routinely perform transition-state-theory (TST) calculations for bimolecular reactions

$$A + B \rightarrow AB^\ddagger \rightarrow Products$$
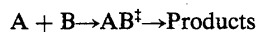
that occur on a potential-energy hypersurface having a saddle point that separates reactants A and B from products. $AB^\ddagger$ is a species that is moving across the saddle point and is usually called an "activated complex." The saddle point is such that in one direction, called the "reaction coordinate," the potential energy is a maximum, and in every direction orthogonal to it, the potential energy is a minimum. The potential-energy hypersurface orthogonal to the reaction coordinate and passing through the saddle point is termed the "transition state." The activated complex $AB^\ddagger$ is located within this hypersurface. The potential energy at the saddle point relative to the potential energy of the reactants is termed the "classical barrier height" or more simply just the "barrier height" and is given the symbol E_c.

The fundamental equation of transition-state theory for such a bimolecular reaction is

$$k = \kappa \frac{RT}{N_A h} \cdot \frac{Q(AB^\ddagger)}{Q(A)Q(B)} \exp(-E_c/RT), \qquad (2)$$

where k is the rate coefficient, κ is the transmission coefficient, R and T are as defined above, N_A is Avogadro's number, h is the Planck constant, $Q(A)$ and $Q(B)$ are partition functions per unit volume of A and B, and $Q(AB^\ddagger)$ is the partition function per unit volume of the activated complex $AB^\ddagger$, calculated treating $AB^\ddagger$ as a normal molecule located within a potential-energy minimum by ignoring the reaction coordinate. $Q(A), Q(B)$, and $Q(AB^\ddagger)$ are calculated with energies measured relative to their respective potential-energy minimums. The factor

$$\frac{Q(AB^\ddagger)}{Q(A)Q(B)} \exp(-E_c/RT)$$

has the form of an equilibrium constant, so Eq. (2) is sometimes written

$$k = \kappa \frac{RT}{N_A h} K^\ddagger. \qquad (3)$$

Substituting Eq. (1) into Eq. (3) yields

$$k = \kappa \frac{(RT)^2}{101.325 N_A h} \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT), \qquad (4)$$

where

$$\Delta S^\ddagger = S^\circ_T(AB^\ddagger) - S^\circ_T(A) - S^\circ_T(B), \qquad (5)$$

and

$$\Delta H^\ddagger = \Delta H^\ddagger_0 + [H^\circ_T(AB^\ddagger) - H^\circ_0(AB^\ddagger)] \\ - [H^\circ_T(A) - H^\circ_0(A)] - [H^\circ_T(B) - H^\circ_0(B)]. \qquad (6)$$

$\Delta S^\ddagger$ is called the "entropy of activation" at temperature T; and $\Delta H^\ddagger$, the "enthalpy of activation." In Eqs. (5) and (6), the subscript zero signifies zero kelvin; and subscript T, the temperature of interest. $S^\circ_T(AB^\ddagger)$ is often written more simply as $S^\ddagger$ and is sometimes referred to as "the entropy of the activated complex," although it is not a true entropy because the reaction coordinate is ignored and $AB^\ddagger$ is confined to a hypersurface orthogonal to the reaction coordinate at the saddle point. $H^\circ_T(AB^\ddagger) - H^\circ_0(AB^\ddagger)$ is often written as $H^\ddagger - H^\ddagger_0$.

As has been pointed out many times in recent years, the transmission coefficient κ is 1 and the transition-state theory is exact if all trajectories over the saddle cross over only once and if tunneling and other quantum effects are absent. If tunneling or recrossing is important, κ will have a temperature-dependent value that differs from unity. See Refs. 3 and 4 for a detailed discussion of transition-state theory and a derivation of Eq. (2).

Our use of transition-state theory differs from the usual approach in that we usually make no attempt to calculate κ or estimate the value of $\Delta H^\ddagger_0$, which depends principally on the barrier height E_c. Instead we write Eqs. (4), (5), and (6) as

$$k = \frac{(RT)^2}{101.325 N_A h} \exp(\Delta S^\ddagger/R)$$

$$\times \exp(-[\Delta H^\ddagger - \Delta H^\ddagger_0]/RT) \exp(-C/RT), \qquad (7)$$

where $C = \Delta H^\ddagger_0 - RT \ln \kappa$. C is treated as a constant, although κ must be of the form $\kappa = \exp(C'/T)$, with C' a constant, for it to be a true constant. C is evaluated from experiment, that is, from a measured value of k; it is an adjustable

parameter that accounts for the barrier height and quantum mechanical tunneling. A brief discussion of the errors that result from treating C as a constant is given in Ref. 5.

In extrapolating a rate coefficient measurement by Eq. (7), the entropy $S^{\ddagger}$ and the enthalpy difference $H^{\ddagger} - H_0^{\ddagger}$ of the activated complex must be computed. This computation is done just as it is for a stable molecule. In many cases, $S^{\ddagger}$ and $H^{\ddagger} - H_0^{\ddagger}$ are calculated by the rigid-rotor, harmonic-oscillator approximation, the method used in preparing the JANAF Thermochemical Tables.[2] This approximation was inadequate for the reaction $F + H_2 \rightarrow HHF^{\ddagger} \rightarrow H + HF$; anharmonic corrections and corrections for the interactions between rotation and bending had to be made.[5] For activated complexes containing many atoms, such as are encountered in the reactions of OH with alkanes, the group additivity method of Benson[6] was used.

Regardless of what method is used, a model of the transition state is required. Such a model might be a description of the potential-energy surface near the saddle point, or, equivalently, it might be a description of the structure of the activated complex including estimates of bond lengths, bond angles, vibrational frequencies, symmetry number, quantum weight of the ground electronic state, barriers to internal rotation, etc. Plausible models, consistent with sound chemical principles, must be formulated; only rarely are there accurate calculations to serve as a guide, and direct experimental measurements are impossible. In general, several plausible models of the transition state will be found that give, by Eq. (7), rate coefficients that agree with experiment over the measured temperature range. It is impossible to decide which model is correct, and usually this does not matter greatly because the different models will extrapolate the experimental data in nearly the same way. The discrepancy between the different extrapolations is an indication of the uncertainty of the TST calculation.

2.5. Recommended Rate Coefficients/Discussion

Recommended rate coefficients are expressed in the form $k = AT^n \exp(-B/T)$, where A, B, and n are constants. The recommendation for k at $T = 298$ is evaluated from this expression. The quotient of the forward and reverse rate coefficients is always taken to be equal to the equilibrium constant, $k_1/k_{-1} = K(T)$. The theoretical possibility that under unusual conditions, e.g., very fast reactions far from equilibrium, this relationship breaks down has never been found to occur to a measurable degree in any laboratory experiment. Recommendations are not extended to temperatures for which k is less than approximately 1 L mol^{-1} s^{-1}.

The section entitled "Discussion" describes how the recommended rate coefficient was chosen.

Uncertainties are assigned to the logarithm of the rec-

ommended rate coefficients. An uncertainty of, say, ± 0.1 in log k_1 indicates that, with a high degree of confidence, the true value of k_1 does not differ from the recommended value by more than a factor of 1.25. [Antilog 0.1 = 1.25, antilog 0.2 = 1.6, antilog 0.3 = 2.0, antilog 0.4 = 2.5, antilog $(-x) = 1/\text{antilog } x$.] Uncertainties are assigned on the basis of the scatter in the experiment data or, if reliable data are lacking, on the results of calculations that use different models for the transition state. A paucity of data or calculations makes the assignments of uncertainties unavoidably subjective.

2.6. State-Specific Kinetics

The rate coefficients reported in these Data Sheets are for reactions between molecules with a thermal distribution of translational and internal energies. Information about the quantum states in which the products are formed is presented only for four reactions important in chemical lasers, namely, $F + H_2 \rightarrow H + HF$, $F + D_2 \rightarrow D + DF$, $H + F_2 \rightarrow F + HF$, and $O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$.

3. Acknowledgments

4. References

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5. Nomenclature

5.1 Symbols Appearing in Data Sheets

$[X]$ — concentration of species X, customarily expressed in mol/L, mol/cm^3, or $molecule/cm^3$.

T — absolute temperature in kelvins.

k_1, $k_1(T)$ — rate coefficient (also called the rate constant) of reaction 1. For an elementary reaction $\Sigma n_i R_i \rightleftharpoons \Sigma m_j P_j$ occurring in a homogeneous, constant-volume system, the rate coefficient is defined by the equation

$$k_1 \, \Pi [R_i]^{n_i} = -\frac{1}{n_i}\frac{d[R_i]}{dt} = \frac{1}{m_j}\frac{d[P_j]}{dt} \ .$$

In these Data Sheets, all reactions have a rate coefficient that is a function of temperature only, and all reacting species are ideal gases.

$k_1(298)$ — k_1 at T = 298 K.

ΔHf^o_{298} — standard enthalpy of formation from the elements at T = 298.15 K (25^oC).

ΔH^o_{298} — enthalpy change for a reaction at 298.15 K (25^oC), sometimes called the heat of reaction. For a gas-phase reaction, the superscript o designates reactants and products as ideal gases; ΔH^o_{298} is independent of pressure. If ΔH^o_{298} is negative, the reaction is said to be exothermic (heat is evolved under conditions of constant pressure); if ΔH^o_{298} is positive, the reaction is endothermic. For the reaction $\Sigma n_i R_i \rightarrow \Sigma m_j P_j$,

$$\Delta H^o_{298} = \Sigma m_j \Delta Hf^o_{298}(P_j) - \Sigma n_i \Delta Hf^o_{298}(R_i) \ .$$

ΔH^o_0 — enthalpy change for a reaction at a temperature of absolute zero.

ΔH^o — enthalpy change for a reaction as a function of temperature or at an unspecified temperature.

S^o_{298} — standard entropy at T = 298.15 K (25^oC). For a species in the gas phase, the word "standard" and the superscript o mean the entropy is calculated assuming the gas is ideal and its partial pressure is 101.325 kPa (1 atm).

ΔS^o_{298} — entropy change for a reaction at 298.15 K (25^oC) when reactants and products are ideal gases each with a partial pressure of 101.325 kPa (1 atm). For the reaction $\Sigma n_i R_i \rightarrow \Sigma m_j P_j$,

$$\Delta S^o_{298} = \Sigma m_j S^o_{298}(P_j) - \Sigma n_i S^o_{298}(R_i) \ .$$

ΔS^o — entropy change for a reaction as a function of temperature or at an unspecified temperature, all species having a partial pressure of one atmosphere.

$K(T)$ — equilibrium constant, which is a function of temperature only. For the reaction $\Sigma n_i R_i \rightarrow \Sigma m_j P_j$,

$$K(T) = \frac{\Pi [P_j]_e^{m_j}}{\Pi [R_i]_e^{n_i}} \ .$$

The subscript e denotes equilibrium concentrations.

log — logarithm to base 10.

‡ — activated complex. For example, $HHF^‡$ is the activated complex in the reaction $F + H_2 \rightarrow H + HF$; it is the species crossing the saddle point that separates reactants from products on the HHF potential energy surface. For the definitions of $\Delta H^‡$, $\Delta S^‡$, and $S^‡$, and for a description of transition-state theory, see section 2.4, "Calculations".

r — internuclear distance; for example, $r(HF-F^‡)$ is the distance between the fluorine atoms in the species $HFF^‡$.

D^o_0 — bond dissociation energy measured at a temperature of absolute zero, or equivalently the dissociation energy measured from the zeroth vibrational level.

$\bar{\omega}$ — vibrational wavenumber of a normal mode.

5.2 Conversion Factors and Fundamental Constants

atm (standard atmosphere) ≡ 101325 N/m^2 = 101.325 kPa

cal (thermochemical calorie) ≡ 4.184 J

L (liter, also abbreviated as l, ℓ, or dm^3) ≡ 10^{-3} m^3

h (Planck constant) = 6.62176×10^{-34} J·s

N_A (Avogadro's number) = 6.022045×10^{23} mol^{-1}

R (gas constant) = 8.31441 $J\ mol^{-1}\ K^{-1}$
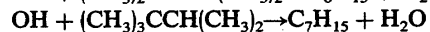
conversion of wavenumber to energy: $1\ cm^{-1}$ = 11.9626 J/mol

6. Data Sheets

6.1. List of Data Sheets

$F + D_2 \rightarrow D + DF$

$F + H_2 \rightarrow H + HF$

$F + HD \rightarrow D + HF, F + HD \rightarrow H + DF$

$H + F_2 \rightarrow F + HF$

$D + F_2 \rightarrow F + DF$

$O_2(^1\Delta) + I(^2P_{1/2}) \rightarrow O_2(^1\Sigma) + I(^2P_{3/2})$

$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma)$

$O + OH \rightarrow H + O_2$

$H + OH \rightarrow O + H_2$

$OH + H_2 \rightarrow H + H_2O$

$OH + OH \rightarrow O + H_2O$

$H + H + M \rightarrow H_2 + M, M = H_2, H$

$H + H + M \rightarrow H_2 + M, M = Ar, N_2, H_2O$

$OH + CH_4 \rightarrow CH_3 + H_2O$

$OH + C_2H_6 \rightarrow C_2H_5 + H_2O$

$OH + C_3H_8 \rightarrow C_3H_7 + H_2O$

$OH + n\text{-}C_4H_{10} \rightarrow C_4H_9 + H_2O$

$OH + i\text{-}C_4H_{10} \rightarrow C_4H_9 + H_2O$

$OH + c\text{-}C_4H_8 \rightarrow C_4H_7 + H_2O$

$OH + c\text{-}C_5H_{10} \rightarrow C_5H_9 + H_2O$

$OH + c\text{-}C_6H_{12} \rightarrow C_6H_{11} + H_2O$

$OH + (CH_3)_4C \rightarrow CH_2C(CH_3)_3 + H_2O$

$OH + (CH_3)_2CHCH(CH_3)_2 \rightarrow C_6H_{13} + H_2O$

$OH + (CH_3)_3CCH(CH_3)_2 \rightarrow C_7H_{15} + H_2O$

$OH + (CH_3)_3CC(CH_3)_3 \rightarrow CH_2C(CH_3)_2C(CH_3)_3 + H_2O$

$Al + O_2 \rightarrow O + AlO$

$B + O_2 \rightarrow O + BO$

$$F + D_2 \underset{-1}{\overset{1}{\rightleftharpoons}} D + DF$$

$\Delta H^o_{298} = -132.71 \pm 1.5 \text{ kJ/mol}^{-1}(-31.72 \text{ kcal/mol}^{-1})$ $\Delta S^o_{298} = -0.66 \pm 0.04 \text{ J mol}^{-1}K^{-1}(-0.16 \text{ cal mol}^{-1}K^{-1})$

$$K(T) = 1.68 \ T^{-0.1} \exp(15957/T)$$

The uncertainty in log $K(T)$ due to uncertainties in ΔH^o_{298} and ΔS^o_T is ±0.2 at 298 K, ±0.07 at 1000 K, ±0.02 at 5000 K.
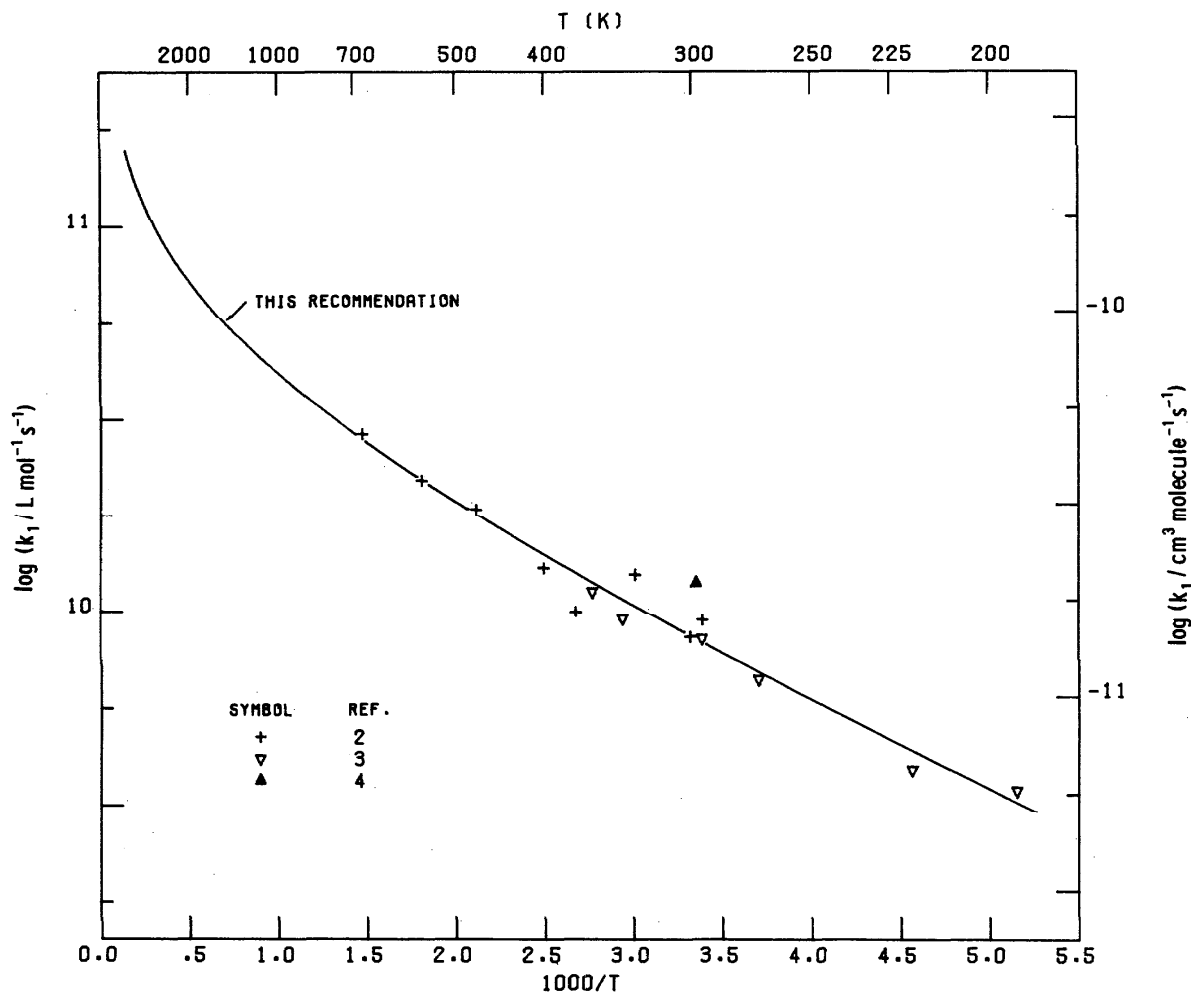
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.0 \times 10^9 \ T^{0.5} \exp(-418/T)$	190-7000 K	8.5×10^9	L mol^{-1}s^{-1}
	$3.3 \times 10^{-12} \ T^{0.5} \exp(-418/T)$		1.4×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.2 \times 10^9 \ T^{0.6} \exp(-16375/T)$	650-7000 K		L mol^{-1}s^{-1}
	$2.0 \times 10^{-12} \ T^{0.6} \exp(-16375/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.15, 190 < T < 700 K, ±0.2 at 2000 K, and ±0.3 at 7000 K. Uncertainty in log k_{-1}: approx. ±0.3, 650 < T < 3000 K, ±0.35 at 7000 K. The uncertainty in log k_{-1} reflects those of log k_1 and log $K(T)$. Below 650 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow. However, the relation $k_1/k_{-1} = K(T)$ should still be valid.

(February 1982)

$F + D_2 \rightleftharpoons D + DF$

THERMOCHEMICAL DATA

Thermochemical data for D, D_2 and DF are taken from unpublished supplements to the JANAF Thermochemical Table; (31 March 1977 and 30 June 1977); data for F are from the second edition of JANAF Tables (1971). The enthalpy change for this reaction may also be calculated from the relation: $\Delta H_0^o = D_0^o(D_2) - D_0^o(HF) - G_0(HF) + G_0(DF)$; where $D_0^o(D_2)$ and $D_0^o(HF)$ are the bond dissociation energies of D_2 and HF, and $G_0(HF)$ and $G_0(DF)$ are the zero-point vibrational energies of HF and DF. Di Lonardo and Douglas[1] measured $D_0^o(HF) = 566.22 \pm 0.8$ kJ/mol. Indisputably accurate measurements have established that $D_0^o(D_2) = 439.61 \pm 0.01$, $G_0(HF) = 24.49$, $G_0(DF) = 17.80$ kJ/mol. Hence $\Delta H_0^o = -133.30 \pm 0.9$ kJ/mol. The data in the JANAF Tables yield $\Delta H_0^o = -132.49$. ΔH_{298}^o calculated from the JANAF Tables is adopted here, even though the value derived from the bond dissociation energy measurements may be slightly more accurate. The analytic expression chosen for K(T) matches the equilibrium constants calculated from JANAF data to within 1% between 298 and 4500 K. The discrepancy at 6000 K is 3%.

MEASUREMENTS

There are six studies reporting direct measurements of k_1. The results of the three most recent studies [2-4] are plotted on the graph. In these studies atomic fluorine was produced by infrared multiphoton dissociation of SF_6 and the rate of reaction determined by monitoring infrared fluorescence from the vibrationally excited product HF. The results from the other studies[5-7] are not included in this evaluation either because too little information was given to assess the accuracy of the measurements or because the interpretation of the experimental data depended on other unknowns besides k_1. In addition five studies have reported values for the ratio k_1/k_2 where k_2 is the rate coefficient for $F + H_2 \overset{2}{\rightleftharpoons} H + HF$; These measurements are discussed in the Data Sheet for Reaction 2.

The experimental measurements of Refs. 2 and 3 were performed with the greatest care and are in agreement. A least-squares fit of these data to the expression $k = AT^{0.5} \exp(-B/T)$ gives $k = 2 \times 10^9 \ T^{0.5} \exp(-418/T)$, $190 < T < 680$, and $k(298) = 8.5 \times 10^9$ L $mol^{-1}s^{-1}$. The temperature dependence of the preexponential factor, $T^{0.5}$, is chosen to agree with the results of the transition-state-theory calculations described below.

CALCULATIONS

Transition-state-theory calculations were performed to extrapolate k_1 to higher temperatures. Several plausible models for the potential-energy surfaces at the transition state were formulated each model being adjusted so that $k_1(298) = 8.5 \times 10^9$ L $mol^{-1}s^{-1}$. Different models give different structures for the activated complex, $DDF^{\ddagger}$. Altogether nine different models or structures were formulated that give rate coefficients that agree with the experimental data from 190 to 680 K. Eight of the models are similar in that they are based in somewhat different ways on the "preliminary" ab initio potential-energy calculations of Bender, Schaefer, Lui, et al.[8] The ninth model is quite different in that it was chosen in accordance with the empirical rules of Benson.[9] These nine models which are consistent with experiment predict nearly same values of k_1 at higher temperatures, up to 7000 K; the maximum disparity in log k_1 (occurring at 7000 K) is ±0.16. The calculated values for k_1 over the temperature range 190 - 7000 K, can be described by the same expression that describes the experimental data over the temperature range 190 - 680 K, namely, $k_1 = 2 \times 10^9 \ T^{0.5} \exp(-418/T)$. The calculations are inconsistent with a two-parameter Arrhenius extrapolation of the experimental data. See Ref. 10 for a fuller discussion.

DISCUSSION

On the basis of the experiments and calculations we recommend $k_1 = 2 \times 10^9 \ T^{0.5} \exp(-418/T)$, $190 < T < 7000$ K. k_1 is not extrapolated to lower temperatures because the effects of quantum mechanical tunneling, which are only crudely accounted for in our calculations, may become important.

STATE SPECIFIC KINETICS

Reaction 1 produces vibrationally excited DF, the distribution of which has been studied in several laboratories. The conclusion of the most recent (and probably most reliable) study[11] is that the first four excited levels, v = 1 - 4, are populated in the ratio of 0.12 : 0.21 : 0.37 : 0.30 at 300 K. The temperature dependences of these ratios have been shown to be small.[12]

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$$F + H_2 \underset{-1}{\overset{1}{\rightleftharpoons}} H + HF$$
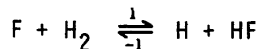
$\Delta H^{o}_{298} = -133.46 \pm 1.5$ kJ mol^{-1} (-31.90 kcal mol^{-1}) $\Delta S^{o}_{298} = -0.94 \pm 0.04$ J mol^{-1}K^{-1} (-0.22 cal mol^{-1}K^{-1})

$$K(T) = 1.64 \ T^{-0.1} \ \exp(16043/T)$$

The uncertainty in log K(T), due to uncertainties in ΔH^{o}_{298} and ΔS^{o}_{T}, is ±0.2 at 298 K, ±0.07 at 1000 K, and ±0.02 at 5000 K.
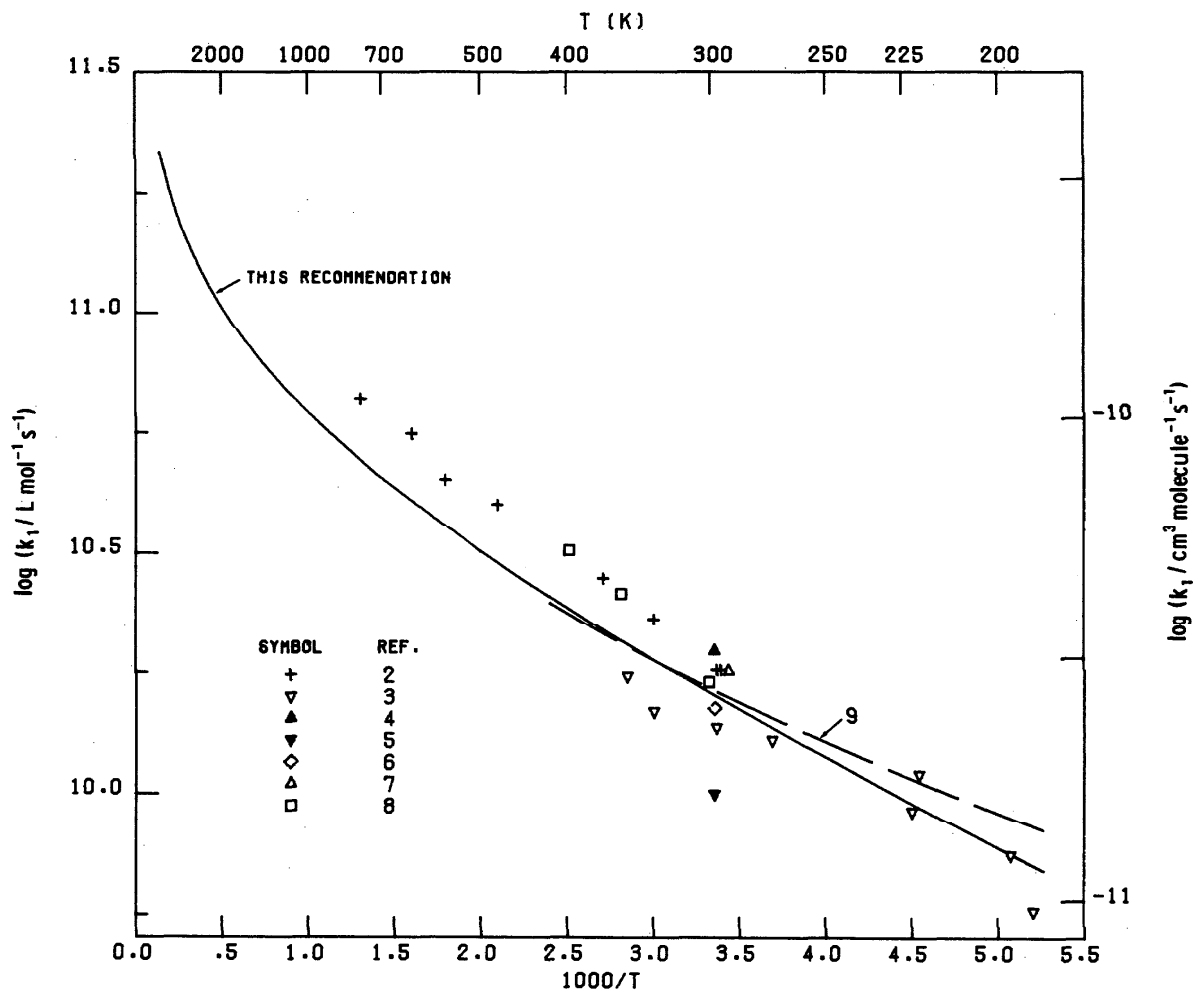
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.7 \times 10^9 \ T^{0.5} \exp(-319/T)$	190-7000 K	1.6×10^{10}	L mol^{-1}s^{-1}
	$4.5 \times 10^{-12} \ T^{0.5} \exp(-319/T)$		2.66×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.65 \times 10^9 \ T^{0.6} \exp(-16362/T)$	650-7000 K		L mol^{-1}s^{-1}
	$2.73 \times 10^{-12} \ T^{0.6} \exp(-16362/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.15, 190 < T < 700, ±0.2 at 2000 K, and ± 0.3 at 7000 K.   Uncertainty in log k_{-1}: approx. ± 0.3, 650 < T < 3000 K, ±0.35 at 7000 K.   The uncertainty in log k_{-1} reflects those of log k_1 and log (T).   Below 650 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow.   However, the relation k_1/k_{-1} = K(T) should still be valid.

(February 1982)

$F + H_2 \rightleftharpoons H + HF$

THERMOCHEMICAL DATA

Thermochemical data for H, H_2 and HF are taken from unpublished supplements to the JANAF Thermochemical Tables (31 March 1977 and 30 June 1977); data for F are from the second edition of the JANAF Tables (1971). The enthalpy change for this reaction may also be calculated from the bond dissociation energies of H_2 and HF: $\Delta H_0^o = D_0^o(H_2) - D_0^o(HF)$. From spectroscopic measurements, Di Lonardo and Douglas[1] found $D_0^o(HF) = 566.22 \pm 0.8$ kJ/mol. $D_0^o(H_2)$ has been accurately determined to be 432.07. These values give $\Delta H_0^o = -134.15 \pm 0.8$ kJ/mol. Data from the JANAF Tables yield $\Delta H_0^o = -133.27$. ΔH_{298}^o calculated from the JANAF Tables is adopted here, even though the value derived from the bond dissociation measurements may be slightly more accurate. The analytic expression chosen for K(T) matches the equilibrium constants calculated from JANAF data to within 2% between 298 and 6000 K.

MEASUREMENTS

There are fifteen studies reporting direct measurements of k_1. The measurements plotted on the graph (from Refs. 2-8) are selected for their precision and probable accuracy. The most recent measurements[2,3] are probably the most accurate of all, even though there is a small discrepancy between them. For example, at 297 K, Heidner et al.[2] report $k_1 = 1.8 \times 10^{10}$, while Wurzberg and Houston[3] find $k_1 = 1.37 \times 10^{10}$ L mol^{-1}s^{-1}. The best value is probably the average of these results or $k_1(298) = 1.6 \times 10^{10}$.

In two studies the ratio k_1/k_2 was measured, where k_2 is the rate coefficient for the reaction $F + D_2 \rightleftharpoons D + DF$. The more precise, and probably more accurate, of these studies is Persky's.[9] His measurements have been combined with our recommendation for k_2, namely, $k_2 = 2 \times 10^9$ $T^{0.5}$ exp(-418/T) to give the values for k_1 plotted on the graph (dashed line). In addition there are three studies in which the ratios k_1/k_3 and k_2/k_3 have been determined, where k_3 is the rate coefficient of some other reaction. These studies, which lack the precision of Persky's measurements, are not used in this evaluation. There are two determinations of k_{-1} reported, both of which are inaccurate. The various measurements of Reaction 1 have been recently reviewed,[10] wherein, except for a recent study,[11] references to the data not used in this evaluation may be found.

CALCULATIONS

As pointed out above, the experimental data for Reaction 1 show small, systematic discrepancies; so a determination of k_1 by a least-squares fit will be subject to a systematic error. Theoretical calculations are needed. Reactions 1 and 2 (F + D$_2$ $\rightleftharpoons$ D + DF) proceed over the same potential-energy surface. The experimental measurements of k_2 show no discrepancies, and, as outlined in the Data Sheet for that reaction, transition-state-theory calculations were performed for several plausible potential-energy surfaces that enabled k_2 to be extrapolated to 7000 K. Using these same potential-energy surfaces, we[12] also calculated k_1/k_2. These calculations have one adjustable constant (chosen so that $k_1/k_2 = 1.88$ at 298 K) which accounts for the neglect of anharmonicity in the calculation of the zero-point energies of DDF‡ and HHF‡, and to a large extent for the fact that the ratio of transmission coefficients may differ from unity. Regardless of which potential-energy surface is used, the calculations of k_1/k_2 are fairly consistent with the expression, $k_1/k_2 = 1.35$ exp(99/T), 190 < T < 7000 K. This expression, combined with our recommendation for k_2, gives $k_1 = 2.7 \times 10^9$ $T^{0.5}$ exp(-319) L mol^{-1}s^{-1}.

