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

N. Cohen, and K. R. Westberg

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

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

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

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I. Introduction

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

In this second compilation, we present an additional forty-nine Data Sheets for as many gas-phase bimolecular reactions (or sets of reactions of the same reagents leading to different products). The reactions fall into three categories: (1) reactions of \( O \) atoms with alkanes; (2) reactions of \( OH \) radicals with haloalkanes; and (3) reactions of importance in the \( O/NH_3 \) system. The process of evaluating these reactions and preparing the Data Sheets resulted in the generation of a good deal more material than could be fitted into the concisely formatted Data Sheets themselves, and consequently separate journal papers were prepared and published. These studies are cited individually in the appropriate Data Sheets.

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

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

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

Measurements/Graph. Each Data Sheet contains a graph on which either \( \ln k \) or \( \ln k_{-1} \) is plotted vs
1000/T. The graph includes the recommended value(s) and those experimental data thought to be the most accurate and precise. For a well-studied reaction, the standard for accuracy is higher than for a less well-studied reaction. In some cases, experimental data have been reanalyzed, and the reanalyzed data are plotted on the graph. The Measurements section of the Data Sheet gives the reasons for preferring some measurements to others, as well as the reasons why some of the data may have been reanalyzed. At the bottom of the graph is a date that indicates when the literature search was concluded.

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

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

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

One of the principal difficulties in using TST is a lack of a general procedure for calculating \( \kappa \). We assume in our calculations that \( \kappa = \exp(C'/T) \), where \( C' \) is a constant. This assumption is equivalent to assuming that tunneling, barrier recrossing, and other nonidealities together lower the effective reaction barrier without changing the shape of the PES in the vicinity of the saddle point. This assumption appears to account accurately (i.e., with ±25% for 1000 < 7K < 200) for tunneling and other quantum effects in the \( \text{H} + \text{para-H}_2 \rightarrow \text{ortho-H}_2 + \text{H} \) reaction calculated on the surface of Porter and Karplus, but it is unlikely to be valid for all reactions. For this reason, we usually use TST calculations to extrapolate data to high temperatures where quantum effects are less important, rather than to lower temperatures, where tunneling could be extensive. As is explained in Ref. 1, the effective barrier height is derived from measured values of the rate coefficient. (In our formulation of TST, the effective barrier \( \Delta H^\ddagger - RC' \), where \( R \) is the gas constant and \( \Delta H^\ddagger \) is the enthalpy of activation at zero kelvin.) The shape of the PES is estimated so as to be maximally consistent with experimental data and with \textit{ab initio} calculations or sound chemical principles.

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

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

**Recommended Rate Coefficients and Uncertainties.** Recommended rate coefficients are always expressed in the form \( k = AT^n \exp(-B/T) \), where \( A, n, \) and \( B \) are constants. The quotient of forward and reverse rate coefficients is taken to be equal to the equilibrium constant for the reaction: \( k_2/k_1 = K(T) \). The uncertainties assigned to the logarithms of the recommended rate coefficients are subjective, rather than statistically precise, because systematic errors in chemical kinetics are almost always larger than the statistically calculable random errors.

**2. Acknowledgments**

We thank S. W. Benson for continued advice and criticisms during the course of this work; and K. Foster for assistance with the preparation of the graphs and with some of the calculations. This work was supported in part by the National Institute of Standards and Technology under Contract No. NB83-NADA-4034.

3. References


4. Data Sheets

4.1 List of Data Sheets

1. \( \text{OH} + \text{CH}_3 \rightarrow \text{O} + \text{CH}_4 \)
2. \( \text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5 \)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>3.</th>
<th>O + C₅H₄ → OH + C₂H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>4.</td>
<td>O + C₆H₁₀ → OH + C₆H₆</td>
</tr>
<tr>
<td>Reaction</td>
<td>5.</td>
<td>O + C₆H₁₂ → OH + C₆H₁₁</td>
</tr>
<tr>
<td>Reaction</td>
<td>6.</td>
<td>O + C₇H₁₄ → OH + C₇H₁₃</td>
</tr>
<tr>
<td>Reaction</td>
<td>7.</td>
<td>O + C₈H₁₆ → OH + C₈H₁₅</td>
</tr>
<tr>
<td>Reaction</td>
<td>8.</td>
<td>O + C₉H₁₈ → OH + C₉H₁₇</td>
</tr>
<tr>
<td>Reaction</td>
<td>9.</td>
<td>O + i-C₄H₁₀ → OH + C₄H₉</td>
</tr>
<tr>
<td>Reaction</td>
<td>10.</td>
<td>O + (CH₃)₂C → OH + C₆H₁₁</td>
</tr>
<tr>
<td>Reaction</td>
<td>11.</td>
<td>O + (CH₃)₂CHCH(CH₃)₂ → OH + C₆H₁₃</td>
</tr>
<tr>
<td>Reaction</td>
<td>12.</td>
<td>O + (CH₃)₂CC(CH₃)₂ → OH + C₆H₁₇</td>
</tr>
<tr>
<td>Reaction</td>
<td>13.</td>
<td>O + C₅H₁₀ → OH + C₅H₅</td>
</tr>
<tr>
<td>Reaction</td>
<td>14.</td>
<td>O + C₆H₁₂ → OH + C₆H₁₁</td>
</tr>
<tr>
<td>Reaction</td>
<td>15.</td>
<td>O + C₇H₁₄ → OH + C₇H₁₃</td>
</tr>
<tr>
<td>Reaction</td>
<td>16.</td>
<td>OH + CH₃F → CH₂F + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>17.</td>
<td>OH + CH₂F₂ → CHF₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>18.</td>
<td>OH + CHF₂ → CF₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>19.</td>
<td>OH + CH₂Cl → CHCl₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>20.</td>
<td>OH + CH₂Cl₂ → CHCl₃ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>21.</td>
<td>OH + CH₂Br → CH₂Br₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>22.</td>
<td>OH + CH₂ClF → CHClF₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>23.</td>
<td>OH + CH₂Cl₂F → CH₂ClF₃ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>24.</td>
<td>OH + CH₂Cl₃F → CH₂Cl₃F + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>25.</td>
<td>OH + CH₂Cl₂F → CH₂Cl₂F + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>26.</td>
<td>OH + CH₂Cl₃F → C₂H₄F + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>27.</td>
<td>OH + CH₃CH₂Cl → C₂H₄Cl + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>28.</td>
<td>OH + CH₃CH₂F₂ → CH₃F₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>29.</td>
<td>OH + CH₃CH₂Cl → C₂H₅Cl + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>30.</td>
<td>OH + CH₃CH₂F₂ → CH₂F₂CHF₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>31.</td>
<td>OH + CH₃BrCH₂Br → CH₃BrCH₂Br + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>32.</td>
<td>OH + CH₃CH₂F₂ → C₂H₅F₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>33.</td>
<td>OH + CH₃CH₂Cl → C₂H₅Cl + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>34.</td>
<td>OH + CH₃CH₂F₂ → CH₂F₂CHF₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>35.</td>
<td>OH + CH₃Cl → CH₂Cl₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>36.</td>
<td>OH + CH₃Cl₂ → CH₂Cl₃ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>37.</td>
<td>OH + CH₃Cl₃ → CH₂Cl₄ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>38.</td>
<td>OH + CH₃Cl₄ → CH₂Cl₅ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>39.</td>
<td>OH + CH₃Cl₅ → CH₂Cl₆ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>40.</td>
<td>OH + CH₃Cl₆ → CH₂Cl₇ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>41.</td>
<td>OH + CH₃Cl₇ → CH₂Cl₈ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>42.</td>
<td>OH + CH₃Cl₈ → CH₂Cl₉ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>43.</td>
<td>OH + CH₃CCl → CH₂CCl₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>44.</td>
<td>OH + NH₃ → NH₂ + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>45.</td>
<td>OH + NH₂ → NH + H₂O</td>
</tr>
<tr>
<td>Reaction</td>
<td>46.</td>
<td>OH + NH ≈ Products</td>
</tr>
<tr>
<td>Reaction</td>
<td>47.</td>
<td>OH + NH₂ ≈ O + NH₃</td>
</tr>
<tr>
<td>Reaction</td>
<td>48.</td>
<td>O + NH₂ ≈ Products</td>
</tr>
<tr>
<td>Reaction</td>
<td>49.</td>
<td>O + NH → Products</td>
</tr>
</tbody>
</table>

4.2. Data Sheets

\[
\text{OH} + \text{CH}_3 = \text{O} + \text{CH}_4
\]

\[
\Delta H^\circ_{298} = -11.6 \pm 1.4 \text{ kJ mol}^{-1} (-2.8 \text{ kcal mol}^{-1})
\]

\[
\Delta S^\circ_{298} = -30.6 \pm 1.3 \text{ J mol}^{-1} \text{ K}^{-1} (-7.3 \text{ cal mol}^{-1} \text{ K}^{-1})
\]

\[K(T) = 1.43 \times 10^{-2} \exp\left(\frac{1580}{T}\right)\]

The uncertainty in log \(K\) is ±0.3 at 298 K, decreasing to ±0.1 at 2000 K.

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>(k)</th>
<th>(k(298))</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>(70 T^{2.2} \exp(-2240/T))</td>
<td>(1.1 \times 10^4)</td>
</tr>
<tr>
<td></td>
<td>(1.16 \times 10^{-19} T^{2.2} \exp(-2240/T))</td>
<td>(1.8 \times 10^{-17})</td>
</tr>
<tr>
<td>(k_{-1})</td>
<td>(4.9 \times 10^3 T^{2.2} \exp(-3820/T))</td>
<td>(4 \times 10^3)</td>
</tr>
<tr>
<td></td>
<td>(8.1 \times 10^{-18} T^{2.2} \exp(-3820/T))</td>
<td>(7 \times 10^{-18})</td>
</tr>
</tbody>
</table>

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

November 1987

II

CH 3

K(T)

was determined from Klemm et

because they are the best measurements above 1755 K. Three other determinations 7-9 of k_1

reaction with methane and what fraction by other, secondary reactions.

values for k_1 are plotted on the graph inasmuch as all determinations of k_1 in the vicinity of 354

the temperature, the larger the value for m. At the lowest temperature, 298 K, m is both large and uncertain, and the plotted

the measurements of Refs.

between

1.7

and is in accord with the sparse, uncertain data at lower temperatures. Calculations with a one-dimensional Eckart potential gave

larger values for K_I bolom,, 500

TST

15. N.

11. F. W. Froben,

13. E. L. Wong and A. E.

17. N.

1. A complete description of the TST calculations is given in Ref. 17. A calculation with the Wigner tunneling correction gave k_1 = 4.9 x 10^3 T^2 exp(-3820/T) L mol^-1 s^-1 250 ≤ T ≤ 2500, which matches experimental data above 500 K

and is in accord with the sparse, uncertain data at lower temperatures. Calculations with a one-dimensional Eckart potential gave larger values for k_1 below 500 K at 298 K, the Wigner correction gives k_1 = 4.9 x 10^3, while the Eckart correction gives 1.7 x 10^4. The Wigner tunneling correction, like all simple tunneling corrections, is imprecise, but the one-dimensional Eckart correction gives too large a correction and hence provides an upper limit to the true value of the rate coefficient.

DISCUSSION

The recommended expression for k_1 below 298 K because the tunneling correction makes k_1 an unknown value in the vicinity of 354 K.

References

$O + C_2H_6 \rightarrow OH + C_2H_5$

$\Delta H_{298}^0 = -6.0 \pm 2 \text{ kJ mol}^{-1} (-1.9 \text{ kcal mol}^{-1})$

$\Delta H_{298}^0 = 4.1 \pm 4 \text{ kJ mol}^{-1} (9.7 \text{ kcal mol}^{-1})$

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

The uncertainty in log $K$ is $\pm 0.6$ at 300 K, decreasing to $\pm 0.3$ at 1500 K.

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.1 \times 10^{-10}$ $\phi_{-5} \exp(140/T)$</td>
<td>298-1300 K</td>
<td>$6.6 \times 10^{5}$</td>
<td>$L \text{ mol}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$1.8 \times 10^{-11}$ $\phi_{-5} \exp(-140/T)$</td>
<td>1300-3000 K</td>
<td>$1.1 \times 10^{-15}$</td>
<td>$cm^3 \text{ molecule}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$2.5 \times 10^{-12}$ $\exp(-7010/T)$</td>
<td>298-1300 K</td>
<td>$6.6 \times 10^{5}$</td>
<td>$L \text{ mol}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$4.3 \times 10^{-9}$ $\exp(-7010/T)$</td>
<td>1300-3000 K</td>
<td>$1.1 \times 10^{-15}$</td>
<td>$cm^3 \text{ molecule}^{-1} \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

| $k_{-1}$| $1.0 \times 10^{-19}$ $\phi_{-8} \exp(-250/T)$   | 298-1500 K    | 256      | $L \text{ mol}^{-1} \text{s}^{-1}$ |
|         | $1.7 \times 10^{-40}$ $\phi_{-8} \exp(-250/T)$   | 1300-3000 K   | $4.3 \times 10^{-19}$ | $cm^3 \text{ molecule}^{-1} \text{s}^{-1}$ |

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

May 1991

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

0 + C2H6 + OH + C2H5

Thermochemical data for C2H5 (ethane) were taken from Stull et al.1 Data for O and OH were taken from JANAF Thermochimical Tables, 3rd edn. (1985). CP and C0 were calculated using vibrational frequencies given by Pacansky and Schrader2 and assigning free internal rotation. The analytic expression chosen for N2H matches equilibrium constants calculated from these data within 8% between 300 and 1500 K.

MEASUREMENTS

As in the case of the reaction of O + C2H6, the measurement of k1 is complicated by the frequent presence of secondary reactions involving the products OH and C2H5 with one or both of the reagents, and by trace impurities, such as C2H4, in the C2H5. Except for the most recent study,3 the room temperature measurements2-5 provide insufficient information to assure the reader that these complications were avoided or accounted for. The reaction has been studied in three different regimes: (a) [O] + [C2H5]; (b) [O] < [C2H5] or (c) [O] >> [C2H5]. In case (a), the stoichiometry, which varies with [O]([C2H5]), T, and extent of reaction, must be determined from product analysis in order to relate the experimentally measured disappearance of either reagent to the elementary rate coefficient k1. In case (b), [C2H5]/[O] must exceed 500 at 370 K for the reaction of OH with O to contribute less than 10% to the rate of O disappearance; under these conditions impurities become a prime concern. At higher temperatures secondary reactions are relatively slower and therefore less important. Ref. 5 used method (a) in a stationary cell with mercury-amplified photodetection of OH as an O atom source and measured rates by competition with the O + C2H5 reaction; Ref. 6 used method (a) in a discharge flow system with EPR detection of O atoms; Ref. 7 used method (a) in a flow system with gas chromatographic analysis of products. Ref. 8 used method (c) at temperatures between 335 and 595 K for the analogous reaction O + C2H2 + OH (OH) + C2H4 (C2H5). In a flow system with mass spectrometric monitoring of the alkanes, their precision is greatly limited by the small amount of alkane consumed during the reaction. Method (c) was also used by Caymax and Peters9 at 500-1630 K with a discharge-flow technique and their work seems to be free of unaccounted complications. Yamanaka and Klemm10 measured k1 over 416-1048 K using a discharge flow technique with C2H5 in excess and obtained somewhat larger values (a factor of 2.5 at 600 K) than reported in Ref. 9; at the reported ratios of [C2H5]/[O] greater than 1000 the technique should have been free from secondary reactions, but full experimental details have not been published. Mannix, Marshall, and Fontijn2 used method (b) in a high-temperature flow reactor at 100 < T/K < 3700, producing atoms by flash photolysis of either O2 or CO2 and atomic resonance fluorescence to monitor [O] decay. They fitted their data by k1 = 1.1 × 107 exp(-485/T) L mol-1 s-1, with log k1(298) = 5.72 ± 0.12. Other work has been reviewed in Refs. 11 and 12.

CALCULATIONS

Transition-state-theory calculations assuming a Wigner tunneling correction, described in detail elsewhere,13 could not match the experimental data of Ref. 4 for the problem is the 0.5 preexponential temperature dependence, which produces a curvature in the plot of log k vs. 1/T that is much larger than usual. The same TST calculations with an Eckart tunneling correction (8 = 1600 cm-1: V = 50.21 kJ/mol, = 0.39, and 5 = 0.21 kJ/mol) fit the experimental data within experimental error. The TST-Eckart results are described by k1 = 7.3 × 105 exp(-1404/T) L mol-1 s-1 for 298 < T/K < 1300 and by 2.6 × 1012 exp(-790/T) L mol-1 s-1 for 1300 < T/K < 3000. The calculations cannot be satisfactorily fitted by a three-parameter expression of the form 4 exp(-A/T) over the entire temperature range of 298 < T/K < 3000.

DISCUSSION

The large extent of curvature in the log k vs. 1/T plot of the results of Ref. 4 is puzzling in that it is not consistent with the behavior of other O + alkane reactions, all of which we have been able to fit by a TST model with a Wigner tunneling correction. We recommend the empirical fit to the results of Ref. 4 For 298 < T/K < 1300, k1 = 1.1 × 1010 exp(-485/T) L mol-1 s-1. If an analytic expression is required for higher temperatures, we recommend the fit to the TST-Eckart calculations described above: 2.6 × 1012 exp(-790/T) L mol-1 s-1 for 1300 < T/K < 3000, with an uncertainty in log k1 of ±0.5. The large degree of curvature in the log k vs. 1/T plot could be due to quantum mechanical tunneling, but other explanations are possible.14 Clearly, further theoretical and experimental work are needed before the tunneling explanation and the low-temperature data can be accepted without reservation.

References

\[ O + C_3H_8 \rightarrow OH + \cdot C_2H_7 \]

\[ \Delta H_{298}^0 = -11.6 \pm 6 \text{ kJ mol}^{-1} (-2.8 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^0 = 37.7 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} (9.0 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

\[ \Delta H_{298}^0 = -25.4 \pm 4 \text{ kJ mol}^{-1} (-6.1 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^0 = 32.2 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} (7.7 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

Recommended rate coefficients:

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A )</td>
<td>( 0.76 T^{2.45} \exp(-1280/T) )</td>
<td>298-2000 K</td>
<td>( 4.0 \times 10^6 )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 1.3 \times 10^{-21} T^{3.5} \exp(-1280/T) )</td>
<td></td>
<td>( 6.6 \times 10^{-15} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_2/k_1 )</td>
<td>( 0.15 T^{0.1} \exp(170/T) )</td>
<td>298-2000 K</td>
<td>13</td>
<td>-</td>
</tr>
</tbody>
</table>

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

(October 1987)
CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

1219

0 + C₃H₇OH + CH₃CH₂CH₃ [n-propyl]
0 + C₃H₇OH + CH₃CH₂CH₂CH₃ [i-propyl]

**THERMOCHEMICAL DATA**

The title represents the sum of two elementary reactions:

0 + C₃H₇OH → CH₃CH₂CH₃ + OH

Thermochmical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). AHᵰ₂⁰₂⁹(C₃H₇OH) and AHᵰ₂⁰₂⁹(C₃H₇OH) are given be -1.7 to -25.9 kJ/mol⁰½ and 12.2 = 2 J mol⁻¹K⁻¹, respectively. Thermochmical data for the two propyl radicals are subject to some uncertainty. We accept AHᵰ₂⁰₂⁹(n-C₃H₇) = 94.6 kJ mol⁻¹ and AHᵰ₂⁰₂⁹(i-C₃H₇) = 80.8 kJ mol⁻¹. However, the former may be too low. Entropies were calculated by group additivity, assuming no barrier to internal rotation about the C-C bond in n-C₃H₇ (63) and 8 kJ/mol in the i-C₃H₇ radical, yielding Aₛᵰ₂⁰₂⁹(n-C₃H₇) = 282.4 and Aₛᵰ₂⁰₂⁹(i-C₃H₇) = 279.5 kJ mol⁻¹K⁻¹. Analytic expressions for k(T) have not been calculated because the reverse reactions will, under all conditions of practical interest, be slower than the competing radical recombination reaction (OH + C₃H₇OH).