DISCUSSION

The calculated expression for k_1, $k_1 = 2.7 \times 10^9$ $T^{0.5}$ exp(-319/T), implies that the experimental values of Heidner et al. are somewhat too great, while for the most part the values of Wurzberg and Houston are too small. At room temperature and above, the calculated values of k_1/k_2 are in almost exact agreement with the measurements of Persky while at 190 K they are 17% lower. We think the calculated expression for k_1 is a good, but not necessarily optimal, fit to the experimental data and recommend it over the temperature range 190-7000 K.

STATE SPECIFIC KINETICS

Reaction 1 produces vibrationally excited HF. The conclusions of the most recent studies are that the first three excited levels, v = 1, 2, and 3, are populated in the ratio of 0.3 : 1.0 : 0.5 at 300 K. Because all studies rely on observing chemiluminescence from the product states, there is no direct evidence on the rate of formation of the v = 0 level. Theoretical calculations indicate that none should be formed. The literature has been reviewed in some detail in Ref. 10c.

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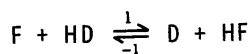$$F + HD \overset{1}{\underset{-1}{\rightleftharpoons}} D + HF \qquad\qquad \& \qquad\qquad F + HD \overset{2}{\underset{-2}{\rightleftharpoons}} H + DF$$
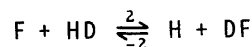
$\Delta H^{o}_{298} = -130.06 \pm 1.5$ kJ mol^{-1} (-31.09 kcal mol^{-1})

$\Delta S^{o}_{298} = -5.43 \pm 0.04$ J mol^{-1} K^{-1} (-1.30 cal mol^{-1} K^{-1})

$K_1(T) = 2.08 \ T^{-0.2} \exp(15545/T)$

$\Delta H^{o}_{298} = -136.75 \pm 1.5$ kJ mol^{-1}(-32.68 kcal mol^{-1})

$\Delta S^{o}_{298} = -8.13 \pm 0.04$ J mol^{-1} K^{-1} (-1.94 cal mol^{-1} K^{-1})

$K_2(T) = 0.76 \ T^{-0.1} \exp(16355/T)$

The data in the left column are for Reaction 1; in the right column, Reaction 2. The uncertainty in $K_1(T)$ or $K_2(T)$ due to uncertainties in ΔH^{o}_{298} and ΔS^{o}_{298} is ±0.2 at 298, ±0.07 at 1000, ±0.02 at 5000 K.
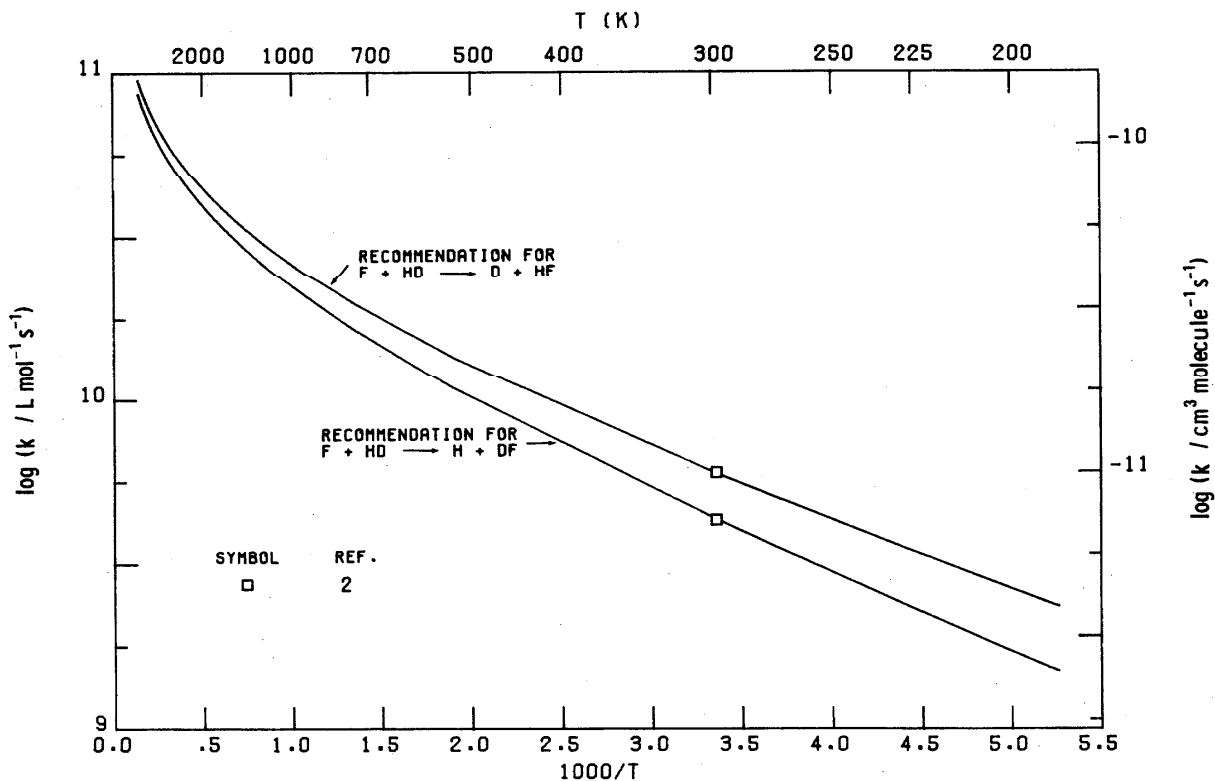
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.2 \times 10^9 \ T^{0.5} \exp(-370/T)$	190-7000 K	6×10^9	L mol^{-1}s^{-1}
	$2.0 \times 10^{-12} \ T^{0.5} \exp(-370/T)$		1×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$5.8 \times 10^8 \ T^{0.7} \exp(-15915/T)$	650-7000 K		L mol^{-1}s^{-1}
	$9.6 \times 10^{-13} \ T^{0.7} \exp(-15915/T)$			cm^3 molecule^{-1}s^{-1}
k_2	$1.1 \times 10^9 \ T^{0.5} \exp(-440/T)$	190-7000 K	4.3×10^9	L mol^{-1}s^{-1}
	$1.83 \times 10^{-12} \ T^{0.5} \exp(-440/T)$		7.2×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-2}	$1.45 \times 10^9 \ T^{0.6} \exp(-16795/T)$	650-7000 K		L mol^{-1}s^{-1}
	$2.4 \times 10^{-12} \ T^{0.6} \exp(-16795/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1 or log k_2: ±0.25 at 298 K, increasing to ±0.3 at 190 and 2000 K, and ±0.35 at 7000 K. Uncertainty in log k_{-1} or log k_{-2}: ±0.4, 650 < T < 7000 K. Below 650 K, both k_{-1} and k_{-2} are less than 1 L mol^{-1}s^{-1} and Reactions -1 and -2 are immeasurably slow. However, the relations $k_1/k_{-1} = K_1(T)$ and $k_2/k_{-2} = K_2(T)$ should still be valid.

(February 1982)

$$F + HD \xrightarrow{\ 1\ } D + HF \qquad\qquad F + HD \xrightarrow{\ 2\ } H + DF$$

THERMOCHEMICAL DATA

Thermochemical data for H, D, HD, HF, and DF are taken from unpublished supplements to the JANAF Thermochemical Tables (31 March 1977 and 30 June 1977); data for F are from the second edition of the JANAF Tables (1971). The enthalpy change for these reactions may also be calculated from the spectroscopically determined bond dissociation energies of HD, HF, and DF, as discussed in the Data Sheets for the reactions $F + H_2 \overset{3}{\rightarrow} H + HF$ and $F + D_2 \overset{4}{\rightarrow} D + DF$. ΔH_0^o so determined differs by less than 1 kJ/mol from the JANAF value. The analytic expressions chosen for $K_1(T)$ and $K_2(T)$ match the equilibrium constants calculated from JANAF data to within 2% between 700 and 6000 K.

MEASUREMENTS

There are no direct measurements of k_1 or k_2, but three studies report relative measurements. One study[1] reports a measurement of k_1/k_3 and k_2/k_4, where k_3 and k_4 are the rate coefficients of $F + H_2 \overset{3}{\rightarrow} H + HF$ and $F + D_2 \overset{4}{\rightarrow} D + DF$. This study, performed by Berry, gives $k_1/k_3 = 0.38$ and $k_2/k_4 = 0.505$. The determination of k_1/k_3 and k_2/k_4 required a knowledge of the vibrational distribution of the products of Reactions 1, 2, 3, and 4, for which Berry used his own determinations. Their uncertainty means the measurements of k_1/k_3 and k_2/k_4 are uncertain by almost ± 0.1. Other systematic errors could also be present. Nevertheless, these are the only measurements of k_1 and k_2 relative to known rate coefficients. With our recommendations for k_3 and k_4, Berry's measurements give $k_1 = 6.0 \times 10^9$ and $k_2 = 4.3 \times 10^9$ L mol^{-1}s^{-1} at 298 K. These values are plotted on the graph. Two studies report measurements of k_1/k_2. Persky[2] measured k_1/k_2 at the following temperatures 165 ± 5, 224 ± 2, 298, and 412 ± 2 K, finding at 298, $k_1/k_2 = 1.46$. In an earlier study, Kompa, Parker, and Pimentel[3] suggested $k_1/k_2 \approx 2.5$ at 300 K on the basis of an assumed, but unproven, reaction mechanism. Berry's measurements of k_1/k_3, k_2/k_4 and our recommendation $k_3/k_4 = 1.88$ at 298 K give $k_1/k_2 = 1.4$, in agreement with Persky's measurement.

Bott[4] has measured $k_{-2} + k_5$ between 2100 and 3900 K, where k_5 is the rate coefficient of the reaction $H + DF \rightarrow D + HF$. An upper limit of $k_2 < 9.4 \times 10^{10} \exp(-440/T)$ L mol^{-1}s^{-1}, 2100 < T < 3900 K, can be readily inferred from his data by assuming he measured only k_{-2} (this would be true if $k_{-2} \gg k_5$) and calculating k_2 from the relation $k_2 = k_{-2} K_2$.

CALCULATIONS

Reactions 1, 2, 3, and 4 proceed over the same potential-energy surface. Experimental data for Reactions 1 and 2 are sparse, while considerably more data exist for Reactions 3 and 4. As outlined in the Data Sheets for these latter reactions, several plausible potential-energy surfaces were found that, when used with transition-state theory, give values for k_3 and k_4 that agree with the experimental data over the measured temperature range, 190 < T < 700 K. Furthermore, each of these surfaces predicts nearly the same values for k_3 or k_4 at higher temperatures, to 7000 K. Using these same potential-energy surfaces, we[5] also calculated k_1/k_3 and k_2/k_4. Each calculation is multiplied by a correction factor containing one adjustable constant which is chosen on the basis of Berry's measurements so that in the calculation of k_1/k_3, $k_1/k_3 = 0.38$ at 298 K, and in the calculation of k_2/k_4, $k_2/k_4 = 0.505$ at 298 K. This adjustable constant accounts for the neglect of anharmonicity in the calculation of the zero-point energies of HHF‡, DDF‡, DHF‡, and HDF‡, and to a large extent, for the fact that the ratio of the transmission coefficients may differ from unity. This correction factor produced only small changes in the calculated values of k_1/k_3 or k_2/k_4 (typically 15% at 298 K, 6% at 700 K, 2% at 2000 K). Regardless of which potential-energy surface is used, the calculations of k_1/k_3 and k_2/k_4 are consistent, within 10%, with the expressions, $k_1/k_3 = 0.43 \exp(-38/T)$ and $k_2/k_4 = 0.55 \exp(-25/T)$, 190 < T < 7000 K. These expressions and our recommendations for k_3 and k_4 give $k_1 = 1.15 \times 10^9\ T^{0.5} \exp(-357/T)$ and $k_2 = 1.1 \times 10^9\ T^{0.5} \exp(-443/T)$ L mol^{-1}s^{-1}.

DISCUSSION

By necessity, we base our recommendations on the measurements of Berry and our transition-state-theory calculations. To avoid the impression of high accuracy, we round-off the calculated expressions for k_1 and k_2 and recommend $k_1 = 1.2 \times 10^9\ T^{0.5} \exp(-370/T)$ and $k_2 = 1.1 \times 10^9\ T^{0.5} \exp(-440/T)$ L mol^{-1}s^{-1}, 190 < T < 7000 K. These expressions imply $k_1/k_2 = 1.1 \exp(70/T)$ which as indicated in the following table is in almost exact agreement with Persky's measurements.

Temperature (K)	224	298	412
k_1/k_2 measured by Persky	1.47	1.46	1.33
$k_1/k_2 = 1.1 \exp(70/T)$	1.50	1.39	1.30

Furthermore, the recommended value of k_2 is lower than the upper limit found by Bott. For example, at 3000 K, Bott's measurements imply $k_2 < 8 \times 10^{10}$, while our recommended value is 5.2×10^{10} L mol^{-1}s^{-1}.

References

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$$H + F_2 \underset{-1}{\overset{1}{\rightleftharpoons}} F + HF$$
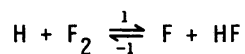
$\Delta H^o_{298} = -411.63 \pm 2.0$ kJ mol^{-1} (-98.38 kcal mol^{-1}) $\qquad \Delta S^o_{298} = 15.02 \pm 0.04$ J mol^{-1}K^{-1} (3.59 cal mol^{-1}K^{-1})

$$K(T) = 180 \ T^{-0.5} \exp(49360/T)$$

The uncertainty in log K(T), due to uncertainties in ΔH^o_{298} and ΔS^o_T, is ±0.3 at 298 K, decreasing to ±0.1 at 1000 K and ±0.03 at 5000 K.
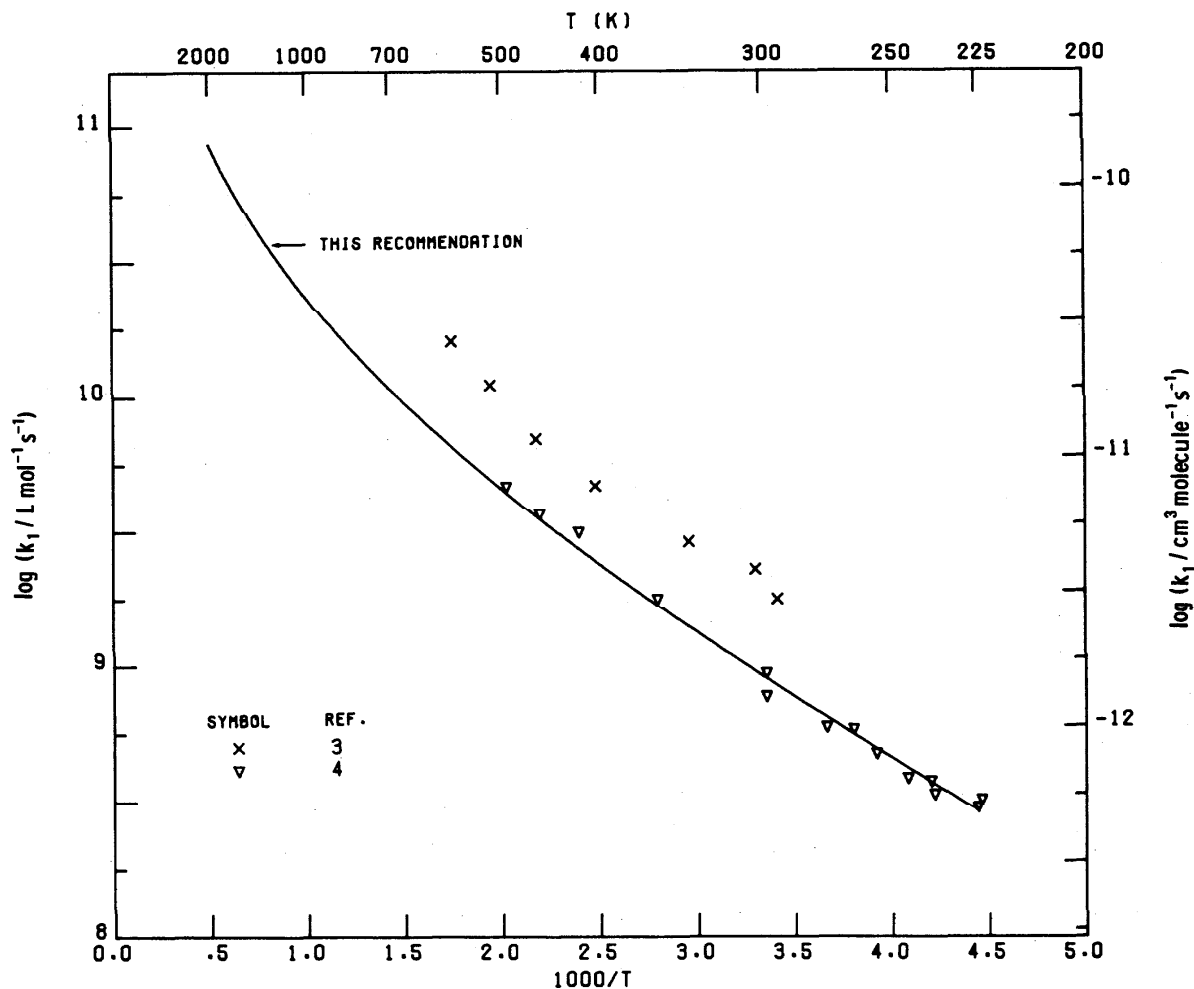
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.9 \times 10^6 \ T^{1.4} \exp(-667/T)$	225-2000 K	9×10^8	L mol^{-1}s^{-1}
	$4.8 \times 10^{-15} \ T^{1.4} \exp(-667/T)$		1.5×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-1}	see below			

Uncertainty in log k_1: $^{+0.3}_{-0.2}$ for 225-500 K, increasing to ±0.4 at 2000 K. Below 2000 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow; however, the relation $k_1/k_{-1} = K(T)$ should still be valid.

(October 1982)

$H + F_2 \rightleftharpoons F + HF$
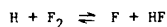
THERMOCHEMICAL DATA

Thermochemical data for H, F_2 and HF are taken from unpublished supplements to the JANAF Thermochemical Tables (31 March 1977 and 30 June 1977); data for F are from the second edition of the JANAF Tables (1971). The enthalpy change for this reaction can also be calculated directly from the bond dissociation energies of F_2 and HF: $\Delta H_0^o = D_0^o(F_2) - D_0^o(HF)$. From spectroscopic measurements, Douglas et al.[1,2] found $D_0^o(F_2) = 154.56 \pm 0.7$ and $D_0^o(HF) = 566.22 \pm 0.8$ kJ/mol. These values give $\Delta H_0^o = -411.66 \pm 1.3$ kJ/mol, in agreement with the JANAF recommendation, $\Delta H_0^o = -411.72$. The analytical expression chosen for K(T) matches equilibrium constants calculated from JANAF data to within 4% between 200 and 5000 K.

MEASUREMENTS

Albright et al.[3] and Homann et al.[4] measured k_1 using a discharge flow system with mass spectrometry to measure reactant and product concentrations. Albright et al. probed a diffusion cloud, while Homann et al. were able to avoid sampling within the mixing region. As is shown on the graph, the results differ by about a factor of 2; e.g., at 298 K, Albright et al. found $k_1 = 2 \times 10^9$ whereas Homann et al. give $k_1 = 9 \times 10^8$ L mol^{-1}s^{-1}. These and other less reliable measurements of k_1 have been reviewed by Foon and Kaufman[5], Cohen and Bott[6], and Baulch et al.[7] A recent relative measurement[8] of k_1 is not used in this evaluation.

CALCULATIONS

Bender et al.[9] and Eades et al.[10] have performed ab initio, quantum mechanical calculations of the shape of the potential-energy surface over which Reaction 1 occurs. Both sets of calculations predict a linear transition state with bond lengths $r(H-FF^{\ddagger}) = 1.7$ and $r(HF-F^{\ddagger}) = 1.5$ Å. Eades et al. give the stretching wavenumber of the activated complex as $\bar{\omega}_s = 934$ cm^{-1} and the bending wavenumber, which has a degeneracy of 2, as $\bar{\omega}_b = 261$ cm^{-1}. The calculations of Bender et al., as analyzed by Carsky and Zahradnik[11], give $\bar{\omega}_s = 690$ and $\bar{\omega}_b = 190$. The electronic degeneracy is 2.

We[12] have calculated k_1 over the temperature range 225-2000 K, using transition-state theory, the above data, and a rigid-rotor, harmonic-oscillator model for the activated complex. The calculations contain an adjustable constant chosen so that $k_1(298) = 9 \times 10^8$ L mol^{-1}s^{-1}. This adjustable constant accounts for the barrier height of the reaction and, to a limited degree, for quantum mechanical tunneling. We find $k_1 = 3.0 \times 10^6$ $T^{1.5}$ exp(-845/T) for the surface of Ref. 9 and $k_1 = 2.9 \times 10^6$ $T^{1.4}$ exp(-667/T) for the surface of Ref. 10. Both expressions for k_1 adequately match the experimental data over the temperature range of the measurements, $225 < T < 500$ K.

DISCUSSION

Our recommendation for k_1 is based on the measurements of Homann, which are probably more accurate than those of Albright because of freedom from mixing complications. In other respects, the measurements are similar. The experimental data are extrapolated with the calculations based on the surface of Ref. 10, giving $k_1 = 2.9 \times 10^6$ $T^{1.4}$ exp(-667/T), $225 < T < 2000$ K. The data are not extrapolated below 225 K because the tunneling correction is approximate or above 2000 K because anharmonicity in HFF‡ has been neglected.

STATE SPECIFIC KINETICS

Reaction 1 is sufficiently exothermic to populate HF up to the 11th vibrational level, and the product distribution has been the subject of several experimental and theoretical investigations. The best experimental study[13] indicates that the v = 3 through v = 6 levels are the most heavily populated, with 7, 14, 35, and 44 percent going into levels 3, 4, 5, and 6 respectively. Very little, if any, of the product HF is formed in higher or lower levels. Since vibrational populations are measured by chemiluminescence, there has been no direct measurement of the population of the v = 0 level; however, theoretical arguments[14] suggest that none should be formed. Experimental data and theoretical studies are summarized in Ref. 6.

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10. R. A. Eades, T. H. Dunning Jr., and D. A. Dixon, J. Chem. Phys. 75, 2008 (1981); 183rd ACS National Meeting, Las Vegas (1982).
11. P. Carsky and R. Zahradnik, Int. J. Quantum Chem. 16, 243 (1979).
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$$D + F_2 \underset{-1}{\overset{1}{\rightleftharpoons}} F + DF$$
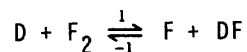
$\Delta H^o_{298.15} = -418.32 \pm 2 \text{ kJ mol}^{-1}$ (-99.98 kcal mol^{-1}) $\Delta S^o_{298.15} = 12.31 \pm 0.04 \text{ J mol}^{-1}\text{K}^{-1}$ (2.94 cal mol^{-1}K^{-1})

$$K(T) = 65 \; T^{-0.4} \exp(50200/T)$$

The uncertainty in log $K(T)$ due to uncertainties in ΔH^o_{298} and ΔS^o_T is ±0.3 at 298 K, ±0.1 at 1000 K.
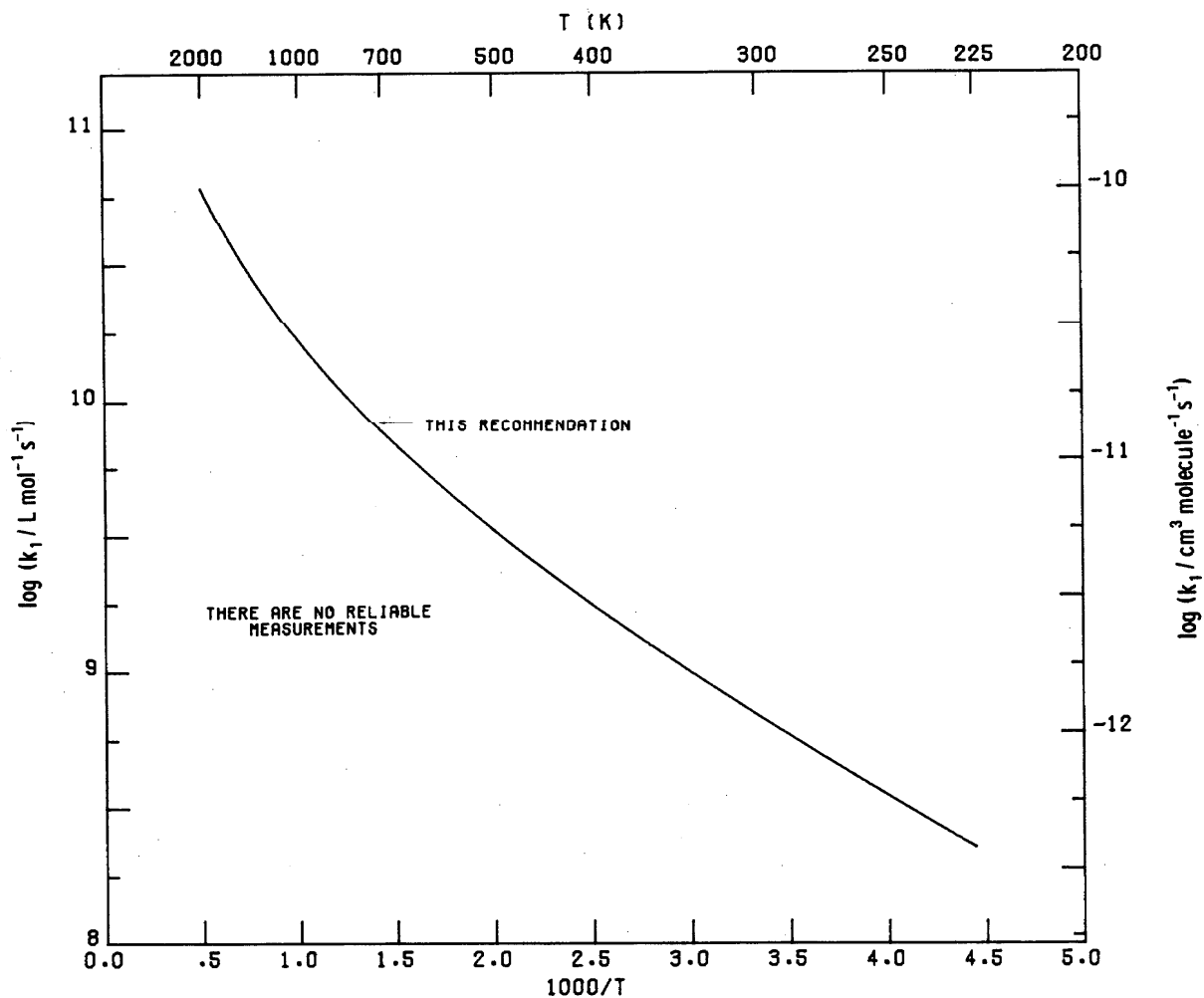
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.2 \times 10^6 \; T^{1.4} \exp(-667/T)$	225-2000 K	6.8×10^8	L mol^{-1}s^{-1}
	$3.7 \times 10^{-15} \; T^{1.4} \exp(-667/T)$		1.13×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-1}	see below			

Uncertainty in log k_1: $^{+0.35}_{-0.25}$ for $225 < T < 500$, increasing to ±0.45 at 2000 K. Below 2000 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow; however, the relation $k_1/k_{-1} = K(T)$ should still be valid.

(October 1982)

$D + F_2 \rightleftharpoons F + DF$
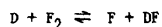
THERMOCHEMICAL DATA

Thermochemical data for D, F_2 and DF are taken from an unpublished supplements to the JANAF Thermochemical Tables (31 March 1977 and 30 June 1977); data for F are from the second edition of the JANAF Tables (1971). The enthalpy change for this reaction can also be calculated from the bond dissociation energies of F_2 and DF: $\Delta H_0^o = D_0^o(F_2) - D_0^o(DF) = D_0^o(F_2) - D_0^o(HF) - G_0(HF) + G_0(DF)$. From spectroscopic measurements, Douglas et al.[1,2] found $D_0^o(F_2) = 154.56 \pm 0.7$ and $D_0^o(HF) = 566.22 \pm 0.8$ kJ/mol. From data given in the JANAF Tables, we calculate the zero-point vibrational energies of HF and DF as $G_0(HF) = 24.49$ and $G_0(DF) = 17.80$ kJ/mol. These values give $\Delta H_0^o = -418.35 \pm 1.3$, in agreement with the JANAF recommendation, $\Delta H_0^o = -418.46$. The analytical expression chosen for K(T) matches equilibrium constants calculated from JANAF data to within 3% between 200 and 5000 K.

MEASUREMENTS

There are no published measurements of k_1.

CALCULATIONS

Reaction 1 occurs on the same potential-energy surface as Reaction 2, $H + F_2 \rightleftharpoons F + HF$. Bender et al.[3] and Eades et al.[4] have performed ab initio, quantum mechanical calculations of the shape of this surface. Some of their results are given on the Data Sheet for Reaction 2. Both sets of calculations predict $r(D-FF^\ddagger) = r(H-FF^\ddagger) = 1.7$ and $r(DF-F^\ddagger) = r(HF-F^\ddagger) = 1.5$ A. The results of Bender et al. give the stretching and bending wavenumbers of DDF‡ as $\bar{\omega}_s = 687$ cm^{-1} and $\bar{\omega}_b = 148$ cm^{-1}. The calculations of Eades et al. give $\bar{\omega}_s = 828$ and $\bar{\omega}_b = 206$ cm^{-1}.

We[5] have calculated k_1/k_2 over the temperature range 225-2000 K, using transition-state theory, the above data, and a rigid-rotor, harmonic-oscillator model for the activated complex. The calculations contain no adjustable parameters. If quantum-mechanical tunneling is neglected, k_1/k_2 decreases monotonically with increasing temperature, from 0.75 to 0.72 for the surface of Bender et al. and from 1.10 to 0.81 for the surface of Eades et al. An estimate for tunneling can be made by assuming the potential-energy surface along the reaction coordinate can be approximated by an Eckart potential with $\omega^\ddagger(HFF^\ddagger) = 392i$, $\omega^\ddagger(DFF^\ddagger) = 282i$, $E_c = 8.0$ kJ/mol for the surface of Bender et al., and $\omega^\ddagger(HFF^\ddagger) = 1277i$, $\omega^\ddagger(DFF^\ddagger) = 1032i$, $E_c = 7.4$ kJ/mol for the surface of Eades et al. (in each case, E_c is chosen so that $k_2(298) = 9 \times 10^8$ L mol^{-1}s^{-1}). With tunneling estimated in this way, k_1/k_2 varies from 0.64 to 0.72 for the surface of Bender et al. and from 0.76 to 0.80 for the surface of Eades et al.

DISCUSSION

We recommend $k_1/k_2 = 0.76$, 225 < T < 2000 K. This expression, combined with our recommendation for k_2, gives $k_1 = 2.2 \times 10^6$ $T^{1.4}$ exp(-667/T) L mol^{-1}s^{-1}. The uncertainty in k_1 is due primarily to the uncertainty in the measurements of k_2 rather than in the calculated values of k_1/k_2.

STATE SPECIFIC KINETICS

Reaction 1 is sufficiently exothermic to populate DF up to the 15th vibrational level, and the product distribution has been the subject of two experimental[6,7] and one theoretical investigation.[8] The more reliable of the two experiments[6] indicates that the v = 2 through the v = 12 levels are populated, with the maximum at v = 10. This is a broader distribution, and peaked higher, than the theoretical calculations, which predict direct formation only of v = 5 through 9, peaking at 8. The results are discussed further in Ref. 9.

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2. E. A. Colbourn, M. Dagenais, A. E. Douglas, and J. W. Raymonda, Can. J. Phys. 54, 1343 (1976).
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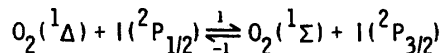9. N. Cohen and J. F. Bott, Review of Rate Data for Reactions of Interest in HF and DF Lasers, Aerospace Corp. Tech. Rept. TR-0082(2603)-2 (1982).

$$O_2(^1\Delta) + I(^2P_{1/2}) \underset{-1}{\overset{1}{\rightleftharpoons}} O_2(^1\Sigma) + I(^2P_{3/2})$$

ΔH^0_{298} = -28.13 ± 0.01 kJ mol^{-1} (-6.72 kcal mol^{-1}) ΔS^0_{298} = 0.17 J mol^{-1}K^{-1} (0.04 cal mol^{-1}K^{-1})

$$K(T) = 0.11 \ \exp(3380/T)$$

The uncertainty in log K is less than ± 0.1 throughout the temperature range.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	3 x 10^8 exp(-460/T)	250 - 400	6.5 x 10^7	L mol^{-1}s^{-1}
	5 x 10^{-13} exp(-460/T)		1.1 x 10^{-13}	cm^3 molecule^{-1}s^{-1}
k_{-1}	2.7 x 10^9 exp(-3840/T)	250 - 400	7.5 x 10^3	L mol^{-1}s^{-1}
	4.5 x 10^{-12} exp(-3840/T)		1.3 x 10^{-17}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 throughout range. Uncertainty in log k_{-1}: ± 0.3 throughout range. This uncertainty reflects those of both k_1 and K.

(September 1980)

$$O_2(^1\Delta) + I(^2P_{1/2}) \rightleftharpoons O_2(^1\Sigma) + I(^2P_{3/2})$$
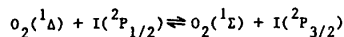
THERMOCHEMICAL DATA

Thermochemical and spectroscopic data for the two states of I atoms are taken from JANAF Thermochemical Tables, 2nd. Edn.; spectroscopic data for O_2 states are taken from Huber and Herzberg.[1] The analytic expression chosen for $K(T)$ matches equilibrium constants calculated with these data to within 2% between 200 and 6000K.

MEASUREMENTS

Two measurements of k_1 at room temperature have been published.[2,3] In both studies, $O_2(^1\Delta)$ and $I(^2P_{1/2})$ were produced in a flow system with a microwave discharge. $O_2(^1\Sigma)$ is produced by energy-pooling collisions involving either $O(^1\Delta)$ and $I(^2P_{1/2})$, reaction 1, or two $O_2(^1\Delta)$ molecules, $2O_2(^1\Delta) \rightleftharpoons O_2(^3\Sigma) + O_2(^1\Sigma)$. If the absolute concentrations of $I(^2P_{1/2})$ and $O_2(^1\Delta)$ are known, a steady state measurement of $[O_2(^1\Sigma)]/[O_2(^1\Sigma)]_o$ under suitably chosen conditions yields the ratio of k_1/k_2. Values of $k_1/k_2 = (1.5 \pm 0.2) \times 10^4$ and $(4.2 \pm 0.8) \times 10^3$ were obtained at 295 K in Refs. 2 and 3, respectively. k_2 has been measured independently by the same workers (see Data Sheet for that reaction). Reaction 1 has also been studied at other temperatures between 268 and 353 K; the results $(k_1/k_2 = (5.6 \pm 1) \times 10^3)$ indicate no measurable temperature dependence for the ratio of k_1/k_2, within experimental error[4].

DISCUSSION

The experimental studies of this reaction have been reviewed by Heidner,[5] on whose review this Data Sheet is largely based. There is no ready explanation for the difference of a factor of 3 between the results of Ref. 2 and the later studies. (This is the discrepancy after the value reported in Ref. 2 is corrected for a persistent typographical error of an order of magnitude.) This recommendation is based on Refs. 3 and 4. Using our recommended expression of $4.2 \times 10^{-7} T^{3.8} \exp(700/T)$ for k_2, we obtain values for k_1 that increase slightly with temperature, from 5.2×10^7 at 268 K to 7.9×10^7 at 353 K. The data are well fitted by $k_1 = 3 \times 10^8 \exp(-460/T)$, which we recommend over the temperature range of 250 - 400 K. Considering the uncertainties in both k_2 and k_1/k_2 the uncertainty in log k_1 is ± 0.2 throughout the range.

It is possible that another reaction takes place in parallel with reaction 1, namely $O_2(^1\Delta) + I^2P_{1/2}) \rightarrow O_2(^3\Sigma) + I(^2P_{3/2})$ — i.e., simultaneous quenching of both species. If only the disappearance of $O_2(^1\Delta)$ is monitored, the sum of $(k_1 + k_3)$ can be measured. This has been done,[3] but the uncertainties are too large to compare the results with those for k_1 and deduce an accurate value for k_3.

References

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2. R. G. Derwent and B. A. Thrush, Disc. Faraday Soc. 53, 162 (1972).
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5. R. F. Heidner, III, to be published.

$$O_2(^1\Delta) + O_2(^1\Delta) \underset{-1}{\overset{1}{\rightleftharpoons}} O_2(^1\Sigma) + O_2(^3\Sigma)$$

$\Delta H^0_{298} = -31.32$ kJ mol^{-1}(-7.49 kcal mol^{-1}) $\Delta S^0_{298} = -2.36 \pm 0.01$ J mol^{-1} K^{-1} (-0.56 cal mol^{-1} K^{-1})

$$K(T) = 0.74 \exp(3780/T)$$

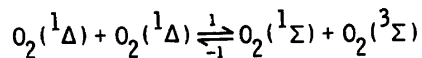The uncertainty in log K is less than ±0.1 throughout the temperature range.

SYMBOL	REF.
×	6
+	7 (25% O_2)
□	7 (46% O_2)
△	7 (100% O_2)
▽	8

THIS RECOMMENDATION
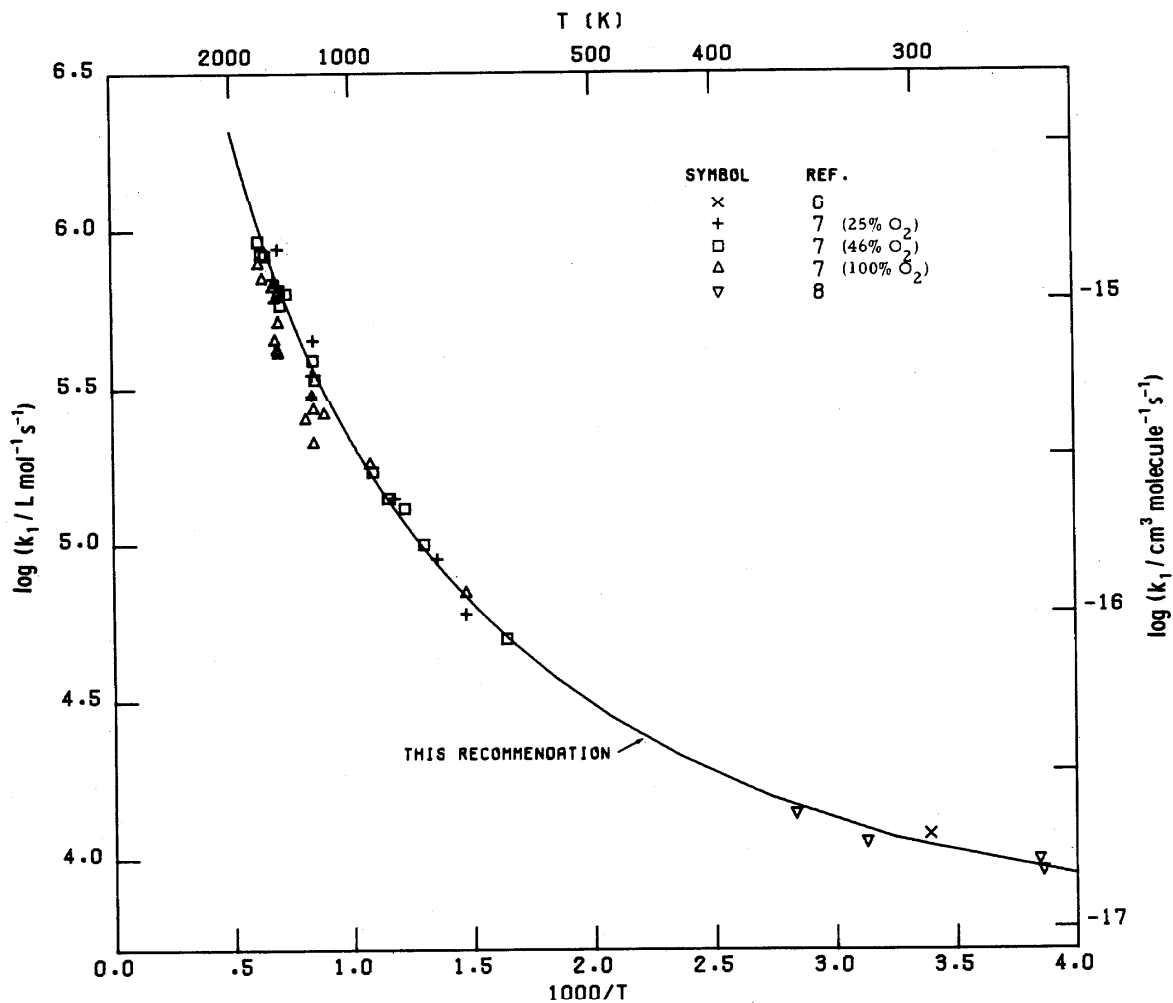
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	4.2×10^{-7} $T^{3.8}$ exp(700/T)	298 - 1650	1.1×10^4	L mol^{-1}s^{-1}
	$7.0 \times 10^{-28}T^{3.8}$ exp(700/T)		1.9×10^{-17}	cm^3 molecule^{-1}
k_{-1}	$5.7 \times 10^{-7}T^{3.8}$ exp(-3080/T)	298 - 1650	5.1×10^{-2}	L mol^{-1}s^{-1}
	$9.4 \times 10^{-28}T^{3.8}$ exp(-3080/T)		8.5×10^{-23}	cm^{3}molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 300 K, increasing to ±0.4 at 1500 K. The uncertainty in log k_{-1} is only slightly larger.

(September 1980)

$$O_2(^1\Delta) + O_2(^1\Delta) \rightleftharpoons O_2(^1\Sigma) + O_2(^3\Sigma)$$
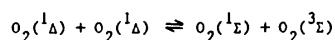
THERMOCHEMICAL DATA

Thermochemical data are calculated from spectroscopic data given by   Huber and Herzberg[1]. The analytic expression chosen for $K(T)$ matches equilibrium constants calculated with these data to within 2% between 250 and 6000 K.

MEASUREMENTS

Five room temperature studies measuring k_1 have been published,[2-6] all using a discharge flow system and differing principally in whether (a) disappearance of reagent or appearance of product was measured or (b) whether time-dependent or steady-state concentrations were measured. All but the last of these are flawed and the results are not shown on the graph. In the one reliable study, $O_2(^1\Delta)$ was produced by microwave discharge through pure O_2; O atoms were removed on an HgO surface. Both $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ were monitored spectroscopically, and the latter state, absolutely by isothermal calorimetry as well. A steady-state measurement of $[O_2(^1\Sigma)]/[O_2(^1\Delta)]^2$ gives the ratio of k_1 to the sum of all quenching processes for $O_2(^1\Sigma)$, which were measured separately in the same experiment. A value of $k_1 = (1.2 \pm 0.3) \times 10^4$ L mol^{-1}s^{-1} was reported. One high-temperature study of k_1 at 650 - 1650 K in a discharge flow/shock tube has also been reported;[7] this study obtained values for $k_1(T)/k_1(300)$ in either pure O_2 or O_2/N_2 mixtures, from which absolute values were calculated using the value of $k_1(300)$ from Ref. 6.

There was a distinct difference in results for pure O_2 and O_2/N_2 mixtures; the authors favored the latter results on the grounds that the emission intensity is considerably enhanced and therefore the measurements more sensitive. However, there is no explanation for the systematic difference between the two sets of data. The accompanying graph compares pure O_2 data with data for either 25% or 42% O_2. (72% and 90% O_2 data are not shown.) The values of $k_1(T)/k_1(300)$ require knowing the similar temperature ratios for all the quenching processes, as in the room temperature experiment; these are measured in the same experiments. Another series of measurements over the temperature range at 259 - 353 K has recently been published.[8] These results indicate very little temperature dependence throughout the latter range of experiments.

DISCUSSION

The experimental data have been reviewed by Heidner,[9] on whose work this Data Sheet and recommendation are based. It is Heidner's conclusion that the only reliable absolute measurement of k_1 is that of Ref. 6; thus an independent confirmation of this result is much to be desired. The high temperature measurements require a separate assessment of the quenching processes, for which independent experiments are also needed. This recommendation relies on Ref. 6 and a best fit through the O_2/N_2 data of Ref. 7, giving $k_1 = 4.2 \times 10^{-7}T^{3.8} \exp(700/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k_1 of $\pm$ 0.4 at 1500 K. This uncertainty reflects only the experimental scatter of Ref. 7, and not the possibility of systematic errors. Within experimental uncertainties, the results of Ref. 9 are consistent with this expression. One possible explanation for the strong non-Arrhenius behavior of k_1 would be the occurence of two parallel mechanisms, one involving long range interactions (weak temperature dependence), the other, repulsive short range interactions (strong temperature dependence at higher temperatures). This suggestion was made by Thomas and Thrush[10].

STATE-SPECIFIC KINETICS

Reaction 1 produces vibrationally excited $O_2(^1\Sigma)$; the relative production rates of v = 0, 1, and 2 have been reported in Ref. 11.

References

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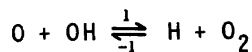9. R. F. Heidner III, to be published.
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11. U. Schurath, J. Photochem. 4, 215 (1975).

$$O + OH \underset{-1}{\overset{1}{\rightleftharpoons}} H + O_2$$

$\Delta H^{\circ}_{298} = -70.89 \pm 1.3 \text{ kJ mol}^{-1}$ (-16.94 kcal mol^{-1}) $\Delta S^{\circ}_{298} = -24.94 \pm 0.06 \text{ J mol}^{-1}\text{K}^{-1}$ (-5.96 cal mol$^{-1}\text{K}^{-1}$)

$$K(T) = 2.7 \times 10^{-3} T^{0.4} \exp(8720/T)$$

The uncertainty in log K(T) is ± 0.2 at 300 K, decreasing to ± 0.02 at 2500 K.
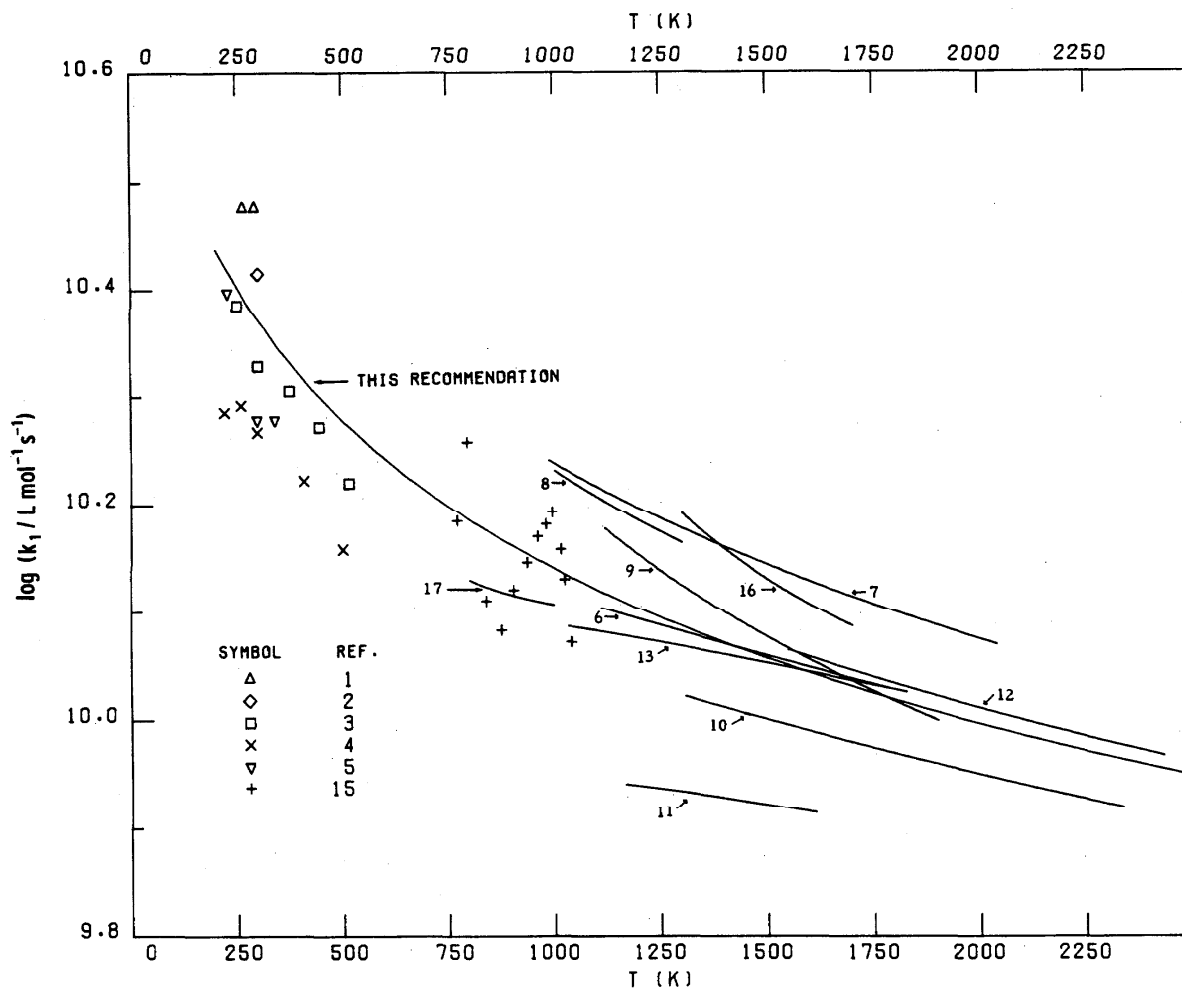
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$4.5 \times 10^{11} T^{-0.5} \exp(-30/T)$	200-2500 K	2.4×10^{10}	L mol^{-1}s^{-1}
	$7.5 \times 10^{-10} T^{-0.5} \exp(-30/T)$		3.9×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.67 \times 10^{14} T^{-0.9} \exp(-8750/T)$	300-2500 K		L mol^{-1}s^{-1}
	$2.77 \times 10^{-7} T^{-0.9} \exp(-8750/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.15 throughout range. Uncertainty in log k_{-1}: ± 0.12 at 1000 K and above, increasing to ± 0.3 at 300 K because of the increasing uncertainty in K(T). Below 300 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow; however, the relation $k_1/k_{-1} = K(T)$ should still be valid.

(June 1982)

$O + OH \rightleftharpoons H + O_2$
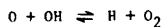
THERMOCHEMICAL DATA

Thermochemical data for all species were taken from unpublished supplements to the JANAF Thermochemical Tables dated 31 March 1977 and 30 June 1977. The analytical expression chosen for K(T) matches equilibrium constants calculated from these data to within 1% between 1000 and 5000 K and to within 4% between 275 and 1000 K.

MEASUREMENTS

The graph contains measurements of both k_1 and k_{-1}. All measurements below 515 K are measurements of k_1, all measurements above 770 K are measurements of k_{-1}, which are plotted as $K(T)k_{-1}$ where K(T) is the equilibrium constant.

There are five reliable measurements of k_1, each made by a somewhat different technique. Clyne and Thrush[1] and Breen and Glass[2] used the reaction of H with NO_2 to produce OH. Two reactions occur, $2OH \rightarrow O + H_2O$, $O + OH \rightarrow H + O_2$; k_1 is determined directly from an absolute measurement of [O] and a relative measurement of [OH]. Clyne and Thrush used chemiluminescence to measure [O]; Breen and Glass used ESR. Howard and Smith[3] produced O atoms by a discharge through O_2, and OH by flash photolysis of H_2O. In this system, O was in excess, and OH decay, measured by resonance fluorescence, gave a direct determination of k_1. Lewis and Watson[4] used a similar procedure except OH was produced by reaction of H with NO_2. The presence of large [H] led to complicating reactions involving H, HO_2, and O_2, which were taken into account by computer modeling. Westenberg et al.[5] produced H and O by passing H_2 and O_2 through a discharge; NO_2 converted H to OH; [H], [O], and [OH] were monitored by ESR. The results of these five sets of measurements are in fairly good agreement at 298 K , all giving, to within 25%, $k_1 = 2.4 \times 10^{10}$ L $mol^{-1}s^{-1}$.

The most precise determinations of k_{-1} have been made by shock heating mixtures of $H_2/O_2/Ar$ and measuring the exponential growth of [O], [OH], [H], or [H_2O] behind the shock front. These measurements[6-13] were recently reanalyzed,[14] with the sensitivity of each measurement to k_{-1} being determined. The lines plotted on the graph are a weighted least-squares fit to the reanalyzed values of k_{-1}. Reaction -1 has also been studied in flames or by measuring explosion limits. Results from the most carefully analyzed flame[15,16] and explosion-limit[17] studies are plotted on the graph; they agree with the shock tube results.

The experimental data for reactions 1 and -1 have been reviewed by Baulch et al.[18,19] and by Dixon-Lewis and Williams[20] wherein, except for four recent studies,[21] references can be found for measurements not used in this evaluation.

CALCULATIONS

Reaction 1 occurs over a potential-energy well inasmuch as HOO is a stable species. As suggested by Benson,[22] reaction is assumed to occur for all trajectories that pass over the so-called "centrifugal barrier." The HO-O bond length at the top of the barrier is calculated as in Ref. 22 (p. 89, Eq. 3.23, $D_0 = 264$ kJ/mol). Below 300 K, the HO-O bond is so long that the OH moiety can rotate unhindered in any direction, which implies that reaction should occur every collision. The gas-kinetic rate coefficient, corrected for electronic degeneracies, is 2.4×10^{10} L $mol^{-1}s^{-1}$ at 298 K, 2.5×10^{10} at 250 K, and 2.7×10^{10} at 200 K. Probably the best measurement[3] of k_1 at 298 K is $(2.3 \pm 0.5) \times 10^{10}$. The agreement with calculation is better than expected. Miller[23] has calculated k_{-1} using classical trajectory methods, obtaining results that agree with the high-temperature experiments.

DISCUSSION

Our recommendations [$k_1 = 4.5 \times 10^{11}$ $T^{-0.5}$ exp(-30/T), $k_{-1} = 1.67 \times 10^{14}$ $T^{-0.9}$ exp(-8750/T), $k_1/k_{-1} = K(T)$] are based on experiment, the results of Refs. 1, 2, 3, 6, and 12 being given the greatest weight. These recommendations are probably accurate to within ± 30% inasmuch as measurements made by several different techniques agree with each other and with theoretical calculations.

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$$H + OH \underset{-1}{\overset{1}{\rightleftharpoons}} O + H_2$$

$\Delta H^o_{298} = -8.54 \pm 1.3$ kJ mol^{-1}(-2.04 kcal mol^{-1}) $\qquad\qquad$ $\Delta S^o_{298} = -6.72 \pm 0.06$ J mol^{-1}K^{-1}(-1.61 cal mol^{-1}K^{-1})

$$K(T) = 0.445 \exp(1030/T)$$

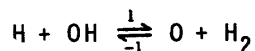The uncertainty in log K is ±0.2 at 298 K, decreasing to ±0.06 at 1000 K and ±0.02 at 5000 K.
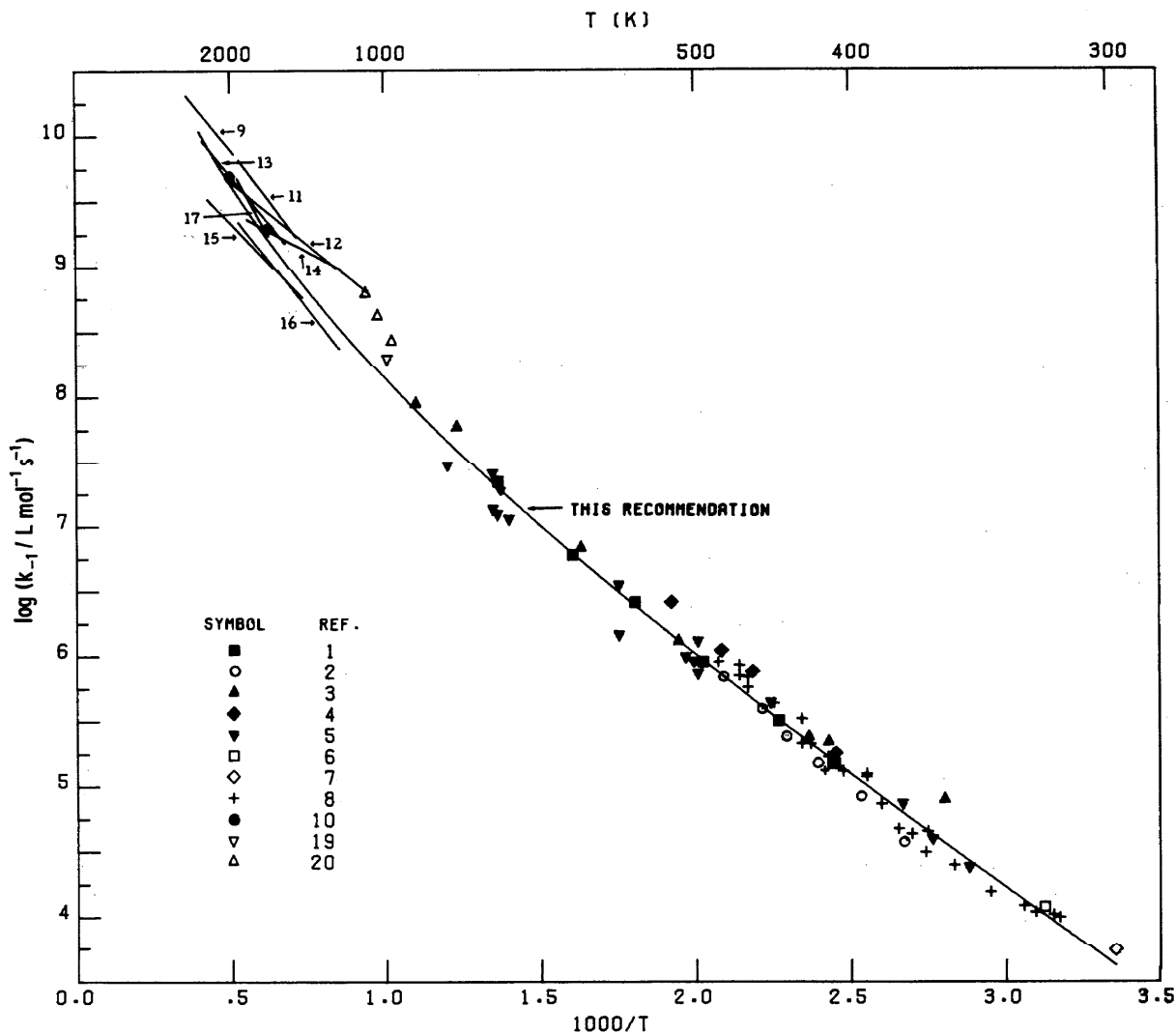
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$4.9\ T^{2.8}\exp(-1950/T)$	298-2500 K	6×10^4	L mol^{-1}s^{-1}
	$8.1 \times 10^{-21}\ T^{2.8}\exp(-1950/T)$		1.0×10^{-16}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$1.1 \times 10^1\ T^{2.8}\exp(-2980/T)$	298-2500 K	4.2×10^3	L mol^{-1}s^{-1}
	$1.8 \times 10^{-20}\ T^{2.8}\exp(-2980/T)$		7×10^{-18}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_{-1}: ±0.2, 350-900 K, increasing to ±0.3 at 298 K and at 1600 K and above. Uncertainty in log k: ±0.3, 400-2500 K, increasing to ± 0.35 at 298 K. k_1 is calculated from k_{-1} and K(T); its uncertainty reflects the uncertainties in both of those quantities.

(December 1982)

$H + OH \rightleftharpoons O + H_2$

THERMOCHEMICAL DATA

Thermochemical data are taken from unpublished supplements to the JANAF Tables dated 31 March 1977 and 30 June 1977. The analytic expression chosen for $K(T)$ matches equilibrium constants calculated from these data to within 1% between 250 and 5000 K.

MEASUREMENTS

There are numerous measurements of k_{-1}, but none of k_1. The most precise determinations of k_{-1} were made in flow tubes between 347 and 910 K. In these studies[1-5] atomic oxygen was produced in a discharge and its rate of removal by reaction -1 was measured by ESR, resonance fluorescence, or chemiluminescence. As shown on the graph, the results are in good agreement.

At lower temperatures, k_{-1} has been determined less precisely. Used in this evaluation are results from two flow tube experiments[6,7] (at 298 and 320 K) and results from a stirred flow reactor[8] (315-490 K).

All high temperature (T > 910 K) determinations of k_{-1} are strongly dependent on rate coefficients of other reactions. Only determinations dependent on the well-established rate coefficient for $N_2O + Ar \overset{2}{\rightleftharpoons} N_2 + O + Ar$ or for $H + O_2 \overset{3}{\rightleftharpoons} O + OH$ are used in the evaluation. Pamidimukkala and Skinner[9] and Frank and Just[10] shock heated mixtures of $N_2O/H_2/Ar$ and determined k_{-1} using $k_2 = 5 \times 10^{11} \exp(-6930/T)$ L $mol^{-1}s^{-1}$ or a nearly equivalent expression. These results are plotted on the graph without reanalysis. Schott et al.[11] deduced $k_{-1}/k_3 \sim 3.6$, 1400 < T < 1900 K, from $[O]_{max}$ behind $H_2/O_2/Ar$ shocks; the expression for k_{-1} plotted on the graph is determined using our recommended value for k_3: $k_3 = 1.67 \times 10^{14} T^{-0.9} \exp(-8750/T)$. There have been several studies[12-17] in which $H_2/O_2/Ar$ mixtures were shock heated and the exponential growth in $[O]$, $[OH]$, or $[H_2O]$ behind the shock front measured. These measurements have recently been reanalyzed[18] with our recommended value for k_3, the sensitivity of each measurement to k_{-1} being determined. The lines plotted on the graph are a weighted least-squares fit to the reanalyzed data. Also included on the graph are our recommended values of k_3 multiplied by k_{-1}/k_3 determined from a pair[19,20] of combustion studies (978 < T < 1067). These determinations of k_{-1}/k_3 are probably uncertain by a factor of 2. Similar determinations at lower temperatures are not shown since better data are available.

Reaction -1 was reviewed by Baulch et al.[21] wherein, except for two recent studies,[22,23] can be found references to papers not used in this evaluation.

CALCULATIONS

Walch et al.[24] have performed ab initio calculations of the shape of the potential energy surface over which reaction -1 occurs. We have used this surface, transition-state theory, and the transmission coefficients calculated by Lee et al.[25] to calculate values for k_{-1}. The barrier height of the reaction was chosen so that the calculated value of k_{-1} at 400 K is 1.2×10^5 L $mol^{-1}s^{-1}$. The bending motion of the activated complex was treated as a two dimensional anharmonic oscillator. Depending on the transmission coefficient used, the calculations yielded $k_{-1} \sim 1.4 \times 10^3 T^{2.2} \exp(-3460/T)$ or $k_{-1} \sim 2.2 \times 10^3 T^{2.1} \exp(-3415/T)$ 300 < T < 2000 K. Both expressions are in fairly good agreement with experiment between 300 and 1000 K but are somewhat lower than the most reliable experimental data at higher temperatures.

DISCUSSION

Based on the experimental data, we recommend $k_{-1} = 11.0 T^{2.8} \exp(-2980/T)$, 298 < T < 2500 K. Below 350 K and above 900 K, the uncertainty and scatter in the data as well as its disagreement with calculation make the recommendation uncertain by as much as a factor of 2. Above 1000 K, the expression $k_{-1} = 7 \times 10^{10} \exp(-5400/T)$ better describes the data.