**MEASUREMENTS**

There are no separate measurements of k₁ and k₂, only of their sum, kᵣ. Of the measurements of kᵣ at or near room temperature, 7-11 the most reliable is that of Ref. 11, carried out in a flow tube with O atoms produced by passing purified H₂ through a microwave discharge and then titrating the O atoms with H₂. Measurements were made by two methods. With method 1, [OH] /[C₃H₇OH] = 1 and kᵣ was determined by measuring propane consumption gas chromatographically. This procedure required knowing the stoichiometry, which varied with the initial ratio of reactants. With method 2, [HC₃H₇] /[C₃H₇OH] = 150 = 250, and kᵣ was determined by monitoring O atom consumption. This gave kᵣ (300) = (4.0 ± 0.5) × 10⁶ L mol⁻¹s⁻¹, compared to method 1, which gave kᵣ (300) = (4.9 ± 0.4) × 10⁶. Of these two techniques, method 2, and hence the smaller value for kᵣ, is preferred.

Of the higher temperature studies, 12-13 that by Azatyan et al. was obtained from ignition limits, a generally unreliable technique. That by Tanawaz et al., obtained by discharge flow-resonance fluorescence, has not been published in sufficient detail for full evaluation. However, in view of the acceptable results for O with other alkanes from the same laboratory (see data sheets for 0 + CH₄ and 0 + (CH₃)₂CO) we consider the results of Ref. 13 to be provisionally reliable.

**CALCULATIONS**

Separate transition-state theory (TST) calculations were carried out for the attack on the primary and on the secondary H atoms. This requires separate values for k₁(298) and k₂(298), the rate coefficients for 0 attack on primary and secondary H atoms at 298 K, respectively. Because the best experimental value for kᵣ at 298 K is 5 to 20 times larger than the rate coefficient at the same temperature for 0 + C₃H₇OH, it was assumed that kᵣ(298) is essentially a measure of k₂(298). k₁(298) was calculated assuming an activation energy the average of the activation energies for the 0 + C₃H₇OH and 0 + neo-C₃H₇OH reactions (see data sheets for those reactions). For additional details see Ref. 14. The resulting values of k₁ and k₂ calculated separately were added together to give kᵣ(T), which could be expressed by kᵣ = 0.76 T⁻²⁻⁵ exp(-1280/T). According to this model, k₁/k₂ is approximately 13 at 298 K, decreasing to approximately 0.6 at 2000 K. Another TST calculation has been described by Michael et al. 15

**DISCUSSION**

Because there are no measurements above 1000 K, we rely on the TST calculations for extrapolating kᵣ to higher temperatures. The calculations in turn depend sensitively on the choice of kᵣ(298); consequently the spread of results near room temperatures is a matter of concern. Although the low temperature values of kᵣ are not sensitive to the contribution from k₁, the high temperature values are. Because the value assumed for k₁ depends on the choice of value for kᵣ(298) for the 0 + C₃H₇OH reaction, it reflects uncertainty in that number. That the chosen model fits data for 0 abstraction from higher alkanes supports its validity, and consequently the accuracy of the high temperature extrapolation. We therefore recommend the expression obtained by TST calculation: kᵣ = 0.76 T⁻²⁻⁵ exp(-1280/T) L mol⁻¹s⁻¹ between 300 and 2000 K, with an uncertainty in log kᵣ of 0.3 throughout the temperature range.

**References**

\[ O + C_4H_{10} \rightarrow OH + C_2H_9 \]

\[ O + C_4H_{10} \rightarrow OH + n-C_2H_9 \]

\[ O + C_4H_{10} \rightarrow OH + s-C_2H_9 \]

\[ \Delta H^\circ_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1} \quad (-2.7 \text{ kcal mol}^{-1}) \]

\[ \Delta S^\circ_{298} = 43.6 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \quad (10.4 \text{ cal mol}^{-1} \text{K}^{-1}) \]

\[ \Delta H^\circ_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1} \quad (-6.9 \text{ kcal mol}^{-1}) \]

\[ \Delta S^\circ_{298} = 38.4 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \quad (9.4 \text{ cal mol}^{-1} \text{K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>■</td>
<td>2</td>
</tr>
<tr>
<td>X</td>
<td>4</td>
</tr>
<tr>
<td>♦</td>
<td>5</td>
</tr>
<tr>
<td>+</td>
<td>6</td>
</tr>
<tr>
<td>○</td>
<td>7</td>
</tr>
<tr>
<td>▽</td>
<td>8</td>
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<tr>
<td>△</td>
<td>9</td>
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<tr>
<td>□</td>
<td>10</td>
</tr>
<tr>
<td>▲</td>
<td>11</td>
</tr>
</tbody>
</table>

\[ k_A = 4.7 \times 10^{-2} \ \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(-780/T) \]

\[ k_A = 7.8 \times 10^{-23} \ \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(-780/T) \]

\[ k_2/k_1 = 8.7 \times 10^{-2} \ \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(1470/T) \]

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

(October 1987)

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

\[ \text{O} + \text{C}_2\text{H}_4 \rightarrow \text{OH} + \text{C}_2\text{H}_3 \]

\[ \text{OH} + \text{n-C}_4\text{H}_9 \rightarrow \text{H}_2\text{O} + \text{n-C}_4\text{H}_{10} \]

\[ \text{H}_2\text{O} + \text{n-C}_4\text{H}_9 \rightarrow \text{OH} + \text{n-C}_4\text{H}_{10} \]

Thermochemical data for \( \text{O} \) and \( \text{OH} \) are from JANAF Thermochemical Tables, 3rd ed. (1985). Differences between the enthalpies and entropies of the two \( \text{C}_4\text{H}_9 \) radicals and of the parent alkane were estimated by group additivity methods outlined by Benson et al. Analytic expressions for \( K(T) \) have not been calculated because the reverse reactions will, under all conditions of interest, be slower than radical recombination (OH + \text{C}_4\text{H}_9 \rightarrow \text{C}_4\text{H}_9\text{OH}).

**Thermochemical Data**

\( k_1 \) and \( k_2 \) have not been measured separately. Cvetanovic\(^2\) reported \( k_3/k_3 = 21 \pm 5 \) where \( k_3 \) is the rate coefficient for \( \text{O} + \text{C}_2\text{H}_4 \). The value shown on the graph is calculated from the value of \( k_3 \) recommended by Herron and Huie.\(^3\) Elias and Schiff\(^4\) measured \( k_2 \) in a fast-flow system; 0 atoms were produced by discharge through \( \text{O}_3 \) and reacted with excess alkane. It was assumed (incorrectly) that the principal reaction is carbon monoxide formation, but its results are not included in this evaluation. Herron and Heicklen\(^6\) measured \( k_3 \) relative to \( \text{O} + \text{C}_2\text{H}_4 \); Stokburger and Helckken,\(^7\) relative to \( \text{O} + \text{C}_3\text{F}_8 \). Herron and Huie\(^8\) produced 0 atoms in large excess in a flow tube and monitored alkane consumption (\( \text{C}_4\text{H}_9\text{OH} \)) by mass spectrometry. The principal shortcoming of the method is the uncertainty in the 0 + \( \text{C}_4\text{H}_9 \) titration used to measure \( [\text{O}] \) and the imprecision in the alkane analysis because small amounts of alkane were consumed (a 5% error in alkane assay means a 25-50% error in \( k_2 \)). They obtained \( k_2(307) = 1.8 \pm 0.4 \times 10^7 \text{L mol}^{-1}\text{s}^{-1} \). Papadopoulos et al.\(^5\) produced 0 by the \( \text{N} + \text{NO} \) reaction in a flow tube with \([\text{O}]_0 = [\text{C}_4\text{H}_{10}]_0 \) and analyzed products by gas chromatography. The value of \( k_2 \) depends on the stoichiometry, which was reported as a function of \([\text{O}]_0/[\text{C}_4\text{H}_{10}]_0 \), but not of \( T \). They reported \( k_2(301) = 6.2 \times 10^7 \text{L mol}^{-1}\text{s}^{-1} \). Atkinson and Pitta\(^10\) produced 0 atoms at 301 K by high-photoionization of \( \text{N}_2 \) in the presence of excess alkane and monitored [O] loss by a phase modulation technique, watching emission from \( \text{O} + \text{NO} \). Corrections for trace butanes in the butane were made later.\(^11\) Atkinson, et al.\(^11\) measured \( k_A \) at 298-493 K by flash photolysis-\( \text{NO}_2 \) chemiluminescence in excess butane. The correction for the 0.05% butanes amounted to almost 30% of the rate at 299 K, decreasing at higher temperatures. The corrected values of \( k_3 \) and \( k_2 \) were determined to give \( k_2(298) = 4.7 \times 10^7 \text{L mol}^{-1}\text{s}^{-1} \).

**Calculations**

Separate transition-state-theory calculations were carried out for the attack of 0 atoms on the primary and the secondary H atoms. This requires separate values for \( k_1(298) \) and \( k_2(298) \), the rate coefficients for 0 attack on primary and secondary H atoms at 298 K, respectively. Because the best experimental value for \( k_2(298) \) is more than 20 times larger than the rate coefficient at the same temperature for \( \text{O} + \text{C}_2\text{H}_4 \), it was assumed that \( k_2(298) \) is essentially \( k_2(298) \). \( k_2(298) \) was calculated assuming the activation energy at 300 K to be the average of those of \( \text{O} + \text{C}_2\text{H}_4 \) and \( \text{O} + \text{neo-C}_5\text{H}_{12} \) (see data sheets for those reactions). For additional details see Ref. 12. The resulting values of \( k_2 \) and \( k_3 \) were determined to give \( k_2(298) = 4.7 \times 10^7 \text{L mol}^{-1}\text{s}^{-1} \) and \( k_3 = 2.5 \times 10^{-9} \text{cm}^3\text{mole}^{-1}\text{s}^{-1} \). The calculated ratio \( k_3/k_2 \) is approximately 35 at 298 K, decreasing to approximately unity at 2000 K.

**Discussion**

The calculations indicate that there should be curvature on an Arrhenius plot (i.e., \log \( k_2 \) vs. \( 1/T \)), making \( k_2(2000) \) about 3 times larger than a linear extrapolation would predict. Our recommendations are based on the calculations described above, which are in good agreement with the experimental data. The range in experimental values for \( k_2 \) is a factor of 3 throughout the temperature range of 250-400 K. This uncertainty adds to the uncertainty inherent in the TST calculations. Thus, we recommend \( k_2 = 4.7 \times 10^7 \text{L mol}^{-1}\text{s}^{-1} \) for the temperature range of 250 - 2000 K, with an uncertainty in \log \( k_2 \) of \pm 0.2 at 298 K, increasing to \pm 0.3 at 2000 K. A reliable high-temperature measurement of \( k_2 \) would be very useful, as would a determination of \( k_1/k_2 \) at any temperature.

**References**

9. C. Papadopoulos, P. G. Ashmore, and R. J. Tyler, 13th Sympl. (Int.) Combust., 261 (1971). The data are presented only graphically; numerical values are taken from Herron and Huie (Ref. 4).
\[ \text{O} + \text{C}_5\text{H}_{12} \rightarrow \text{OH} + \text{C}_5\text{H}_{11} \]

\[ \Delta H_{298} = -11.3 \pm 6 \text{ kJ mol}^{-1} \quad (\text{-2.7 kcal mol}^{-1}) \]
\[ \Delta S_{298} = 43.6 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \quad (\text{10.4 cal mol}^{-1} \text{K}^{-1}) \]

\[ \text{O} + \text{C}_5\text{H}_{12} \rightarrow \text{OH} + \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3 \]
\[ \Delta H_{298} = -28.9 \pm 7 \text{ kJ mol}^{-1} \quad (\text{-6.9 kcal mol}^{-1}) \]
\[ \Delta S_{298} = 36.4 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \quad (\text{9.4 cal mol}^{-1} \text{K}^{-1}) \]

\[ \text{O} + \text{C}_5\text{H}_{12} \rightarrow \text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]
\[ \Delta H_{298} = -32.2 \pm 11 \text{ kJ mol}^{-1} \quad (\text{-7.7 kcal mol}^{-1}) \]
\[ \Delta S_{298} = 32.6 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \quad (\text{7.8 cal mol}^{-1} \text{K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A )</td>
<td>( 38 \times 10^{-3} \exp(-1010/T) )</td>
<td>250-2000 K</td>
<td>( 3.5 \times 10^{7} ) \ L mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 6.3 \times 10^{-20} \times 3.0 \exp(-1010/T) )</td>
<td></td>
<td>( 5.9 \times 10^{-14} ) \ cm(^3)molecule(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>( k_2/k_1 )</td>
<td>( 0.21 \times 3 \exp(1650/T) )</td>
<td>298-2000 K</td>
<td>90</td>
</tr>
</tbody>
</table>

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

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THERMOCHEMISTRY

The title reaction is the sum of three separate processes: attack on one of the six equivalent primary H atoms,
\[ \text{O} + \text{C}_2\text{H}_5\text{CH} \rightarrow \text{O} + \text{C}_2\text{H}_5\text{CH}_2 \]
attack on one of the four equivalent secondary H atoms on the number 2 carbons,
\[ \text{O} + \text{C}_2\text{H}_5\text{CH}_2 \rightarrow \text{O} + \text{C}_2\text{H}_5\text{CH}_2 \]
and attack on one of the two equivalent secondary H atoms on the number 3 carbon,
\[ \text{O} + \text{C}_2\text{H}_5\text{CH}_2 \rightarrow \text{O} + \text{C}_2\text{H}_5\text{CH}_2 \]
Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules\(^1\) were used to estimate the differences between \(\Delta H_f^\circ\) and \(\Delta S^\circ\) for the three pentyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between pentyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions \(\text{OH} + \text{C}_2\text{H}_5\text{CH}_2 \rightarrow \text{OH} + \text{C}_2\text{H}_5\text{CH}_2 \).

MEASUREMENTS

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

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. Trial calculations on the two different kinds of secondary H atoms suggested that the differences in the two calculations were too slight, and the respective uncertainties too large, to justify carrying out separate calculations. Consequently, \(k_{2a}\) and \(k_{2b}\) were grouped together and only their sum, \(k_2\), was calculated. This requires separate values for \(k_1\) (298 K) and \(k_2\) (298 K), the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for \(k_A\) at 298 K is approximately 50 times larger than the rate coefficient at the same temperature for \(O + C_2H_6\), it was assumed that \(k_2\) (298 K) is essentially a measure of \(k_2\) at 298 K, and was assumed to be \(3.8 \times 10^5\) L mol\(^{-1}\) s\(^{-1}\), a value obtained by calculating the entropy of activation by the usual method and assuming approximately the same activation energy at 300 K as for the reaction of \(O + C_4H_10\). The vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of \(O + C_6H_{14}\) (see data sheet for that reaction). For further details, see Ref. 4. The resulting values of \(k_1\) and \(k_2\) calculated separately were added together to give \(k_A\), which could be expressed by \(k_A = 38 \times 10^7 \text{ exp}(-1010/T)\) L mol\(^{-1}\) s\(^{-1}\) over the temperature range of 250-2000 K. The calculated ratio \(k_2/k_1\) is approximately 90 at 298 K, decreasing to approximately 1 at 2000 K.

DISCUSSION

Although there is only one set of experimental data, its consistency with data for O atom reaction with higher alkanes (see data sheets for \(O + C_6H_{14}\), \(O + C_7H_{16}\), and \(O + C_8H_{18}\)), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthens the reliability of both the experiments and the calculations. Consequently, we recommend \(k_A = 38 \times 10^7 \text{ exp}(-1010/T)\) L mol\(^{-1}\) s\(^{-1}\) for 250-2000 K, with an uncertainty in log \(k_A\) of \pm 0.2 at 298 K, increasing to \pm 0.3 at 2000 K.

References

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\[ O + C_6H_{14} \rightarrow OH + C_6H_{13} \]

\[ O + C_6H_{14} \rightarrow OH + CH_3CH(CH_2)CH_3 \]

\[ O + C_6H_{14} \rightarrow OH + CH_3CH_2CH(CH_3)_2 \]

\[
\begin{align*}
\Delta H_{298}^0 &= -11.3 \pm 6 \text{ kJ mol}^{-1} \left( -2.7 \text{ kcal mol}^{-1} \right) \\
S_{298}^0 &= 43.6 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1} \left( 10.4 \text{ cal mol}^{-1} \text{ K}^{-1} \right)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^0 &= -28.9 \pm 7 \text{ kJ mol}^{-1} \left( -6.9 \text{ kcal mol}^{-1} \right) \\
S_{298}^0 &= 38.4 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1} \left( 9.4 \text{ cal mol}^{-1} \text{ K}^{-1} \right)
\end{align*}
\]

\[
\begin{align*}
\Delta H_{298}^0 &= -32.2 \pm 11 \text{ kJ mol}^{-1} \left( -7.7 \text{ kcal mol}^{-1} \right) \\
S_{298}^0 &= 38.4 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1} \left( 9.4 \text{ cal mol}^{-1} \text{ K}^{-1} \right)
\end{align*}
\]

**Recommended Rate Coefficients**

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<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
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<td>( k_A )</td>
<td>100 ( T^{5.9} \exp(-1000/T) )</td>
<td>250-2000 K</td>
<td>( 5.5 \times 10^7 )</td>
<td>L mol(^{-1})s(^{-1})</td>
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<td></td>
<td></td>
<td></td>
<td>( 9.1 \times 10^{-14} )</td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( k_2/k_1 )</td>
<td>0.19 ( T^{0.2} \exp(1610/T) )</td>
<td>298-2000 K</td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_A \): ±0.2 near 298 K, increasing to ±0.3 at 2000 K. Uncertainty in \( \log k_2/k_1 \): ±0.5. Expressions for \( K, k_{-1} \)

and \( k_2 \) are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

The title reaction is the sum of three separate processes: attack on one of the six equivalent primary H atoms,
\[ O + CH_3(CH_2)_2CH_3 \rightarrow CH_3(CH_2)_2CHO + C_2H_6 \]
attack on one of the four equivalent secondary H atoms on the number 2 carbons,
\[ O + CH_3(CH_2)_2CH_3 \rightarrow CH_3CH(CH_2)_2CHO + C_2H_6 \]
and attack on one of the equivalent secondary H atoms on the number 3 carbons,
\[ O + CH_3(CH_2)_2CH_3 \rightarrow O + CH_3CH(CH_2)_2CHO + C_2H_6 \]
Thermochernical data for 0 and OH are from the JANAF Thermochernical Tables, 3rd edn. (1985). Group contribution rules were used to estimate the differences between \( \Delta H_f^\circ \) and \( \Delta S_f^\circ \) for the three hexyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between hexyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (0 + C_6H_{13} + C_6H_{13}O).

**MEASUREMENTS**

Herron and Huie measured \( k_A \) over the temperature range of 247 - 597 K in a flow system, with \([OH]/[C_6H_{13}] > 15\), by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, \( k_A = 4.7 \times 10^7 \) L mol\(^{-1}\)s\(^{-1}\), and interpolated \( k_A \) at 298 K to be \( 5.6 \times 10^7 \) L mol\(^{-1}\)s\(^{-1}\).