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$$OH + H_2 \underset{-1}{\overset{1}{\rightleftharpoons}} H + H_2O$$
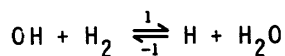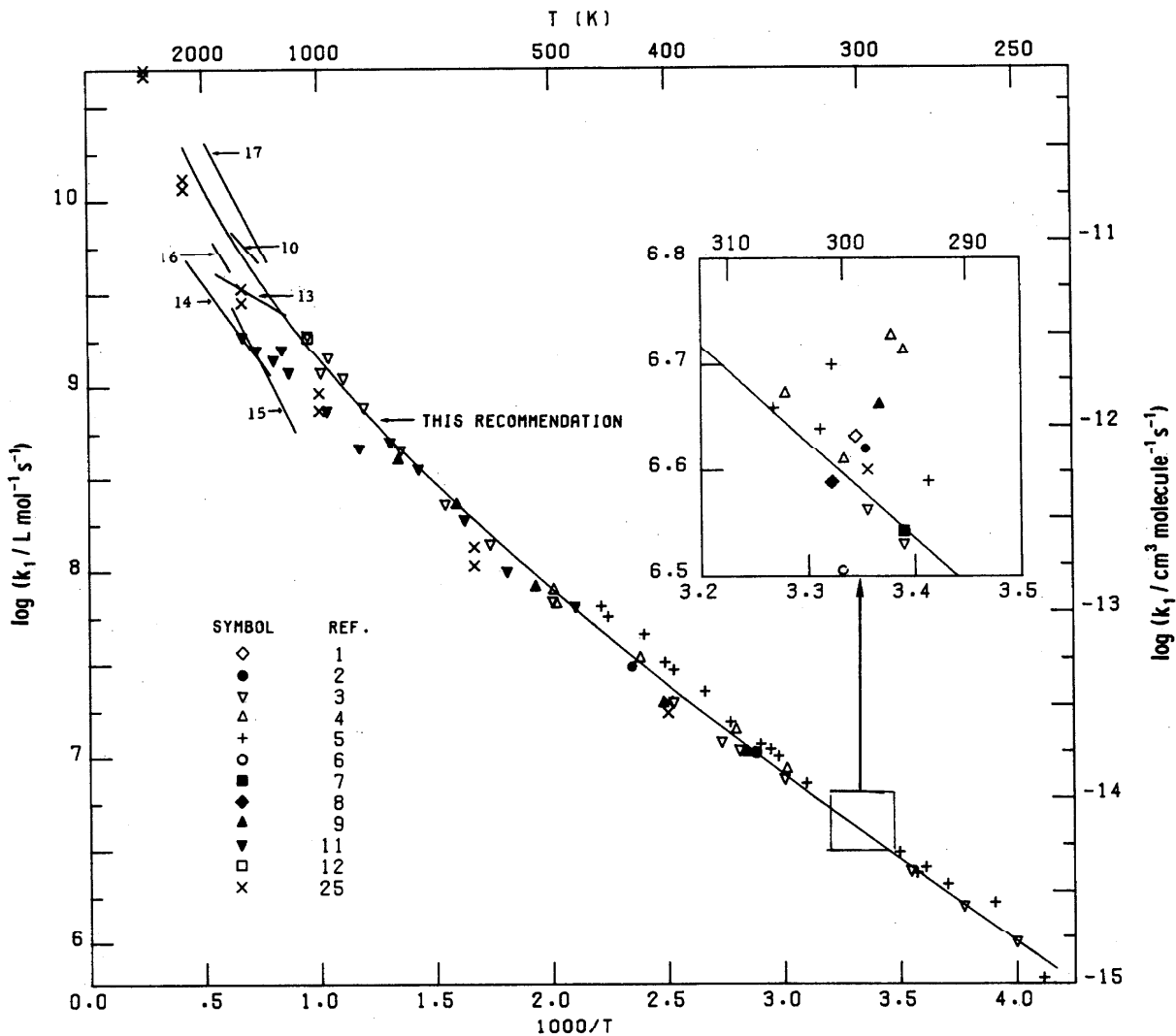
$\Delta H^o_{298} = -63.54 \pm 1.3$ kJ mol^{-1} (-15.19 kcal mol^{-1}) $\Delta S^o_{298} = -10.87 \pm 0.06$ J mol^{-1}K^{-1} (-2.60 cal mol^{-1}K^{-1})

$$K(T) = 0.102 \ T^{0.1} \ \exp(7775/T)$$

The uncertainty in log K(T) is ±0.2 at 300 K, decreasing to ±0.08 at 1000 K and to ±0.03 at 4000 K.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$6.3 \times 10^3 \ T^2 \ \exp(-1490/T)$	240-2400 K	3.8×10^6	L mol^{-1}s^{-1}
	$1.06 \times 10^{-17} \ T^2 \ \exp(-1490/T)$		6.3×10^{-15}	cm^{3}molecule^{-1}s^{-1}
k_{-1}	$6.2 \times 10^4 \ T^{1.9} \ \exp(-9265/T)$	400-2400 K		L mol^{-1}s^{-1}
	$1.03 \times 10^{-16} \ T^{1.9} \ \exp(-9265/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.05 at 300 K, increasing to ±0.15 at 250 and 1000 K; and to ±0.3 at 2000 K and ±0.4 at 2400 K.
Uncertainty in log k_{-1}: ±0.3 at 400 K increasing to ±0.4 at 2400 K. Below 400 K, k_{-1} is less than 1 L mol^{-1}s^{-1} and Reaction -1 is immeasurably slow; however, the relation k_1/k_{-1} = K(T) should still be valid.

(December 1982)

$OH + H_2 \rightleftharpoons H + H_2O$
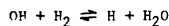
THERMOCHEMICAL DATA

Thermochemical data for H, H_2 and OH are taken from unpublished supplements to the JANAF Thermochemical Tables (31 March 1977 and 30 June 1977); data for H_2O are from the second edition of the JANAF Tables (1971). The analytical expression chosen for K(T) agrees with equilibrium constants calculated from these data to within 5 percent between 298 and 5000 K.

MEASUREMENTS

Between 246 and 1050 K, k_1 has been measured directly by three different techniques: flash-photolysis, resonance-fluorescence,[1-3] flash-photolysis, ultraviolet-absorption,[4-7] and discharge-flow, ESR spectroscopy.[8,9] The results of these measurements are plotted on the graph. For the most part, they are in good agreement; at 298 K, all measurements give $k_1 \approx 4 \pm 1 \times 10^6$ L mol^{-1} s^{-1}. There are, in addition, numerous indirect determinations of k_1, derived by analysis of a complex system with substantial corrections for competing reactions. These determinations were not used to evaluate k_1 between 246 and 1050 K.

At temperatures greater than 1050 K, there are no direct measurements of k_1, only indirect ones. Plotted on the graph are those high-temperature determinations of k_1 that appear to be most accurate.[10-18] Gardiner et al.[10] determined k_1 from a measurement of $[OH]_{max}$ behind $H_2/O_2/Ar$ shocks. Eberius et al.[11] determined k_1 from measurements of $[H_2]$, $[O_2]$, $[H_2O]$, $[H]$, and $[OH]$ in low-pressure H_2/O_2 flames. Dixon-Lewis et al.[12] determined k_1 from numerous measurements in atmospheric-pressure $H_2/N_2/O_2$ flames. Jackimowski and Houghton,[13] Getzinger et al.,[14] Brabbs et al.,[15] Schott,[16] and Pamidimukkala and Skinner[17] measured the exponential growth of [O], [OH], or $[H_2O]$ behind $H_2/O_2/Ar$ shocks; these measurements were reanalyzed[18] to give values for the product k_1k_2 where k_2 is the rate coefficient of the reaction $O + H_2 \rightarrow H + OH$. A sensitivity analysis of each measurement gave an uncertainty to each determination of k_1k_2; the lines plotted on the graph were calculated from a weighted least-squares fit to the data and our recommended value for k_2.

The experimental data for this reaction have been reviewed and evaluated by Baulch et al.[19,20] and by Dixon-Lewis and Williams[12] wherein, except for two recent studies,[21,22] references can be found for measurements of k_1 not used in this evaluation. There is only one study[23] reporting absolute measurements of k_{-1}; its results are not used in this evaluation.

CALCULATIONS

Walch and Dunning[24] have performed ab initio calculations of the shape of the potential-energy surface over which Reaction 1 occurs. Isaacson and Truhlar[25] calculated k_1 using this potential-energy surface, variational transition-state theory, and two different models for quantum mechanical tunneling. We have modified their calculations by multiplying each calculated value of k_1 by $exp(-\Delta E_c/RT)$, where ΔE_c is chosen to make calculation and experiment agree at 298 K. This modification is equivalent to changing the barrier height by an amount ΔE_c. Depending on the model Isaacson and Truhlar used for tunneling, ΔE_c is +1.1 or -1.7 kJ/mol, which is smaller than the uncertainty in the calculated barrier height. The modified calculations are plotted on the graph; for each temperature, two points are plotted, corresponding to the two different models for tunneling.

DISCUSSION

We recommend $k_1 = 6.3 \times 10^3$ T^2 $exp(-1490/T)$ L $mol^{-1}s^{-1}$, $240 < T < 2400$ K. The recommendation is based heavily, but not exclusively, on the measurements of Ravishankara et al.[3] and Gardiner et al.[10] No recommendation is made for T < 240 K, because both calculation[25] and experiment[5] are approximate.

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$$OH + OH \overset{1}{\underset{-1}{\rightleftharpoons}} O + H_2O$$

$\Delta H^o_{298} = -72.08 \pm 2.5$ kJ mol^{-1} (-17.23 kcal mol^{-1})　　　　　$\Delta S^o_{298} = 17.60 \pm 0.06$ J mol^{-1}K^{-1} (-4.21 cal mol^{-1}K^{-1})

$$K(T) = 4.54 \times 10^{-2} T^{0.1} \exp(8805/T)$$

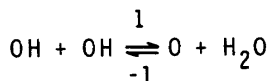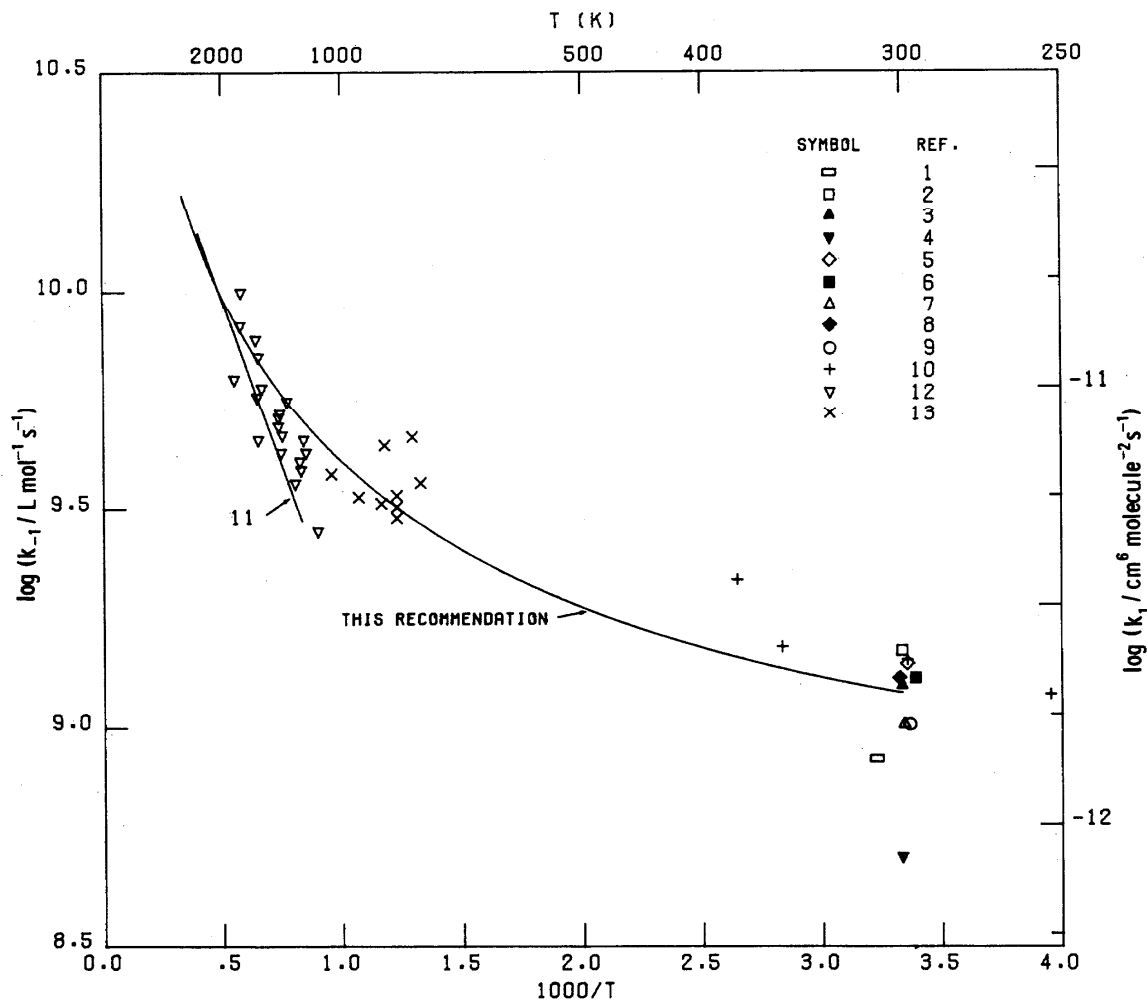The uncertainty in log K(T) is ±0.3 at 298 K, decreasing to ±0.1 at 1000 K and ±0.05 at 5000 K.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$2.1 \times 10^5 \ T^{1.4} \exp(200/T)$	300-2000 K	1.2×10^9	L mol^{-1}s^{-1}
	$3.5 \times 10^{-16} \ T^{1.4} \exp(200/T)$		2.0×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$4.6 \times 10^6 \ T^{1.3} \exp(-8605/T)$	400-2000 K		L mol^{-1}s^{-1}
	$7.6 \times 10^{-15} \ T^{1.3} \exp(-8605/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 300 K increasing to ±0.3 at 2000 K.　Uncertainty in log k_{-1}: ±0.4 throughout this range.　k_{-1} is calculated from k_1 and K(T); its uncertainty reflects the uncertainties in both of those quantities.

(October 1982)
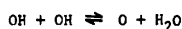
N. COHEN AND K. R. WESTBERG

$OH + OH \rightleftharpoons O + H_2O$

THERMOCHEMICAL DATA

Thermochemical data for H_2O are taken from the second edition of the JANAF Thermochemical Tables (1971); data for O and OH are taken from unpublished supplements to the JANAF Tables dated March 1977 and June 1977, respectively. The analytical expression chosen for K(T) matches equilibrium constants calculated from these data to within 6% over the temperature range of 298-5000 K.

MEASUREMENTS

There have been 10 good measurements of k_1 at or near room temperature[1-10], all but one of which agree on a value of $1.2 \pm 0.3 \times 10^9$ L $mol^{-1}s^{-1}$; the discordant result is lower by a factor of about 2. There have been two shock tube studies [11-12] in the 1000-2000 K temperature range; in addition one shock tube study of the reverse reaction has been reported[13] that covers the temperature range of 750-1050 K. Some earlier, discarded measurements are discussed in more detail in reviews by Baulch et al.[14], Wilson,[15] and Dixon-Lewis and Williams.[16]
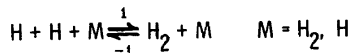
CALCULATIONS

A transition-state-theory calculation was made for k_1 assuming a bent configuration for O...H...O, with the other H atom out of the plane and treated as a hindered internal rotor (1 kcal/mol barrier to internal rotation). The vibrational frequencies of the TS were estimated, using the methods of Benson[17], to be 3700, 1500, 1000, and 500 cm^{-1}. It was further assumed that the TS is an electronic triplet state. The barrier height to reaction was chosen to give agreement with experimental data at 300 K (log k(300) = 9.08). These assumptions yield for k_1 the expression $2.1 \times 10^5 T^{1.4} \exp(200/T)$ L $mol^{-1}s^{-1}$. This expression agrees with experimental data within 25%. A slightly different TST calculation was described in Ref. 10; similar results (within a factor of 2) were reported.

DISCUSSION

All the room temperature measurements except for Ref. 4 are in good agreement on the value of k_1 within 25%. Possible reasons for the lower value of Ref. 4 have been discussed in detail in Ref. 6. Hence we base our recommendation in part on a value of 1.2×10^9 at 300 K. The two shock tube studies[11,12] are essentially in accord with one another, although the former is based on computer simulations and the latter gives insufficient details to evaluate the work critically. These studies suggest a much stronger temperature dependence in the 1000-2000 K range than earlier reviews proposed (e.g., see Ref. 14, p. 120). The single study of the reverse reaction is consistent with the other data. The calculated expression for k_1 described above is in very good agreement with the experimental data; however, it suggests a smaller temperature dependence in the 1500-2000 K regime than Refs. 11 and 12 determined. Since the absolute disagreement is very small, we recommend the rate expression calculated from theory, namely $k_1 = 2.1 \times 10^5 T^{1.4} \exp (200/T)$ 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.

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$$H + H + M \underset{-1}{\overset{1}{\rightleftharpoons}} H_2 + M \qquad M = H_2, H$$

$\Delta H^O_{298} = -436.00 \pm 0.01$ kJ mol^{-1} (-104.206 kcal mol^{-1}) $\Delta S^O_{298} = -98.645 \pm 0.035$ J mol^{-1}K^{-1} (-23.58 cal mol^{-1}K^{-1})

$$K(T) = 1.18 \times 10^{-4}T^{0.1} \exp(52530/T) \text{ L mol}^{-1} - 1.96 \times 10^{-25}T^{0.1} \exp(52530/T) \text{ cm}^3 \text{ molecule}^{-1}$$

The uncertainty in log K(T) is ±0.03 for 600 < T < 6000 K. This uncertainty is primarily due to the imprecision of the chosen analytic expression; the uncertainty due to uncertainties in ΔH^O_{298} and ΔS^O_T is probably not greater than ±0.005.
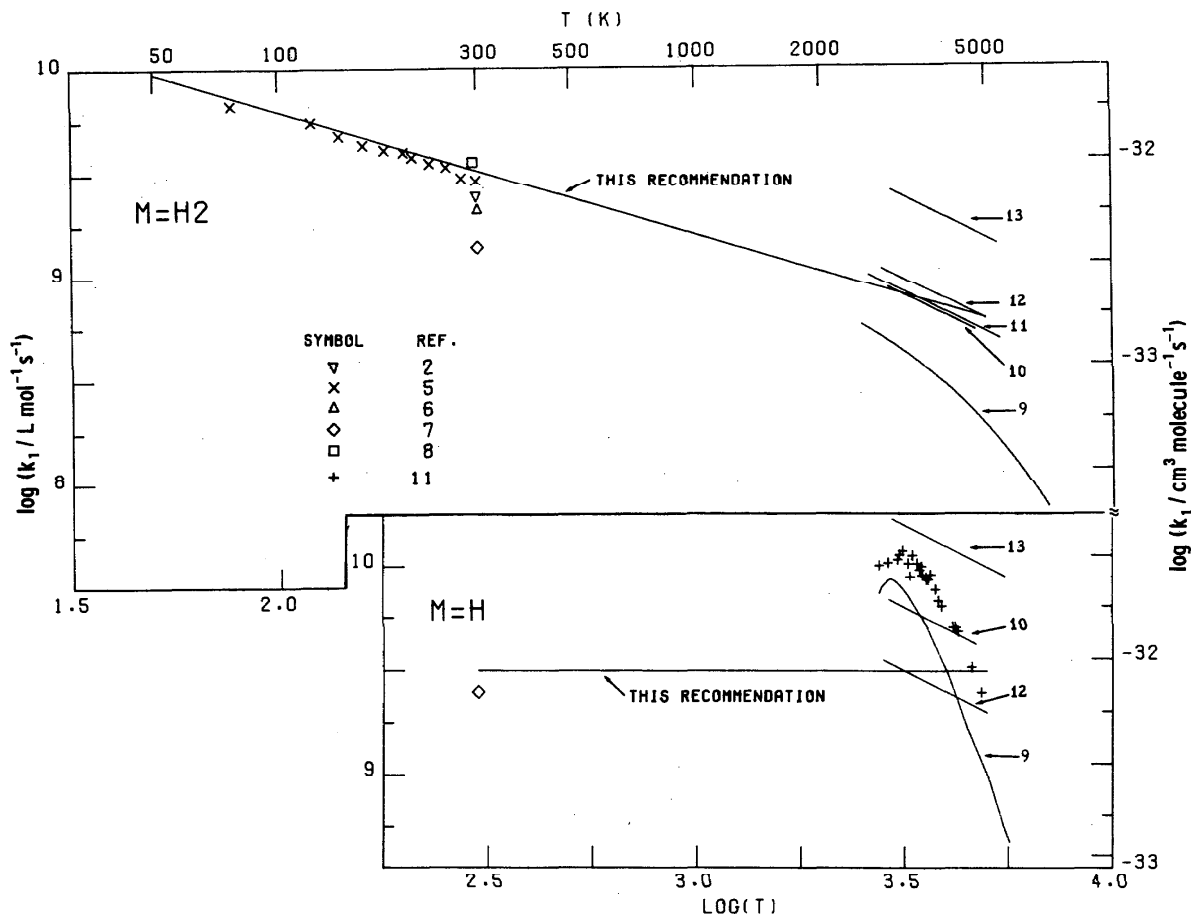
RECOMMENDED RATE COEFFICIENTS

k,M	k(T)	Range	k(298)	Units
$k_1(H_2)$	$1.0 \times 10^{11}T^{-0.6}$	50-5000 K	3.3×10^9	L^2 mol^{-2}s^{-1}
	$2.8 \times 10^{-31}T^{-0.6}$		9.0×10^{-33}	cm^6 molecule^{-2}s^{-1}
$k_1(H)$	3.2×10^9	50-5000 K	3.2×10^9	L^2 mol^{-2}s^{-1}
	8.8×10^{-33}		8.8×10^{-33}	cm^6 molecule^{-2}s^{-1}
$k_{-1}(H_2)$	$8.47 \times 10^{14}T^{-0.7} \exp(-52530/T)$	600-5000 K		L mol^{-1}s^{-1}
	$1.43 \times 10^{-6}T^{-0.7} \exp(-52530/T)$			cm^3 molecule^{-1}s^{-1}
$k_{-1}(H)$	$2.71 \times 10^{13}T^{-0.1} \exp(-52530/T)$	600-5000 K		L mol^{-1}s^{-1}
	$4.49 \times 10^{-8}T^{-0.1} \exp(-52530/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log $k_1(H_2)$ and log $k_{-1}(H_2)$: ±0.2 at T < 300 K, increasing to ±0.4 at T = 5000 K. Uncertainty in log $k_1(H)$ and log $k_{-1}(H)$: ±0.5 throughout range.

(October 1979)
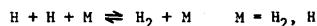
$$H + H + M \rightleftharpoons H_2 + M \qquad M = H_2, H$$

THERMOCHEMICAL DATA

Thermochemical data for both H and H_2 were taken from an unpublished supplement (31 March 1977) to the JANAF Thermochemical Tables. The analytical expression chosen for K(T) matches the equilibrium constants calculated from JANAF data to within 6% between 600 and 6000 K.

MEASUREMENTS

Over 50 separate studies of hydrogen recombination/dissociation published prior to 1972 were reviewed by Baulch et al;[1] three additional studies have since been reported.[2-4] The experiments fall into four categories: discharge-flow studies at low temperatures (77-300 K);[2-8] flame studies at intermediate temperatures (1000-2000 K); and shock tube or nozzle expansion studies at high temperatures (1700-7000 K).[9-14] The early discharge-flow studies (prior to 1960) have been discarded, mainly for reasons discussed in Refs. 1, 5, and 7. The flame studies, conducted in H_2/O_2/diluent systems, are, in retrospect, chemically too complex to afford precise rate coefficient data and have been discarded in this evaluation. The nozzle expansion studies have been neglected because of fluid dynamic complications still not thoroughly understood.

The flow tube studies all monitored H disappearance and measured k_1 directly; most of the shock tube studies observed the dissociation of H_2 and hence measured k_{-1}; their results are reported as k_1 by the relation, $k_1 = k_{-1}K(T)$.

CALCULATIONS

Theoretical calculations for recombination with $M = H_2$ have been reported; however, the experimental data seem sufficient for making recommendations over a wide temperature range with reasonable confidence. Of greater interest are calculations by Shui[16] for $M = H$, for which data are ambiguous. Shui's results over the temperature range of 300-5000 K can be expressed within 20% by $k_1(H) = 10^{10.8}T^{-0.35} L^2 mol^{-2}s^{-1}$ (his calculated result at 10,000 K falls considerably below this expression when extrapolated). For more recent calculations for various M, see Refs. 16 (and the papers cited therein) and 17.
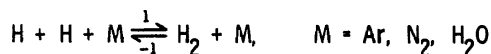
DISCUSSION

As the accompanying graph shows, the low temperature (77-300 K) data for $M = H_2$ are in reasonable agreement and suggest a temperature dependence of $T^{-0.6}$ for $k_1(H_2)$. The high temperature shock tube data show considerably more spread—exceeding a factor of five at some temperatures. Except for Ref. 9, which reports considerably steeper temperature dependences (the validity of which has been questioned[15]), the shock tube studies all report T^{-1} dependences, but in most cases this relation is assumed, not deduced directly from the data. The recommendation of Ref. 1 is based principally on Ref. 11 for $M = H_2$, and we see no reason to favor an alternative in the high temperature regime. Our recommendation is based principally on Refs. 2, 3, 5, and 11; a two-parameter expression is chosen, namely $k_1(H_2) = 10^{11}T^{-0.6}$, because the precision of the data does not seem to justify anything more elaborate.

The data for $M = H$ are considerably more uncertain, with only one useful low temperature measurement,[7] and that an upper limit only. For reasons outlined in Ref. 5, this result may well be low by a factor of 2-3.

The shock tube results show considerable scatter, a result of the fact that $k_1(H)$ must be extracted from systems in which $k_1(H_2)$ and $k_1(M)$ (with M usually Ar) dominate. Both experimental and theoretical indications are that $k_1(H)$ is considerably larger than $k_1(H_2)$—possibly by as much as an order of magnitude, but even at that extreme the practical significance of the reaction is certain to be small, since in all systems of practical interest $[H_2] > 10[H]$. Any recommendation made at this time for $k_1(H)$ must have an uncertainty of at least ± 0.4 in log $k_1(H)$ at $T \sim 2000$ K, and larger yet at lower T. Hence, while the data suggest that $k_1(H)$ passes through a maximum at some intermediate T, nothing more elaborate than a constant value of log $k_1(H) = 9.5 \pm 0.5$ throughout the full temperature range seems justified at present. The theoretical results of Ref. 15 fall within this range of values for 300 < T < 5000 K.

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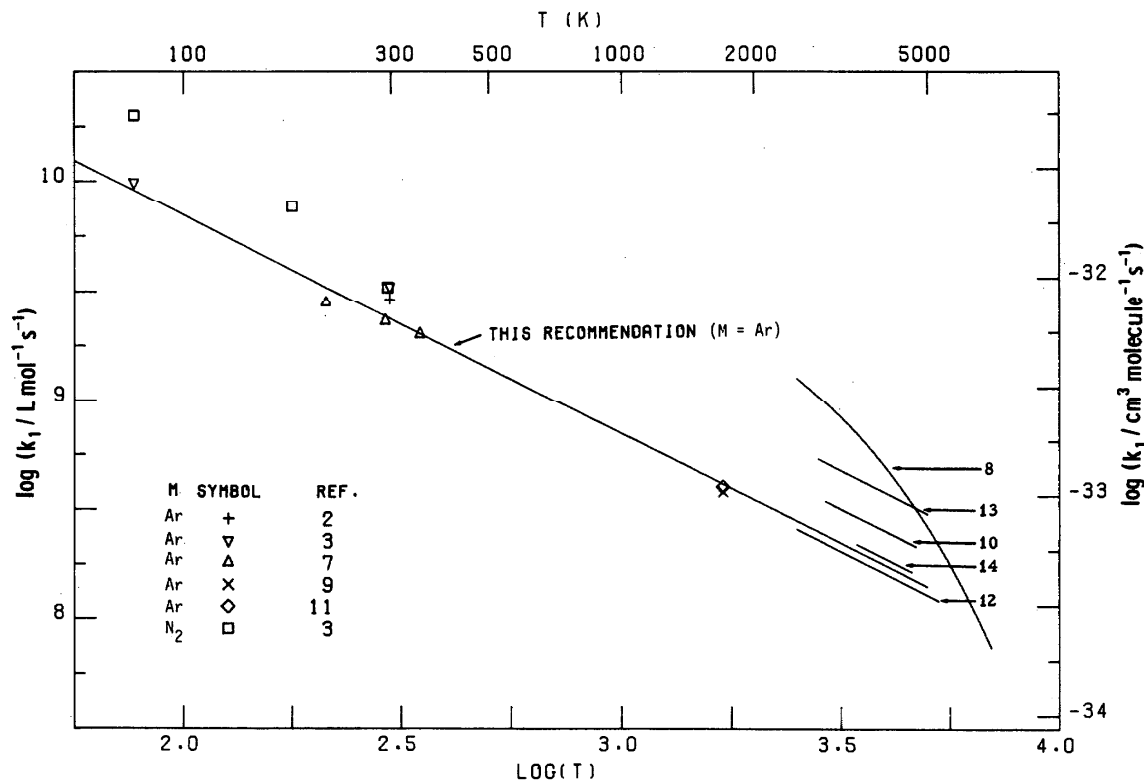18. A. A. Levitskii and L. S. Polak, High Energy Chem. 12, 291 (1978) [p. 245 in English edn.].

$$H + H + M \underset{-1}{\overset{1}{\rightleftharpoons}} H_2 + M, \qquad M = Ar, N_2, H_2O$$

$\Delta H^o_{298} = -436.00 \pm 0.01 \text{ kJ mol}^{-1}$ (-104.206 kcal mol^{-1}) $\Delta S^o_{298} = -98.645 \pm 0.035 \text{ J mol}^{-1}K^{-1}$ (-23.58 cal mol$^{-1}K^{-1}$)

$$K(T) = 1.18 \times 10^{-4} \ T^{0.1} \ \exp(52530/T) \ \text{L mol}^{-1} = 1.96 \times 10^{-25} \ T^{0.1} \ \exp(52530/T) \ \text{cm}^3 \ \text{molecule}^{-1}$$

The uncertainty in log K(T) is ±0.03 for 600 < T < 6000 K. This uncertainty is primarily due to the imprecision of the chosen analytic expression; the uncertainty due to uncertainties in ΔH^o_{298} and ΔS^o_T is probably not greater than ±0.005.

M	SYMBOL	REF.
Ar	+	2
Ar	▽	3
Ar	△	7
Ar	×	9
Ar	◇	11
N₂	□	3

RECOMMENDED RATE COEFFICIENTS

k(M)	k(T)	Range	k(298)	Units
$k_1(Ar)$	$7.0 \times 10^{11} \ T^{-1}$	77-5000	2.3×10^9	$L^2 \ mol^{-2}s^{-1}$
	$1.9 \times 10^{-30} \ T^{-1}$		6.4×10^{-33}	$cm^6 \ molecule^{-2}s^{-1}$
$k_1(N_2)$	$5.4 \times 10^{12} \ T^{-1.3}$	77-2000	3.2×10^9	$L^2 \ mol^{-2}s^{-1}$
	$1.5 \times 10^{-29} \ T^{-1.3}$		9.0×10^{-33}	$cm^6 \ molecule^{-2}s^{-1}$
$k_1(H_2O)$	$1.0 \times 10^{13} \ T^{-1}$	300-2000	3.3×10^{10}	$L^2 \ mol^{-2}s^{-1}$
	$2.8 \times 10^{-29} \ T^{-1}$		9.2×10^{-32}	$cm^6 \ molecule^{-2}s^{-1}$
$k_{-1}(Ar)$	$5.93 \times 10^{15} \ T^{-1.1} \ \exp(-52530/T)$	600-5000		$L \ mol^{-1}s^{-1}$
	$9.69 \times 10^{-6} \ T^{-1.1} \ \exp(-52530/T)$			$cm^3 \ molecule^{-1}s^{-1}$
$k_{-1}(N_2)$	$4.58 \times 10^{16} \ T^{-1.4} \ \exp(-52530/T)$	600-2000		$L \ mol^{-1}s^{-1}$
	$7.60 \times 10^{-5} \ T^{-1.4} \ \exp(-52530/T)$			$cm^3 \ molecule^{-1}s^{-1}$
$k_{-1}(H_2O)$	$8.47 \times 10^{16} \ T^{-1.1} \ \exp(-52530/T)$	600-2000		$L \ mol^{-1}s^{-1}$
	$1.43 \times 10^{-4} \ T^{-1.1} \ \exp(-52530/T)$			$cm^3 \ molecule^{-1}s^{-1}$

Uncertainty in log $k_1(Ar)$ and log $k_{-1}(Ar)$: ±0.3 throughout range. Uncertainty in log $k_1(N_2)$ and $k_{-1}(N_2)$: ±0.3 for T < 300; ±0.5 for 300 < T < 2000 K. Uncertainty in log $k_1(H_2O)$ and log $k_{-1}(H_2O)$: ±1.0 throughout range. The uncertainty due to that in K(T) is negligible.

(October 1982)

THERMOCHEMICAL DATA

Thermochemical data for both H and H_2 were taken from an unpublished supplement (31 March 1977) to the JANAF Thermochemical Tables. The analytical expression chosen for $K(T)$ matches the equilibrium constants calculated from JANAF data to within 6% between 600 and 6000 K.