**CALCULATIONS**

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. As in the case of \( O + n-C_6H_{12} \) (see data sheet for that reaction), \( k_{A2} \) and \( k_{B2} \) were grouped together and only their sum, \( k_{A2} \), was calculated. This requires separate values for \( k_{A2}(298) \) and \( k_{B2}(298) \), the rate coefficients for 0 attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for \( k_B \) at 298 K is approximately 100 times larger than the rate coefficient at the same temperature for \( O + C_6H_{14} \), it was assumed that \( k_{B2}(298) \) is essentially a measure of \( k_{A2}(298) \). \( k_{B2}(298) \) was estimated by the same procedure used for the \( O + n-C_6H_{13}O \) reaction. Similarly, the vibrational frequencies of the two activated complexes and effect of the OH atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of \( O + n-C_6H_{13}O \) (see data sheet for that reaction). For further details, see Ref. 4. The resulting values of \( k_1 \) and \( k_2 \) calculated separately were added together to give \( k_A(T) \), which could be expressed by \( k_A = 100 T^{1.9} \exp(-1000/T) \) L mol\(^{-1}\)s\(^{-1}\) over the temperature range of 250-2000 K. The calculated ratio \( k_2/k_1 \) is approximately 125 at 298 K, decreasing to approximately 2 at 2000 K.

**DISCUSSION**

Although there is only one set of experimental data, its consistency with data for 0 atom reaction with homologous alkanes (see data sheets for \( O + C_6H_{14}, O + C_6H_{15}, \) and \( O + C_6H_{16} \)), and the success of the same model yields transition-state-theory calculations that fit all four reactions as well, strengthens the reliability of both the experiments and the calculations. Consequently, we recommend \( k_A = 100 T^{1.9} \exp(-1000/T) \) L mol\(^{-1}\)s\(^{-1}\) for 250-2000 K, with an uncertainty in log \( k_A \) of ±0.2 at 298 K, increasing to ±0.3 at 2000 K.

**References**

\[ O + \text{C}_7\text{H}_{16} \rightarrow \text{OH} + \text{C}_7\text{H}_{15} \]

\[ \Delta H^{\circ} = -11.3 \pm 6 \text{ kJ mol}^{-1} \] (-2.7 kcal mol\(^{-1}\))

\[ \Delta S^{\circ} = 41.6 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \] (10.4 cal mol\(^{-1}\) K\(^{-1}\))

\[ O + \text{C}_7\text{H}_{16} \rightarrow \text{H} + \text{C}_7\text{H}_{15} \]

\[ \Delta H^{\circ} = -28.9 \pm 7 \text{ kJ mol}^{-1} \] (-6.9 kcal mol\(^{-1}\))

\[ \Delta S^{\circ} = 38.4 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \] (9.4 cal mol\(^{-1}\) K\(^{-1}\))

\[ O + \text{C}_7\text{H}_{16} \rightarrow \text{OH} + \text{C}_7\text{H}_{14}(\text{CH}_2) \]

\[ \Delta H^{\circ} = -32.2 \pm 11 \text{ kJ mol}^{-1} \] (-7.7 kcal mol\(^{-1}\))

\[ \Delta S^{\circ} = 38.4 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \] (9.4 cal mol\(^{-1}\) K\(^{-1}\))

\[ O + \text{C}_7\text{H}_{16} \rightarrow \text{OH} + \text{C}_7\text{H}_{14}(\text{CH}_2)_2 \]

\[ \Delta H^{\circ} = -32.2 \pm 11 \text{ kJ mol}^{-1} \] (-7.7 kcal mol\(^{-1}\))

\[ \Delta S^{\circ} = 32.6 \pm 8 \text{ J mol}^{-1} \text{K}^{-1} \] (7.8 cal mol\(^{-1}\) K\(^{-1}\))

**RECOMMENDED RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>( k_\text{A} )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 93 \times 10^{-9} \exp(-880/T) )</td>
<td>250-2000 K</td>
<td>( 7.6 \times 10^7 )</td>
<td>( 1.3 \times 10^{13} )</td>
<td>L mol(^{-1}) s(^{-1}) cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( 1.5 \times 10^{-19} \exp(-860/T) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_\text{A} \): \( \pm 0.2 \) near 298 K, increasing to \( \pm 0.3 \) at 2000 K. Uncertainty in \( \log k_2/k_1 \): \( \pm 0.5 \) from 300 to 2000 K.

Expressions for \( k_1 \) and \( k_2 \) are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

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

\[ O + CH_3(CH_2)_3CH_3 \rightarrow OH + CH_3(CH_2)_3CH_2 \]

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

\[ O + CH_3(CH_2)_3CH_3 \rightarrow 2OH + CH_3CH(OH)(CH_2)_3CH_3 \]

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

\[ O + CH_3(CH_2)_3CH_3 \rightarrow 2OH + CH_3CH(OH)(CH_2)_3CH_3 \]

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

\[ O + CH_3(CH_2)_3CH_3 \rightarrow 2OH + CH_3CH(OH)(CH_2)_3CH_3 \]

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group contribution rules were used to estimate the differences between enthalpies and entropies for the four heptyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between heptyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (OH + C_7H_15 + C_7H_15 OH).

Measurements

Herron and Huie measured \( k_A \) over the temperature range of 247 - 597 K in a flow system, with \[ \frac{[D_2]}{[C_7H_16]} > 20 \], by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 307 K, \( k_A = (9.7 \pm 6) \times 10^{-7} \text{ mol}^{-1} \text{s}^{-1} \), and interpolated \( k_A \) at 298 K to be \( 7.7 \times 10^{-7} \). Herron and Heicklen generated O atoms from N_2-sensitized photodecomposition of N_2O in the presence of C_7F_16 and alkane at 307-398 K. \( k_A \) was determined relative to the rate coefficient \( k_5 \) for the \( O + C_7F_16 \) reaction by measuring the decrease in oxygenated fluorocarbon products gas chromatographically. \( k_3 \) had been determined previously. Their room temperature result is close to that of Ref. 2 but their activation energy is noticeably smaller.

Calculations

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. As in the case of \( O + \text{n-C}_7\text{H}_16 \) (see data sheet for that reaction), \( k_{2a}, k_{2b}, \) and \( k_5 \) were grouped together and only their sum, \( k_2 \), was calculated. This requires separate values for \( k_2(298) \) and \( k_5(298) \). The rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for \( k_A \) at 298 K is more than 100 times larger than the rate coefficient at the same temperature for \( O + \text{n-C}_7\text{H}_16 \), it was assumed that \( k_2(298) \) is essentially a measure of \( k_2(298) \) and \( k_2(298) \) was assumed to be \( 7.5 \times 10^{-7} \text{ mol}^{-1} \text{s}^{-1} \), a value obtained by the same procedure as used for \( O + \text{n-C}_7\text{H}_{10} \). Similarly, the vibrational frequencies of the two activated complexes and effect of the O atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of \( O + \text{n-C}_7\text{H}_{10} \) (see data sheet for that reaction). For further details, see Ref. 6. The resulting values of \( k_2 \) and \( k_5 \) calculated separately were added together to give \( k_2(7) \), which could be expressed by \( k_2 = 93 \times 10^7 \exp(-880/T) \text{ mol}^{-1} \text{s}^{-1} \) over the temperature range of 250-2000 K. The calculated ratio \( k_2/k_4 \) is approximately 298 at 298 K, decreasing to approximately 3 at 2000 K.

Discussion

The data of Ref. 2 are preferred because of the directness of the method. The consistency with data for O atom reaction with other alkanes (see data sheets for \( O + \text{C}_6\text{H}_{14}, O + \text{C}_8\text{H}_{18}, \) and \( O + \text{C}_7\text{H}_{15} \)), and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthen the reliability of both the experiments and the calculations. Consequently, we recommend \( k_A = 93 \times 10^7 \exp(-880/T) \text{ mol}^{-1} \text{s}^{-1} \) for 230-2000 K, with an uncertainty in \( \log k_A \) of \pm 0.2 at 298 K, increasing to \pm 0.5 at 2000 K.

References:

\[ \text{O} + \text{C}_8\text{H}_{18} \rightarrow \text{OH} + \text{C}_8\text{H}_{17} \]

\[ \Delta H_{98} = -11.3 \pm 6 \text{ kJ mol}^{-1} \quad \text{(-2.7 kcal mol}^{-1}) \]

\[ \Delta S_{298} = 38.4 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{(9.4 cal mol}^{-1} \text{ K}^{-1}) \]

**SYMBOL**

\[ \text{A} \quad \text{REF. 2} \]

**RECOMMENDED RATE COEFFICIENTS**

\[ k_A = 1.9 \times 10^9 \tau^{7.8 \text{ exp(-840/T)}} \]

\[ 3.2 \times 10^{-19} \tau^{2.8 \text{ exp(-840/T)}} \]

\[ k_2/k_1 = 0.28 \tau^{2.2 \text{ exp(1880/T)}} \]

Uncertainty in \( \log k_A \): \( \pm 0.2 \) near 298 K, increasing to \( \pm 0.3 \) at 2000 K. Uncertainty in \( \log k_2/k_1 \): \( \pm 0.5 \) from 298 to 2000 K.

Expressions for \( k_1 \), \( k_{-1} \) and \( k_{-2} \) are not given because the reverse reactions are unlikely to be important at any temperature.

(October 1987)

The title reaction is the sum of four separate elementary processes: Attack on one of the six equivalent primary H atoms,  
\[ O + \text{C}_8\text{H}_{17} \rightarrow \text{OH} + \text{C}_8\text{H}_{15} \]
attack on one of the four equivalent secondary H atoms on the number 2 carbons,  
\[ O + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4 \rightarrow \text{OH} + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_3 \]
attack on one of the four equivalent secondary H atoms on the number 3 carbons,  
\[ O + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4 \rightarrow \text{OH} + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_3 \]
and attack on one of the four equivalent secondary H atoms on the number 4 carbons  
\[ O + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_4 \rightarrow \text{OH} + \text{CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{C}_2\text{H}_3 \]

Thermochemical data for O and OH are from the JANAF Thermochemical Tables, 3rd edn. (1985). Group contribution rules were used to estimate differences between enthalpies and entropies for the four heptyl radicals and for the alkane itself. Equilibrium constant expressions have not been calculated because the reverse reactions (between octyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (OH + C\text{H}_17 \rightarrow \text{C}_9\text{H}_{17} \cdot \text{OH}).

**MEASUREMENTS**

Herron and Huie\(^2\) measured \(k_A\) over the temperature range of 297 - 597 K in a flow system, with [O]/[C\text{H}_17] > 14, by monitoring alkane disappearance by mass spectrometry. The method should be free from complications due to impurities or secondary reactions. They obtained, at 375 K, \(k_A = (1.23 \pm 0.16) \times 10^8\) L mol\(^{-1}\) s\(^{-1}\), and interpolated \(k_A\) at 298 K to be \(1.0 \times 10^8\). An earlier measurement\(^3\) gave values of \(k_A\) in the temperature range of 353 to 473 K smaller by a factor of approximately 5 than those reported in Ref. 2. Because these values, and others from the same laboratory, are inconsistent with the majority of measurements for other homologous alkanes, they are not used in this evaluation.

**CALCULATIONS**

Separate transition-state-theory calculations were carried out for the attack on the primary and on the secondary H atoms. In the case of \(O + \text{C}_8\text{H}_{12}\) (see data sheet for that reaction), \(k_{2a}, k_{2b}, k_{2c}\) were grouped together and only their sum, \(k_2\), was calculated. This requires separate values for \(k_{2a}(298)\) and \(k_{2b}(298)\), the rate coefficients for \(O\) attack on primary and secondary H atoms at 298 K, respectively. Because the experimental value for \(k_2\) at 298 K is approximately 300 times larger than the rate coefficient at the same temperature for \(O + \text{C}_8\text{H}_6\), it was assumed that \(k_2(298)\) is essentially a measure of \(k_{2b}(298)\). \(k_{2a}(298)\) was estimated to be \(2.2 \times 10^5\) L mol\(^{-1}\) s\(^{-1}\), by the same procedure used for the \(O + \text{C}_9\text{H}_{17}\) reaction. Similarly, the vibrational frequencies of the two activated complexes and effect of the 0 atom on the barriers to internal rotation were assumed to be the same as in the case of the analogous reactions of \(O + \text{C}_8\text{H}_{12}\) (see data sheet for that reaction). For further details, see Ref. 5. The resulting values of \(k_A\) and \(k_2\) calculated separately were added together to give \(k_A(T)\), which could be expressed by \(k_A = 1.9 \times 10^8 e^{-840/T}\) L mol\(^{-1}\) s\(^{-1}\) over the temperature range of 250-2000 K. The calculated ratio \(k_2/k_A\) is approximately 450 at 298 K, decreasing to approximately 3 at 2000 K.

**DISCUSSION**

The consistency of the data of Ref. 2 with data for \(O\) atom reactions with similar alkanes (see data sheets for \(O + \text{C}_8\text{H}_{12}, O + \text{C}_8\text{H}_6, O + \text{C}_9\text{H}_{14},\) and \(O + \text{C}_9\text{H}_{16}\)) and the success of the same model yielding transition-state-theory calculations that fit all four reactions as well, strengthen the reliability of both the experiments and the calculations. Consequently, we recommend \(k_A = 1.9 \times 10^8 e^{-840/T}\) L mol\(^{-1}\) s\(^{-1}\) for 250-2000 K, with an uncertainty in log \(k_A\) of ±0.2 at 298 K, increasing to ±0.3 at 2000 K.

References

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

$\Delta H^0_{298} = -18.2 \pm 6 \text{ kJ mol}^{-1} (-4.4 \text{ kcal mol}^{-1})$

$\Delta S^0_{298} = 38.5 \pm 8.1 \text{ J mol}^{-1} \text{ K}^{-1} (9.2 \text{ cal mol}^{-1} \text{ K}^{-1})$

$\Delta H^0_{298} = -59.1 \pm 8.1 \text{ kJ mol}^{-1} (-14.0 \text{ kcal mol}^{-1})$

$\Delta S^0_{298} = 52.0 \pm 8.1 \text{ J mol}^{-1} \text{ K}^{-1} (12.0 \text{ cal mol}^{-1} \text{ K}^{-1})$

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**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_A$</td>
<td>$2.0 \times 10^{-2} \cdot 3.9 \exp(-80/T)$</td>
<td>298-2000 K</td>
<td>$7 \times 10^7$</td>
<td>L mol$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$3.3 \times 10^{-23} \cdot 3.9 \exp(-80/T)$</td>
<td></td>
<td></td>
<td>cm$^3$ molecule$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>$k_2/k_1$</td>
<td>$3.7 \times 10^{-2} \cdot 0.1 \exp(2315/T)$</td>
<td>298-2000 K</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

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

(October 1987)
0 + (CH₃)₂OH → OH + (CH₃)₂COH₡

THERMOCHEMISTRY

The title reaction is the sum of two elementary reactions: removal of one of the nine equivalent primary H atoms to form isobutyl:  
0 + (CH₃)₂OH → OH + (CH₃)₂CHCH₂

and removal of the single tertiary H to form t-butyl:  
0 + (CH₃)₂OH → OH + (CH₃)₂C₆H₁₃

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Data for isobutane are from Stull et al.¹ AH°₂₉₈(a-C₄H₉) = 57.3 kJ mol⁻¹ is taken from Benson² AH°₂₉₈(t-C₄H₉) has been the subject of considerable disagreement, as reviewed by McMillen and Golden.³ We use their recommended value of 36.4 kJ mol⁻¹, but the uncertainty is at least ±8 kJ mol⁻¹. S°₂₉₈(a-C₄H₉) was calculated to be 310.5 J mol⁻¹ K⁻¹ using group additivity methods and assuming that the barrier to rotation about the C-C bond is 1.2 kJ mol⁻¹.⁴ S°₂₉₈(t-C₄H₉) was taken to be 318 J mol⁻¹ K⁻¹.⁵

MEASUREMENTS

Four measurements of kₐ have been reported, all near room temperature.⁶⁻⁹ Of these, the earliest⁶ is discarded because it is based on an incorrect mechanism and furthermore the method is too indirect to be reliable. The second⁷ was cited in a footnote of another study and has not been reported in detail; consequently it is not possible to evaluate it properly, although it does agree within a factor of 2 with the two remaining, and most reliable, measurements. Washida and Bayes⁸ produced O atoms in a fast-flow reactor by passing O₂/He through a microwave discharge. Isobutane or isobutane-deuterated (CH₃)₂CD at pressures comparable to 0.02 atm pressure (approximately 1 - 0.3 mPa) was added to the flow. Alkyl radical concentrations were monitored by photionization mass spectrometry. Based on the results with the deuteroalkane, those workers concluded that abstraction of the tertiary hydrogen was the dominant but not exclusive pathway. kₐ at room temperatures was reported to be (6 ± 1.2) x 10⁻⁷ L mol⁻¹ s⁻¹. Jewell et al.⁹ produced O atoms by the N + NO reaction, N atoms being formed in a microwave discharge through N₂. Hydrocarbon was added downstream. Kinetic measurements were made by monitoring gas chromatographic consumption of isobutane in the presence of excess O atoms. They reported kₐ = (7.9 ± 1.4) x 10⁻⁷ L mol⁻¹ s⁻¹ at 307 K. There are no measurements at higher temperatures.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack of O atoms on the primary and on the tertiary H atoms. This requires separate values for kₐ(298) and kₐ(298), the rate coefficients for O attack on primary and secondary H atoms at 298 K, respectively. Because experimental evidence indicates that kₐ(298) is approximately 50 times larger than k₂(298) for the O + (CH₃)₂C₆H₁₃ reaction, it was assumed that kₐ(298) is essentially a measure of kₐ(298). kₐ(298) was assumed to be 5 x 10⁻⁸ L mol⁻¹ s⁻¹, a value obtained by calculating the entropy of reaction by the usual methods and taking the activation energy at 298 K to be the same as for tertiary attack on 2,3-dimethylbutane (see data sheet for that reaction). The vibrational frequencies and effects of O adduct on the internal rotations of the two activated complexes were assumed to be the same as in the case of O + 2,3-dimethylbutane as well. For additional details, see Ref. 10. This model gave good agreement with experimental data in the case of the latter molecule. The resulting values of kₐ and k₂ were added together to give kₐ(T), which could be represented over the temperature range of 298-2000 K by the expression, kₐ(T) = 2 x 10⁻² T⁻³⁻⁹ exp(-807/T) L mol⁻¹ s⁻¹. According to this model k₂/k₁ = 150 at 298 K, decreasing to 0.3 at 2000 K.

DISCUSSION

There is very good agreement between the two most reliable measurements of kₐ near room temperature,⁸,⁹ but no measurements at higher temperatures. Consequently we rely entirely on the calculations to extrapolate kₐ to 2000 K. The reliability of the model used to do this depends on the success of the same model for the analogous reaction of O + 2,3-dimethylbutane. The model agrees well with experiments for that reaction, and there is no reason to doubt its accuracy in this case. Consequently, we recommend kₐ(T) = 2 x 10⁻² T⁻³⁻⁹ exp(-807/T) L mol⁻¹ s⁻¹, with an uncertainty in log kₐ of ±0.2 at 300 K, increasing to ±0.4 at 2000 K.

References

N. COHEN AND K. R. WESTBERG

O + (CH₃)₄C → OH + C₅H₁₁

$\Delta H^{\circ}_{298} = -5.0 \pm 4.4 \text{ kJ mol}^{-1} (-12 \text{ kcal mol}^{-1})$

$\Delta S^{\circ}_{298} = 48.6 \pm 8.3 \text{ J mol}^{-1} \text{ K}^{-1} (11.6 \text{ cal mol}^{-1} \text{ K}^{-1})$

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.5 \times 10^3 T^{2.5} \exp(-2720/\text{T})$</td>
<td>298-2000 K</td>
<td>$4.5 \times 10^5$</td>
<td>L mol$^{-1}$s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$4.2 \times 10^{-18} T^{2.5} \exp(-2720/\text{T})$</td>
<td></td>
<td>$7.5 \times 10^{-16}$</td>
<td>cm$^3$ molecule$^{-1}$s$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty in log $k_1$: ±0.3 throughout range. Because the reverse reaction is unimportant at any temperature, values for $k_1$ and $k(T)$ have not been recommended.