MEASUREMENTS

Over 50 separate studies of hydrogen recombination/dissociation published prior to 1972 were reviewed by Baulch et al;[1] four additional studies have since been reported.[2-5] The experiments fall into four categories: discharge-flow studies at low temperatures (77-300 K);[2-7] flame studies at intermediate temperatures (1000-2000 K); and shock tube or nozzle expansion studies at high temperatures (1700-7000 K).[8-16] The early discharge flow studies (prior to 1960) have been discarded, mainly for reasons discussed in Refs. 1 and 6. The flame studies, conducted in H_2/O_2/diluent systems, are, in retrospect, too chemically complex to afford precise rate coefficient data and have been discarded in this evaluation. The nozzle expansion studies have been neglected because of fluid dynamic complications still not thoroughly understood.

The flow tube studies all monitored H disappearance and measured k_1 directly; most of the shock tube studies observed the dissociation of H_2 and hence measured k_{-1}; their results are reported as k_1 by the relation, $k_1 = k_{-1} K(T)$.

CALCULATIONS

Theoretical calculations for recombination with M = Ar have been reported (see Ref. 17 and papers cited therein); however, the experimental data seem sufficient for making recommendations over a wide temperature range with reasonable confidence.

DISCUSSION

As the accompanying graph shows, the low temperature (77-300 K) data for M = Ar are in reasonable agreement and suggest a temperature dependence of T^{-1} for $k_1(Ar)$. The high temperature shock tube data show considerably more spread--exceeding a factor of five at some temperatures. Except for Ref. 8, which reports considerably steeper temperature dependences (the validity of which has been questioned[18]), the shock tube studies all report T^{-1} dependences, but in most cases this relation is assumed, and cannot be deduced directly from the data. Our recommendations are based principally on Refs. 2, 3, 7, and 12; a two-parameter expression is chosen, namely $k_1(Ar) = 7 \times 10^{11} T^{-1} L^2 mol^{-2} s^{-1}$, because the precision of the data does not seem to justify anything more elaborate.

Numerous data have been reported for other M, two of which are of great practical interest: N_2 and H_2O. The most reliable data for M = N_2 are at 77-300 K (Ref. 3), and suggest $k_1(N_2) = 5.4 \times 10^{12} T^{-1.3} L^2 mol^{-2} s^{-1}$. The data for M = H_2O show considerable scatter; we concur with the statement of Ref. 1 that $k_1(H_2O)/k_1(Ar)$ probably lies between 10 and 20, but with considerable uncertainty; hence all that can be said at present is that $\log k_1(H_2O) = (13 \pm 1) - \log T$.

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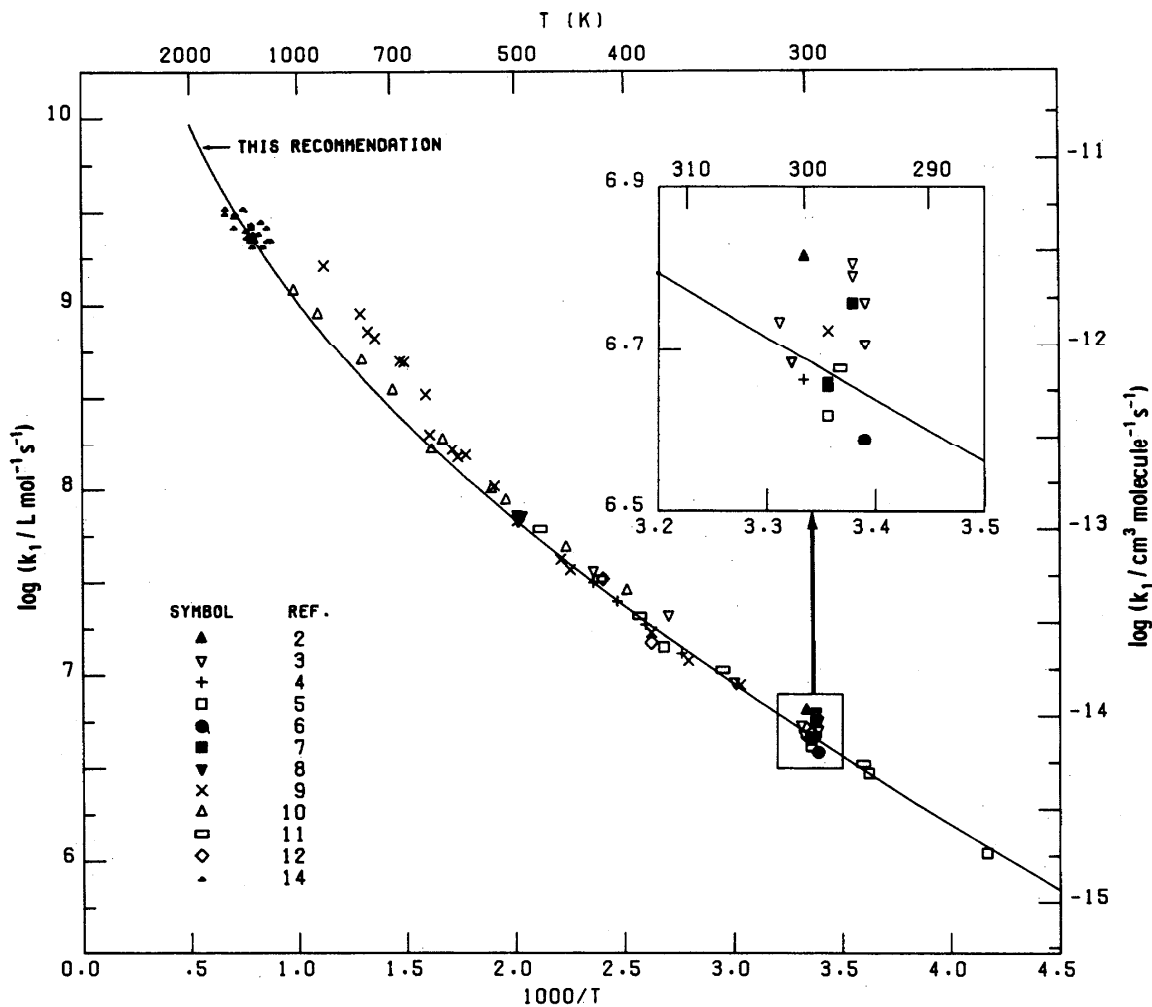18. V. H. Shui, J. Chem. Phys. 58, 4868 (1973).

$$OH + CH_4 \underset{-1}{\overset{1}{\rightleftharpoons}} CH_3 + H_2O$$
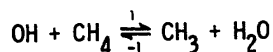
$\Delta H^{o}_{298} = -59.1 \pm 2 \text{ kJ mol}^{-1} \ (-14.12 \text{ kcal mol}^{-1})$ $\Delta S^{o}_{298} = 13.04 \pm 1.2 \text{ J mol}^{-1}\text{K}^{-1} \ (3.12 \text{ cal mol}^{-1}\text{K}^{-1})$

$$K(T) = 400 \ T^{-0.5} \ \exp(6420/T)$$

The uncertainty in log K is ±0.2 at 700 K decreasing to ±0.1 at 2000 K.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.9 \times 10^2 T^{2.4} \exp(-1060/T)$	240-3000 K	4.9×10^6	$\text{L mol}^{-1}\text{s}^{-1}$
	$3.2 \times 10^{-19}T^{2.4} \exp(-1060/T)$		8.1×10^{-15}	$\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$
k_{-1}	$4.8 \times 10^{-1}T^{2.9} \exp(-7480/T)$	700-3000 K		$\text{L mol}^{-1}\text{s}^{-1}$
	$8.0 \times 10^{-22}T^{2.9}\exp(-7480/T)$			$\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$

Uncertainty in log k_1: ±0.1 in the range 240-500 K, increasing to ±0.2 at 2000 K and ±0.3 at 3000 K. Uncertainty in log k_{-1}: ±0.3 throughout range of 700-3000 K. This uncertainty reflects the uncertainties in both log k_1 and log K(T).

(May 1982)

$$OH + CH_4 \rightleftharpoons CH_3 + H_2O$$
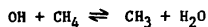
THERMOCHEMICAL DATA

Thermochemical data for CH_4, H_2O and CH_3 are taken from the second edition of the JANAF Thermochemical Tables (1971), except that the enthalpy of formation of CH_3 at 298 K is taken to be 146.9 ± 0.7 kJ/mol, in accordance with recent measurements.[1] Thermochemical data for OH are taken from an unpublished supplement to the JANAF Tables dated 30 June 1977.

The analytic expression chosen for K(T) matches equilibrium constants calculated from the above data to within 2% between 700 and 6000 K.

MEASUREMENTS

Ten measurements of k_1 at room temperature are in very close agreement on a value of $(4.9 \pm 1.0) \times 10^6$ L mol^{-1}s^{-1}. The most reliable of these used flash photolysis of H_2O[3,5,9,10] or a discharge through H_2/He, titrated with NO_2[11] as an OH radical source and monitored the reaction by following [OH] diminution by either kinetic spectroscopy[3], resonance fluorescence[5,10,11] or resonance absorption[9]. These same studies, and one absolute determination by pulse radiolysis of H_2O and absorption spectroscopy[12], also provide the best information on k_1 at intermediate temperatures (up to 1000 K). These studies are in excellent agreement up to about 600 K, above which there is a spread of a factor of approximately 2. In this temperature regime the principal studies are those of Refs. 8 and 9. Above 1000 K there is one shock tube study[13] in which H_2O_2 was decomposed in the presence of CH_4 and k_1 measured relative to the rate coefficient, k_3, for the reaction between OH and H_2; this value has not been used in this evaluation because the computer analysis neglected several reactions of probable importance. There is also a combined flash photolysis-shock tube study[14] in which H_2O was the OH source; the subsequent OH decay was monitored by uv absorption.

CALCULATIONS

Ernst et al.[14] reported a transition state theory (TST) calculation for a 5-atom nonlinear TS in which a BEBO calculation was used to aid in obtaining vibrational frequencies and the barrier height; the results were scaled by a multiplicative factor to give agreement with experiments at 300 K. They obtained an expression for k_1 of $1.5 \times 10^3 T^{2.13} \exp(-1234/T)$, in excellent agreement with the low temperature data and with the higher temperature data of Refs. 10 and 13. A TST calculation was carried out by us using CH_4 as a model compound for the activated complex $CH_3HOH^{\pm}$, in accordance with the techniques discussed by Benson.[15,16] The vibrational frequencies in the activated complex were taken to be those of CH_4, less a C-H stretch (3000 cm^{-1}) and two HCH bends (1500, 1300); with the following additional frequencies: 3700, 2200, 1000, 1000, 1000, and 600 cm^{-1}. The partition functions $Q_f(300)$ for the two hindered internal rotors and their potential energy barriers were assumed to be 4.8 and 3.6; and 8400 and 4200 J/mol, respectively (see Ref. 15, p. 305). The resulting values of k_1 could be well-fitted by the expression, $k_1 = 1.7 \times 10^5 T^{1.5} \exp(-1560/T)$. This gives slightly smaller values than the calculations of Ref. 14.

DISCUSSION

The agreement among the various measurements below 500 K is excellent and leaves no doubt that log k_1 is known to ±0.1 units between 240 and 500 K. At higher temperatures, the best measurements seem to be those of Refs. 9 and 10, though neither report gives details on how the data were analyzed. In principle, the technique of Ref. 10 should be the more precise, and we favor it in reaching our own recommendation. The value of 8×10^9 at 2000 K obtained by our TST calculations is probably as reliable as the experiments above 1000 K. These considerations suggest an expression for k_1 of $1.9 \times 10^2 T^{2.4} \exp(-1060/T)$ L mol^{-1}s^{-1}, with an uncertainty in log k of ±0.1 for 240-500 K, increasing to ±0.2 at 2000 K.

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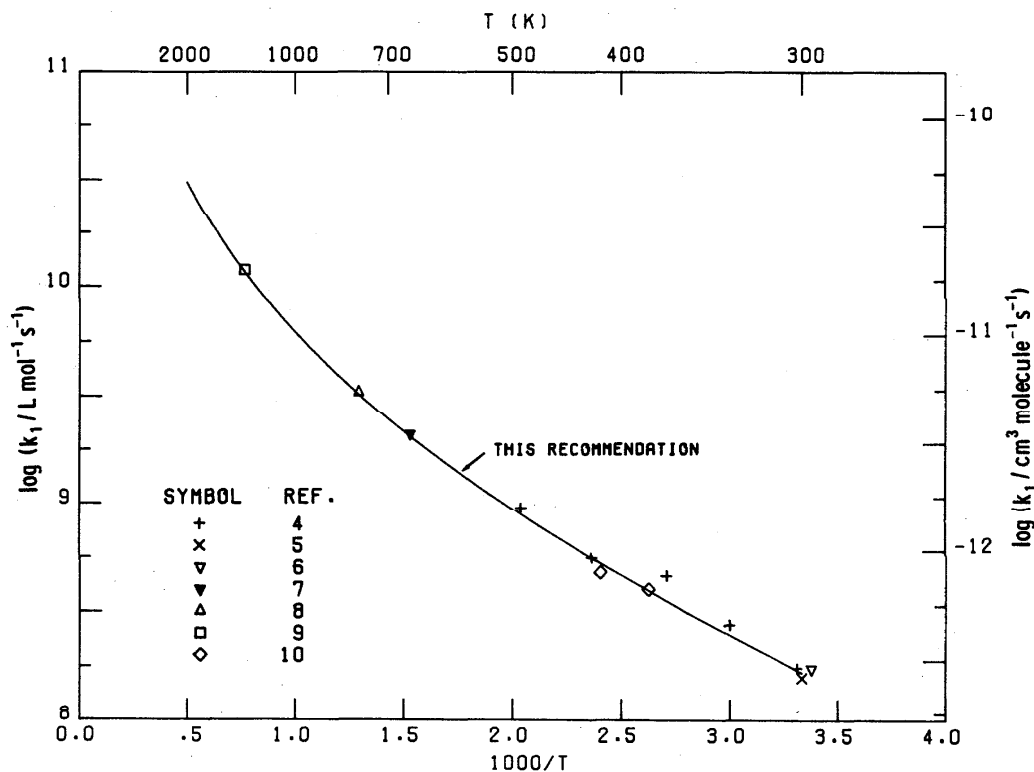16. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + C_2H_6 \overset{1}{\underset{-1}{\rightleftharpoons}} C_2H_5 + H_2O$$
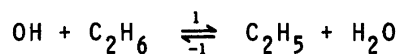
$\Delta H^o_{298} = -78 \pm 8$ kJ mol^{-1}(-18.7 kcal mol^{-1}) $\Delta S^o_{298} = 23.4$ J mol^{-1} K^{-1} (5.6 cal mol^{-1}K^{-1})

$$K(T) = 2.6 \times 10^3 \ T^{-0.4} \exp (9240/T)$$

The uncertainty in log K is ±1.4 at 300 K, decreasing to ±0.2 at 2000 K.

RECOMMENDED RATE COEFFICENTS

k	k(T)	Range	k(298)	Units
k_1	$2.2 \times 10^4 \ T^{1.9} \exp(-570/T)$	300 - 2000 K	1.7×10^8	L mol^{-1}s^{-1}
	$3.6 \times 10^{-17} \ T^{1.9} \exp(-570/T)$		2.8×10^{-13}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$8.5 \ T^{2.3} \exp(-9810/T)$	1000 - 2000 K		L mol^{-1}s^{-1}
	$1.4 \times 10^{-20} \ T^{2.3} \exp(-9810/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.1 at 300 K, increasing to ±0.3 at 2000 K. Uncertainty in log k_{-1}: ±0.6 at 1000 K, decreasing to ±0.5 at 2000 K. This uncertainty reflects those of both log k_1 and log K(T).

(June 1981)

$OH + C_2H_6 \longrightarrow C_2H_5 + H_2O$
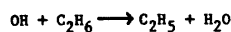
THERMOCHEMICAL DATA

Thermochemical data for H_2O were taken from the 2nd edition of JANAF Thermochemical Tables (1971); data for OH were taken from an unpublished supplement to the JANAF Tables dated 30 June 1977. Data for C_2H_6 are taken from Stull et al.[1] ΔHf°_{298} (C_2H_5) was assumed[2] to be 118 kJ mol^{-1}; S°_{298} was taken to be[3] 247.5 J mol^{-1} K^{-1}. K(T) above 300 K was calculated from Cp data for the four species given in the above references.

The analytic expression chosen for K(T) matches equilibrium constants calculated with the above data to within 1% between 300 and 1500 K.

MEASUREMENTS

Three accurate measurements[4-6] of k_1 at room temperature agree on a value of $1.7 \pm 0.1 \times 10^8$ L $mol^{-1}s^{-1}$. All three used flash photolysis of H_2O vapor as a source of OH radicals, and monitored the course of reaction either by kinetic spectroscopy of OH in the ultraviolet, or by laser magnetic resonance spectrometry. At higher temperatures, in addition to Ref. 4, there are four reliable measurements, one absolute[7] and three relative.[8-10] In the former, OH was produced by pulse radiolysis of H_2O vapor/alkane mixtures at 381 and 416 K, and the rate of reaction monitored by following the decay of OH absorption at 3087 A. Results of 4.0×10^8 (381 K) and 4.8×10^8 (416 K) were reported. Two of the relative measurements were made by comparison with k_2, the rate coefficient for the reaction $OH + H_2 \rightarrow H + H_2O$. In one of these[8], small amounts of C_2H_6 were added to H_2-O_2 mixtures and the ratio of k_1/k_2 measured at 773 K. This ratio was obtained from a gas chromatographic measurement of ethane consumption and a pressure change measurement to determine hydrogen disappearance. A ratio of k_1/k_2 ~ 5.7 was reported; using our own recommended value for k_2, this gives $k_1 = 3.3 \times 10^9$ L $mol^{-1}s^{-1}$. The other determination[9] was a shock tube study in which OH was generated by decomposition of H_2O_2 at 1300 K in the presence of C_2H_6 additive. OH decay was monitored by uv absorption. The ratio of $k_1/k_2 = 3.95$ was reported; using our own recommended value of k_2, this yields $k_1 = 1.2 \times 10^{10}$. This result has not been heavily weighted in our evaluation because the computer analysis neglected some reactions of probable importance. In the third relative measurement k_1/k_3 was determined in aged boric acid-coated reactors at 653 K where k_3 is the rate coefficient for the reaction $OH + CH_4 \rightarrow CH_3 + H_2O$. OH was produced by thermal decomposition of H_2O_2 vapor. Hydrocarbon concentrations were measured by gas chromatography; the residual H_2O_2 was assayed by trapping out at 195 K and titrating with $KMnO_4$ solution. Values for k_1/k_3 of 9.0 ± 2.0 were obtained. This value is subject to minor corrections for the effects of HO_2 radicals in the system. Using our own recommended value of k_3 gives a value of $k_1 = 2.1 \times 10^8$ L $mol^{-1}s^{-1}$.

CALCULATIONS

A transition-state-theory calculation was carried out using C_2H_5OH as a model compound for the activated complex $C_2H_5HOH^{\ddagger}$, in accordance with the techniques discussed by Benson.[11] Details are given in Ref. 12. The vibrational frequencies in the activated complex were thus taken to be those of C_2H_6, less a C-H stretch (3100 cm^{-1}), an HCH bend (1400), and a CCH bend (1100); with the following additional frequencies: 3700, 2200, 1000, 1000, 350, 300 cm^{-1}. The partition functions $Q_f(300)$ for the two hindered internal rotors and their potential energy barriers were assumed to be 5.6 and 3.9; and 8400 and 4200 J/mol respectively (see Ref. 11, p. 305). The resulting values of k_1 could be well-fitted by the expression, $k_1 = 7.8 \times 10^3 T^{2.0} \exp(-430/T)$ L $mol^{-1}s^{-1}$, in excellent agreement with the experimental data.

DISCUSSION

Although the seven experiments cited above are all consistent with one another, some more direct measurements, either in the 400-500 K range or above 1500 K would be very useful to reduce the uncertainty in k_1. In Ref. 8 a general expression for the ratio of rate coefficients for OH reaction with any alkane to that of $OH + H_2$ was given; when this is used for C_2H_6, an expression for k_1 of $1.4 \times 10^6 T^{1.3} \exp(-765/T)$ results, which is very similar to our TST expression for temperatures up to about 1500 K; at higher temperatures, the TST expression yields larger values for k_1 (by a factor of 1.6 at 2000 K). At this time we favor a three-parameter expression obtained by fitting to the three experimental values cited above. (Taken alone, the experimental data, with their uncertainties, would not justify a three-parameter expression in preference to an Arrhenius expression; however, the TST calculations clearly suggest curvature to the Arrhenius plot, and the fit to the experimental data agrees well with the TST expression given above.) Hence, we recommend $k_1 = 2.2 \times 10^4 T^{1.9} \exp(-570/T)$ L $mol^{-1}s^{-1}$ over the temperature range of 300-2000 K. The uncertainty in log k_1 is ± 0.1 at 300 K, increasing to ± 0.3 at 2000 K.

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11. See S. W. Benson, Thermochemical Kinetics, 2nd. ed. (Wiley, New York, 1976), pp 148ff.
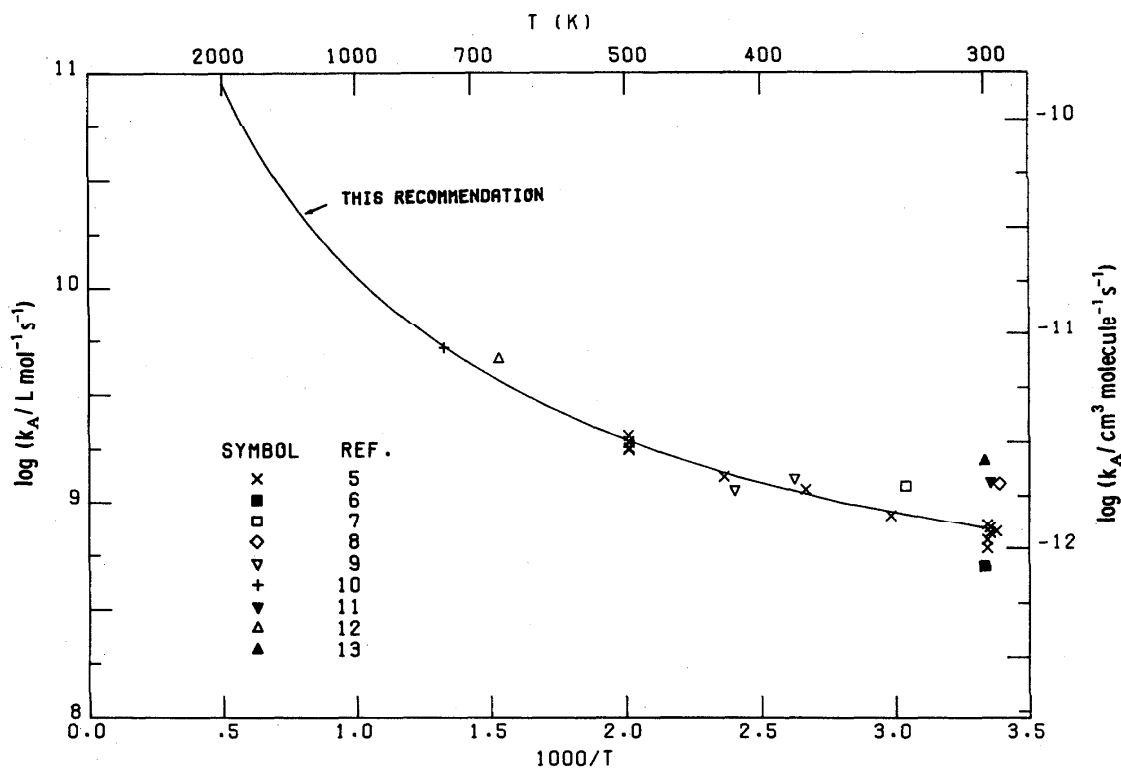12. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + C_3H_8 \xrightarrow{A} C_3H_7 + H_2O$$

$OH + C_3H_8 \xrightarrow{1} n-C_3H_7 + H_2O$
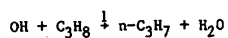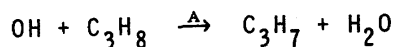
$\Delta H^o_{298.15} = -82 \pm 10$ kJ mol^{-1} (-19.7 kcal mol^{-1})

$\Delta S^o_{298.15} = 23.7 \pm 2$ J mol^{-1}K^{-1} (5.6 cal mol^{-1}K^{-1})

$OH + C_3H_8 \xrightarrow{2} i-C_3H_7 + H_2O$
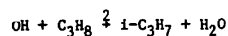
$\Delta H^o_{298.15} = -96 \pm 5$ kJ mol^{-1} (-23.0 kcal mol^{-1})

$\Delta S^o_{298.15} = 23.0 \pm 2.3$ J mol^{-1}K^{-1} (5.5 cal mol^{-1}K^{-1})

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$0.4 \, T^{3.4} \exp(590/T)$	300 – 2000 K	7.6×10^8	L mol^{-1}s^{-1}
	$7.0 \times 10^{-22} \, T^{3.4} \exp(590/T)$		1.3×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_1/k_2	$4 \exp(-800/T)$	300 – 2000 K	0.28	___

Uncertainty in log k_A: ±0.3 from 300 to 750 K, increasing to ±0.5 at 2000 K. Uncertainty in log k_1/k_2: ±0.3. The reverse reactions are unimportant at any temperature; hence, values for K(T), k_{-1}, and k_{-2} are not recommended.

(June 1981)

$$OH + C_3H_8 \xrightarrow{A} C_3H_7 + H_2O$$
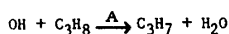
THERMOCHEMICAL DATA

Because there are two different kinds of H atoms on propane (C_3H_8), the title reaction actually represents two separate elementary reactions, so that k_A is the sum of k_1 and k_2. The n-C_3H_7 has the structure $\dot{C}H_2CH_2CH_3$; i-C_3H_7 has the structure $CH_3\dot{C}HCH_3$, where the dot indicates the location of the unpaired electron and hence the reactive site.

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to the JANAF Tables dated 30 June 1977. Data for C_3H_8 are from Stull et al.[1] Enthalpies for n-C_3H_7 and i-C_3H_7 radicals are from O'Neal and Benson,[2] and Baldwin et al.,[3] respectively. However the former value may be too low, in view of the recent revisions in enthalpies for other alkyl radicals. Entropies are from O'Neal and Benson.[4] Analytic expressions for $K(T)$ have not been calculated because the reverse reactions (between propyl radicals and H_2O) are not important: at low temperatures they are too endothermic to occur and at high temperatures the propyl radicals are unstable.

MEASUREMENTS

Five absolute measurements of k_A have been reported: by flash photolysis-kinetic spectroscopy (one at 300-500 K,[5] the other at 295 K[8]); discharge flow-ESR (298 K);[6] Hg-photosensitization flow-modulation spectroscopy (329 K);[7] and pulse radiolysis-kinetic spectroscopy (381-416 K).[9] The most direct measurements, least subject to errors, are the two flash photolysis and the pulse radiolysis experiments, in which OH was monitored directly by kinetic absorption spectroscopy. However, the room-temperature results of Refs. 5 and 8 differ by a factor of 1.7.

In addition, measurements of k_A have been made relative to the following reactions: $OH + H_2 \overset{3}{\rightarrow} H + H_2O$ at 753 K;[10] $OH + CO \overset{4}{\rightarrow} H + CO_2$ at 298 K;[11] $OH + C_2H_6 \overset{5}{\rightarrow} C_2H_5 + H_2O$ at 653 K;[12] and $OH + n-C_4H_{10} \overset{6}{\rightarrow} C_4H_9 + H_2O$ at 300 K.[13] The values shown on the graph were calculated using our own recommended values for k_3 and k_5; the value for k_4 recommended by Baulch et al.;[14] and a value for k_6 based on an average of Refs. 5 and 15.

Because of the complications of secondary reactions, it is difficult to measure k_1 and k_2 separately. Using a computer program and the results of product analysis, Baker et al.[16] derived a preliminary value of $k_2/k_1 = 1.2 \pm 0.1$ at 753 K, but in a subsequent unpublished corrigendum cautioned against reliance on this derivation.
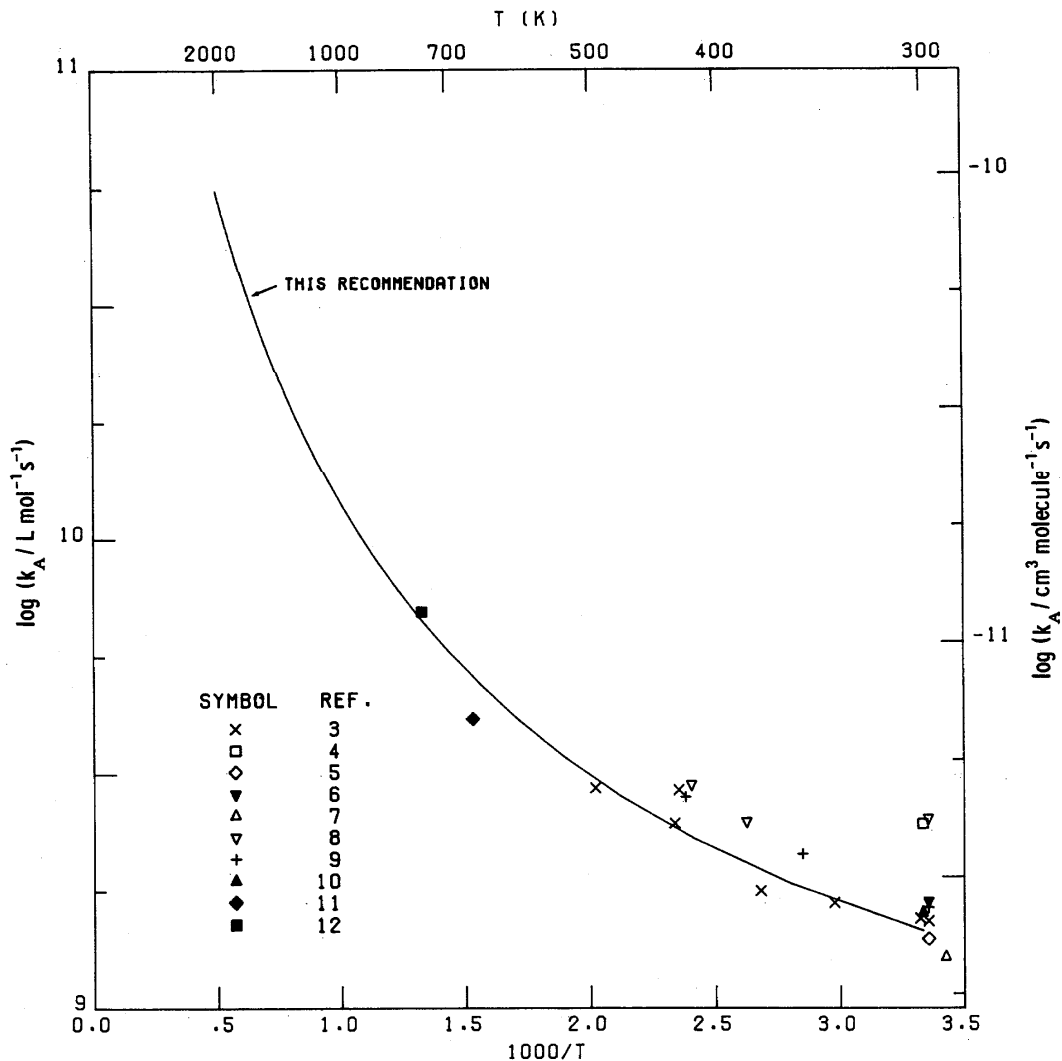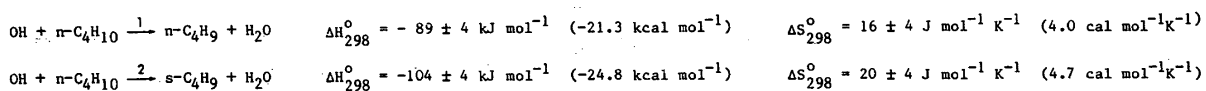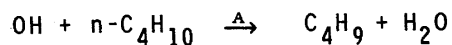
DISCUSSION

Although the room-temperature measurements reported in Refs. 5 and 8 are intrinsically of equal merit, we chose to base our recommendation on those of Ref. 5 only because these are more consistent with data at other temperatures. Ref. 5 also yields a value for k_A of 1.9×10^9 L $mol^{-1}s^{-1}$ at 500 K. For a higher temperature point we rely on the relative measurement of Ref. 10, but use our own evaluation for the rate coefficient for $OH + H_2$ to obtain an absolute value. These three measurements determine a 3-parameter expression of $k_A = 0.4\ T^{3.4}\ exp(590/T)$ L $mol^{-1}s^{-1}$, which fits the results of Ref. 9 within 15% and all the other experimental data within a factor of less than 2. It also agrees closely with the expression $k_A = 1.38 \times 10^6\ T^{1.3}exp(-765/T) + 0.38 \times 10^6\ T^{1.3}\ exp(-15/T)$ calculated in Ref. 10 from three "universal" rate coefficients for primary, secondary, and tertiary H atom abstraction that were derived by assuming that the rate coefficients for these processes do not depend on the alkane from which H atom is being abstracted. The uncertainty in log k_A is ±0.5 at 2000 K. It should be recalled that the unusual values for the 3 parameters of k_A are a result of the reaction being the sum of two parallel processes. The parameters for the "universal" rate coefficients are reasonable in terms of transition state theory.

From the "universal" rate coefficients for primary and secondary H abstraction given in Ref. 10, a ratio of $k_1/k_2 = 3.7$ exp $(-750/T)$ can be calculated. However, in the absence of a reliable experimental measurement of k_1/k_2, any recommendation for k_1/k_2 must be regarded as having a factor of 2 uncertainty; we recommend 4 exp $(-800/T)$.

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$$OH + n\text{-}C_4H_{10} \xrightarrow{A} C_4H_9 + H_2O$$

$OH + n\text{-}C_4H_{10} \xrightarrow{1} n\text{-}C_4H_9 + H_2O$ $\Delta H^{\circ}_{298} = -89 \pm 4$ kJ mol^{-1} (-21.3 kcal mol^{-1}) $\Delta S^{\circ}_{298} = 16 \pm 4$ J mol^{-1} K^{-1} (4.0 cal mol^{-1}K^{-1})

$OH + n\text{-}C_4H_{10} \xrightarrow{2} s\text{-}C_4H_9 + H_2O$ $\Delta H^{\circ}_{298} = -104 \pm 4$ kJ mol^{-1} (-24.8 kcal mol^{-1}) $\Delta S^{\circ}_{298} = 20 \pm 4$ J mol^{-1} K^{-1} (4.7 cal mol^{-1}K^{-1})

SYMBOL	REF.
×	3
□	4
◇	5
▼	6
△	7
▽	8
+	9
▲	10
◆	11
■	12

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	2.6×10^2 $T^{2.5}$ exp(390/T)	300-2000 K	1.5×10^9	L mol^{-1}s^{-1}
	4.3×10^{-19} $T^{2.5}$ exp(390/T)		2.5×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_1/k_2	1.7 exp(-750/T)	300-2000 K	0.14	---

Uncertainty in log k_A: ±0.1 at 300 K, increasing to ±0.5 at 2000 K. Uncertainty in log k_1/k_2: ±0.3. Because the reverse reactions are unimportant at any temperature; values for K(T), k_{-1} and k_{-2} are not recommended.

(December 1981)

$$OH + n\text{-}C_4H_{10} \xrightarrow{A} C_4H_9 + H_2O$$

THERMOCHEMICAL DATA

Because there are two different kinds of H atoms on $n\text{-}C_4H_{10}$—6 on primary C atoms (attached to only one other C atom) and 4 on secondary C atoms (attached to two other C atoms)—there are two different reactions represented by the title reaction:

$$OH + n\text{-}C_4H_{10} \rightarrow n\text{-}C_4H_9 + H_2O \qquad (n\text{-}C_4H_9 \text{ is } \cdot CH_2CH_2CH_2CH_3)$$
$$\rightarrow s\text{-}C_4H_9 + H_2O \qquad (s\text{-}C_4H_9 \text{ is } CH_3CHCH_2CH_3)$$

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $n\text{-}C_4H_{10}$ were taken from Stull et al.[1]. Data for the two C_4H_9 radicals were estimated by group additivity methods outlined by Benson et al.[2]; these estimates give, for $n\text{-}C_4H_9$, $\Delta Hf^\circ_{298} = 65.8$ kJ mol^{-1}, $S^\circ_{298} = 321$ J mol^{-1} K^{-1}, $Cp^\circ_{298} = 97.3$ J mol^{-1} K^{-1}, and for $s\text{-}C_4H_9$, $\Delta Hf^\circ_{298} = 51.1$ kJ mol^{-1}, $S^\circ_{298} = 324$ J mol^{-1} K^{-1}, $Cp^\circ_{298} = 96.7$ J mol^{-1} K^{-1}. Analytic expressions for K(T) have not been calculated because the reverse reactions will never be important; at low temperatures they are too endothermic to occur and at high temperatures the butyl radicals are unstable.

MEASUREMENTS

The most direct measurements of k_A utilized either the flash photolysis[3,5,9,10] or radiolysis[8] of H_2O in the presence of butane and diluent. OH was monitored either by absorption[3,8] or resonance fluorescence.[5,9,10] Other, less direct measurements involved fast flow discharge (OH produced by H + NO_2 reaction)[4], photolysis of $H_2O_2/CO/O_2/C_4H_{10}$ mixtures,[6] photolysis of $H_2O_2/NO_2/CO/C_4H_{10}$ mixtures,[7] thermal decomposition of H_2O_2 at 653 K in the presence of C_4H_{10},[11] and the inhibition of H_2/O_2 flames at 753 K by C_4H_{10}.[12] In several studies k_A was obtained relative to the rate coefficient for the reaction of OH with CO,[6,7] with H_2,[12] with C_3H_8,[11] or with C_3H_6.[4] The values plotted have been recomputed with our own recommended values of $k_{OH + H_2}$ and $k_{OH + C_3H_8}$; and with that of Baulch et al.[14] for $k_{OH + CO}$. In three studies, measurements were made over a range of temperatures: 298-495 K in Ref. 3, 298-420 K in Ref. 9, and 298-416 K in Ref. 8. All the measurements[3,5,7,9,10] at 292-300 K except two[4,8] agree on $k_A = 1.5 \pm 0.2 \times 10^9$ L mol^{-1}s^{-1}; the latter two are 67% higher. One measurement of $k_1/k_2 = 2.2 \pm 0.5$ at 753 K has been reported.[13] This was calculated from C_2H_6 yields, assuming that H, O, and OH are equally selective in attacking primary or secondary H atoms in C_4H_{10}. A more refined treatment suggests values of k_1/k_2 somewhat smaller.

CALCULATIONS

Transition state theory calculations were made for k_1 and k_2. The thermochemical properties of the transition states were estimated using C_4H_9OH and $s\text{-}C_4H_9OH$ as model compounds (Ref. 1, pp. 425-26). It was assumed that both activated complexes have the same vibrational frequencies: those of $n\text{-}C_4H_{10}$ less a C-H stretch (3100 cm^{-1}), an HCH bend (1400), and a CCH bend (1100). The additional assumed frequencies were 3700, 2200, 1000, 1000, 350, and 300. The partition functions $Q_f(300)$ for the two hindered internal rotors and their potential energy barriers were assumed to be 5.6 and 3.9; and 8400 and 4200 J/mol respectively (see Ref. 2a, p. 305). It was assumed that for both activated complexes $g_e^{\ddagger} = 2$. These assumptions resulted in $\Delta S^{\ddagger}(300) = -100.3$ J mol^{-1} K^{-1} for Reaction 1 and -104.5 J mol^{-1} K^{-1} for Reaction 2. In the absence of reliable activation energies, $k_1(300)$ and k_2 (300) were estimated from $k_A = k_1 + k_2 = 1.5 \times 10^9$ L mol^{-1}s^{-1} at 300 K and from the branching ratio for primary and secondary radical formation in the analogous OH + C_3H_8 reaction (see Data Sheet for that reaction.) It was assumed, based on statistics, that k_1/k_2 for C_4H_{10} is 0.5 times the analogous ratio for C_3H_8, so that $k_1/k_2 = 0.14$. The results of the separate calculations for k_1 and k_2, when added together, are described by the equation $k_A = 2.6 \times 10^2$ $T^{2.5}$ exp(390/T), which agrees well with the experimental data. The calculated ratio k_1/k_2 is approximately 1.7 exp(-750/T). This calculated ratio is in fair agreement with ratios derived by Baldwin and Walker[12] and by Greiner[3] from experimental data on different alkanes and the assumption that the Arrhenius parameters for all primary H atoms are the same, and similarly for secondary and tertiary H atoms. From Baldwin and Walker's expression one calculates $k_1/k_2 = 1.9$ exp(-750/T); from Greiner's, 0.6 exp(-395/T).
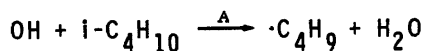
DISCUSSION

Based on directness of technique and detailed description of results, the preferred experimental studies are Refs. 3, 5, 9, 10, and 12, all of which are in excellent agreement with one another. The explanation for the different value obtained in Ref. 8 is not obvious; Ref. 4 may have been flawed by unaccounted side reactions in the flow discharge or by flow nonuniformities.

The calculated value of k_A agrees with the preferred experimental studies, which cover the range of 298-753 K, and provides a suggested extrapolation to higher temperatures. The calculated ratio k_1/k_2 is in good agreement with Ref. 13. We recommend $k_A = 2.6 \times 10^2$ $T^{2.5}$ exp(390/T) and $k_1/k_2 \approx 1.7$ exp(-750/T), 300 < T < 2000 K.
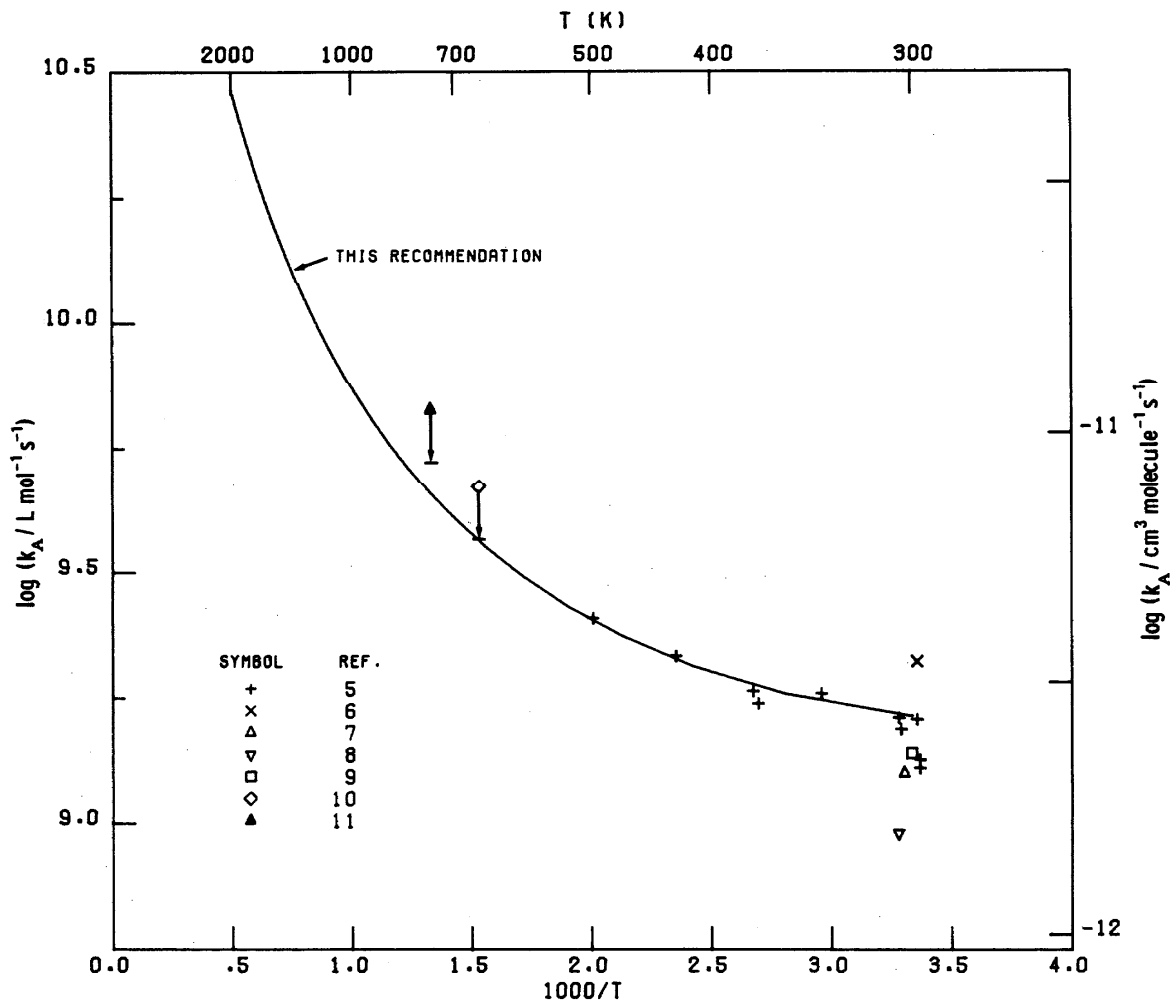
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$$OH + i\text{-}C_4H_{10} \xrightarrow{A} \cdot C_4H_9 + H_2O$$

OH + i-C$_4$H$_{10}$ $\xrightarrow{1}$ i-C$_4$H$_9$ + H$_2$O ΔH^o_{298} = -88.2 ± 4.2 kJ mol^{-1} (-21.2 kcal mol^{-1}) ΔS^o_{298} = 21.5 ± 5 J mol^{-1} K^{-1} (5.2 cal mol^{-1} K^{-1})

OH + i-C$_4$H$_{10}$ $\xrightarrow{2}$ t-C$_4$H$_9$ + H$_2$O ΔH^o_{298} = -111 ± 8.5 kJ mol^{-1} (-26.5 kcal mol^{-1}) ΔS^o_{298} = 12.1 ± 14.6 J mol^{-1} K^{-1} (2.9 cal mol^{-1} K^{-1})

SYMBOL	REF.
+	5
×	6
△	7
▽	8
□	9
◇	10
▲	11

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	2.6 x 10^2 T$^{2.4}$ exp(590/T)	300 - 2000 K	1.6 x 10^9	L mol^{-1}s^{-1}
	4.3 x 10^{-19} T$^{2.4}$ exp(590/T)		2.7 x 10^{-12}	cm^3 molecule^{-1}s^{-1}
k_1/k_2	15 exp(-1230/T)	300 - 2000 K	0.25	--

**Uncertainty** in log k_A: ±0.12 near 300 K, increasing to ±0.5 at 2000 K. Uncertainty in log k_1/k_2: ±0.3 near 300 K, increasing to ±0.6 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.

February 1982

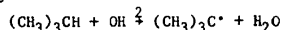$$OH + i\text{-}C_4H_{10} \xrightarrow{A} C_4H_9 + H_2O$$
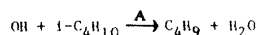
THERMOCHEMISTRY

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

$$(CH_3)_3CH + OH \xrightarrow{1} (CH_3)_2CH\dot{C}H_2 + H_2O$$
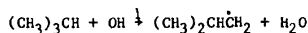
and removal of the single tertiary H to form t-butyl:

$$(CH_3)_3CH + OH \xrightarrow{2} (CH_3)_3C^\cdot + H_2O$$

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement (June 1977) to those tables. Data for isobutane are from Stull et al.[1] Both the entropy and enthalpy of formation of the t-butyl are in dispute; values given by Benson[2] (for both radicals) are used here.

MEASUREMENTS

Greiner[3] produced OH by flash photolysis of H_2O at 300-500 K and monitored its decay by kinetic absorption spectroscopy. Gorse and Volman[4] produced OH by photolysis of H_2O_2 at 300 K and measured k_A relative to k_3 for the reaction $OH + CO \xrightarrow{3} CO_2 + H$. Butler et al.[6] used a very similar procedure except their data analysis required knowing both k_3 and k_4, the latter for the reaction $OH + H_2O_2 \xrightarrow{4} HO_2 + H_2O$. Assuming values for k_4 recommended by Baulch et al.[7] and pressure-dependent values of k_3 recommended by Atkinson et al.[8] we obtain values of k_A between 7.8 and 11.4 x 10^8 L $mol^{-1}s^{-1}$. Darnall et al.[9] measured k_A relative to k_5 for the reaction of $OH + n$-butane. Our own recommended value for k_5 of 1.5 x 10^9 L $mol^{-1}s^{-1}$ at 300 K yields a value for k_A of 1.4 x 10^9. Hucknall et al.[10] studied the oxidation of pairs of alkanes at 653 K in aged boric-acid-coated reactors in the presence of decomposing H_2O_2. They reported k_A/k_6 to be 1.28 ± 0.07 where k_6 pertains to the reaction of $OH + C_3H_8$. Our own recommended value for k_6 yields 4.7 x 10^9 for k_A. However, this value is sensitive to the choice of values for k_7 for the recombination of HO_2, for which Hucknall et al. used Lloyd's[11] recommended value of 5 x 10^9. More recent evidence[12] suggests k_7 is probably smaller by at least a factor of 30, which would lower k_A by about 30%. Baldwin et al.[13] extracted k_A by the effect of small quantities of alkane on the kinetics of the $H_2 - O_2$ system at 753 K. The analysis in their complex system requires many side reactions to be taken into account. The resulting value for k_A of 6.7 x 10^9 was obtained assuming H atoms (rather than HO_2 radicals) to be the second-most important species removing RH, a conclusion that may be subject to revision in view of the recently revised value of k_7. If the HO_2 radicals dominate over H atoms in this way, then k_A would be smaller by about 25%.

CALCULATIONS

k_1 and k_2 were separately calculated by the semi-empirical transition-state-theory method described elsewhere.[14] This requires values for $k_1(300)$ and $k_2(300)$. $k_1(300)$ was taken to be the same as that for alkanes with only primary H atoms, weighted by the number of primary H atoms on $i\text{-}C_4H_{10}$, i.e., 9 x (3.7 x 10^7 L $mol^{-1}s^{-1}$). $k_2(300)$ was calculated from $k_A = k_1 + k_2$ where 1.6 x 10^9 was taken as the best experimental value for $k_A(300)$. These assumptions resulted in $\Delta S_1^{\ddagger}(300)$ and $\Delta S_2^{\ddagger}(300)$ values of -102.8 and -125.2 J mol^{-1} K^{-1} respectively. Values of k_A obtained from $k_1 + k_2$ could be fitted within 15% by the expression $k_A = 9T^{2.8}$ $\exp(910/T)$ L $mol^{-1}s^{-1}$, and $k_1/k_2 = 14.9 \exp(-1230/T)$.

DISCUSSION

A comparison of the $OH + i\text{-}C_4H_{10}$ reaction with those involving alkanes with only primary H atoms indicates that near room temperature k_A is approximately 80% due to k_2, reaction with the tertiary H atom (which has almost no activation energy), but above 500 K k_1 dominates. Nevertheless, if the rate of removal of the primary H atoms is the same as for C_2H_6 and neopentane, which have only primary H atoms, then the values of k_A reported in Refs. 10 and 11 are about 50% faster than the calculated rate coefficients. However, there are good grounds for believing that both of those experimental values are somewhat too large because of unaccounted complications in the system. At this time we recommend an expression for k_A based on the experimental values of 1.6 x 10^9 L $mol^{-1}s^{-1}$ at 300 K and 2.5 x 10^9 at 500 K, and on the corrected values of approximately 3.3 x 10^9 and 5 x 10^9 at 653 K and 753 K, respectively. These give $k_A = 2.6$ x 10^2 $T^{2.4}$ $\exp(590/T)$ L $mol^{-1}s^{-1}$, which agrees with the calculated value described in the preceeding section within 25%. For k_1/k_2 we recommend the calculated value of 15 $\exp(-1230/T)$. The uncertainty in log k_A is estimated to be ±0.12 at 300 K, increasing to ±0.5 at 2000 K.

References

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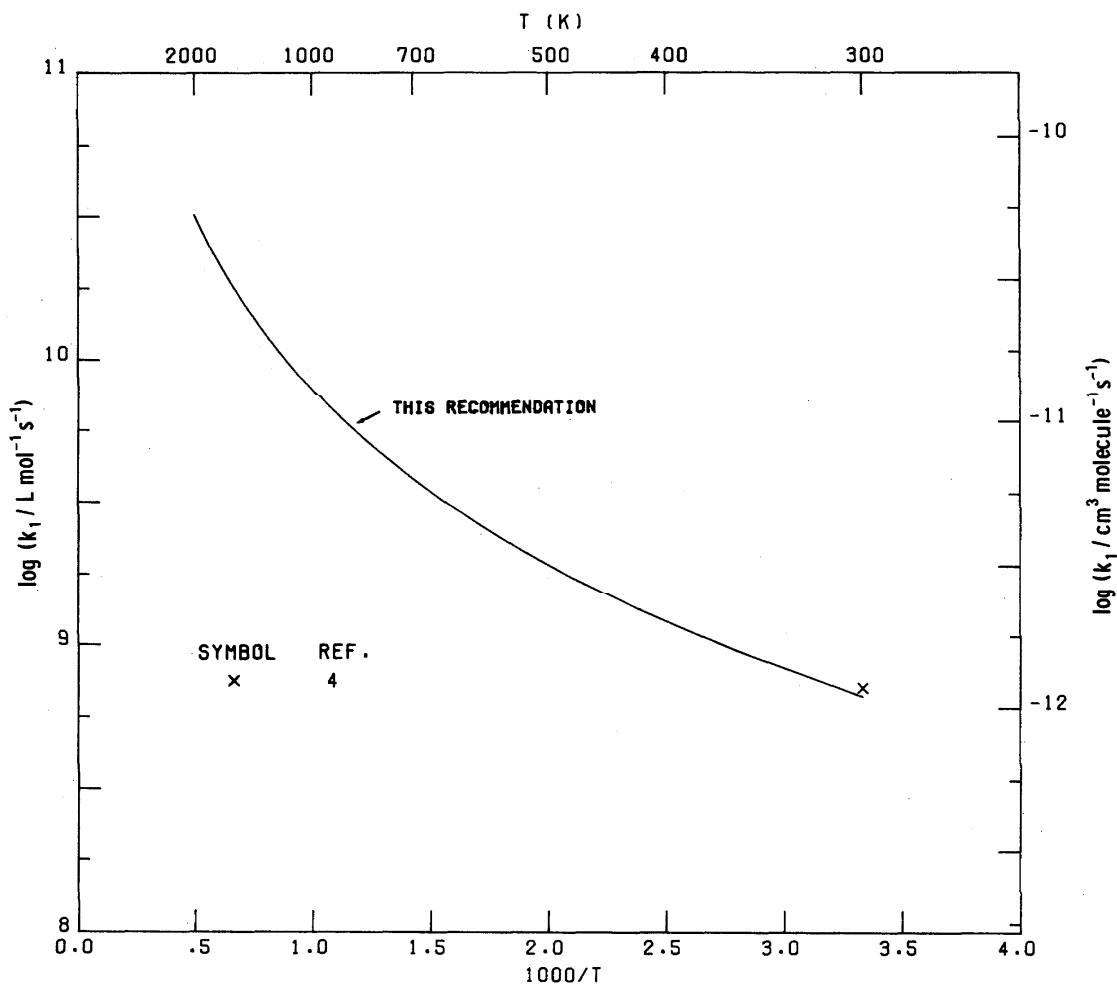14. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + c\text{-}C_4H_8 \underset{-1}{\overset{1}{\rightleftharpoons}} c\text{-}C_4H_7 + H_2O$$
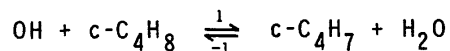
$\Delta H^o_{298} = -94 \pm 5$ kJ mol^{-1} (-22.4 kcal mol^{-1}) $\Delta S^o_{298} = 21 \pm 5$ J mol^{-1} K^{-1} (5.1 cal mol^{-1} K^{-1})

$$K(T) = 1.22 \times 10^3 \ T^{-0.3} \ \exp(11120/T)$$

The uncertainty in log K is ±1 at 298 K, decreasing to ±0.4 at 2000 K.

RECOMMENDED RATE COEFFICIENTS

$\underline{k}$	$\underline{k(T)}$	Range	K(300)	Units
k_1	$8.4 \times 10^3 \ T^{2.0} \ \exp(-30/T)$	298 - 2000 K	6.6×10^8	L mol^{-1}s^{-1}
	$1.4 \times 10^{-17} \ T^{2.0} \ \exp(-30/T)$		1.1×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$6.8 \ T^{2.3} \ \exp(-11150/T)$	1000 - 2000 K		L mol^{-1}s^{-1}
	$1.2 \times 10^{-20} \ T^{2.3} \ \exp(-11150/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.2 at 298 K, increasing to ±0.5 at 2000 K. Uncertainty in log k_{-1}: ±0.9 throughout range. k_{-1} is calculated from k_1 and K; its uncertainty reflects the uncertainties in both of these quantities.

(December 1981)
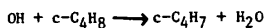
$$OH + c-C_4H_8 \longrightarrow c-C_4H_7 + H_2O$$

THERMOCHEMISTRY

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $c-C_4H_8$ (cyclobutane) are taken from Stull et al.[1] Data for the cyclobutyl radical at 298 K are taken from Kerr and Parsonage;[2] C_p's at higher temperatures were estimated by group additivity methods.[3] The analytic expression chosen for K(T) matches equilibrium constants calculated from these data to within 3% between 298 and 2000 K.

MEASUREMENTS

A single measurement for k_1 at room temperature has been reported.[4] In this study, mixtures of H_2O_2, CO, O_2, and alkane were photolyzed and the effect of the alkane on CO_2 yields measured. Under the conditions of the experiment, CO_2 yields could be related to the ratio of k_1/k_2, where k_2 is the rate coefficient for the reaction OH + CO → CO_2 + H. Using the value of k_2 recommended by Baulch et al.[5] and correcting the results for the small C_4H_{10} impurity in the $c-C_4H_8$, one obtains $k_1 = 6.6 \times 10^8$ L $mol^{-1}s^{-1}$.

CALCULATIONS

Transition state theory (TST) calculations were carried out for k_1 in order to extrapolate the rate coefficient to higher temperatures. $S^{\ddagger}(300)$ was estimated by group additivity methods, using $c-C_4H_8$ as a model compound. Vibrational frequencies were taken to be the same as for cyclobutane except for the removal of a C-H stretch (3100 cm^{-1}), an HCH bend (1400), and a CCH bend (1100); and the addition of the following frequencies: 3700, 2200, 1000, 1000, 350, and 300 cm^{-1}. The two new internal rotors were assumed to have partition functions $Q_f(300) = 5.6$ and 3.9, and barriers to rotation V = 8.4 and 4.2 kJ mol^{-1}, respectively. The electronic degeneracy of the activated complex, $g_e^{\ddagger}$, was assumed to be 2. These assumptions yielded a value for $\Delta S^{\ddagger}(300)$ of -99.9 J mol^{-1} K^{-1}. $k_1(300)$ was assumed to be 6.6×10^8 L $mol^{-1}s^{-1}$. The resulting values of $k_1(T)$ are well-fitted by the expression $k_1 = 8.4 \times 10^3$ $T^{2.0}$ exp(-30/T).

DISCUSSION

Like cyclopentane and cyclohexane, cyclobutane has only secondary H atoms, so there is only one product of the OH attack. However, the C-H bonds in cyclobutane are approximately 9 kJ mol^{-1} stronger than in the other two cycloalkanes, so the activation energy for H abstraction would be expected to be slightly higher. We recommend the expression determined from the TST calculations described above, which are based on the experimental 300 K measurement of Ref. 4. Thus, $k_1 = 8.4 \times 10^3$ $T^{2.0}$ exp(-30/T) L $mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ±0.2 at 300 K, increasing to ±0.5 at 2000 K.

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$$OH + c\text{-}C_5H_{10} \xrightarrow{1} c\text{-}C_5H_9 + H_2O$$
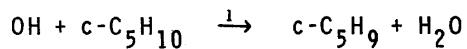
$\Delta H^o_{298} = -103 \pm 5 \text{ kJ mol}^{-1} \ (-24.7 \text{ kcal mol}^{-1})$ $\qquad\qquad\qquad$ $\Delta S^o_{298} = 23 \pm 5 \text{ J mol}^{-1}K^{-1} \ (5.5 \text{ cal mol}^{-1}K^{-1})$
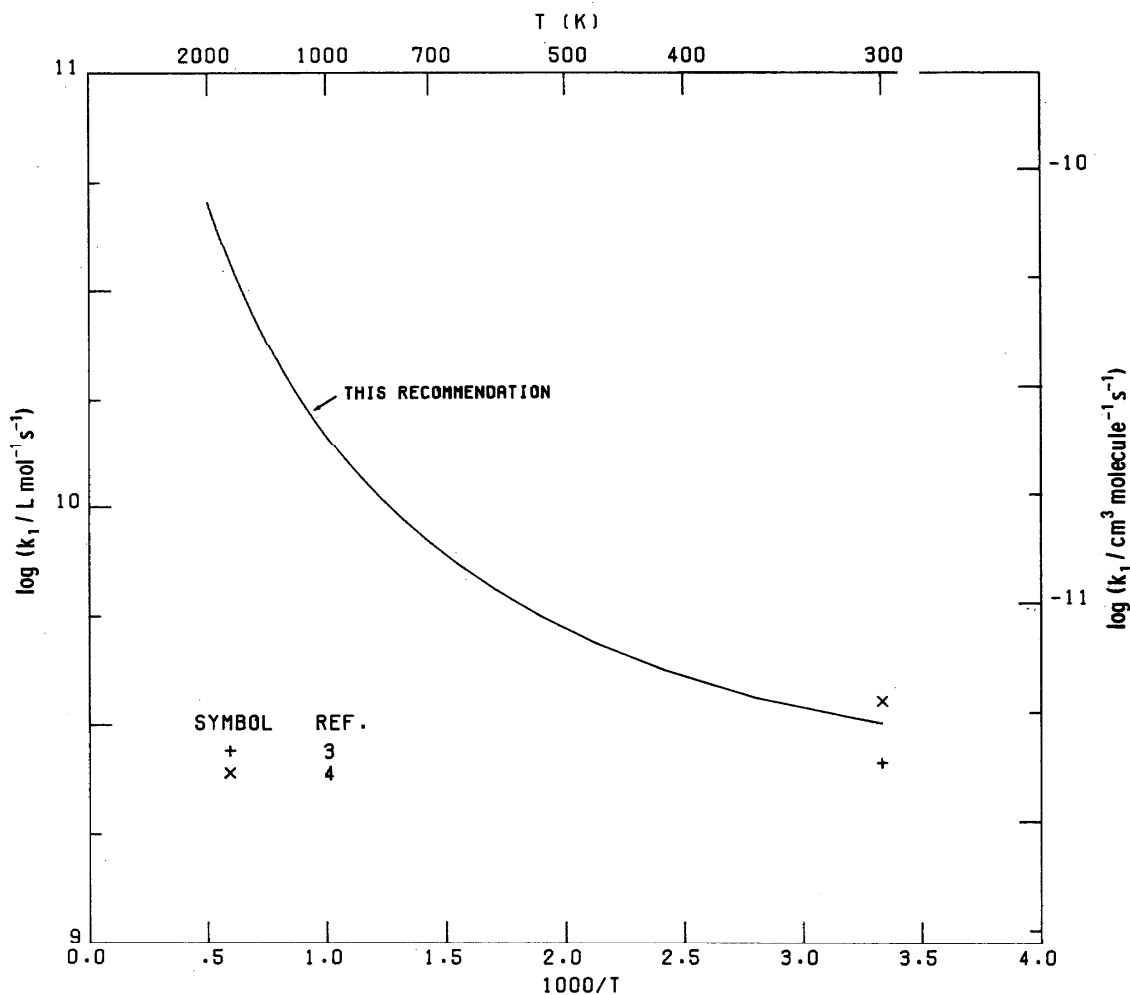
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(300)	Units
k_1	$4.8 \times 10^3 \ T^{2.1} \exp(430/T)$	300–2000 K	3.2×10^9	$L \ mol^{-1}s^{-1}$
	$8.0 \times 10^{-18} \ T^{2.1} \exp(430/T)$		6.5×10^{-12}	$cm^3 \ molecule^{-1}s^{-1}$

Uncertainty in log k_1: ± 0.2 at 300 K, increasing to ± 0.5 at 2000 K.

(December 1981)
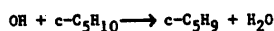
$$OH + c-C_5H_{10} \longrightarrow c-C_5H_9 + H_2O$$

THERMOCHEMISTRY

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $c-C_5H_{10}$ (cyclopentane) are taken from Stull et al.[1] Data for the cyclopentyl radical are taken from Kerr and Parsonage.[2] An analytic expression for K(T) has not been calculated because the reverse reaction will not be important over the temperature range for which values of k_1 are recommended.