(October 1987)

O + (CH₃)₂C• \rightarrow \text{OH} + (CH₃)₂CH₂

**THERMOCHEMISTRY**

Thermochemical data for O and OH are taken from JANAF Thermocheral Tables, 3rd edn. (1985). Data for (CH₃)₂C• (2,2-dimethylpropane, or neopentane) are taken from Stull et al. The bond dissociation energy of (CH₃)₂C•, D₀¹⁰⁺ (CH₃)₂CCH⁺H⁻, was determined relative to that of CH₄, from which D₀¹⁰⁺ can be calculated to be -5.0 kJ mol⁻¹ for the reaction. The difference between the entropies of the radical and of the parent alkane was calculated by group additivity methods to be 26.0 J mol⁻¹ K⁻¹, assuming a near-zero barrier to internal rotation about the n-CC bond. An analytic expression for K(T) has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the competing radical recombination reaction, OH + (CH₃)₂CH⁺ + (CH₃)₂CH⁺OH.

**MEASUREMENTS**

Of the three measurements of k₁, the most reliable is that of Michael et al., made by both flash photolysis-resonance fluorescence (41S-528 K) and discharge flow-resonance fluorescence (427-922 K). With [(CH₃)₂C•]₀/([O]) always greater than 200, the contribution from secondary reactions should always have been less than 10%. The reported rate coefficients (calculated without taking secondary reactions into account) therefore require small if any, corrections. Herron and Huie measured k₁ between 276 and 597 K in a flow system, with [OH]₀/[C₅H₁₂]₀ > 10 (2000 at low temperatures), by monitoring alkane disappearance by mass spectrometry. Under their conditions the reaction should be free from secondary processes. Nevertheless, their rate coefficients are consistently larger than those of Ref. 7 by a factor of 2-3. There are no obvious flaws with their procedure, except possibly that the small change in alkane concentration (less than 10% at T > 307 K) means limited precision in measuring k₁ (a 5% error in [OH]₀ or [RH]₀ means a 10% error in k₁). The only likely source of systematic error is the ethylene titration technique needed to measure absolute [O]. If the stoichiometry is greater than assumed value of 5 atoms O consumed per molecule of C₅H₁₂, then [O] will be larger than was assumed, and k₁ consequently smaller. The results of Wright are not used in this evaluation because the method was too indirect and the conclusions are based on an incorrect mechanism.

**CALCULATIONS**

A transition-state-theory calculation (TST) was carried out assuming that k(T) = 1.1 x 10⁻⁷ L mol⁻¹ s⁻¹ (ref. 7) and assuming linear geometry for the C-H-O structure. Further details are given in Ref. 8. With these assumptions, the resulting rate coefficients can be fitted by the expression k = 2.5 x 10⁻⁷ T².⁵ exp(-2720/T) L mol⁻¹ s⁻¹. Another TST calculation has been described by Michael et al.

**DISCUSSION**

Although it is difficult to pinpoint errors in the measurements of Ref. 6 we favor the more recent technique used in Ref. 7 which produced lower values for k₁. We recommend the expression for k₁ obtained by TST calculations, which also gives good agreement with the experimental data: k₁ = 2.5 x 10⁻⁷ T².⁵ exp(-2720/T) L mol⁻¹ s⁻¹. The uncertainty in k₁ is a factor of 2 throughout the temperature range of 298-2000 K.

**References**

\[ O + (\text{CH}_3)_2\text{CHCH(CH}_3)_2 \rightarrow \text{OH} + \text{C}_6\text{H}_{13} \]

\[ \Delta H_{298} = -10.0 \pm 8 \text{ kJ mol}^{-1} (-2.4 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298} = 35.2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} (8.4 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

\[ \Delta H_{298} = -36.2 \pm 6 \text{ kJ mol}^{-1} (-8.7 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298} = 51.9 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1} (12.4 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

The recommended rate coefficients are:

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A )</td>
<td>( 2.3 \times 10^{-1} \times 10^{-6} \exp(-140/T) )</td>
<td>250-2000 K</td>
<td>( 1.2 \times 10^{8} )</td>
<td>L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 3.9 \times 10^{-22} \times 10^{-6} \exp(-140/T) )</td>
<td></td>
<td>( 2.0 \times 10^{-13} )</td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>( k_2/k_1 )</td>
<td>( 6.0 \times 10^{0.1} \exp(2330/T) )</td>
<td>298-2000 K</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

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

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

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

$$O + (CH_3)_2CHCH(CH_3)_2 \rightarrow OH + (CH_3)_3CCH(CH_3)_2$$

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

$$O + (CH_3)_2CHCH(CH_3)_2 \rightarrow OH + (CH_3)_2CHCH(CH_3)_2$$

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). $\Delta H_{298}^0$ and $\Delta S_{298}^0$ for both reactions are estimated by comparison with the analogous reactions of $i-C_4H_{10}$, with appropriate corrections for symmetry differences and for the effects of gauche interactions.

Analytic expressions for $K(T)$ have not been calculated because the reverse reactions (between dimethylbutyl radicals and OH) will, under all conditions of practical interest, be slower than the competing radical recombination reactions (OH + C$_6$H$_{13}$).

MEASUREMENTS

Herron and Huie produced O atoms in large excess in a flow tube by the $N + NO$ reaction and monitored alkane consumption by mass spectrometry. The principal shortcoming of the method is the uncertainty in the O + C$_2$H$_4$ titration used to measure [O]. They obtained values of $k_A$ from 247 to 597 K; at 307 K they found $k_A = 1.5 \pm 0.3 \times 10^8$ L mol$^{-1}$ s$^{-1}$, and interpolated $k_A(298)$ to be $1.2 \times 10^8$.

CALCULATIONS

Separate transition-state-theory calculations were carried out for the attack of O atoms on the primary and on the tertiary H atoms. This requires separate values for $k_1(298)$ and $k_2(298)$, the rate coefficients for O attack on primary and tertiary H atoms at 298 K, respectively. Because experimental evidence indicates that $k_A(298)$ is approximately 30 times larger than $k_A(298)$ for the O + (CH$_3$)$_2$C reaction, it was assumed that $k_A(298)$ is essentially a measure of $k_2(298)$. $k_1(298)$ was assumed to be $5 \times 10^5$ L mol$^{-1}$ s$^{-1}$, an estimation arrived at by calculating the entropy of reaction by the usual methods and taking the activation energy at 298 K to be the average of the activation energies of the reactions of O with C$_2$H$_6$ and with (CH$_3$)$_4$C. For additional details, see Ref. 4. The resulting values of $k_1$ and $k_2$ were added together to give $k_A(T)$, which could be represented over the temperature range of 250-2000 K by the expression, $k_A(T) = 0.23 T^{3.6} \exp(-140/T)$ L mol$^{-1}$ s$^{-1}$. This expression agrees well with the experimental data. These calculations suggest $k_2/k_1$ to be $250$ at 298 K, rapidly decreasing with temperature.

DISCUSSION

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

References:

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

$\Delta H_{298}^0 = -17.5 \pm 8 \text{ kJ mol}^{-1} (-4.2 \text{ kcal mol}^{-1})$

$\Delta S_{298}^0 = 44.4 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (10.6 \text{ cal mol}^{-1} \text{ K}^{-1})$

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.2 \times 10^3 \tau^{2.5} \exp(-2360/T)$</td>
<td>298-2000 K</td>
<td>$2 \times 10^6$</td>
<td>$L \text{ mol}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$5.3 \times 10^{-18} \tau^{2.5} \exp(-2360/T)$</td>
<td></td>
<td>$3.4 \times 10^{-15}$</td>
<td>$cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

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

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

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0 + (CH₃)₂CC(CH₃)₂→ OH + CH₃C(CH₃)₂C(CH₃)₂

Thermochemistry

Thermochemical data for O and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules¹ were used to estimate differences between the enthalpies and entropies of the neopentyl radical, and of the alkane itself, assuming a near-zero barrier to internal rotation about the α-CC bond. An analytic expression for K(T) has not been calculated because the reverse reaction, between OH and neopentyl radicals, will, under all conditions of practical interest, be slower than the competing radical combination process (OH + C₆H₁₃ + C₆H₁₇ → ).

Measurements

A single measurement of k₁ at 307 K has been reported.² The value obtained, 8 × 10⁶ L mol⁻¹ s⁻¹, is 2.4 times faster than the same workers reported for k₂, the rate coefficient for the analogous reaction of O + neopentane. The measurement was made in a flow system with 0 atoms in large excess; alkane disappearance was monitored by mass spectrometry, and [0] was determined by titration with ethylene.

Calculations

A transition-state-theory calculation was carried out assuming that k(298) = 2 × 10⁶ L mol⁻¹ s⁻¹ and using the same model for the activated complex that was used for the reaction of O + neopentane (see data sheet for that reaction). Details are given in Ref. 3 (except that there, k(298) was assumed to be 1 × 10⁶). With these assumptions, the resulting rate coefficients can be fitted by the expression, k₁ = 3.2 × 10³ T²/5 exp(-2360/T) L mol⁻¹ s⁻¹.

Discussion

At 298 K, the calculated entropy of activation for reaction 1 is only 0.5 cal mol⁻¹ K⁻¹ larger than that for reaction 2, O + neopentane. The C-H bond dissociation energy in neopentane has not been measured but is expected to be slightly lower (by 5–10 kJ/mol) than that of neopentane (41 kJ/mol), which would make the activation energy smaller by approximately 1–2 kJ/mol, and k(298) larger by a factor of 1.3 – 2.7. The recommended value for k₁(298) is 1 × 10⁶. The measured value of k₁(307) is 8 × 10⁶, which seems too large because it implies that either the activation energy of reaction 1 is 5 kJ/mol less than that of reaction 2 or that one of the calculated entropies of activation is significantly in error. A more plausible explanation is that the measured value of k₁ is too high.⁴ In Ref. 2, k₂ was also measured using the same technique. We concluded that their measurements of k₂ were also too high; see the data sheet for that reaction for a further discussion. We recommend k₁(298) = 2 × 10⁶ and the calculated expression for k₁(T) based on this value, namely, k₁ = 3.2 × 10³ T²/5 exp(-2360/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.4 throughout the range of 298 K < T < 2000 K.

References

\[
\Delta G_{298}^o = -32.7 \pm 5 \text{ kJ mol}^{-1} (-7.8 \text{ kcal mol}^{-1})
\]

\[
\Delta f_{298}^o = 48.5 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} (11.4 \text{ cal mol}^{-1} \text{ K}^{-1})
\]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.9 \times 10^3 \frac{2.6}{T} e^{-1390/T} )</td>
<td>298 - 2000 K</td>
<td>( 7.5 \times 10^7 )</td>
<td>L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 4.8 \times 10^{-19} \frac{2.6}{T} e^{-1390/T} )</td>
<td></td>
<td></td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
</tbody>
</table>

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

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

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THERMOCHEMISTRY

Thermochemical data for O and OH are from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules\(^1\) were used to estimate differences between RH\(^0\) and RH\(^\circ\) for the cyclopentyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction (OH + c-C\(_5\)H\(_9\) → c-C\(_5\)H\(_9\)OH).

MEASUREMENTS

The most reliable measurements are those of Huie and Herron,\(^2\) who studied the reaction at 307-652 K in a flow tube, producing O atoms by passing a few percent of O\(_2\) in Ar through a microwave discharge. O atoms were kept in considerable excess over alkane. Relative [O] was determined by mass spectrometry, put on an absolute basis by titration with NO\(_2\). The alkane concentration was also measured by mass spectrometry. Because [O] was kept in excess and at most 10% of the alkane was consumed, the method was free of complications caused by secondary reactions. However, since \(k\) is proportional to \(\ln([RH]_0/[RH])\), a 5% error in measuring either [RH]\(_0\) or [RH] results in a 50% error in \(k\). From their own data, they later\(^3\) extrapolated a value of \(k/\text{H}(00)\) of \(7.5 \times 10^7\) L mol\(^{-1}\) s\(^{-1}\). An earlier measurement\(^4\) of \(k_1\) relative to the rate of reaction of O atoms with C\(_3\)F\(_6\), in turn measured relative to the rate of O with 1-C\(_4\)H\(_8\), is not used in this evaluation because of its indirectness.

CALCULATIONS

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

DISCUSSION

The calculations are in reasonable agreement with the data of Ref. 3, and also consistent with data and calculations for reactions of O with 1-C\(_4\)H\(_8\) and with c-C\(_5\)H\(_9\) (see data sheets for those reactions). We therefore recommend \(k_1 = 2.9 \times 10^3 T^{2.6} \exp(-1390)\) L mol\(^{-1}\) s\(^{-1}\), with an uncertainty in \(\log k_1\) of ±0.3 at 298 K, increasing to ±0.5 at 2000 K.

References

N. COHEN AND K. R. WESTBERG

\[ \text{O} + \text{c-C}_6\text{H}_{12} \rightarrow \text{OH} + \text{c-C}_6\text{H}_{11} \]

\[ \Delta H^0_{298} = -32.7 \pm 5 \text{ kJ mol}^{-1} (-7.8 \text{ kcal mol}^{-1}) \]

\[ \Delta G^0_{298} = 53.0 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} (12.7 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

**RECOMMENDED RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.6 \times 10^7 \pm 2.6 \times 1240/T )</td>
<td>298 - 2000 K</td>
<td>( 8.3 \times 10^7 )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 4.3 \times 10^{-18} \pm 2.6 \times 1240/T )</td>
<td></td>
<td>( 1.4 \times 10^{-13} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): ±0.3 at 298 K, increasing to ±0.5 near 2000 K. Expressions for \( k(T) \) and \( k_2 \) are not given because the reverse reaction is unlikely to be important at any temperature.

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

0 \cdot C_6H_{12} + OH \rightarrow C_6H_{11}

THERMOCHEMISTRY

Thermochemical data for 0 and OH are taken from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules were used to estimate differences between \( \Delta H^\circ \) and \( \Delta G^\circ \) for the cyclohexyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction (OH + c-C_6H_{11} + c-C_6H_{11}OH).

MEASUREMENTS

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

Kim and Timmons studied the reaction in a discharge flow facility, the O atoms being generated by the reaction between H and NO. Two procedures were used: in one, \( [O] \) was in excess and \( [C_6H_{12}] \) was monitored mass spectrometrically; in the other, \( [C_6H_{12}] \) was in excess and \( [O] \) was measured by epr. The epr results were not corrected for stoichiometry and hence are not useful as they stand. The mass spectrometric data, at 300–840 K, are in good agreement with the results of Huie and Herron; at 300 K they reported \( k \cdot 1 \cdot 10^8 \). Washida and Takagi used photoionization mass spectrometry to monitor \( c-C_6H_{12} \) disappearance in the presence of excess 0 atoms and obtained a value for \( k \) about 30% smaller than the \( 8.3 \times 10^7 \) value recommended by Herron and Huie; however, details of their data reduction are not given. Two earlier measurements are not used in this evaluation: that by Avramenko, for reasons discussed by Kaufman, and that by Stuckey and Heicklen because \( k \) was measured relative to the rate of reaction of \( O + C_2F_6 \), which in turn was measured relative to the rate of \( O + 1-C_6H_5 \).

CALCULATIONS

Transition-state theory calculations were carried out for \( k_1 \) in order to extrapolate the rate coefficients to higher temperatures. \( S^\circ(298) \) was estimated by group additivity methods, using the parent cycloalkane as a model compound. The C-H-O geometry was assumed to be linear. Vibrational frequencies for the activated complex were taken to be the same as for the reaction of \( O + c-C_6H_{12} \). For further details, see Ref. 9. With an assumed value for \( k_1(298) \) of \( 8.3 \times 10^7 \) L mol\(^{-1}\) s\(^{-1}\) from Ref. 5, this model gives values for \( k_1 \) that are fitted by the expression, \( k_1 \cdot 2.6 \times 10^5 \cdot 10^2 \cdot 10^{-1240/T} \) L mol\(^{-1}\) s\(^{-1}\).

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

DISCUSSION

The calculations, based on experimental values of \( k_1(300) \) of Refs. 2 and 3, are in good agreement with higher temperature data of those studies. Apart from this, there is no reason to invalidate the result of Ref. 4. We recommend the calculated expression of \( k_1 \cdot 2.6 \times 10^5 \cdot 10^2 \cdot 10^{-1240/T} \) L mol\(^{-1}\) s\(^{-1}\), with an uncertainty in log \( k_1 \) of ±0.3 at 298 K, increasing to ±0.5 at 2000 K.

References

\[ \text{O} + \text{c-C}_2\text{H}_{14} \rightarrow \text{OH} + \text{c-C}_2\text{H}_{13} \]

\[ \Delta H^{\circ} = -32.7 \pm 5 \text{ kJ mol}^{-1} \ (-7.8 \text{ kcal mol}^{-1}) \]

\[ \Delta G^{\circ} = 54.2 \pm 5.3 \text{ kJ mol}^{-1} \ (13.0 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.3 \times 10^3 \exp^{-2.6 \times 10^{-20}/T} )</td>
<td>298 - 2000 K</td>
<td>( 2.0 \times 10^8 )</td>
<td>L mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 3.8 \times 10^{-18} \exp^{-2.6 \times 10^{-20}/T} )</td>
<td></td>
<td>( 3.3 \times 10^{-13} )</td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
</tbody>
</table>

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

(October 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

O + c-C₈H₁₈ → OH + c-C₇H₁₃

THERMOCHEMISTRY

Thermochemical data for O and OH are from JANAF Thermochemical Tables, 3rd edn. (1985). Group additivity rules were used to estimate differences between AH°₂₉₈ and AH°₃₃₁ for the cyclohexyl radical and for the parent alkane itself. An analytic expression for the equilibrium constant has not been calculated because the reverse reaction will, under all conditions of practical interest, be slower than the radical recombination reaction (OH + c-C₇H₁₃ → c-C₇H₇OH).

MEASUREMENTS

A single series of experimental measurements of k₁ has been reported. Muir and Herron produced O atoms by passing a flow of argon with a few percent O₂ through a microwave discharge and added reagent gas downstream. O atoms were kept in considerable excess. Relative [O] was determined by mass spectrometry, put on an absolute basis by titration with NO₂. Alkane concentration was also measured by mass spectrometry. Measurements were made between 331 and 652 K. Because [O] was kept in excess and at most 10% of the alkane was consumed, the method was free of complications caused by secondary reactions. However, since k is proportional to \ln([OH]/[RH]), a 5% error in measuring either [OH] or [RH] can mean a 50% error in k. The scatter in the data reflects this shortcoming. From their data, they extrapolated a value of k₁(298) of 1.6 × 10⁸ L mol⁻¹ s⁻¹, by assuming a linear Arrhenius plot.

CALCULATIONS

Transition-state theory calculations were carried out for k₁ in order to extrapolate the rate coefficients to higher temperatures. S¹(298) was estimated by group additivity methods, using the parent cycloalkane as a model compound. The C-H-O structure was assumed to be linear. Vibrational frequencies for the activated complex were taken to be the same as reaction of O + c-C₇H₇O. For further details, see Ref. 4. With an assumed value for k₁(298) of 2.0 × 10⁸ L mol⁻¹ s⁻¹, this model gives values for k₁ that are fitted by the expression, k₁ = 2.3 × 10³ T².6 exp(-1020/T) L mol⁻¹ s⁻¹. (This expression was obtained by treating the reaction as if there were a symmetry change of 1 → 1. Strictly speaking c-C₇H₇ has a symmetry of 1 and one should treat the problem as if there were 1 separate H atom abstraction reactions with (possibly) varying enthalpies and entropies of activation. The expected variations, though, are so slight that the calculation can effectively be carried out by assuming o(c-C₈H₁₄) = 14.)

DISCUSSION

The calculations are in reasonable agreement with experiment, though the latter possibly suggest more curvature in the plot of log k vs 1/T than the former. Until there are more precise measurements available, we recommend an expression for k₁ derived from the calculations: k₁ = 2.3 × 10³ T².6 exp(-1020/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.3 at 298 K, increasing to ±0.5 at 2000 K.

REFERENCES

N. COHEN AND K. R. WESTBERG

OH + CH₃F → CH₂F + H₂O

ΔH°₂₉₈ = -80.3 ± 8 kJ mol⁻¹ (-19.2 kcal mol⁻¹)  
ΔS°₂₉₈ = -10.8 ± 6 J mol⁻¹ K⁻¹ (2.6 cal mol⁻¹ K⁻¹)

---

Recommended rate coefficients

|   |  
|---|---|
| k₁ | 2.6 × 10⁵ T⁻¹.₅ exp(-1480/T)  
|   | 4.3 × 10⁻¹⁶ T⁻¹.₅ exp(-1480/T)  
|   | 250-2000 K  
|   | 9.3 × 10⁵  
|   | 1.6 × 10⁻¹⁹  

Units:  
L mol⁻¹ s⁻¹  
cm³ molecule⁻¹ s⁻¹

Uncertainty in log k₁: ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K. Expressions for K and k⁻¹ are not given because the reverse reaction is unlikely to be important at any temperature.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,¹ DH²⁹(C₃F₇) = -233 ± 8 and DH²⁹(C₂F₅) = -32.6 ± 8 kJ mol⁻¹. We estimate DH²⁹(C₂F₅) = DH²⁹(C₃F₇) + AH, assuming that the radical is nonplanar and that b₂ = 2. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

MEASUREMENTS

Howard and Evenson² measured k₁ at 295 K at 0.8 - 10 torr total pressure in a discharge flow system, using the H + NO₂ reaction to generate 10⁷ - 10¹ OH radicals/cm³ and using laser magnetic resonance at 84.3 μm for radical detection. They obtained (9.6 ± 2.1) x 10⁶ L mol⁻¹ s⁻¹. Nip et al.³ produced OH at 297 K by VUV flash photolysis of 0.3 torr H₂O and monitored OH decay by resonance absorption at 308.2 nm. They reported k₁ = (4.5 ± 0.8) x 10⁷ exp(-1890/T) L mol⁻¹ s⁻¹, with a 292 K value of (8.8 ± 0.5) x 10⁷. Bera and Hanrahan⁶ measured k₁ at room temperature using pulse radiolysis-absorption spectroscopy, and reported (1.0 ± 0.16) x 10⁷ L mol⁻¹ s⁻¹.

The spread among the room temperature values is thus approximately 0.2 units in log k₁, or 60% in k₁.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The value of k(298) required for the calculation was taken from Ref. ⁴. The model for the activated complex was based on that used previously for the reaction of OH with CH₄ with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data within 25% for T ≥ 298 K, could be described by the expression, k₁ = 2.6 x 10⁵ T⁻¹ S exp(-1480/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. ⁷.

DISCUSSION

The calculations are in very good agreement with the data of Ref. ⁴ throughout the range of experiments. Hence, we rely on them to extrapolate k₁ to higher temperatures and recommend k₁ = 2.6 x 10⁵ T⁻¹ S exp(-1480/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and higher.

References


\( \Delta H_{298} = -76.1 \pm 8 \text{ kJ mol}^{-1} (-18.2 \text{ kcal mol}^{-1}) \)

\( \Delta S_{298} = -16.1 \pm 8 \text{ kJ mol}^{-1} (-18.2 \text{ kcal mol}^{-1}) \)

\( T \) (K)

\( 10^0 \)

\( 5 \)

\( 1000/T \)

\( 0.0 \)

\( 0.5 \)

\( 1.0 \)

\( 1.5 \)

\( 2.0 \)

\( 2.5 \)

\( 3.0 \)

\( 3.5 \)

\( 4.0 \)

\( 1000/T \)

**RECOMMENDED RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.8 \times 10^4 T^{-1.7} \exp(-1290/T) )</td>
<td>250-2000 K</td>
<td>( 5.9 \times 10^6 )</td>
<td>L mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 4.7 \times 10^{-17} T^{1.7} \exp(-1290/T) )</td>
<td></td>
<td>( 9.9 \times 10^{-15} )</td>
<td>cm(^3) molecule(^{-1})s(^{-1})</td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): ±0.1 at 298 K, increasing to ±0.2 at 250 K and to ±0.3 at 1000 K and higher. Expressions for \( k \) and \( k_1 \) are not given because the reverse reaction is unlikely to be important at any temperature.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH TEMPERATURE REACTIONS

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,¹ and our own measurements.

Based on the review of McMillen and Golden,¹ we estimate

\[ \Delta H_{298}(\text{CHF}_2) = -247.6 \text{ kJ mol}^{-1} \]

and

\[ \Delta H_{298}(\text{CH}_2\text{F}_2) = -452.2 \text{ kJ mol}^{-1} \]

We estimate \( \Delta S_{298}(\text{CHF}_2) = \Delta S_{298}(\text{CH}_2\text{F}_2) \) based on the assumption that the reaction is unimolecular and that \( \Delta H = 2 \).

An analytic expression for \( K(T) \) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range</th>
<th>P (torr)</th>
<th>Method</th>
<th>( \log k_{298} ) (L mol(^{-1}) s(^{-1}))</th>
<th>( \log A )</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>293-429</td>
<td>1.5-2</td>
<td>discharge flow-resonance fluorescence</td>
<td>6.54</td>
<td>9.65</td>
<td>2100</td>
</tr>
<tr>
<td>3, 4</td>
<td>250-492</td>
<td>3</td>
<td>discharge flow-resonance fluorescence</td>
<td>6.83</td>
<td>9.41</td>
<td>1700</td>
</tr>
<tr>
<td>5</td>
<td>296</td>
<td>0.8-9.8</td>
<td>discharge flow-resonance fluorescence</td>
<td>6.97</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>297</td>
<td>50</td>
<td>flash photolysis-resonance absorption</td>
<td>6.86</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>(298)</td>
<td>600</td>
<td>pulse radiolysis-resonance absorption</td>
<td>6.72</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate \( k_1 \) to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₂F, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The room temperature value of \( k_1 \) used in the calculations was based on the results of Ref. 3. The results, in agreement with the data of Ref. 3 within 25%, could be described by the expression:

\[ k_1 = 2.8 \times 10^4 \text{ T}^{1.7} \text{ exp}(-1290/T) \text{ L mol}^{-1}\text{s}^{-1} \]

For further details, see Ref. 8.

DISCUSSION

The calculations are used as a basis for extrapolating \( k_1 \) to temperatures above the range of experimental data. Thus we recommend:

\[ k_1 = 2.8 \times 10^4 \text{ T}^{1.7} \text{ exp}(-1290/T) \text{ L mol}^{-1}\text{s}^{-1} \]

with an uncertainty in \( \log k_1 \) of 0.1 at 298 K, increasing to 0.3 at 1000 K and above. This expression differs from all the data (except the lowest-temperature value of Ref. 2) by no more than 25%.

References

\[ \Delta G^\circ_{298} = -52.3 \pm 4 \text{ kJ mol}^{-1} \] 

\[ \Delta H^\circ_{298} = 10.8 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} \] 

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(298) )</th>
<th>( x(298) )</th>
<th>( u(298) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 5.7 \times 10^3 \text{ mol}^{-1} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 9.5 \times 10^{-18} \exp(-2160/T) )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): ±0.2 at 298 K, increasing to ±0.3 at 3000 K. Expressions for \( k \) and \( k_1 \) are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

and Golden, 1 4 kJ/mol. We estimate observed practically no temperature variation between the two
with an extrapolation based on the relative relative
A linear extrapolation on an Arrhenius plot
shock-heated complex
and to test for
with the high
frequl'mcies,
with the high
China. The model for the activated complex was based on that used previously for the reaction of OH with CH4, with appropriate changes for the vibrations, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 3 within 25% for T ≥ 298 K, could be described by the expression, k 1 = 5.7 x 103 T 1.6 exp(-21601/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 16.

**DISCUSSION**

The calculations described above are in excellent agreement with all the data of Refs. 4 and 6 and in reasonable agreement with the high temperature datum of Refs. 8 and 9. The data of Ref. 3 are discounted, leaving only the room temperature value of T 1 being unaccountably high by nearly a factor of 2. We rely on the expression obtained from the calculations and recommend k1 = 5.7 x 105 T 1.0 exp(-21601/T) L mol⁻¹ s⁻¹, with an uncertainty in log k1 of ±0.2 at 300 K, increasing to ±0.3 at 2000 K.

**References**

OH + CH₃Cl → CH₂Cl + H₂O

ΔG°₂₉₈ = -76.5 ± 8 kJ mol⁻¹ (-18.3 kcal mol⁻¹)
ΔH°₂₉₈ = 10.6 ± 6 J mol⁻¹K⁻¹ (2.6 cal mol⁻¹K⁻¹)

This recommendation

Recommended Rate Coefficients

<table>
<thead>
<tr>
<th>k_1</th>
<th>k(T)</th>
<th>Range</th>
<th>k(298)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 x 10⁴</td>
<td>7.1.6 exp(-1040/T)</td>
<td>250-2000 K</td>
<td>2.6 x 10⁷</td>
<td>L mol⁻¹s⁻¹</td>
</tr>
<tr>
<td>1.5 x 10⁻¹⁶</td>
<td>7.1.6 exp(-1040/T)</td>
<td></td>
<td>4.3 x 10⁻¹⁴</td>
<td>cm³ molecule⁻¹s⁻¹</td>
</tr>
</tbody>
</table>

Uncertainty in log k₁: ±0.1 at 298 K, increasing to ±0.2 at 290 K and to ±0.3 at 1000 K and above. Expressions for K and k₁ are not given because the reverse reaction is unlikely to be important at any temperature.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

1251

OH + CHClOC + Cl + H2O

THERMOCHEMICAL DATA

Thermochemical data for H2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,1 

The radical is non-planar and that geometrical calculations were based on that used previously for the reaction of OH with CHCl3. With an analytic expression for \( k(T) \) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range (K)</th>
<th>P (torr)</th>
<th>Method</th>
<th>( \log k(298) )</th>
<th>( k = A^R \exp(-B/T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>296</td>
<td>0-8.9</td>
<td>discharge flow-magnetic resonance</td>
<td>7.34</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>290-350</td>
<td>20-200</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.39</td>
<td>9.05</td>
</tr>
<tr>
<td>4</td>
<td>298</td>
<td>20-50</td>
<td>flash photolysis-resonance fluorescence</td>
<td>1.42</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>297</td>
<td>[30-250]</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.39</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>241-483</td>
<td>5</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.30</td>
<td>9.26</td>
</tr>
<tr>
<td>7</td>
<td>295-800</td>
<td>750</td>
<td>laser photolysis-laser induced fluorescence</td>
<td>7.47</td>
<td>4.81</td>
</tr>
<tr>
<td>8</td>
<td>1600-2100</td>
<td>30</td>
<td>flames</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate \( k_1 \) to temperatures beyond the range of experimental data and to test for consistency of the data with results for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CHCl3, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. With an assumed value for log \( k_1(298) \) of 7.37, the results could be described by the expression, \( k_1 = 5.0 \times 10^9 \exp(-1230/K) \) L mol\(^{-1}\) s\(^{-1}\). This expression is in good agreement with results of Ref. 8 (except at their lowest temperature of 295 K), but overpredicts results of Refs. 3 and 6. The calculated value of log \( k_1 \) is proportional to \((295/T) \log k_1(298)\). For further computational details, see Ref. 10.

DISCUSSION

The flame study of Ref. 9 is considered too imprecise to be of use in this evaluation. Two other room temperature studies11,12 disagree significantly with Refs. 2-6. The most recent results of Ref. 8 agree with earlier data near 335 K, but are systematically larger at other temperatures: at the highest temperature of Ref. 6, Ref. 8 is 40% larger; at 295 K, 23% larger. (Note that the analytic fit of Ref. 8—given in the table above—underpredicts their own datum at 295 K by 35%.) There is thus an unresolvable systematic discrepancy in the experimental record at temperatures over ca. 400 K (increasing with temperature), notwithstanding the similarity in techniques. Instead as the results of Ref. 8 cover the broadest temperature range and are in nice agreement with the TST calculations, we tend to favor them. We recommend an expression very similar to both but with slightly more curvature, to decrease the discrepancy with Refs. 3 and 6 and 250 K: \( k_1 = 5.3 \times 10^9 \exp(-1060/K) \) L mol\(^{-1}\) s\(^{-1}\). The uncertainty in log \( k_1 \) is ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above. An additional experimental study to resolve the experimental discrepancies would be instructive.

References

\[ \Delta H_{298}^0 = -84.5 \pm 8.4 \text{ kJ mol}^{-1} \] (-20.2 kcal mol\(^{-1}\))

\[ \Delta C_{298}^0 = 10.8 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} \] (2.6 cal mol\(^{-1}\)K\(^{-1}\))

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>v</td>
<td>2</td>
</tr>
<tr>
<td>x</td>
<td>3</td>
</tr>
<tr>
<td>+</td>
<td>4</td>
</tr>
<tr>
<td>△</td>
<td>5</td>
</tr>
<tr>
<td>△</td>
<td>6</td>
</tr>
<tr>
<td>o</td>
<td>7</td>
</tr>
</tbody>
</table>

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>(k)</th>
<th>(k(T))</th>
<th>Range</th>
<th>(k(298))</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>(6.0 \times 10^6 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
<td>250-2000 K</td>
<td>(9.5 \times 10^7)</td>
<td>(9.5 \times 10^7) \text{ L mole}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td></td>
<td>(1.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
<td></td>
<td>(1.6 \times 10^{-13})</td>
<td>(1.6 \times 10^{-13}) cm(^3) molecules(^{-1}) s(^{-1})</td>
</tr>
</tbody>
</table>

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

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**Inhalation Health Effects**

This recommendation is made because of the potential for the formation of highly reactive species.

**References**

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

OH + CHCl₂ - CHCl₂ + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden, the radical nonplanar and that geometric is unlikely. These results are based on that used previously for the complex was based on that used previously for the reaction with CHCl₂. We estimate \( \Delta H_{\text{f}}(\text{OH}) = -95.4 \) and \( \Delta H_{\text{f}}(\text{CHCl}_2) = 100.8 \) kJ mol⁻¹. We estimate \( \Delta H_{\text{f}}(\text{CHCl}_2) = \Delta H_{\text{f}}(\text{OH}) + \text{Rin} \Delta \mu \), assuming that the radical nonplanar and that \( \mu = 2 \). An analytic expression for \( K(T) \) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range (K)</th>
<th>Method</th>
<th>( \log k(298) ) (L mol⁻¹s⁻¹)</th>
<th>( k = A^\text{n} \exp(-B/T) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>298</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.94</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>245-375</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.83</td>
<td>9.41 0.40</td>
</tr>
<tr>
<td>4</td>
<td>296</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.97</td>
<td>---</td>
</tr>
<tr>
<td>5, 6</td>
<td>291-455</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.96</td>
<td>9.52 0.40</td>
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<tr>
<td>7</td>
<td>298-775</td>
<td>laser photolysis-laser induced fluorescence</td>
<td>8.03</td>
<td>4.96 1.58 622</td>
</tr>
<tr>
<td>8</td>
<td>298</td>
<td>HONO photolysis-NO yield</td>
<td>7.86</td>
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</tr>
<tr>
<td>9</td>
<td>300-400</td>
<td>pulse radiolysis-absorption spectroscopy</td>
<td>7.94</td>
<td>9.61 0.40</td>
</tr>
</tbody>
</table>

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

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate \( k_1 \) to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of C by heavy halogen atoms. The results, in agreement with all the data (except those of Ref. 3) within 25% for \( T_{298} \) K, could be described by the expression, \( k = 6.0 \times 10^8 T^{1.6} \exp(-520/T) \) L mol⁻¹s⁻¹. For further computational details, see Ref. 10.

DISCUSSION

The data are all in good agreement with the exception of Ref. 3. The calculations, based on the room temperature value of Ref. 5, are also in good agreement at other temperatures with all the data excluding Ref. 3. Consequently, we rely on the calculations to extrapolate \( k_1 \) to higher temperatures than the range of experimental data: \( k_1 = 6.0 \times 10^8 T^{1.6} \exp(-520/T) \) L mol⁻¹s⁻¹, with an uncertainty in \( \log k_1 \) of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and higher.

References

$\Delta H_{298} = -97.9 \pm 8.4 \text{ kJ mol}^{-1} (-23.4 \text{ kcal mol}^{-1})$

$\Delta G_{298} = 10.8 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (2.6 \text{ cal mol}^{-1} \text{ K}^{-1})$

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k_{\text{f}}$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k_{298}$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$10.2 \times 10^2 \exp(-100/T)$</td>
<td>250-2000 K</td>
<td>$6.2 \times 10^7$</td>
<td>L mol$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$1.7 \times 10^{-20} \exp(-100/T)$</td>
<td></td>
<td>$1.0 \times 10^{-13}$</td>
<td>cm$^3$ molecule$^{-1}$s$^{-1}$</td>
</tr>
</tbody>
</table>

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

May 1991

**CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS**

**THERMOCHEMICAL DATA**

Thermochromic data for \( \text{H}_2\text{O} \) and \( \text{OH} \) are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden.\(^1\) \( \Delta H^E_{298}(\text{CCl}_3) = -103.3 \) and \( \Delta H^E_{298}(\text{CCl}_4) = -79.5 \text{ kJ mol}^{-1} \). We estimate \( \Delta G^E_{298}(\text{CCl}_3) = \Delta G^E_{298}(\text{CCl}_4) + R \ln \kappa_0 \), assuming that the radical is nonplanar and that \( \kappa_0 = 2 \). (JANAF Tables are based on the assumption that \( \text{CCl}_3 \) is planar.) An analytic expression for \( K(T) \) has not been calculated because the reverse reaction is unlikely ever to be important.

**EXPERIMENTAL DATA**

The reaction has been studied by Davis et al.\(^2\) over the temperature range of 245 to 375 K by flash photolysis-resonance fluorescence, using \( \text{H}_2\text{O} \) as an \( \text{OH} \) radical source in the presence of a large excess of helium diluent; by Howard and Evenson,\(^3\) using discharge flow-laser magnetic resonance at 296 K; and by Taylor et al.\(^4\) at 296 - 775 K using laser photolysis-laser induced fluorescence. All four studies are in excellent agreement.

Transition-state-theory calculations were carried out to extrapolate \( k_1 \) to temperatures beyond the range of experimental data and test for consistency of the data with data for reactions of \( \text{OH} \) with other haloethanes. The model for the activated complex was based on that used previously for the reaction of \( \text{OH} \) with \( \text{CH}_4' \) with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of \( \text{H} \) by heavy halogen atoms. The results could be described by the expression, \( k_1 = 6.6 \times 10^3 T^{1.7} \exp(-1701/T) \text{ L mol}^{-1}\text{ s}^{-1} \). For further computational details, see Ref. 8. Unlike all the other haloethanes considered, the calculations were in poor agreement with experimental data, underpredicting \( k(T) \) more severely with increasing temperature, up to an error of a factor of approximately 2.5 at 775 K. There is no obvious reason why the model should fail in this one case.

**DISCUSSION**

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

**References**

**N. COHEN AND K. R. WESTBERG**

**OH + CH₂Br → CH₂Br + H₂O**

\[ \Delta H°_{298} = -71.9 \pm 8.4 \text{ kJ mol}^{-1} (-17.2 \text{ kcal mol}^{-1}) \]

\[ \Delta G°_{298} = 10.8 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} (2.6 \text{ cal mol}^{-1} \text{K}^{-1}) \]

---

**RECOMMENDED RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 7.6 \times 10^3 \text{ s}^{-1} \exp(-500/T) )</td>
<td>250-2000 K</td>
<td>( 2.3 \times 10^9 )</td>
<td>L mol(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \exp(-500/T) )</td>
<td></td>
<td>( 3.9 \times 10^{-14} )</td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): ±0.2 at 298 K and below, increasing to ±0.4 at 1000 K and above. Expressions for \( k \) and \( k_1 \) are not given because the reverse reaction is unlikely to be important at any temperature.