MEASUREMENTS

Two measurements of k_1 at 300 K have been reported. Darnall et al.[3] used irradiated NO_x-hydrocarbon-air mixtures in a 5500 L teflon bag at 1 atm total pressure, sampling periodically and assaying alkane concentrations by gas chromatography. OH radicals were produced by a series of reactions involving NO, NO_2, and H_2O. Both cyclopentane and n-butane were present and the relative rates determined. k_1 was evaluated assuming $k_2 = 1.64 \times 10^9$ L $mol^{-1}s^{-1}$ for the reaction of OH + $n-C_4H_{10}$. Using instead our own recommended rate coefficient for k_2 of 1.5×10^9 (see Data Sheet for that reaction) we obtain $k_1 = 2.6 \times 10^9$. A second measurement of k_1 (relative to k_3 for the reaction between OH and CO) has been reported by Volman,[4] but no details are given.

CALCULATIONS

Transition state theory (TST) calculations were carried out for k_1 in order to extrapolate the rate coefficient to higher temperatures. $S^{\ddagger}(300)$ was estimated by group additivity methods, using $c-C_5H_{10}$ as a model compound. Vibrational frequencies were taken to be the same as for cyclopentane except for the removal of a C-H stretch (3100 cm^{-1}), an HCH bend (1400) and a CCH bend (1100); and the addition of the following frequencies: 3700, 2200, 1000, 1000, 350, and 300 cm^{-1}. The two new internal rotors were assumed to have partition functions $Q_f(300) = 5.6$ and 3.9, and barriers to rotation V = 8.4 and 4.2 kJ mol^{-1}, respectively. The electronic degeneracy of the activated complex, $g_e^{\ddagger}$, was assumed to be 2. These assumptions yielded a value for $\Delta S^{\ddagger}(300)$ of −97.8 J mol^{-1} K^{-1}. $k_1(300)$ was assumed to be 3.2×10^9 L $mol^{-1}s^{-1}$. The resulting values of $k_1(T)$ are well-fitted by the expression $k_1 = 4.8 \times 10^3$ $T^{2.1}$ exp(430/T).

DISCUSSION

Cyclopentane, like cyclohexane and cyclobutane, has only secondary H atoms, so there is only one product of the OH attack. If the rate of OH attack is the same for all secondary H atoms regardless of the structure of the alkane, then k_1 should be 0.83 k_2, where k_3 is the rate coefficient for OH + $c-C_6H_{12}$. Our recommended value for k_3 is 4.8×10^9 L $mol^{-1}s^{-1}$, so k_1 should be 4×10^9, over 50% larger than the corrected experimental value of Ref. 3. We therefore adopt 3.2×10^9 for $k_1(300)$ and use the TST calculations for the temperature dependence. The recommended expression, then, is $k_1 = 4.8 \times 10^3$ $T^{2.1}$ exp(430/T) L $mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ±0.2 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, New York, 1969), p. 344.
2. J. A. Kerr and M. J. Parsonage, Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals (Butterworths, London, 1976), p. 61.
3. K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., J. Phys. Chem. 82, 1581 (1978).
4. D. H. Volman, Int. J. Chem. Kinet., Symp. 1, 358 (1975).

$$OH + c\text{-}C_6H_{12} \xrightarrow{1} c\text{-}C_6H_{11} + H_2O$$

$\Delta H^o_{298} = -103 \pm 5 \text{ kJ mol}^{-1}$ ($-24.7 \text{ kcal mol}^{-1}$) $\Delta S^o_{298} = 25 \pm 5 \text{ J mol}^{-1}K^{-1}$ (6 cal mol^{-1}K^{-1})

T (K)

THIS RECOMMENDATION

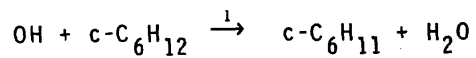| SYMBOL	REF.
+	3
x	4

1000/T
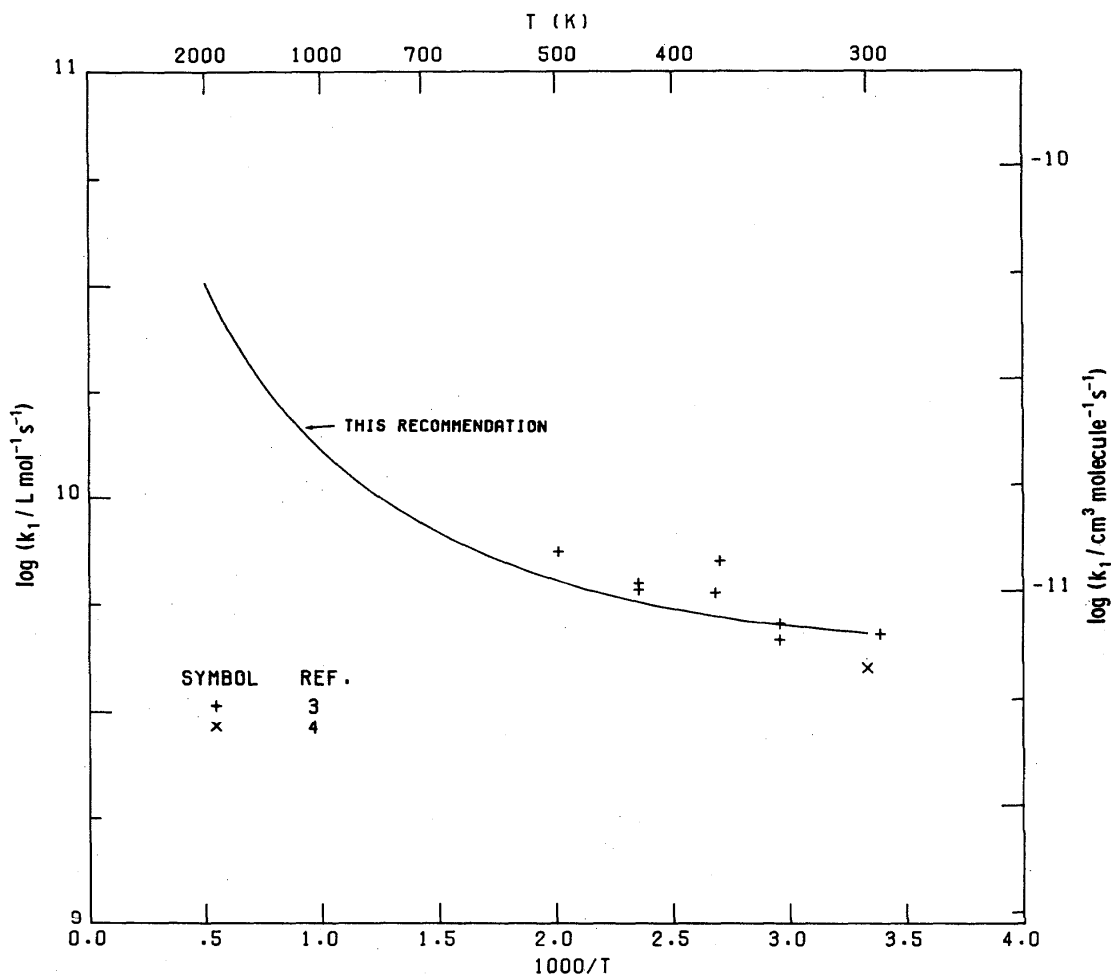
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(300)	Units
k_1	$1.4 \times 10^5 T^{1.6} \exp(400/T)$	300-2000 K	4.8×10^9	L mol^{-1}s^{-1}
	$2.3 \times 10^{-16} T^{1.6} \exp(400/T)$		8×10^{-12}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 for 300-500 K, increasing to ± 0.5 at 2000 K.

(May 1981)
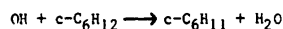
$$OH + c\text{-}C_6H_{12} \longrightarrow c\text{-}C_6H_{11} + H_2O$$

THERMOCHEMISTRY

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $c\text{-}C_6H_{12}$ (cyclohexane) are taken from Stull et al.[1] Data for the cyclohexyl radical are taken from Benson.[2] An analytic expression for $K(T)$ has not been calculated because the reverse reaction will not be important over the temperature range for which values of k_1 are recommended.

MEASUREMENTS

Three experimental studies of this reaction have been reported. Greiner[3] measured k_1 over the temperature range of 294-497 K using flash photolysis of H_2O as an OH source, monitoring OH disappearance by kinetic absorption spectroscopy. His results for other alkanes, obtained by the same technique, are in good agreement with those reported by other workers. Gorse and Volman[6] measured the room temperature ration k_1/k_2 where k_2 is the rate coefficient for the reaction, $OH + CO \rightarrow H + CO_2$. Using the value of k_2 recommended by Baulch et al.[5] one obtains a value of $k_1 = 4.0 \times 10^9$ L mol^{-1}s^{-1}, slightly smaller than the value of (4.79 ± 0.26) $\times 10^9$ obtained by Greiner. The third measurement[6] of k_1 was made relative to the rate coefficient for OH + cis-2-butene, and is not used in this evaluation.

CALCULATIONS

Transition state theory (TST) calculations were carried out for k_1 in order to extrapolate the rate coefficient beyond the temperature range of experimental data. $S^{\ddagger}(300)$ was estimated by group additivity methods, using $c\text{-}C_6H_{12}$ as a model compound. Vibrational frequencies were taken to be the same as for cyclohexane except for the removal of a C-H stretch (3100 cm^{-1}) an HCH bend (1400) and a CCH bend (1100); and the addition of the following frequencies: 3700, 2200, 1000, 1000, 350, and 300. The two new internal rotors were assumed to have partition functions $Q_f(300) = 5.6$ and 3.9, and barriers to rotation $V = 8.4$ and 4.2 kJ mol^{-1}, respectively. The electronic degeneracy of the activated complex, $g_e^{\ddagger}$, was assumed to be 2. These assumptions yielded a value for $\Delta S^{\ddagger}(300)$ of -102.4 J mol^{-1} K^{-1}. The experimental value of $k_1(300)$ obtained by Greiner was used. The resulting values of $k_1(T)$ are well-fitted by the expression, $k_1 = 1.4 \times 10^5$ $T^{1.6}$ exp(400/T) L mol^{-1} s^{-1}, in good agreement with Greiner's data.

DISCUSSION

Cyclohexane is of theoretical interest because it contains only secondary H atoms, so there is only one product of the OH attack. (This assumes that the "chair" and "boat" conformations of cyclohexane interconvert rapidly at temperatures above 300 K.) Using the "universal" rate coefficient expression of Baldwin and Walker[6] (adjusted with our own recommended value for k_{H_2+OH}) we calculate $k_1 = 2.3 \times 10^6$ $T^{1.3}$ exp(-15/T) mol^{-1}s^{-1}, which agrees, within 20% for 300-2000 K with the TST result described in the above section. We recommend the expression $k_1 = 1.4 \times 10^5$ $T^{1.6}$ exp(400/T) L mol^{-1}s^{-1} over the temperature range of 300-2000 K, with an uncertainty in log k_1 of ± 0.2 up to 500 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, New York, 1969), p. 344.
2. S. W. Benson. Thermochemical Kinetics. 2nd ed. (Wiley. New York. 1976). p. 299.
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7. R. R. Baldwin and R. W. Walker, J. Chem. Soc. Faraday Trans. I, 75, 140 (1979).

$$OH + (CH_3)_4C \xrightarrow{1} \cdot CH_2 C(CH_3)_3 + H_2O$$
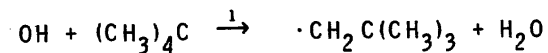
$\Delta H^o_{298} = -79.1 \pm 4.2$ kJ mol^{-1}(-18.9 kcal mol^{-1}) $\Delta S^o_{298} = 28.4 \pm 4$ J mol^{-1} K^{-1}(6.8 cal mol^{-1} K^{-1})

SYMBOL   REF.

Δ	4
×	5
∇	6
□	7
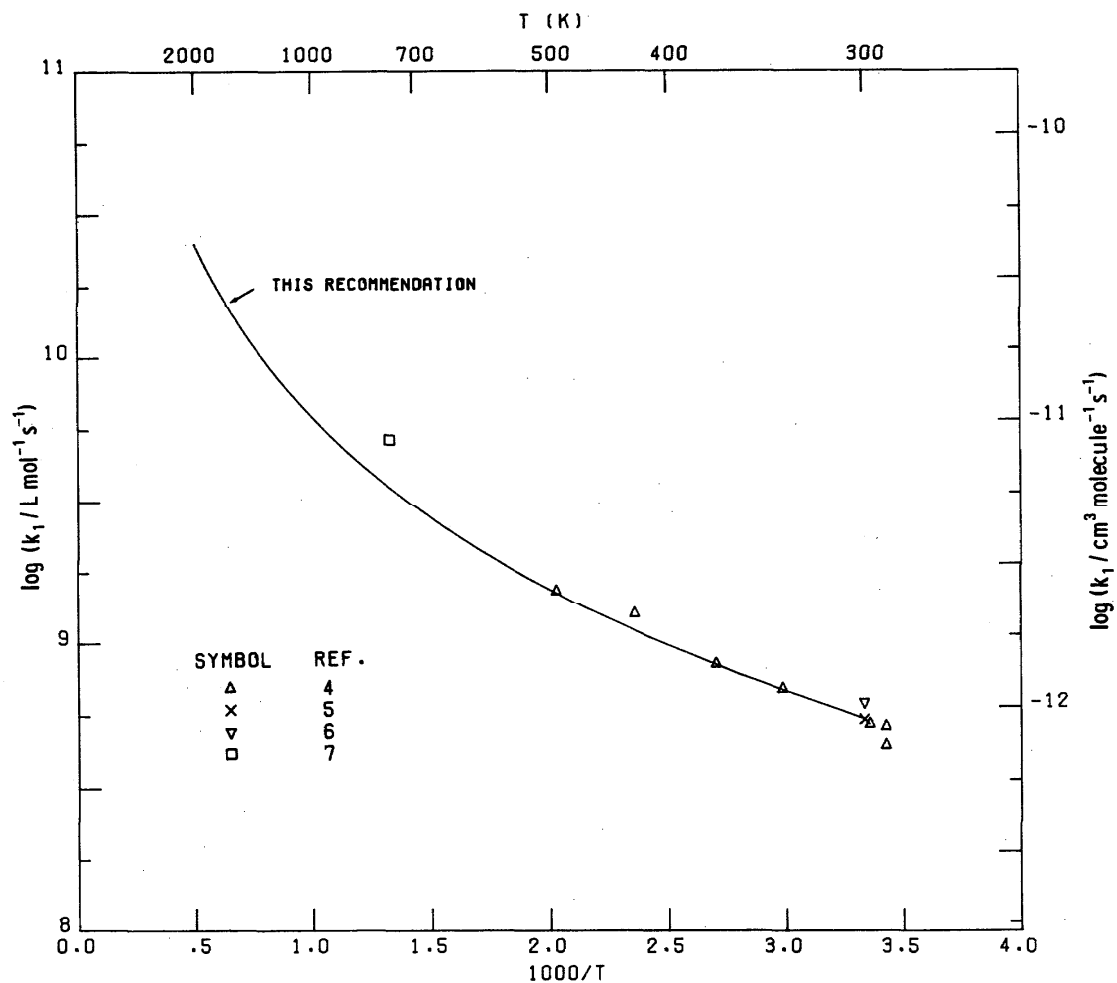
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	6.3×10^3 T$^{2.0}$ exp (-10/T)	300-2000 K	5.5×10^8	L mol^{-1}s^{-1}
	1.1×10^{-17} T$^{2.0}$ exp(-10/T)		9.1×10^{-13}	cm^{3}molecule^{-1}s^{-1}

Uncertainty in log k_1:   ±0.1 at 298 K, increasing to ±0.5 at 2000 K.   Because the reverse reaction is unimportant at any temperature, values for K(T) and k_{-1} are not recommended.
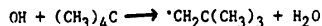
(December 1981)

$$OH + (CH_3)_4C \longrightarrow {}^{\bullet}CH_2C(CH_3)_3 + H_2O$$

THERMOCHEMISTRY

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $(CH_3)_4C$ (2,2-dimethylpropane, or neopentane) are taken from Stull et al.[1] D^o_{298}(neopentyl-H) is reported[2] as 419.25 ± 4.2 kJ mol^{-1}, from which ΔHf^o_{298} can be calculated to be 35.7 kJ mol^{-1} for the neopentyl radical. S^o_{298} for the radical was calculated[3] to be 329.4 J $mol^{-1}K^{-1}$.

An analytic expression for $K(T)$ has not been calculated because the reverse reaction will never be important; at low temperatures it is too endothermic to occur, and at high temperatures the neopentyl radicals are unstable.

MEASUREMENTS

Four experimental measurements of k_1 have been reported. Greiner[4] made observations over the temperature range of 292–493 K using flash photolysis of H_2O as an OH source, monitoring OH disappearance by kinetic absorption spectroscopy. Two room temperature measurements[5,6] were made both using flash photolysis of H_2O and resonance fluorescence to monitor OH disappearance. In the case of one of these,[6] the measurement was made relative to reaction between OH and n-C_4H_{10}. Using our own recommended rate coefficient for the latter reaction (which is about 10% smaller than that used in Ref. 6), we obtain $k_1 = 5.7 \times 10^8$ L $mol^{-1}s^{-1}$. The three room temperature measurements then agree within better than 10%; the average value is $5.5 \pm 0.3 \times 10^8$ L $mol^{-1}s^{-1}$. Baker et al.[7] measured k_1/k_2, where k_2 is the rate coefficient for $OH + H_2 \rightarrow H + H_2O$, by adding trace amounts of neopentane to H_2-O_2 mixtures at 753 K. Using our own recommended value for k_2 (see Data Sheet for that reaction) we obtain $k_1 = 5.2 \times 10^9$ L $mol^{-1}s^{-1}$.

CALCULATIONS

Transition state theory calculations were carried out for k_1 in order to extrapolate the rate coefficient beyond the temperature range of the experimental data.[8] $S^{\ddagger}(298)$ was calculated to be 388.3 J mol^{-1} K^{-1} using neopentane as a model compound, giving $\Delta S^{\ddagger} = -102$ J $mol^{-1}K^{-1}$. Vibrational frequencies were taken to be the same as for neopentane except for the removal of a C–H stretch (3100 cm^{-1}), an HCH bend (1400) and a CCH bend (1100); and the addition of the following frequencies: 3700 (OH stretch), 2200 (C$\cdot$H) stretch; 1000, 1000, 350 and 300 (deformations). The two new hindered internal rotors were assumed to have partition functions $Q_f(300) = 5.6$ and 3.9, and barriers to rotation $V = 8.4$ and 4.2 kJ mol^{-1}, respectively. The electronic degeneracy of the activated complex, $g^{\ddagger}_e$, was assumed to be 2. The resulting values of $k_1(T)$ are well-described by the expression $k_1 = 6.3 \times 10^3$ $T^{2.0}$ $exp(-10/T)$ L $mol^{-1}s^{-1}$. This expression, derived using the experimental value of $k_1(300) = 5.5 \times 10^8$, is in good agreement with the experimental data at higher temperatures.

DISCUSSION

This reaction is of theoretical interest because neopentane contains only one kind of H atom (primary), so that there is only one reaction taking place, in contrast with straight-chain alkanes with more than 2 carbon atoms.

The experimental data are in good accord; the discrepancy among the three room temperature measurements is too small to suggest any real problems. Since our calculated expression agrees with all the experimental data within experimental uncertainty, we use it for the recommended expression. Thus we recommend $k_1 = 6.3 \times 10^3$ $T^{2.0}$ $exp(-10/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_1 of ± 0.1 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, New York, 1969), p. 247.
2. C. W. Larson, E. A. Hardwidge, and B. S. Rabinovitch, J. Chem. Phys. 50, 2769 (1969).
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7. R. R. Baker, R. R. Baldwin, and R. W. Walker, Combust. Flame 27, 147 (1976).
8. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{\text{A}} \cdot C_6H_{13} + H_2O$$

$OH + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{1} \dot{C}H_2CH(CH_3)CH(CH_3)_2 + H_2O$

$\Delta H^o_{298} = -88.2 \pm 5$ kJ mol^{-1} (-21.1 kcal mol^{-1})
$\Delta S^o_{298} = 24.3 \pm 3$ J mol^{-1}K^{-1} (5.8 cal mol^{-1}K^{-1})

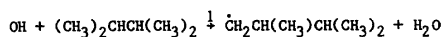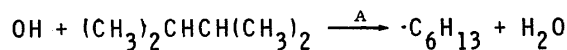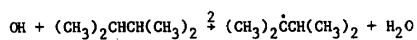$OH + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{2} (CH_3)_2\dot{C}CH(CH_3)_2 + H_2O$

$\Delta H^o_{298} = -117.0 \pm 5$ kJ mol^{-1} (-28.0 kcal mol^{-1})
$\Delta S^o_{298} = 22.2 \pm 3$ J mol^{-1}K^{-1} (5.3 cal mol^{-1}K^{-1})
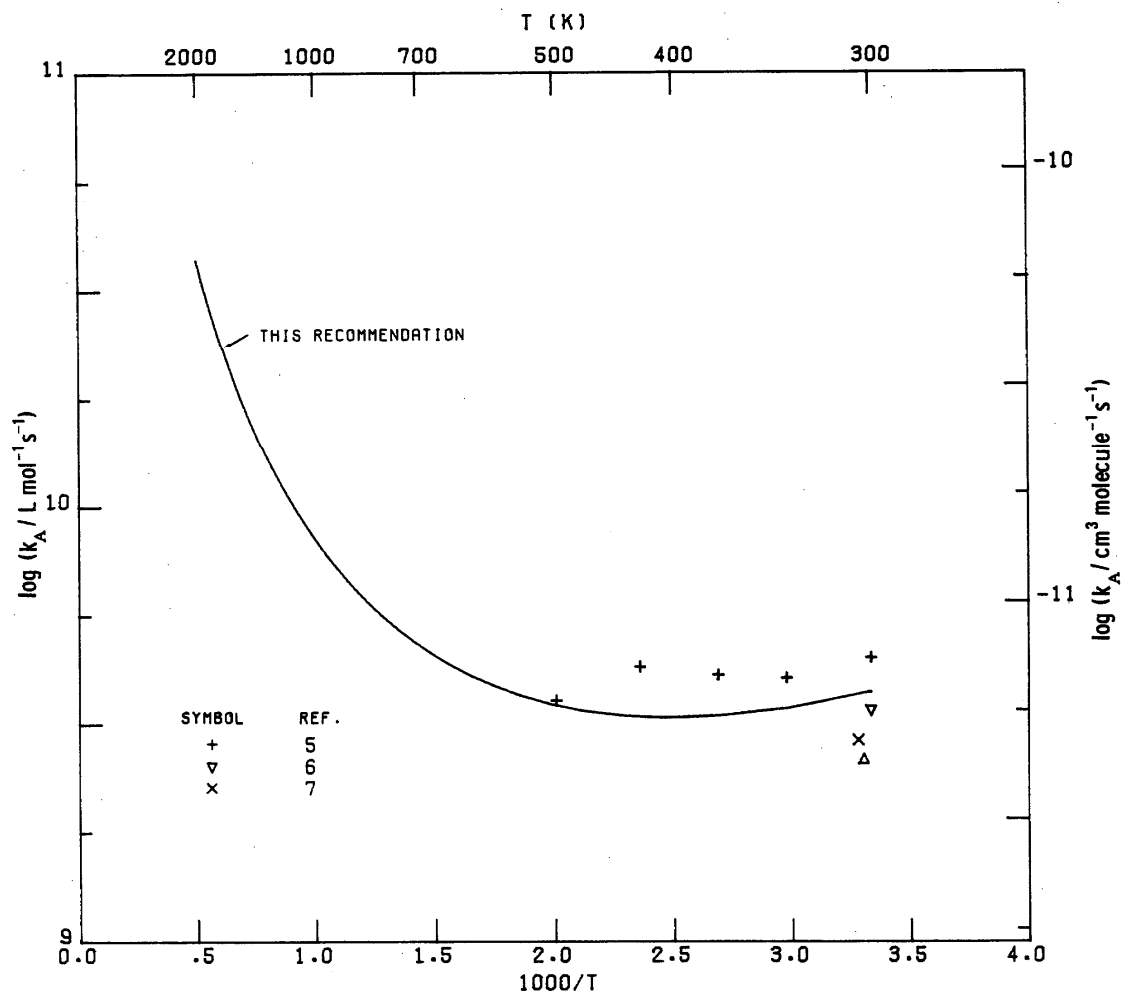
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_A	$2.5 \ T^3 \ exp(1200/T)$	298 - 2000 K	3.7×10^9	L mol^{-1}s^{-1}
	$4.1 \times 10^{-21}T^3 \ exp(1200/T)$		6.2×10^{-12}	cm^3 molecule^{-1}s^{-1}
k_1/k_2	$10 \ exp(-1300/T)$	298 - 2000 K	0.13	---

Uncertainty in log k_A: ±0.2 near 300 K_1 increasing to ±0.5 at 2000 K. Uncertainty in log k_1/k_2: ±0.3 near 300 K increasing to ±0.7 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 temperatures.

(February 1982)
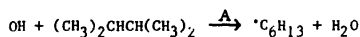
$$OH + (CH_3)_2CHCH(CH_3)_2 \xrightarrow{A} {}^{\bullet}C_6H_{13} + H_2O$$

THERMOCHEMISTRY

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

$$(CH_3)_2CHCH(CH_3)_2 + OH \xrightarrow{1} {}^{\bullet}CH_2CH(CH_3)CH(CH_3) + H_2O$$

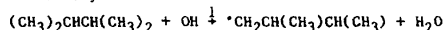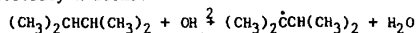and removal of one of the two equivalent tertiary H atoms:

$$(CH_3)_2CHCH(CH_3)_2 + OH \xrightarrow{2} (CH_3)_2\overset{\bullet}{C}CH(CH_3)_2 + H_2O$$

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement (June 1977) to those tables. Data for 2,3-dimethylbutane (2,3-DMB) are from Stull et al.[1] The value for ΔHf^o_{298} given by Cox and Pilcher[2] is larger by 7.3 kJ mol^{-1}. Entropy and enthalpy values for both 2,3-dimethylbutyl radicals are calculated by group additivity methods[3,4] using 2,3-DMB as the model compound. Values thus calculated for the primary radical are: $\Delta Hf^o_{298} = 7.0$ kJ mol^{-1} and $S^o_{298} = 385$ J mol^{-1} K^{-1}; those for the tertiary radical are, respectively, -21.8 kJ mol^{-1} and 382.8 J mol^{-1} K^{-1}. The uncertainty in ΔHf^o_{298} of the alkane affects those of the radicals, but cancels out of the calculation for ΔH_{rxn}.

MEASUREMENTS

There have been three published studies of k_A. Greiner[5] produced OH radicals by flash photolysis of H_2O over the temperature range of 300 - 500 K and monitored its decay by kinetic absorption spectroscopy. Because he observed slight decreases in rate constant with increasing alkane concentrations, corrections were made for an assumed recombination reaction between OH and the alkyl radicals with an assumed temperature- and radical-independent recombination rate constant of 10^{11} L $mol^{-1}s^{-1}$. At 300 K a value of $k_A = 4.5 \times 10^9$ L $mol^{-1}s^{-1}$ was reported, with little or no temperature dependence up to 500 K. In Ref. 6, k_A was measured relative to k_3 at 300 K for the reaction between OH and isobutene; this study was not used in the present evaluation. In Ref. 7, k_A was measured at 300 K relative to k_4 for the reaction between OH and n-butane. OH was generated by a series of reactions involving photolysis of NO_x - H_2O mixtures; alkane loss was measured by gas chromatography. Our own recommended value for k_4 of 1.5×10^9 L $mol^{-1}s^{-1}$ at 300 K yields a value for k_A of 3.1×10^9 L $mol^{-1}s^{-1}$.
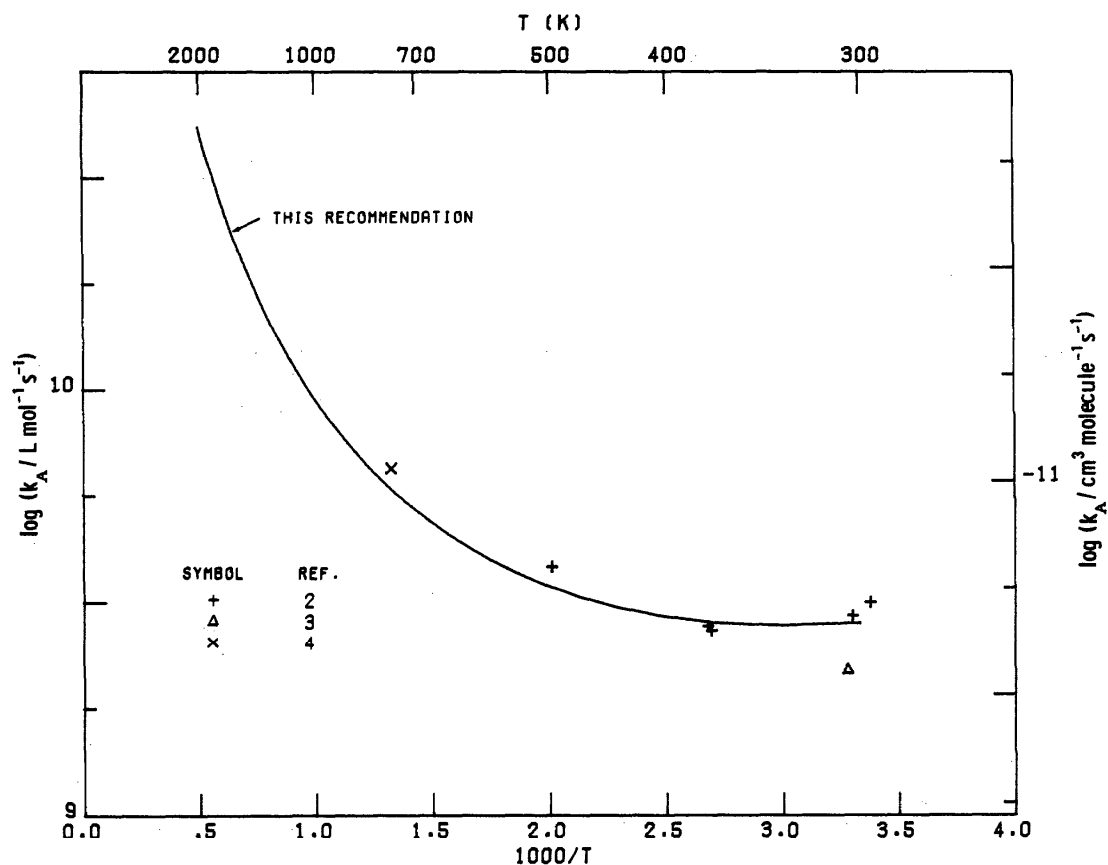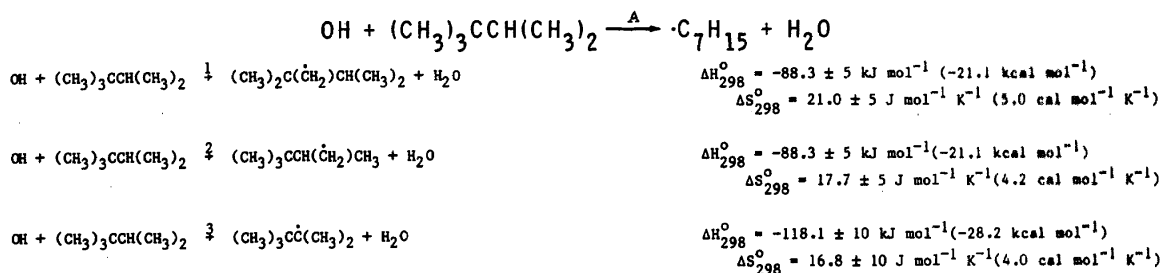
CALCULATIONS

k_1 and k_2 were separately calculated by the semi-empirical transition-state-theory method described elsewhere.[8] This requires values for $k_1(300)$ and $k_2(300)$. $k_1(300)$ was taken to be the same as that for alkanes with only primary H atoms, weighted by the number of primary H atoms on 2,3-DMB, i.e., $12 \times (3.7 \times 10^7$ L $mol^{-1}s^{-1})$. $k_2(300)$ was calculated from $k_A = k_1 + k_2$ where 3.7×10^9 was taken as the best experimental value for $k_A(300)$. 2,3-DMB was taken as the model compound for the calculation of $S^{\ddagger}$ of the activated complexes. Further details are given in Ref. 8. These assumptions resulted in $\Delta S^{\ddagger}_1(300)$ and $\Delta S^{\ddagger}_2(300)$ values of -99.9 and -118.9 J mol^{-1} K^{-1} respectively. Values of k_A obtained for $k_1 + k_2$ could be fitted within 15% by the expression $k_A = 2.5$ T^3 $exp(1200/T)$ L $mol^{-1}s^{-1}$; k_1/k_2 could be fitted well by 9.9 $exp(-1300/T)$.