May 1991

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THERMOCHEMICAL DATA

Thermochemical data for H2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,\(^1\) \(\Delta H_{298}^o(\text{CH}_3\text{Br}) = -35.2\) and \(\Delta H_{298}^o(\text{CH}_2\text{Br}) = 173.6\) kJ mol\(^{-1}\). We estimate \(\Delta G_{298}^o(\text{CH}_2\text{Br}) = \Delta G_{298}^o(\text{CH}_3\text{Br}) + \text{Rln} \, \varepsilon_a\), assuming that the radical is nonplanar and that \(\varepsilon_a = 2\). An analytic expression for \(K(T)\) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Howard and Evenson\(^2\) reported a value for \(k_1\) at 296 K of \((2.1 \pm 0.5) \times 10^7\) L mol\(^{-1}\) s\(^{-1}\) obtained in a discharge flow system with the \(\text{H} + \text{H}_2\text{O}\) reaction as an OH radical source and laser magnetic resonance as the means of detecting OH disappearances. Davis et al.\(^3\) studied the reaction at temperatures between 244 and 350 K in 20-200 torr Helium diluent. Flash photolysis of H\(_2\)O provided the OH radicals, whose disappearance was monitored by resonance fluorescence. They reported \(k_1 = (4.8 \pm 0.5) \times 10^8\) exp\((-890 \pm 58) / T\) L mol\(^{-1}\) s\(^{-1}\), with a room temperature value of \(2.4 \times 10^7\). The flame studies of Wilson et al.\(^4,5\) are subject to too many uncertainties to be useful in this evaluation.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate \(k_1\) to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH\(_4\), with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data within 60\%, for \(T \geq 298\) K, could be described by the expression, \(k_1 = 8.3 \times 10^5\, \tau^{-1.3}\exp(-500/T)\) L mol\(^{-1}\) s\(^{-1}\). For further details, see Ref. 6.

DISCUSSION

The calculations suggest a weaker temperature dependence in \(k_1\) than the results of Ref. 3 show, though the discrepancy in absolute values over the limited temperature range of the experiments is no more than 60%. There are no data for other brominated halomethanes for comparison. We recommend an expression for \(k_1\) based on a fit through the experimental data but forced to have a \(\tau^{-1.3}\) dependence as suggested by the calculations. This yields \(k_1 = 7.6 \times 10^5\, \tau^{-1.3}\exp(-900/T)\) L mol\(^{-1}\) s\(^{-1}\), with an uncertainty in log \(k_1\) of 0.2 at 298 K, increasing to 0.4 at 1000 K and above.

References

OH + CH₂CIF → CHCIF + H₂O

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

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

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OH + CH₂ClF → CH₂ClF + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). According to Chen et al.,¹ ΔH°₂₉₈(CHClF) = -264 kJ mol⁻¹. We estimate ΔH°₂₉₈(CH₂ClF) to be 290 ± 20 kJ mol⁻¹, and ΔH°₂₉₈(CH₂ClF) = ΔH°₂₉₈(CHClF) + Rln k, assuming that the radical nonplanar and that s₂ = 2. An analytic expression for K(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarized as follows:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range (K)</th>
<th>P (torr)</th>
<th>Method</th>
<th>log k(T)/mol⁻¹s⁻¹</th>
<th>k = A exp(-B/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>log A B</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>245-375</td>
<td>40</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.42</td>
<td>9.23 1259</td>
</tr>
<tr>
<td>3</td>
<td>278-373</td>
<td>12-20</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.54</td>
<td>9.47 1320</td>
</tr>
<tr>
<td>4, 5</td>
<td>250-466</td>
<td>3</td>
<td>discharge flow-response fluorescence</td>
<td>7.47</td>
<td>9.16 1140</td>
</tr>
<tr>
<td>6</td>
<td>296</td>
<td>0.8-9.8</td>
<td>discharge flow-magnetic resonance</td>
<td>7.34</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>297</td>
<td>[30-250?]</td>
<td>flash photolysis-resonance absorption</td>
<td>7.43</td>
<td>---</td>
</tr>
</tbody>
</table>

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 4 within 25% for T ≥ 298 K, could be described by the expression, k₁ = 5.6 × 10⁴ T⁻¹.6 exp(-870/T) L mol⁻¹s⁻¹. For further computational details, see Ref. 8.

DISCUSSION

The experimental data are all in close agreement, except at the lowest temperatures, for which the data of Refs. 4 and 2, when the temperature dependence is taken into account, disagree by approximately 50%. The calculations described above are in good agreement with all the data, splitting the difference in the lowest temperature values. Consequently we rely on the calculated curve to extrapolate k to temperatures above those of the experiments and recommend k₁ = 5.6 × 10⁴ T⁻¹.6 exp(-870/T) L mol⁻¹s⁻¹. The uncertainty in log k₁ is ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above.

References


**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 4.9 \times 10^3 \text{ } T^{1.8} \exp(-1180/T) )</td>
<td>250-2000 K</td>
<td>( 2.7 \times 10^5 )</td>
<td>L mol(^{-1})s(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 8.1 \times 10^{-18} \text{ } T^{1.8} \exp(-1180/T) )</td>
<td>250-2000 K</td>
<td>( 4.4 \times 10^{-15} )</td>
<td>cm(^3) molecule(^{-1})s(^{-1})</td>
</tr>
</tbody>
</table>

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

February 1987

OH + CHClF₂ + CClF₂ + H₂O

THERMOCHEMICAL DATA

Thermocchemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the review of McMillen and Golden,¹ AH°(OH) = -476 ± 8 and AH°(H₂O) = -269 ± 8 kJ/mol. We estimate ΔS°(OH) = 298k = 1 R ln kₑ assuming that the radical is nonplanar and that kₑ = 2. An analytic expression for k(T) has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

Experimental results are summarised as follows:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range (K)</th>
<th>P(torr)</th>
<th>Method</th>
<th>log k(298) (L mol⁻¹ s⁻¹)</th>
<th>k = A exp(-B/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>297-434</td>
<td>15-25</td>
<td>flash photolysis-resonance fluorescence</td>
<td>6.46</td>
<td>8.86 1635</td>
</tr>
<tr>
<td>3</td>
<td>296</td>
<td>0.8-10</td>
<td>discharge flow-magnetic resonance</td>
<td>6.31</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>250-350</td>
<td>40-200</td>
<td>flash photolysis-resonance fluorescence</td>
<td>6.46</td>
<td>8.75 1575</td>
</tr>
<tr>
<td>5</td>
<td>253-427</td>
<td>2.3-5.8</td>
<td>discharge flow-magnetic resonance</td>
<td>6.41</td>
<td>8.86 1657</td>
</tr>
<tr>
<td>6</td>
<td>263-373</td>
<td>10-30</td>
<td>flash photolysis-resonance fluorescence</td>
<td>(6.53)</td>
<td>9.10 1780</td>
</tr>
<tr>
<td>7</td>
<td>294-426</td>
<td>1.5-2</td>
<td>discharge flow-magnetic resonance</td>
<td>6.39</td>
<td>9.76 2300</td>
</tr>
<tr>
<td>8</td>
<td>297</td>
<td>[2307]</td>
<td>flash photolysis-resonance fluorescence</td>
<td>6.44</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>293-482</td>
<td>~3</td>
<td>discharge flow-magnetic resonance</td>
<td>6.45</td>
<td>8.88 1660</td>
</tr>
</tbody>
</table>

¹ interpolated value

For reasons that are not apparent, Clyne and Holt obtained a stronger temperature dependence than the other workers, recording larger values of k₁ at their higher temperatures and lower at 296 K than other measurements indicate. The lowest temperature results of Chang and Kaufman are also out of line with respect to other measurements.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 9 within 25% for T ≥ 298 K, could be described by the expression, k₁ = 4.9 × 10³ ¹.8 exp(-1180/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 10.

DISCUSSION

Except for the data of Ref. 7, the variations among the experimental data seem random. The calculated values, based on a room temperature value near the cluster of points from Refs. 2, 4, 5, 6, 8, and 9, are in good agreement with the data at other temperatures. Thus, we rely on the calculations to extrapolate k₁ to temperatures above the range of the data and recommend k₁ = 4.9 × 10³ ¹.8 exp(-1180/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.1 at 298 K, increasing to ±0.3 at 1000 K and above.

References

\[ \Delta G_{298} = -92.0 \pm 20 \text{ kJ mol}^{-1} (-22.0 \text{ kcal mol}^{-1}) \]

\[ \Delta H_{298} = -10.8 \pm 6.0 \text{ J mol}^{-1} \text{K}^{-1} (2.6 \text{ cal mol}^{-1} \text{K}^{-1}) \]

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

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

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OH + CHCl$_2$F + Cl$_2$F$^-$ + H$_2$O

THERMOCHEMICAL DATA

Thermochemical data for H$_2$O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Based on the reviews of Chen et al.\textsuperscript{1} and McMillen and Golden,\textsuperscript{2} AM$^0$(CHCl$_2$F) = -284.9 and AM$^0$(Cl$_2$F) = -96.2 kJ mol$^{-1}$. We estimate AM$^0$(Cl$_2$F) = -220 kJ mol$^{-1}$, assuming that the radical is nonplanar and that $k_p = 2$. An analytic expression for $K(T)$ has not been calculated because the reverse reaction is unlikely ever to be important.

EXPERIMENTAL DATA

$k_1$ has been measured in eight separate experiments spanning the temperature range of 240 to 483 K. Except for Ref. 10, the discrepancy among the different results is less than a factor of 1.8 throughout the temperature range, and if the results of Ref. 7 are discounted, the spread in values is only 35% or less. Experimental conditions and results are tabulated below:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temp. Range (K)</th>
<th>P(torr)</th>
<th>Method</th>
<th>log $k$(298) (L mol$^{-1}$s$^{-1}$)</th>
<th>$k = A \exp(-E/R)$</th>
<th>Log A</th>
<th>E/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>298-422</td>
<td>50</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.21</td>
<td>9.02</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>296</td>
<td>0.8 10</td>
<td>discharge flow-magnetic resonance</td>
<td>7.20</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>295-375</td>
<td>40-200</td>
<td>flash photolysis-resonance fluorescence</td>
<td>7.26</td>
<td>9.05</td>
<td>1245</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>291 396</td>
<td>2.2 5.9</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.26 (296 K) 8.84</td>
<td>1073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>293-413</td>
<td>1.5-2</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.33 (293 K) 9.46</td>
<td>1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>297</td>
<td>[20-2000]</td>
<td>flash photolysis-resonance absorption</td>
<td>7.31</td>
<td>---</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>250-483</td>
<td>3</td>
<td>discharge flow-resonance fluorescence</td>
<td>7.31</td>
<td>8.86</td>
<td>1050</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>300-400</td>
<td>760</td>
<td>pulse radiolysis-absorption spectroscopy</td>
<td>6.49</td>
<td>9.04</td>
<td>1787</td>
<td></td>
</tr>
</tbody>
</table>

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate $k_1$ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halomethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH$_3$O, with appropriate changes for the vibrational frequencies, moments of inertia, etc., resulting from the substitution of H by heavy halogen atoms. The results, in agreement with the data of Ref. 9 within 35% for $T \geq 298$ K, could be described by the expression, $k_1 = 9.1 \times 10^3 \, T^{1.7} \exp(-610/T)$ L mol$^{-1}$s$^{-1}$. For further computational details, see Ref. 11.

DISCUSSION

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

References

\[
\text{OH} + \text{CH}_3\text{CH}_2\text{F} \rightarrow \text{C}_2\text{H}_4\text{F} + \text{H}_2\text{O}
\]

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{CH}_2\text{F} & \rightarrow \text{CH}_3\text{CH}_2\text{F} + \text{H}_2\text{O} & \Delta H_{298}^0 & = -82.4 \pm 8 \text{ kJ mol}^{-1} \quad (-19.7 \text{ kcal mol}^{-1}) \\
\text{OH} + \text{CH}_3\text{CH}_2\text{F} & \rightarrow \text{C}_2\text{H}_4\text{F} + \text{H}_2\text{O} & \Delta H_{298}^0 & = -76.2 \pm 8 \text{ kJ mol}^{-1} \quad (-18.2 \text{ kcal mol}^{-1})
\end{align*}
\]

\[
\Delta G_{298}^0 = 16.7 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} \quad (4.0 \text{ cal mol}^{-1} \text{ K}^{-1})
\]

\[
\Delta G_{298}^0 = 16.4 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1} \quad (3.9 \text{ cal mol}^{-1} \text{ K}^{-1})
\]

\[
\text{THIS RECOMMENDATION}
\]

**RECOMMENDED RATE COEFFICIENTS**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Reference</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A )</td>
<td>( 9.3 \times 10^4 \text{ s}^{-1} \exp(-550/T) )</td>
<td>298 - 2000 K</td>
<td>( 1.4 \times 10^8 )</td>
<td>L mol(^{-1}\text{s}^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 1.5 \times 10^{-16} \text{ s}^{-1} \exp(-550/T) )</td>
<td></td>
<td>( 1.3 \times 10^{-13} )</td>
<td>cm(^3) molecule(^{-1}\text{s}^{-1})</td>
</tr>
</tbody>
</table>

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

February 1987

OH + CH₂CH₂F → CH₂CF + H₂O
≈ CH₂CH₂F + H₂O

THERMOCHEMICAL DATA

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

OH + CH₂CH₂F → CH₂CF + H₂O

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

OH + CH₂CH₂F → CH₂CH₂F + H₂O

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

Thermochemical data for H₂O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for fluoroethanes are from Stull et al. Data for fluoroethyl radicals are not available. Based on the predictions of Ref. 1, we estimate ΔH₂⁹⁰_C-C = -62.6 ± 12 kJ mol⁻¹ and TΔS₂⁹⁰_C-C = -56.5 ± 12 kJ mol⁻¹. The entropies of the two radicals were estimated to be 276.6 ± 5 and 276.2 ± 5 J mol⁻¹ K⁻¹, assuming barriers to internal rotation of 0 and 4 kJ mol⁻¹, respectively.

MEASUREMENTS

kₐ has been measured at 297 K by Nip et al. using VUV flash-photolysis of water vapor to produce OH radicals and resonance absorption to monitor their disappearance. From 18 separate measurements, a value of kₐ = (1.4 ± 0.22) x 10⁸ L mol⁻¹ s⁻¹ was determined. In a separate study, Singleton et al. determined that 85 ± 15 of the abstraction occurs at the α positions, whence k₁/k₂ = 5.7 ± 1.6.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out for k₁ and k₂ to extrapolate the room temperature results of Refs. 3 and 4 to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other halothanes. The model for the activated complex was based on that used previously for the reaction of OH with haloethanes, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results for k₁ and k₂ were added together to give kₐ, which could be described by the expression, kₐ = 9.3 x 10⁸ T⁻¹.6 exp(-155017) L mol⁻¹ s⁻¹. For further computational details, see Ref. 5.

DISCUSSION

For many or more experimental data, we are forced to rely on the single experimental measurements of kₐ and k₁/k₂, and the TST calculations based upon them. The experimental finding that k₁/k₂ = 6 requires an activation energy difference of E₂ - E₁ = 6.5 kJ mol⁻¹, since calculations suggest that the activation entropy for β-abstraction exceeds that for α-abstraction by -2.2 gibbs mol⁻¹. While such a large difference may seem questionable, it is consistent with the lower experimental values for rate coefficients for OH with haloethanes with only β-atoms. Hence, we recommend kₐ = 9.3 x 10⁸ T⁻¹.6 exp(-155017) L mol⁻¹ s⁻¹, with an uncertainty in log kₐ(298) of ±0.3, increasing to ±0.6 at 2000 K.

References

OH + CH₃CH₂Cl → C₂H₄Cl + H₂O

\( \Delta H_{298}^0 = -78 \pm 12 \text{ kJ mol}^{-1} \) (-18.6 kcal mol\(^{-1}\))

\( \Delta S_{298}^0 = 17.6 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} \) (4.2 cal mol\(^{-1}\) K\(^{-1}\))

\( \Delta H_{298}^0 = -70 \pm 12 \text{ kJ mol}^{-1} \) (-16.8 kcal mol\(^{-1}\))

\( \Delta S_{298}^0 = 17.3 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1} \) (4.1 cal mol\(^{-1}\) K\(^{-1}\))

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_A )</td>
<td>( 65 \times 10^{1.6} \exp(110/T) )</td>
<td>298 - 2000 K</td>
<td>( 2.3 \times 10^8 )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 1.1 \times 10^{-19} \times 2.6 \exp(110/T) )</td>
<td></td>
<td>( 3.9 \times 10^{-13} )</td>
<td>( \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>

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

May 1991

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

\[
\text{OH} + \text{CH}_2\text{CHCl} \rightarrow \text{CH}_3\text{CHCl} + \text{H}_2\text{O}
\]

and abstraction of one of the three \( \beta \)-hydrogen atoms:

\[
\text{OH} + \text{CH}_2\text{CHCl} \rightarrow \text{CH}_2\text{CH}_2\text{Cl} + \text{H}_2\text{O}
\]

The three \( \beta \)-H atoms are not exactly equivalent because there is a barrier to rotation about the C-C bond. Hence, the properties of the H atom trans to the Cl atom (opposite it, when viewed along the C-C axis) will differ slightly from those of the two gauche \( \beta \)-H atoms. (Once one H atom is removed by reaction, there is practically free rotation about the C-C bond in the chloroethyl radical, and the products are almost equivalent.) McKean et al.\(^1\) predict the bond strengths of the trans and gauche \( \beta \)-H atoms to be 815.0 and 829.7 kJ \text{ mol}^{-1}, respectively; and that of the \( a \)-H atoms to be 428.9 kJ \text{ mol}^{-1}.\(^2\) These values have not been verified experimentally, and considering the usual uncertainties measuring bond strengths, the trans/gauche difference may be unmeasurable. We assume hereafter that the reactions involving the two different conformations are indistinguishable.

Thermochemical data for \( \text{H}_2\text{O} \) and \( \text{OH} \) are taken from the third edition of JANAF Thermochemical Tables (1985). Data for chloroethanes are from Stull et al.\(^3\). Data for the chloroethyl radicals are not available. Based on the predictions of Ref. 1, we estimate \( \Delta H^\circ_{(298)} \text{(CH}_2\text{CHCl)} = 91.6 \pm 12 \text{ kJ mol}^{-1} \) and \( \Delta H^\circ_{(298)} \text{(CH}_2\text{CH}_2\text{Cl)} = 99.2 \pm 12 \text{ kJ mol}^{-1} \). The entropies of the two radicals were estimated to be 282.3 and 287.9 \( \pm 5 \) \text{ J mol}^{-1}\text{ K}^{-1}, assuming barriers to internal rotation of 0 and 4 \text{ kJ mol}^{-1}, respectively.

**MEASUREMENTS**

\( k_3 = k_1 + k_2 \) was measured by Howard and Evenson\(^5\) at 296 K in a discharge flow system using the \( \text{H} + \text{NO}_2 \) reaction as a source of \( \text{OH} \) radicals and laser magnetic resonance for monitoring \( \text{OH} \) consumption. From 9 separate measurements they determined \( k_3 \) to be \( (2.3 \pm 0.4) \times 10^{6} \text{ mol}^{-1}\text{ s}^{-1} \). Paraskevopoulos et al.\(^6\) used UV flash photolysis of \( \text{H}_2\text{O} \) at 297 K and monitored \( \text{OH} \) disappearance by resonance absorption. They reported \( k_A = (2.37 \pm 0.32) \times 10^{6} \text{ mol}^{-1}\text{ s}^{-1} \), in excellent agreement with the earlier study. Neither group monitored the chloroethyl radicals produced and consequently could make no determination of \( k_1 \) or \( k_2 \). Kasner et al.\(^7\) used laser photolysis--laser-induced fluorescence to measure \( k_A \) at 294 \( \pm \) 7 K \( \pm 789 \) and 780 torr and reported \( k_A = 68.4 \times 10^{-9} \text{ exp}(115/T) \).

**CALCULATIONS**

Transition-state-theory calculations were carried out to extrapolate \( k_1 \) to temperatures above 298 K and to test for consistency of the data with data for reactions of \( \text{OH} \) with other haloethanes. It was assumed that \( k_3 \gg k_2 \), so that the experimental measurement of \( k_3 \) (296) is essentially a measurement of \( k_1 \). This assumption is justified by (a) the much smaller rate coefficients for \( \text{OH} \) reactions with haloethanes having only \( \beta \)-hydrogen atoms (e.g., \( \text{CH}_2\text{CF}_3, \text{CH}_2\text{CCl}_3 \)); and (b) the experimental determination that \( a \)-hydrogen abstraction from \( \text{CH}_2\text{CHCl} \) accounts for approximately 85% of the total reaction.\(^8\) The model for the activated complex was based on that used previously for the reaction of \( \text{OH} \) with \( \text{CH}_4 \), with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results could be described by the expression, \( k_1 = 5.8 \times 10^6 \text{ exp}(-590/T) \text{ mol}^{-1}\text{ s}^{-1}. \) For further computational details, see Ref. 7.

**DISCUSSION**

The transition state theory calculations described above underpredict results of Ref. 6 by up to 18% at their highest temperatures. Lacking a measurement of \( k_1/k_2 \) at any temperatures, we had to assume \( k_1 \gg k_2 \) at room temperature, and that \( k_4 = k_1 \) throughout the temperature range. However, the neglect of contributions from \( k_2 \) means that the TST estimate of \( k_4 \) will be a lower limit at temperatures above 296 K. We thus recommend the results of Ref. 6, namely \( k_A = 65 \times 10^{-9} \text{ exp}(110/T) \text{ mol}^{-1}\text{ s}^{-1}, \) with an estimated uncertainty in \( \log k_A \) of \( +0.2 \) at 298 K, increasing to \( +0.3 \) at 3000 K.

**References**

N. COHEN AND K. R. WESTBERG

**OH + CH₂BrCH₂Br → CH₂BrCHBr + H₂O**

$\Delta_{298}^0 \mu = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1})$

$\Delta_{298}^0 S = 22.6 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} (5.4 \text{ cal mol}^{-1} \text{K}^{-1})$

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$1.8 \times 10^8 , \text{T}^{1.7} \exp(-180/\text{T})$</td>
<td>298 - 2000 K</td>
<td>$1.6 \times 10^8$</td>
<td>L mol$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$3.0 \times 10^{-17} , \text{T}^{1.7} \exp(-180/\text{T})$</td>
<td></td>
<td>$2.6 \times 10^{-13}$</td>
<td>cm$^3$ molecule$^{-1}$s$^{-1}$</td>
</tr>
</tbody>
</table>

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

February 1987

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

OH + CH₂BrCH₂Br + CHBrCH₂Br + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from the third edition of JANAF Thermochemical Tables (1985). Data for 1,2-dibromoethane are given by Stull et al.¹ Data for the 1,2-dibromoethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹ whence ΔH°₂⁹⁸ (CHBrCH₂Br) = 289 ± 10 kJ mol⁻¹; ΔS°₂⁹⁸ (CHBrCH₂Br) is estimated to be 397 ± 6 J mol⁻¹K⁻¹.

MEASUREMENTS

k₁ has been measured at 296 K by Howard and Evenson² in a discharge flow system using the H + NO₂ reaction as a source of OH radicals and laser magnetic resonance to monitor OH consumption. From 19 separate measurements they determined k₁ to be (1.5 ± 0.3) x 10⁸ L mol⁻¹ s⁻¹.

CALCULATIONS

Transition-state-theory calculations were carried out to extrapolate k₁ to temperatures above 298 K and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results could be described by the expression, k₁ = 1.8 x 10⁴ T¹.⁷ exp(-180/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 3.

DISCUSSION

In the absence of experimental data above room temperature, we rely on the TST calculations based on the single reliable measurement of Ref. 2. We recommend k₁ = 1.8 x 10⁴ T¹.⁷ exp(-180/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.2 at 298 K increasing to ±0.5 at 3000 K.

References


OH + CH₂FCHF₂ → C₂H₆F₃ + H₂O

\[ \text{OH} + \text{CH}_2\text{FCHF}_2 \rightarrow \text{C}_2\text{H}_6\text{F}_3 + \text{H}_2\text{O} \]

\[ \Delta H_{298}^\circ = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^\circ = 23.0 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (5.5 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

Recommended Rate Coefficients

\[ k_A = 3.1 \times 10^7 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \times 10^{-17} \exp(-930/T) \]

Range: 298 - 2000 K

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

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

OH + CH₃FCH₂F₂ → CHFCHF₂ + H₂O
and abstraction of the single H-atom to form 1,1,2-trifluoroethyl:

OH + CH₃FCH₂F₂ → CH₂FCF₂ + H₂O

THERMOCHEMICAL DATA

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

OH + CH₂FCHF₂ → CHFCHF₂ + H₂O

and abstraction of the single H-atom to form 1,1,2-trifluoroethyl:

OH + CH₃FCH₂F₂ → CH₂FCF₂ + H₂O

Thermochemical data for H₂O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for 1,2,2-trifluoroethane and for the radicals are not available. In the absence of such data we assume both C-H bond dissociation energies to be 423 ± 10 kJ mol⁻¹, whence ∆H°₂⁹⁸ = -77 ± 10 kJ/mol for both reactions. ∆S°₂⁹⁸ for each reaction is estimated to be 23 ± 6 J mol⁻¹ K⁻¹.

MEASUREMENTS

Clyne and Holt¹ produced OH in a discharge-flow system by the reaction of H atoms with NO₂, and monitored OH consumption by resonance fluorescence. Because products were not monitored, their measurements gives only kA, the sum of k₁ + k₂. Over the temperature range of 293 - 441 K, they reported log kₐ = (8.95 ± 0.14) - (430 ± 43)/T; however, their data suggest considerable curvature on an Arrhenius plot of log k versus 1/T.

Martin and Paraskevopoulos² studied the reaction at 298 K, generating OH radicals by VUV flash photolysis of H₂O vapor and monitoring OH disappearance by resonance absorption. They obtained log kₐ(298) = 7.04, about a factor of 3 lower than Clyne and Holt's value of 7.47 at the same temperature. Both groups claim experimental uncertainties of ±10% in kₐ.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate kₐ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log kₐ(298) was assumed to be 7.37. k₁ and k₂ were calculated separately, assuming k₁(298) = 2k₂(298), and the results added together to give kₐ. The model for the activated complex was based on that used previously for the reaction of OH with CH₄ with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 25%, could be described by the expression, kₐ = 3.1 × 10⁴ T⁻¹.⁷ exp(-930/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 3; however, a slightly larger value of k₁(298) was assumed there.

DISCUSSION

Although Clyne and Holt obtained log kₐ = 7.47 at 298 K, in view of the scatter of the data at other temperatures, a value of 7.37 is consistent with their results. However, Ref. 2 suggests that kₐ is smaller by as much as a factor of 3 at room temperature. We have our recommendation on the TST calculations described above, recognizing that this may be subject to revision when another, decisive measurement of kₐ(298) is made. An additional contribution to the uncertainty comes from having to apportion kₐ(298) arbitrarily between k₁ and k₂; we assumed an equal reaction rate coefficient for each of the 3 H atoms. Thus we recommend kₐ = 3.1 × 10⁴ T⁻¹.⁷ exp(-930/T) L mol⁻¹ s⁻¹, with an uncertainty in log kₐ of ±0.3 at 298 K, increasing to ±0.5 at 2000 K. A negative error is more probable than a positive one.

References


N. COHEN AND K. R. WESTBERG

\[ \text{OH} + \text{CH}_2\text{CICHCl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_3 + \text{H}_2\text{O} \]

\[ \Delta H^\circ = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \]

\[ \Delta S^\circ = 19.2 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1} (11.6 \text{ cal mol}^{-1} \text{ K}^{-1}) \]

\[ \text{THIS RECOMMENDATION} \]

**Recommended Rate Coefficients**

- \( k_A \): 
  - \( 1.6 \times 10^4 \times 1.6 \exp(30/7) \) ~ \( 250 - 2000 \text{ K} \)
  - \( 2.7 \times 10^{-17} \times 1.6 \exp(30/7) \) ~ \( 3.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)

Uncertainty in \( \log k_A \): ±0.2 at 298 K, increasing to ±0.4 at 2000 K and ±0.3 at 290 K. \( k_A \) is the sum of \( k_1 + k_2 \); separate values for \( k_1 \) and \( k_2 \) are not recommended. Because the reverse reactions are unlikely to be important at any temperature, values for equilibrium constants and reverse rate coefficients are not recommended.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

\[
\text{OH} + \text{CH}_2\text{CICH}_2 \text{Cl} \rightarrow \text{CHCICHCl}_2 + \text{H}_2\text{O} \\
\text{OH} + \text{CH}_2\text{CICH}_2 \text{Cl} \rightarrow \text{CHClCHCl}_2 + \text{H}_2\text{O}
\]

THERMOCHEMICAL DATA

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

\[
\text{OH} + \text{CH}_2\text{CICH}_2 \text{Cl} \rightarrow \text{CHClCHCl}_2 + \text{H}_2\text{O}
\]

and abstraction of the single H-atom to form 1,1,2-trichloroethyl:

\[
\text{OH} + \text{CH}_2\text{ClCH}_2 \text{Cl} \rightarrow \text{CH}_2\text{ClCCl}_2 + \text{H}_2\text{O}
\]

Thermochemical data for H\(_2\)O and OH are taken from the third edition of JANAF Thermochemical Tables (1985). Data for 1,1,2-trichloroethane are from Stull et al.\(^1\), data for the rest are not available. In the absence of such data we assume both C-H bond dissociation energies to be 423 ± 10 kJ mol\(^{-1}\), whence \(\Delta H^\text{f}_{298} = -77 ± 10 \text{ kJ mol}^{-1}\) for each reaction.

MEASUREMENTS

The only published study of this reaction is that of Jeong and Kaufman,\(^2\) who produced OH in a discharge flow system by the reaction of H with NO\(_2\), and monitored its consumption by resonance fluorescence. Over the temperature range of 277 to 461 K, they reported\(^3\) 

\[
k_A = (9.9 \pm 1.6) \times 10^8 \text{ exp}[-(960 \pm 110)/T] \text{ L mol}^{-1}\text{s}^{-1},
\]

an expression only slightly different from that given in the earlier paper. Since products were not monitored, this represents the sum of \(k_1 + k_2\).

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate \(k_A\) to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Separate calculations were carried out for the two kinds of H atoms assuming \(k_1(298) = 2k_2(298)\), and the resulting values of \(k_1\) and \(k_2\) were added together to give \(k_A\). The model for the activated complex was based on that used previously for the reaction of OH with CH\(_4\), with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 25\%, could be described by the expression, \(k_A = 1.6 \times 10^4 T^{1.7} \text{ exp}(-100/T) \text{ L mol}^{-1}\text{s}^{-1}\). For further computational details, see Ref. 4.

DISCUSSION

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

References


N. COHEN AND K. R. WESTBERG

**OH + CH₂FCF₃ → CHFCF₃ + H₂O**

\[ \Delta H_{298}^{°} = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^{°} = 19.2 \pm 4 \text{ J mol}^{-1} \text{K}^{-1} (4.6 \text{ cal mol}^{-1} \text{K}^{-1}) \]

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### Recommended Rate Coefficients

<table>
<thead>
<tr>
<th>K</th>
<th>K(298)</th>
<th>Range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 2.1 \times 10^5 \ T^{-1.7} \exp(-1110/T) )</td>
<td>250 - 2000 K</td>
<td>( 3.0 \times 10^6 ) L mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>( 3.5 \times 10^{-18} \ T^{-1.7} \exp(-1410/T) )</td>
<td></td>
<td>( 5.0 \times 10^{15} ) cm³ molecule⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

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

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

OH + CH₂F₂C₃F₇ → CH₂F₅ + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1,2-tetrafluoroethane and for the 1,2,2,2-tetrafluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹, whence ΔH₂⁰ for the reaction is -77 ± 10 kJ mol⁻¹. ΔS₂⁰ for the reaction is estimated to be 19.2 ± 4 J mol⁻¹ K⁻¹.

MEASUREMENTS

There are two temperature-dependent measurements of k₁, both by the same method: in a discharge flow system, OH was generated by the reaction of H atoms with NO₂ and its disappearance monitored by resonance fluorescence. Clyne and Holt² made measurements at temperatures from 294 to 429 K, while Jeong et al.³ from 249 to 493 K. Except at room temperature, the results are in fair agreement, but the two groups reported different Arrhenius parameters. Clyne and Holt gave log k₁ = (9.29 ± 0.23) - (780 ± 87)/T in L mol⁻¹ s⁻¹ units; Jeong et al. reported log k₁ = (8.82 ± 0.88) - (620 ± 15)/T. Martin and Paraskevopoulos² measured k₁ at 298 K using VUV flash photolysis of H₂O and resonance absorption detection and obtained (3.10 ± 0.35) × 10⁶ L mol⁻¹ s⁻¹, in near agreement with Clyne and Holt's value of (5.08 ± 0.42) × 10⁶. Liu et al.⁴ measured by flash photolysis-resonance fluorescence at 270 < T/K < 400. Their values for k₁ agree with the other measurements at their highest temperature but diverge increasingly as temperature decreases, giving 3.1 × 10⁶ at 298 K.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k₁ to temperatures above the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k₁(298) was assumed to be 6.48. The model for the activated complex was based on that used previously for the reaction of OH with CH₃, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data within 35%, except at the lowest temperature, could be described by the expression, k₁ = 2.1 × 10⁷ T¹⁻¹ exp(-1270/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 5, where a different value for k₁(298) was used.

DISCUSSION

The TST calculations are in good agreement with Ref. 4, which should be the most reliable measurements. Consequently, we recommend k₁ = 2.1 × 10⁷ T¹⁻¹ exp(-1270/T) L mol⁻¹ s⁻¹ for 250 < T/K < 2000, with an uncertainty in log k₁ of ±0.1 at 300 K, increasing to ±0.2 at 250 K and to ±0.3 at 2000 K.

References

$\Delta H^\circ_{298} = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1})$

$\Delta H^\circ_{298} = 20.5 \pm 4 \text{ J mol}^{-1} \text{K}^{-1} (4.9 \text{ cal mol}^{-1} \text{K}^{-1})$

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$k(T)$</th>
<th>Range</th>
<th>$k(298)$</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.6 \times 10^6 T^{1.7} \exp(-1020/T)$</td>
<td>250 - 2000 K</td>
<td>$8.4 \times 10^6$</td>
<td>L mol$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$2.7 \times 10^{-17} T^{1.7} \exp(-1020/T)$</td>
<td></td>
<td>$1.4 \times 10^{-14}$</td>
<td>cm$^3$ molecule$^{-1}$s$^{-1}$</td>
</tr>
</tbody>
</table>

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

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**THERMOCHEMICAL DATA**

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for the 1-chloro,2,2,2-trifluoroethyl radical and enthalpy data for 2-chloro,1,1,1-trifluoroethane are not available. The H-CH₂Cl₂F₃ bond dissociation energy is given by McMillen and Golden. From these data, ΔH°₂⁹⁸ for the reaction is calculated to be -73 ± 10 kJ/mol. ΔS°₂⁹⁸ for the reaction is estimated to be 20.5 ± 4 J mol⁻¹ K⁻¹, assuming that the three ligands on the unsaturated C atom of the radical are nonplanar.

**MEASUREMENTS**

Handwerk and Zellner studied the reaction at temperatures between 263 and 373 K in a static system, using flash photolysis of H₂O to generate OH radicals and monitoring their disappearance by resonance absorption. They reported k₁ = (6.62 ± 1.8) × 10⁸ exp[-(1260 ± 60)/T] L mol⁻¹ s⁻¹. Clyne and Holt made measurements between 294 and 427 K in a discharge flow system, using the reaction between H and NO₂ to produce OH and monitoring its consumption by resonance fluorescence. They reported log k₁ = (10.37 ± 0.34) - (1000 ± 130)/T in L mol⁻¹ s⁻¹ units. Howard and Evenson reported a measurement near 296 K made in a discharge flow system also using the H + NO₂ reaction as an OH source but with laser magnetic resonance as a means of monitoring OH consumption. They reported k₁ = (6.32 ± 1.38) × 10⁶ L mol⁻¹ s⁻¹, in close agreement with the value of Clyne and Holt, but much smaller than Handwerk and Zellner's result of (9.03 ± 1.81) × 10⁶ at 293 K.

**CALCULATIONS**

Transition-state-theory (TST) calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k₁(298) was assumed to be 6.95. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in agreement with the data generally within a factor of 2, could be described by the expression, k₁ = 1.6 × 10⁶ T⁻¹⁻⁷ exp(-1020/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 5.

**DISCUSSION**

The results of Ref. 3 exhibit a much stronger temperature dependence than do those of Ref. 2; however, the scatter in the data is so much greater that we are inclined to give more weight to Ref. 2. The TST calculations predict a slightly larger temperature dependence than the results of Ref. 1. Until another, definitive measurement of k₁ is made, we recommend the results of the TST calculation: k₁ = 1.6 × 10⁶ T⁻¹⁻⁷ exp(-1020/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.2 at 298 K, increasing to ±0.5 at 2000 K and to ±0.3 at 2500 K.

**References**


\[ \Delta H_{298}^\circ = -77 \pm 10 \text{ kJ mol}^{-1} \quad (-18.4 \text{ kcal mol}^{-1}) \]
\[ \Delta G_{298}^\circ = 19.2 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} \quad (4.6 \text{ cal mol}^{-1} \text{K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Expression</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 1.5 \times 10^8 , T^{\gamma - 7} \exp(-810/T) )</td>
<td>250 - 2000 K</td>
<td>( 1.6 \times 10^9 )</td>
<td>L mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td></td>
<td>( 2.6 \times 10^{17} , T^{1.7} \exp(-810/T) )</td>
<td></td>
<td>( 2.6 \times 10^{-14} )</td>
<td>cm(^3) molecule(^{-1}) s(^{-1})</td>
</tr>
</tbody>
</table>

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

(February 1987)

OH + CH₂CIF₂Cl → CHClF₂Cl + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,2-dichloro,1,1-difluoroethane and for the 1,2-dichloro,2,2-difluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹, whence ΔH°₂₉₈ for the reaction is -77 ± 10 kJ mol⁻¹. ΔS°₂₉₈ for the reaction is estimated to be 19.2 ± 6 J mol⁻¹ K⁻¹.

MEASUREMENTS

Jeong et al.¹ measured k₁ in a discharge-flow apparatus, using the H + NO₂ reaction to produce OH radicals and monitoring their disappearance by resonance fluorescence. Over the temperature range of 249 - 473 K they could express k₁ by (1.22 ± 0.12) × 10⁹ exp[-(1260 ± 35)/T] L mol⁻¹ s⁻¹, but noted that their data suggested considerable curvature on an Arrhenius plot.

Watson et al.² used flash photolysis-resonance fluorescence at 250, 298, and 350 K, with the source of OH radicals being 50 - 400 mtorr of H₂O. They reported k₁ = (1.8 ± 0.6) × 10⁹ exp[(-1580 ± 230)/T] L mol⁻¹ s⁻¹, with an estimated correction made for the presence of 450 ppm of halogenated C₂ alkenes. Their approximate room temperature value of (1 ± 0.1) × 10⁷ is about 2/3 of the value obtained by Jeong et al.¹

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc. A value of log k₁(298) = 7.2 was assumed. The results, in agreement with all the data within 40%, could be described by the expression, k₁ = 1.5 × 10⁸ T⁻¹.⁷ exp[(-810/T)] L mol⁻¹ s⁻¹. For further computational details, see Ref. 3.