DISCUSSION

There are no separate measurements of k_1 or k_2, only k_A. At present the best choice for a value of $k_A(300)$ is 3.8×10^9 L $mol^{-1}s^{-1}$, obtained by averaging results of Refs. 5 and 7. If we assume $k_A = k_1 + k_2 = 12k_p + 2k_t$, where k_p and k_2 are, respectively, the rate coefficients for OH attack per primary or per tertiary H atom, and assume further that k_p can be calculated from OH attack on alkanes with only primary H atoms, then $k_1(300) = 4.4 \times 10^8$ and $k_2(300) = 3.4 \times 10^9$ L $mol^{-1}s^{-1}$. In other words, $k_A(300)$ is 87% due to tertiary attack, which has a negligible activation energy. However, calculations indicate that by 700 K, the reaction is over 60% due to primary attack, and the activation energy of k_A will begin to resemble that for primary attack, although experiments were not performed at high enough temperatures to show this. Since the calculated value of k_A described in the preceding section is in good agreement with the data over the entire temperature range of the experiments, our recommendation is based on the calculations. Thus we recommend $k_A = 2.5$ T^3 $exp(1200/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_A of ±0.2 at 300 K, increasing to ±0.5 at 2000 K; and $k_1/k_2 = 10$ $exp(-1300/T)$, with an uncertainty in log k_1/k_2 of ±0.3 near 300 K, increasing to ±0.7 at 2000 K.

References:

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4. S. W. Benson, Thermochemical Kinetics, 2nd edn. (Wiley, New York, 1976), Appendix A.1.
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8. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + (CH_3)_3CCH(CH_3)_2 \xrightarrow{A} \cdot C_7H_{15} + H_2O$$

$OH + (CH_3)_3CCH(CH_3)_2 \xrightarrow{1} (CH_3)_2C(\dot{C}H_2)CH(CH_3)_2 + H_2O$

$\Delta H^o_{298} = -88.3 \pm 5$ kJ mol^{-1} (-21.1 kcal mol^{-1})
$\Delta S^o_{298} = 21.0 \pm 5$ J mol^{-1} K^{-1} (5.0 cal mol^{-1} K^{-1})

$OH + (CH_3)_3CCH(CH_3)_2 \xrightarrow{2} (CH_3)_3CCH(\dot{C}H_2)CH_3 + H_2O$

$\Delta H^o_{298} = -88.3 \pm 5$ kJ mol^{-1}(-21.1 kcal mol^{-1})
$\Delta S^o_{298} = 17.7 \pm 5$ J mol^{-1} K^{-1}(4.2 cal mol^{-1} K^{-1})

$OH + (CH_3)_3CCH(CH_3)_2 \xrightarrow{3} (CH_3)_3C\dot{C}(CH_3)_2 + H_2O$

$\Delta H^o_{298} = -118.1 \pm 10$ kJ mol^{-1}(-28.2 kcal mol^{-1})
$\Delta S^o_{298} = 16.8 \pm 10$ J mol^{-1} K^{-1}(4.0 cal mol^{-1} K^{-1})

RECOMMENDED RATE COEFFICIENTS

| k	k(T)	Range	k(298)	Units
k_A	$15 \ T^{2.8} \exp(920/T)$	298 - 2000 K	2.9×10^9	L mol^{-1}s^{-1}
	$2.5 \times 10^{-20} \ T^{2.8} \exp(920/T)$		4.8×10^{-12}	cm^3 molecule^{-1}s^{-1}
$(k_1 + k_2)/k_3$	$49 \ T^{-0.1} \exp(-1410/T)$	298 - 2000 K	0.25	---
k_1/k_2	1.5	298 - 2000 K	1.5	---

Uncertainty in log k_A: ±0.2 at 298 K, increasing to ± 0.5 at 2000 K. Uncertainty in log $(k_1 + k_2)/k_3$: ±0.3 at 298 K, increasing to ±0.7 at 2000 K. Uncertainty in log k_1/k_2: ±0.15 throughout temperature range. No recommendations are made for k_{-1}, k_{-2}, and k_{-3}, or $K_{1,-1}$, $K_{2,-2}$, and $K_{3,-3}$ because the reverse reactions are unlikely to be important at any temperature.
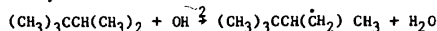
(February 1982)

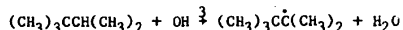$$OH + (CH_3)_3CCH(CH_3)_2 \xrightarrow{A} \cdot C_7H_{15} + H_2O$$
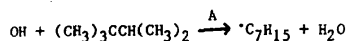
THERMOCHEMISTRY

The title reaction is the sum of three elementary reactions: (1) removal of one of the nine equivalent primary H atoms:

$$(CH_3)_3CCH(CH_3)_2 + OH \xrightarrow{1} (CH_3)_2C(\dot{C}H_2)CH(CH_3)_2 + H_2O$$
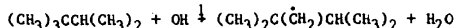
(2) removal of one of the six equivalent primary H atoms:

$$(CH_3)_3CCH(CH_3)_2 + OH \xrightarrow{2} (CH_3)_3CCH(\dot{C}H_2) CH_3 + H_2O$$

and (3) removal of the single tertiary H atom:

$$(CH_3)_3CCH(CH_3)_2 + OH \xrightarrow{3} (CH_3)_3C\dot{C}(CH_3)_2 + H_2O$$

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement (June 1977) to those tables. Data for $(CH_3)_3CCH(CH_3)_2$, which is 2,2,3-trimethylbutane (2,2,3-TMB), are from Stull et al.[1] The enthalpy and entropy of the different radicals were calculated by group additivity rules; it was assumed that all primary C-H bonds have the same bond dissociation energy.

MEASUREMENTS

There have been three published studies of k_A. Greiner[2] produced OH radicals by flash photolysis of H_2O over the temperature range of 300-500 K and monitored its decay by kinetic absorption spectroscopy. Because he observed slight decreases in rate constants with increasing alkane concentrations, corrections were made for an assumed recombination reaction between OH and the alkyl radicals with an assumed temperature- and radical-independent recombination rate constant of 10^{11} L $mol^{-1}s^{-1}$. At 296-303 K values of $k_A = 3.04 \pm 0.18 \times 10^9$ L $mol^{-1}s^{-1}$ were obtained, increasing slightly to $3.81 \pm 0.11 \times 10^9$ at 497 K. Darnall et al.[3] measured k_A/k_4 at 300 K where k_4 is the rate coefficient for the reaction of OH with isobutene. Their resulting value for k_A is shown on the graph but was not considered in this evaluation. Baldwin et al.[4] measured k_A/k_5 from the effect of small quantities of 2,3,3-TMB on H_2-O_2 kinetics at 753 K where k_5 is for the reaction of OH + H_2. The course of the reaction was monitored by gas chromatographic analysis of reaction products. They deduced a value for k_A/k_5 of 12.2, which, using our own recommended value for k_5 yields a value for k_A of 6.5×10^9 L $mol^{-1}s^{-1}$. Corrections were required for competing processes involving attack on the alkane by O, H, and HO_2.

CALCULATIONS

k_1, k_2 and k_3 were separately calculated by the semi-empirical transition-state-theory method described elsewhere.[5] This requires values for $k_1(300)$, $k_2(300)$ and $k_3(300)$. $k_1(300)$ and $k_2(300)$ were taken to be the same as that for alkanes with only primary H atoms, weighted by the number of primary H atoms of each kind. $k_3(300)$ was calculated from $k_A = k_1 + k_2 + k_3$ where 3.0×10^9 was taken as the best experimental value for $k_A(300)$. For further details see Ref. 5. These assumptions resulted in $\Delta S_1^{\ddagger}(300)$, $\Delta S_2^{\ddagger}(300)$ and $\Delta S_3^{\ddagger}(300)$ values of -102.4, -105.8, and -124.8 J mol^{-1} K^{-1}, respectively. Values of k_A obtained from $k_1 + k_2 + k_3$ could be fitted, within 12%, by the expression $k_A = 15 \ T^{2.8} \exp(920/T)$. The ratio of primary to tertiary attack $(k_1 + k_2)/k_3$ could be expressed, within 10%, as $49 \ T^{-0.1} \exp(-1410/T)$. Since all primary H atoms were assumed equivalent, $k_1/k_2 = 1.5$.

## DISCUSSION

There are no separate measurements of k_1, k_2, or k_3, only the combined k_A. The best choice at present for $k_A(300)$ is that of Ref. 2: 3.0×10^9 L $mol^{-1}s^{-1}$. If we assume $k_A = k_1 + k_2 + k_3 = 15k_p + k_t$, where k_p and k_t are, respectively the rate coefficients for HO attack per primary or per tertiary H atom (atoms of each group considered equivalent), and assume further that k_p can be calculated from OH attack on alkanes with only primary H atoms, then $k_1 (300) = 3.4 \times 10^8$, $k_2(300) = 2.2 \times 10^8$, and $k_3(300) = 2.4 \times 10^9$ L $mol^{-1}s^{-1}$. There are theoretical reasons why k_1/k_2 should not be precisely equal to 9/6, the ratio of the two kinds of primary H atoms, but the deviation from this value is probably small compared to other uncertainties in the calculations and in the measurements. Near 300 K, the above assumptions indicate that the total observed rate constant k_A is over 80% due to tertiary attack, which has a negligible activation energy. However, calculations indicate that by 700 K, the reaction is almost 80% due to primary attack.

The calculated value of k_A described in the preceding section is in good agreement with all the experimental data of Refs. 2 and 4; consequently we base our recommendation on it. Thus we recommend $k_A = 15 \ T^{2.8} \exp(920/T)$ L $mol^{-1}s^{-1}$, with an uncertainty in log k_A of ± 0.2 near 300 K, increasing to ± 0.5 at 2000 K; $(k_1 + k_2)/k_3 = 50 \ T^{-0.1} \exp(-1410/T)$, with an uncertainty in log $(k_1 + k_2)/k_3$ of ± 0.3 at 298, increasing to ± 0.7 at 2000 K; $k_1/k_2 = 1.5$ with an uncertainty in log k_1/k_2 of ± 0.15 throughout the temperature range.

References:

1. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, The Chemical Thermodynamics of Organic Compounds (Wiley, New York, 1969), p. 252.
2. N. R. Greiner, J. Chem. Phys. 53, 1070 (1970).
3. K. R. Darnall, A. M. Winer, A. C. Lloyd, and J. N. Pitts, Jr., Chem. Phys. Lett. 44, 415 (1976).
4. R. R. Baldwin, R. W. Walker, and R. W. Walker, J. Chem. Soc., Faraday Trans. I, 77, 2957 (1981).
5. N. Cohen, Int. J. Chem. Kinet. 14, 1339 (1982).

$$OH + (CH_3)_3CC(CH_3)_3 \xrightarrow{1} \cdot CH_2C(CH_3)_2C(CH_3)_3 + H_2O$$
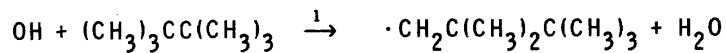
$\Delta H_{298}^o = -90.8 \pm 4$ kJ mol^{-1} (-21.7 kcal mol^{-1}) $\Delta S_{298}^o = 26.0 \pm 5$ J mol^{-1} K^{-1} (6.2 cal mol^{-1} K^{-1})
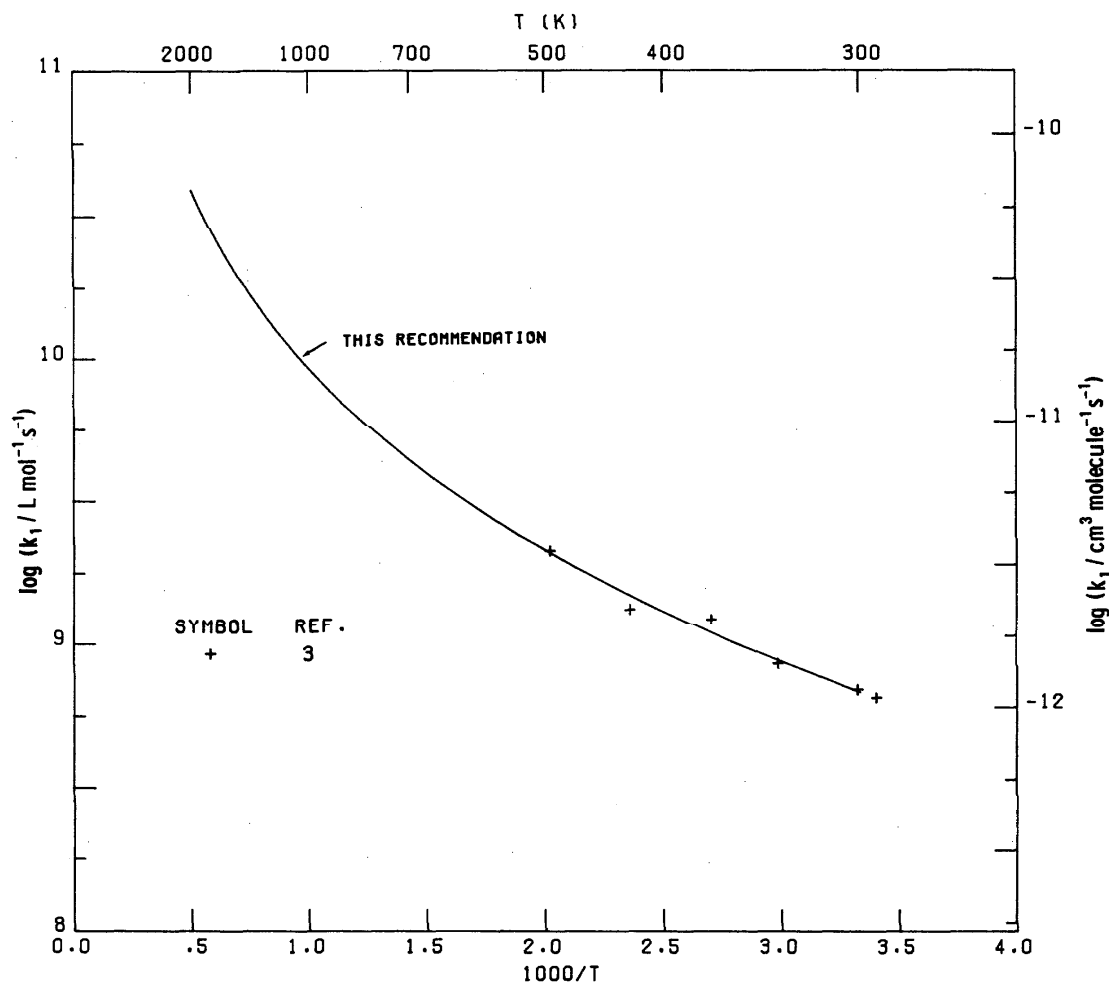
RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	$1.0 \times 10^4\ T^{2.0}\ \exp(-90/T)$	300-2000 K	6.9×10^8	L mol^{-1}s^{-1}
	$1.7 \times 10^{-17}\ T^{2.0}\ \exp(-90/T)$		1.1×10^{-12}	cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ± 0.2 for 300-750 K, increasing to ± 0.4 at 2000 K. Because the reverse reaction will be unimportant at any temperature, values for K(T) and k_{-1} are not recommended.
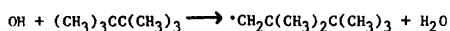
(December 1981)

$$OH + (CH_3)_3CC(CH_3)_3 \longrightarrow {}^{\cdot}CH_2C(CH_3)_2C(CH_3)_3 + H_2O$$

THERMOCHEMISTRY

Thermochemical data for H_2O are taken from the second edition of JANAF Thermochemical Tables (1971); data for OH are from an unpublished supplement to those tables dated June 1977. Data for $(CH_3)_3CC(CH_3)_3$ (2,2,3,3-tetramethylbutane, or neooctane) are taken from Stull et al.[1] Data for the neooctyl radical are taken from Kerr and Parsonage.[2] An analytic expression for $K(T)$ has not been calculated because the reverse reaction will never be important: at low temperatures it is too endothermic to occur, and at high temperatures the neooctyl radicals are unstable.

MEASUREMENTS

Only one experimental study of this reaction has been reported. Greiner[3] measured k_1 over the temperature range of 294-495 K using flash photolysis of H_2O as an OH source, monitoring OH disappearance by kinetic absorption spectroscopy. His results for other alkanes, obtained by the same technique, are in good agreement with those reported by other workers.

CALCULATIONS

Transition state theory (TST) calculations were carried out for k_1 in order to extrapolate the rate coefficient beyond the temperature range of the experimental data. $S^{\ddagger}(300)$ was estimated to be 475.7 J $mol^{-1}K^{-1}$ by group additivity methods, using neooctane as a model compound.[4] Vibrational frequencies were taken to be the same as for neooctane except for the removal of a C-H stretch (3100 cm^{-1}) an HCH bend (1400) and a CCH bend (1100); and the addition of the following frequencies: 3700 (OH stretch), 2200 (C·H stretch); 1000, 1000, 350, and 300 (deformations). The two new internal rotors were assumed to have partition functions $Q_f(300) \sim 5.6$ and 3.9, and barriers to rotation $V \sim 8.4$ and 4.2 kJ mol^{-1}, respectively. The electronic degeneracy of the activated complex, $g_e^{\ddagger}$ was assumed to be 2. The resulting values of $k_1(T)$ are well-fitted by the expression, $k_1 = 1.0 \times 10^4 \ T^{2.0} \exp(-90/T)$ L $mol^{-1}s^{-1}$, in good agreement with the other data of Ref. 3.

DISCUSSION

Neooctane, like neopentane, is of theoretical interest because it contains only primary H atoms, so there is only one product of the OH attack. Using the "universal" rate coefficient of Baldwin and Walker[5] (adjusted with our own recommended value for k_{H_2+OH}) we calculate $k_1 = 4.2 \times 10^6 \ T^{1.3} \exp(-765/T)$, which agrees, within 50% for 300-2000 K, with the TST result described in the above section. We therefore recommend the expression $k_1 = 1.0 \times 10^4 \ T^{2.0} \exp(-90/T)$ L $mol^{-1}s^{-1}$ over the temperature range of 300 - 2000 K, with an uncertainty in log k_1 of ±0.2 up to 750 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. 259.
2. J. A. Kerr and M. J. Parsonage, Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals (Butterworths, London, 1976), p. 58.
3. N. R. Greiner, J. Chem. Phys. 53, 1070 (1970).
4. See, for example, S. W. Benson, Thermochemical Kinetics, 2nd ed. (Wiley, New York, 1976).
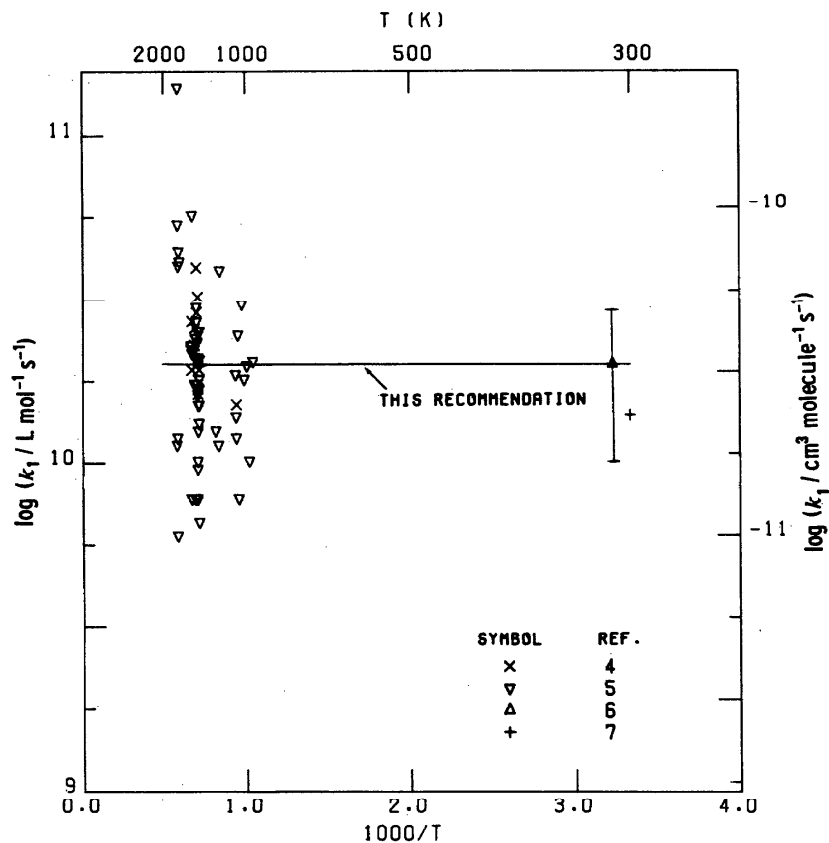5. R. R. Baldwin and R. W. Walker, J. Chem. Soc. Faraday Trans. I, 75, 140 (1979).

$$Al + O_2 \underset{-1}{\overset{1}{\rightleftharpoons}} AlO + O$$
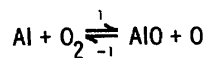
$\Delta H^o_{298} = -8.6 \pm 8$ kJ mol^{-1} (-2.1 kcal mol^{-1}) $\qquad\qquad \Delta S^o_{298} = 9.74 \pm 0.07$ J mol^{-1} K^{-1} (2.33 cal mol^{-1} K^{-1})

$$K(T) = 0.1\ T^{0.5}\ exp(1200/T)$$

The uncertainty in log K is at least ±1.3 at 298 K, ±0.4 at 1000 K, and ±0.1 at 5000 K.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	2×10^{10}	300-2000 K	2×10^{10}	L mol^{-1}s^{-1}
	3×10^{-11}		3×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$2 \times 10^{11}T^{-0.5}$ exp(-1200/T)	300-2000 K	2×10^8	L mol^{-1}s^{-1}
	$3 \times 10^{-10}T^{-0.5}$ exp(-1200/T)		3×10^{-13}	cm^3 molecule^{-1}s^{-1}

The uncertainty in log k_1 is ±0.3 throughout the temperature range; that in log k_{-1} is ±1.6 at 298 K, decreasing to ±0.7 at 1000 and ±0.4 at 2000 K. The uncertainty in log k_{-1} reflects those of k_1 and K(T).

(August 1980)

Al + O$_2$ $\rightleftharpoons$ AlO + O
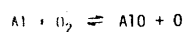
THERMOCHEMICAL DATA

Thermochemical data for Al are taken from the second edition of the JANAF Thermochemical Tables (1971); data for O and O$_2$ are taken from an unpublished supplement (dated 31 March 1977) to these Tables; data for AlO are from the 1978 Supplement to the JANAF Tables. These Tables give D_0^o(Al-O) as 502 ± 8 kJ/mol. Recent measurements by Pasternack and Dagdigian[1] give D_0^o(Al-O) = 506 kJ/mol, while measurements by Fontijn and Felder[2] yield D_0^o(Al-O) ⩾ 527 kJ/mol.

The analytic expression chosen for K(T) matches equilibrium constants calculated from the JANAF Tables to within 6% between 200 and 6000 K.

MEASUREMENTS

The gas-phase reaction of atomic aluminum with oxygen has been examined in a fast-flow reactor over a wide range of temperatures by Fontijn and co-workers.[3-6] In this technique a resistance-heated metal atom vaporizer provides the source for Al atoms, which are entrained in a stream of carrier gas down a cylindrical tube, into which is injected O$_2$. Relative [Al] as a function of distance downstream is determined by atomic absorption spectroscopy. By a special modular construction technique and the introduction of water coolant, the apparatus has been adapted to measurements at room temperature.[6] Results at both 300 K and in the range of 1000-1700 K yield a rate coefficient of (2.0 ± 1.3) x 10^{10} L mol^{-1}s^{-1}.

Another measurement by a diffusion flame technique at 300 K has also been reported;[7] this result is (1.4 ± 0.5) x 10^{10} L mol^{-1}s^{-1}. Because of gasdynamic complications, this experimental result is less reliable than the former, in spite of the higher reported precision.

CALCULATIONS

A Transition-State-Theory calculation was made for k_1 assuming that the reaction intermediate, AlOO, has a stable ground state and that the transition state (TS) is loose, following the procedure outlined by Benson and Golden.[8,9] The Al-O$_2$ bond strength was taken to be 230 kJ/mol less than that of Al-OH, by analogy with the difference between H-O$_2$ and H-OH, giving a value of 305 kJ/mol; whence, using Eq. (3.23) of Ref. 8, the Al-O$_2$ bond length in the TS at different temperatures can be calculated. It was further assumed that the AO-O stretch, the only vibrational degree of freedom contributing to $s^{\ddagger}$, is the same as in O$_2$; and that the TS is an electronic doublet state. These assumptions would lead to values for log k_1 of 10.5 ± 0.3 for 300 - 1000 K if the reaction were very exothermic. For a thermoneutral reaction the calculated k_1 would be smaller by a factor of 2; if the reaction were endothermic, the reduction could be considerably greater. Our assumed thermochemistry leads to values for log k_1 of 10.4 ± 0.5 for 300 - 1000 K.

DISCUSSION

The results of the calculation described above are in agreement with experimental data. We therefore recommend the values obtained by Fontijn et al., namely log $(k_1/\text{Lmol}^{-1}\text{s}^{-1})$ = 10.3 ± 0.3 for 300 - 2000 K.

References

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2. A. Fontijn and W. Felder, J. Chem. Phys. 71, 4854 (1979).
3. A. Fontijn, S. C. Kurius, and J. J. Houghton, 14th Symp. (Int.) Combust., 167 (1973).
4. A. Fontijn, W. Felder, and J. J. Houghton, Chem. Phys. Lett. 27, 365, (1974).
5. A. Fontijn, W. Felder, and J. J. Houghton, 15th Symp (Int.) Combust., 775 (1975).
6. A. Fontijn, W. Felder, and J. J. Houghton, 16th Symp. (Int.) Combust., 871 (1977).
7. U. C. Sridharan, T. G. DiGiuseppe, D. L. McFadden, and P. Davidovits, J. Chem. Phys. 70, 5422 (1979).
8. S. W. Benson, Thermochemical Kinetics, 2nd ed. (Wiley, New York, 1976), pp. 89ff.
9. S. W. Benson and D. M. Golden, "Methods for the Estimation of Rate Parameters of Elementary Processes," in Physical Chemistry: An Advanced Treatise, Vol. VII, Henry Eyring, ed. (Academic Press, New York, 1975), pp. 75ff.
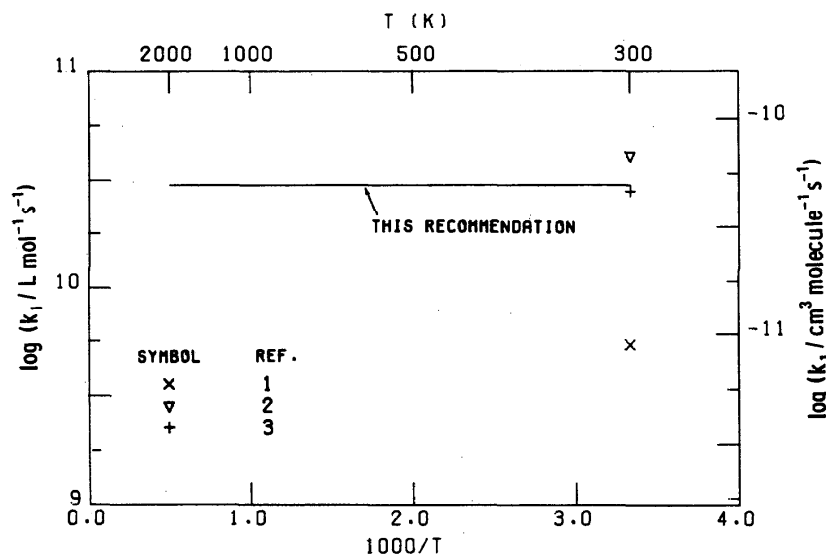
$$B + O_2 \underset{-1}{\overset{1}{\rightleftharpoons}} BO + O$$
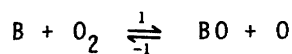
$\Delta H^o_{298} = -306.5 \pm 8$ kJ mol (-73.2 kcal/mol) $\Delta S^o_{298} = 5.93 \pm 0.03$ J mol^{-1} K^{-1}(1.42 cal mol^{-1} K^{-1})

$$K(T) = 4.1 \, T^{-0.1} \, \exp(36860/T)$$

The uncertainty in log K is ±1.2 at 298 K, ±0.4 at 1000 K and ±0.1 at 5000 K.

RECOMMENDED RATE COEFFICIENTS

k	k(T)	Range	k(298)	Units
k_1	3×10^{10}	300-2000	3×10^{10}	L mol^{-1}s^{-1}
	5×10^{-11}		5×10^{-11}	cm^3 molecule^{-1}s^{-1}
k_{-1}	$7.3 \times 10^9 \, T^{0.1} \, \exp(-36860/T)$	1000-2000		L mol^{-1}s^{-1}
	$1.2 \times 10^{-11} \, T^{0.1} \, \exp(-36860/T)$			cm^3 molecule^{-1}s^{-1}

Uncertainty in log k_1: ±0.3 at 300 K, increasing to ±0.5 at 2000 K. Uncertainty in log k_{-1}: ±1.5 at 300, decreasing to ±0.8 at 2000 K. This uncertainty reflects those of both k_1 and K(T).

(May 1981)

$$B + O_2 \rightleftharpoons BO + O$$
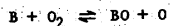
THERMOCHEMICAL DATA

The thermochemical data for B and BO are taken from the second edition of the JANAF Thermochemical Tables (1971); data for O and O_2 are taken from an unpublished supplement to these Tables, dated 31 March 1977. The analytic expression chosen for $K(T)$ matches equilibrium constants calculated from the JANAF tables to within 4% between 700 and 6000 K.

MEASUREMENTS

Two studies of this reaction at 300 K from the same laboratory have been published.[1,2] In the second and more reliable,[2] B atoms were produced in a microwave discharge through a dilute B_2H_6-Ar mixture in a flow tube. Consumption of B atom was monitored by atomic absorption spectrometry with a B resonance lamp. A value for k_1 of $(2.8 \pm 1.1) \times 10^{10}$ L $mol^{-1}s^{-1}$ was deduced. Corrections were made for flow non-ideality and for wall losses. Another study has been reported[3] in which a larger value for k_1, namely $(4.1 \pm 0.8) \times 10^{10}$ L $mol^{-1}s^{-1}$, was obtained.

CALCULATIONS

A transition state theory calculation was made for k_1 assuming that BOO has a stable ground state and that the transition state (TS) is "loose", following the procedure outlined by Benson and Golden.[4,5] The B-O_2 bond strength was taken to be 238 kJ/mol less than the HB-O bond (774 kJ/mol), based on comparison with HO_2/HOH and AlOH/HAlO analogs; whence, using Eq. (3.23) of Ref. 3, the B-O_2 bond length in the TS can be calculated at different temperatures. It was further assumed that the B-O stretch in the TS, the only vibration contributing to $S^{\ddagger}$, is 1900 cm^{-1}, and that the TS is an electronic doublet state. With these assumptions, it can be shown that B reacts with O_2 on every collision at temperatures of 300K or less, so $k_1(300)$ should be calculable by ordinary collision theory. The result is log k(300) = 10.5 ± 0.2. A loose TS implies very weak temperature dependence. However, at temperatures greater than about 1500-2000 K, the B-O_2 bond length in the TS becomes too short for it to be "loose" as defined in Ref. 4 or 5.

DISCUSSION

The calculation described above predicts a negligible temperature dependence and a value for $k_1(300)$ in good agreement with Refs. 2 and 3. Consequently, we recommend the temperature dependence suggested by the calculation: log k_1 = 10.5, with an uncertainty in log k of ±0.3 at 300 K increasing to ±0.5 at 2000 K.

References

1. U. C. Sridharan, T. G. DiGiuseppe, D. L. McFadden, and P. Davidovits, J. Chem. Phys. 70, 5422 (1979).
2. T. G. DiGiuseppe and P. Davidovits, J. Chem. Phys. 74, 3287 (1981).
3. G. C. Light and S. S. Goldberg, Bull. Amer. Phys. Soc. 26, 362 (1981).
4. S. W. Benson, Thermochemical Kinetics, 2nd ed. (Wiley, New York, 1976), pp. 89ff.
5. S. W. Benson and D. M. Golden, "Methods for the Estimation of Rate Parameters of Elementary Processes," in Physical Chemistry: An Advanced Treatise, Vol. VII, Henry Eyring, ed. (Academic Press, New York, 1975), pp. 75ff.