DISCUSSION

The results of Ref. 2 are consistently lower than those of Ref. 1, especially at the lowest temperature of both studies (250 K), where the discrepancy is a factor of 1.8. We see no compelling reason for preferring one set of results over the other, though we have made our TST calculations based on a value of k₁(298) consistent with the results of Ref. 1. Until a third, decisive measure of k₁ is made, we recommend the results of the TST calculation: k₁ = 1.5 × 10⁸ T⁻¹.⁷ exp[(-810/T)] L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.2 at 298 K, increasing to ±0.4 at 2000 K and to ±0.3 at 250 K.

References

\[ \Delta H_{298}^{0} = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \]

\[ \Delta G_{298}^{0} = 20.5 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} (4.9 \text{ cal mol}^{-1} \text{K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(298) )</th>
<th>( k(1000) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 1.6 \times 10^6 \exp(-1330/T) )</td>
<td>( 2.7 \times 10^{-17} \exp(1330/T) )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 3.0 \times 10^6 )</td>
<td>( 4.9 \times 10^{-15} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): \( \pm 0.3 \) at \( 298 \text{ K} \), increasing to \( \pm 0.6 \) at \( 2000 \text{ K} \). Expressions for \( k \) and \( k^{-1} \) are not given because the reverse reaction is unlikely to be important at any temperature.

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\[ \text{OH} + \text{CF}_2\text{CF}_2 \cdot \rightarrow \text{CF}_2\text{CF}_2 \cdot + \text{H}_2\text{O} \]

THERMOCHEMICAL DATA

Thermochemical data for \( \text{H}_2\text{O} \) and \( \text{OH} \) are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,2,2-tetrafluoroethane and for the 1,1,2,2-tetrafluoroethyl radical are not available. We estimate the C-H bond dissociation energy to be \( 423 \pm 10 \text{ kJ/mol} \), whence \( \Delta H_{298}^0 \) for the reaction is \( -77 \pm 10 \text{ kJ/mol} \). \( \Delta G_{298}^0 \) for the reaction is estimated to be \( 20.5 \pm 6 \text{ J mol}^{-1}\text{K}^{-1} \).

MEASUREMENTS

The single published study of this reaction to date is by Clyne and Holt,\(^1\) who used a discharge flow system in which \( \text{OH} \) was generated by the reaction between \( \text{H} \) atoms and \( \text{NO}_2 \) and its consumption monitored by resonance fluorescence. For 4 temperatures between 294 and 434 K they reported \( \log k_1 = (9.22 \pm 0.53) - (780 \pm 170)/T \) in L mol\(^{-1}\) s\(^{-1} \) units, with considerable deviation from linearity on an Arrhenius plot.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate \( k_1 \) to temperatures above 298 K and to test for consistency of the data with data for reactions of \( \text{OH} \) with other haloethanes. \( \log k_1(298) \) was assumed to be 6.50. The model for the activated complex was based on that used previously for the reaction of \( \text{OH} \) with \( \text{CH}_3 \), with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results in reasonable agreement with the data considering the scatter, could be described by the expression, \( k_1 = 1.6 \times 10^8 T^{1.7} \text{exp}(-1330/T) \text{ L mol}^{-1}\text{ s}^{-1} \). For further computational details, see Ref. 2.

DISCUSSION

As the graph shows, the four data points of Ref. 1 exhibit considerable uncertainty in temperature dependence. \( \log k_1 \) at room temperature could easily be in error by \( \pm 0.25 \) units. The "universal" rate coefficient expression derived in Ref. 3 predicts a value of \( \log k_1(298) \) of over 7.35. On the other hand, in the case of several other haloethanes the results of Ref. 1 are significantly larger than those of other workers. With some hesitancy, therefore, we rely on the TST calculations based on room temperature value of \( k_1 \) determined in Ref. 1, recognizing that another measurement is badly needed. We recommend \( k_1 = 1.6 \times 10^8 T^{1.7} \text{exp}(-1330/T) \text{ L mol}^{-1}\text{ s}^{-1} \), with an uncertainty in \( \log k_1 \) of \( \pm 0.3 \) at 298 K, increasing to \( \pm 0.6 \) at 3000 K.

References

N. COHEN AND K. R. WESTBERG

OH + CHF<sub>2</sub>CF<sub>3</sub> → CF<sub>2</sub>CF<sub>3</sub> + H<sub>2</sub>O

ΔH<sup>0</sup><sub>298</sub> = -68 ± 8 kJ mol<sup>-1</sup> (-16.2 kcal mol<sup>-1</sup>)

ΔS<sup>0</sup><sub>298</sub> = 12.6 ± 4 J mol<sup>-1</sup>K<sup>-1</sup> (3.0 cal mol<sup>-1</sup>K<sup>-1</sup>)

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>k</th>
<th>k(T)</th>
<th>Range</th>
<th>k(298)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>k&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1.4 × 10&lt;sup&gt;6&lt;/sup&gt; exp(-1270/T)</td>
<td>298 - 2000 K</td>
<td>3.2 × 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>L mol&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>2.3 × 10&lt;sup&gt;-17&lt;/sup&gt; exp(-1270/T)</td>
<td></td>
<td>5.2 × 10&lt;sup&gt;-15&lt;/sup&gt;</td>
<td>cm&lt;sup&gt;3&lt;/sup&gt; molecule&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Uncertainty in log k<sub>1</sub>: ±0.3 at 298 K, increasing to ±0.6 at 2000 K. Expressions for K and k<sub>-1</sub> are not given because the reverse reaction is unlikely to be important at any temperature.

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OH + CF$_2$CF$_3$ → CF$_2$CF$_3$ + H$_2$O

THERMOCHEMICAL DATA

Thermochemical data for H$_2$O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for pentfluoroethane are from Chen et al.$^1$. Data for the pentfluoroethyl radical are from Rogers,$^2$ who cites AH$_{298}^\circ$ = -591 ± 4 kJ mol$^{-1}$ and E$_{298}^\circ$ = 341.2 J mol$^{-1}$K$^{-1}$. The uncertainty in AH$_{298}^\circ$ for the reaction results primarily from the uncertainties in the barriers to internal rotation in both the haloalkane and the radical.

MEASUREMENTS

The only temperature-dependent study of this reaction to date is by Clyne and Holt$^3$, who used a discharge flow system in which OH was generated by the reaction between H atoms and NO$_2$ and its consumption monitored by resonance fluorescence. For 4 temperatures between 294 and 441 K they reported log $k_1$ = (8.01 ± 0.20) - (478 ± 43)/T in L mol$^{-1}$s$^{-1}$ units. Their room temperature value (294 K) was (3.0 ± 1.1)$ \times 10^6$. A much smaller value of (1.5 ± 0.17)$ \times 10^6$ L mol$^{-1}$s$^{-1}$ at 298 K was reported by Martin and Paraskevopoulos$^4$, who used flash photolysis of H$_2$O vapor as an OH source and monitored the disappearance of OH radicals by resonance absorption.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate $k_1$ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log $k_1$(298) was assumed to be 6.28. The model for the activated complex was based on that used previously for the reaction of OH with CH$_4$, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data though suggesting stronger temperature dependence, could be described by the expression, $k_1 = 1.4 \times 10^9 T^{1.6} \exp(-1270/T)$ L mol$^{-1}$s$^{-1}$. For further computational details, see Ref. 5; however, a slightly larger value of $k_1$(298) was assumed there.

DISCUSSION

The room temperature value of $k_1$ reported in Ref. 4 is smaller by more than a factor of 2 than the value of Ref. 3; but it is consistent with higher temperature data of the latter study if the temperature dependence is as determined by the TST calculations described above. In view of the unsatisfactory agreement between the experimental studies, we rely on the TST calculations until another, definitive experiment is published. We recommend $k_1 = 1.4 \times 10^9 T^{1.6} \exp(-1270/T)$ L mol$^{-1}$s$^{-1}$, with an uncertainty in log $k_1$ of ±0.3 at 298 K, increasing to ±0.6 at 2000 K.

References


**OH + CHClF₃ → CCIF₃ + H₂O**

\[ \Delta G^{\circ}_{298} = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \]

\[ \Delta G^{\circ}_{298} = 15.5 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} (3.7 \text{ cal mol}^{-1} \text{K}^{-1}) \]

---

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(298) ) Range</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 5.0 \times 10^3 \ t^{-1/2} \exp(-770/T) )</td>
<td>250 - 2000 K</td>
</tr>
<tr>
<td>( 8.3 \times 10^{-18} \ t^{-1/2} \exp(-770/T) )</td>
<td>1.0 \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

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

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OH + CHFCF₃ → CCIFCF₃ + H₂O

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1,2-tetrafluoro-2-chloroethane and for the 1,2,2,2-tetrafluoro-1-chloroethane radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹, whence Δ²⁹⁸ for the reaction is estimated to be -77 ± 10 kJ mol⁻¹. Δ²⁹⁸ for the reaction is estimated to be 15.5 ± 6 J mol⁻¹ K⁻¹.

MEASUREMENTS

Watson et al.¹ measured k₁ at 250, 301, and 375 K using flash photolysis of 50 - 200 torr H₂O as an OH source and resonance fluorescence to monitor its disappearance. They reported k₁ = (3.69 ± 0.24) × 10⁸ exp[-(124 ± 90)/T] L mol⁻¹ s⁻¹, with a value at 301 K of (5.7 ± 0.2) × 10⁶. Howard and Evenson² obtained a slightly higher room temperature value of (7.5 ± 1.1) × 10⁶ (296 K) using the H₊ NO₂ reaction in a discharge flow to generate OH radicals and laser magnetic resonance to detect their disappearance.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. Log k₁(298) was assumed to be 6.80. The model for the activated complex was based on that used previously for the reaction of OH with CH₄, with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data considering the scatter, could be described by the expression, k₁ = 5.0 × 10³ T¹.⁷ exp(-770/T) L mol⁻¹ s⁻¹. For further computational details, see Ref. 3; however, a slightly larger value of k₁(298) was assumed there.

DISCUSSION

The experimental data are within approximately 25% of the values of k₁ calculated by TST; hence we recommend the TST expression of k₁ = 5.0 × 10³ T¹.⁷ exp(-770/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.2 at 298 K, increasing to ±0.5 at 2000 K.

References


OH + CHCl₂CF₃ → CCl₂CF₃ + H₂O

ΔH°₂⁹₈ = -77 ± 10 kJ mol⁻¹ (-18.4 kcal mol⁻¹)

ΔS°₂⁹₈ = 20.1 ± 2.0 J mol⁻¹ K⁻¹ (4.1 cal mol⁻¹ K⁻¹)

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ref.</th>
<th>k₁</th>
<th>K(T)</th>
<th>Range</th>
<th>k₂⁹₈</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ</td>
<td>2</td>
<td>4.4 × 10³ T⁻¹⁷ exp(-370/T)</td>
<td>250 - 2000 K</td>
<td>2.0 × 10⁷</td>
<td>L mol⁻¹ s⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.3 × 10⁻¹⁸ T⁻¹⁷ exp(-370/T)</td>
<td></td>
<td>3.4 × 10⁻¹⁴</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

Uncertainty in log k₁: ±0.2 at 250 to 300 K, increasing to ±0.4 at 2000 K. Expressions for k and k⁻¹ are not given because the reverse reaction is unlikely to be important at any temperature.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THermoCHEMICAL DATA

Thermochemical data for \( \text{H}_2 \text{O} \) and \( \text{OH} \) are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1-trifluoro-2,2-dichloroethane (except for \( \Delta H^0_{298} \) -- see Ref. 1) and for the 2,2,2-trifluoro-1,1-dichloroethyl radical are not available. We estimate the C-H bond dissociation energy to be \( 423 \pm 20 \) kJ \( \text{mol}^{-1} \), whence \( \Delta H^0_{298} \) for the reaction is \(-77 \pm 10 \) kJ \( \text{mol}^{-1} \). \( \Delta H^0_{298} \) for the reaction is estimated to be \( 17.2 \pm 6 \) J \( \text{mol}^{-1} \text{K}^{-1} \).

MEASUREMENTS

Clyne and Holt\(^2\) used a discharge flow system to measure \( k_1 \) at \( 4 \) temperatures between 293 and 429 K. \( \text{OH} \) was generated by the reaction between \( \text{H} \) atoms and \( \text{NO}_2 \), and its consumption monitored by resonance fluorescence. They reported \( \log k_1 = (8.83 \pm 0.02) - (435 \pm 44) / T \) in L \( \text{mol}^{-1} \text{s}^{-1} \) units. At 293 K they obtained \( k_1 = (2.32 \pm 0.11) \times 10^7 \) L \( \text{mol}^{-1} \text{s}^{-1} \). Howard and Evenson\(^3\) obtained a smaller room temperature value of \( (1.71 \pm 0.26) \times 10^7 \) in a similar experiment except that the \( \text{OH} \) was monitored by laser magnetic resonance. Watson et al.\(^4\) used flash photolysis resonance fluorescence at 295, 298, and 375 K and reported a rate coefficient of \( (6.4 \pm 0.2) \times 10^8 \exp[-(1102 \pm 57)/T] \) L \( \text{mol}^{-1} \text{s}^{-1} \). Their room temperature result of \( (2.2 \pm 0.2) \times 10^7 \) agrees with that of Ref. 1. (The higher and lower values shown for Ref. 4 on the graph represent experiments at 40 and 300 torr diluent, respectively.) Liu et al.\(^5\) measured \( k_1 \) by flash photolysis-resonance fluorescence at \( 270 < T/\text{K} < 400 \). Their values for \( k_1 \) agree with the other measurements.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate \( k_1 \) to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of \( \text{OH} \) with other halogenoethanes. The model for the activated complex was based on that used previously for the reaction of \( \text{OH} \) with \( \text{CH}_3 \), with appropriate changes for the vibrational frequencies, moments of inertia, etc. \( \log k_1(298) \) was assumed to be 7.3. The results, in agreement with the data generally within \( 25\% \), could be described by the expression \( k_1 = 4.4 \times 10^3 \times \exp(-370/T) \) L \( \text{mol}^{-1} \text{s}^{-1} \). For further computational details, see Ref. 5; however, a slightly larger value of \( k_1(298) \) was assumed there.

DISCUSSION

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

References

**N. COHEN AND K. R. WESTBERG**

**OH + CH₃CF₃ → CH₂CF₃ + H₂O**

\[ \Delta H_{298}^{o} = -53 \pm 8 \text{ kJ mol}^{-1} (-12.6 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^{o} = 20.1 \pm 4.2 \text{ mol}^{-1} \text{K}^{-1} (4.8 \text{ cal mol}^{-1} \text{K}^{-1}) \]

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k_1 )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.1 \times 10^6 \text{ T}^{-1.1} \exp(-2380/T) )</td>
<td>298 - 2000 K</td>
<td>( 7.3 \times 10^5 )</td>
<td>L mol⁻¹ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>( 6.8 \times 10^{-15} \text{ T}^{-1.1} \exp(-2380/T) )</td>
<td></td>
<td>( 1.2 \times 10^{-15} )</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

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

February 1987

\[ \text{OH} + \text{CH}_2\text{CF}_3 \rightarrow \text{CHO} + \text{CF}_3 \text{H} \]

**THERMOCHEMICAL DATA**

Thermochemical data for \( \text{H}_2\text{O} \) and \( \text{OH} \) are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1,1,1-trifluoroethane are from Stull et al.\(^1\). Data for the 2,2,2-trifluoroethyl radical are from Rogers,\(^2\) who cites \( \Delta_{298}^{\circ} G = -517 \pm 8 \text{ kJ mol}^{-1} \) and \( \Delta_{298}^{\circ} H = -59.4 \text{ J mol}^{-1} \text{K}^{-1} \). The uncertainty in \( \Delta_{298}^{\circ} G \) for the reaction results primarily from the uncertainties in the barriers to internal rotation in both the haloalkane and the radical.

**EXPERIMENTAL DATA**

Clyne and Holt\(^3\) studied the reaction at 4 temperatures between 293 and 425 K in a discharge-flow system. The OH was produced by the reaction of H atoms with \( \text{N}_2\text{O} \), and its disappearance monitored by resonance fluorescence. They expressed their results by \( \log k_1 = (10.62 \pm 0.40) - (1390 \pm 220)/T \) in \( \text{L mol}^{-1} \text{s}^{-1} \) units. At 293 K they obtained only an upper limit to \( k_1 \) of \( 6.0 \times 10^5 \). Martin and Paraskevopoulos\(^4\) obtained a larger value for \( k_1 \) at 298 K of \( (1.03 \pm 0.26) \times 10^6 \). This result was obtained by flash photolysis of \( \text{H}_2\text{O} \) in the VUV to produce \( \text{OH} \) radicals, whose disappearance was then monitored by resonance absorption. Their fluoroacetone was of measured purity 99.6%, with 0.4% \( \text{CF}_3\text{Cl} \) impurity. Assuming a reactivity of the latter compound characteristic of olefins with \( \text{OH} \), there is sufficient impurity present to contribute significantly to the measured rate coefficient at room temperature. Clyne and Holt's reagent was stated to be 99.9% pure or better.

**CALCULATIONS**

Transition-state-theory (TST) calculations were carried out to extrapolate \( k_1 \) beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other haloethanes. \( \log k_1 \) was assumed to be 5.9. The model for the activated complex was based on that used previously for the reaction of OH with \( \text{CH}_4 \), with appropriate changes for the vibrational frequencies, amounts of limiting, etc.,. The results, in agreement with the data (within a factor of 2), could be described by the expression, \( k_1 = 4.1 \times 10^6 \text{T}^{-1.5}\text{exp}(-2380/T) \text{L mol}^{-1} \text{s}^{-1} \). For further computational details, see Ref. 5; however, a slightly larger value of \( k_1(298) \) was assumed there.

**DISCUSSION**

Both room temperature measurements of \( k_1 \) leave something to be desired: that of Ref. 4 may be too large because of possible impurities; the lower value of Ref. 3 is given as only an upper limit. A value of \( \log k_1(298) = 5.9 \) is consistent with both measurements, but may still be too large. The TST calculation based on this value for \( k_1(298) \) predicts values at higher temperatures consistently lower than the other results of Ref. 3. However, values for the rate coefficient for the analogous reaction of OH with \( \text{CH}_3\text{Cl} \) obtained in Ref. 3 are consistently higher than results of other workers (see Data Sheet for that reaction). The TST calculation for that reaction is in good agreement with the most reliable experimental data. Hence, we chose to rely on the TST calculations in this case, not withstanding the disagreement with Ref. 3. We recommend \( k_1 = 4.1 \times 10^6 \text{T}^{-1.5}\text{exp}(-2380/T) \text{L mol}^{-1} \text{s}^{-1} \), with an uncertainty in \( \log k_1 \) of \( \pm 0.3 \) at 300 K, increasing to \( \pm 0.5 \) at 2000 K.

**References**

\( \Delta G^0 = -77 \pm 10 \text{ kJ mol}^{-1} (-18.4 \text{ kcal mol}^{-1}) \)

\( \Delta G^0 = 17.7 \pm 5 \text{ J mol}^{-1} \text{K}^{-1} (4.2 \text{ cal mol}^{-1} \text{K}^{-1}) \)

### Recommended Rate Coefficients

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 3.4 \times 10^5 \ y^{1.1} \ \text{exp}(-1300/T) )</td>
<td>250 - 2000 K</td>
<td>( 2.3 \times 10^6 )</td>
<td>L \text{ mol}^{-1} \text{s}^{-1}</td>
</tr>
<tr>
<td></td>
<td>( 5.7 \times 10^{-16} \ y^{1.1} \ \text{exp}(-1300/T) )</td>
<td></td>
<td>( 3.8 \times 10^{-15} )</td>
<td>cm(^3) \text{ molecule}^{-1} \text{s}^{-1}</td>
</tr>
</tbody>
</table>

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

May 1991

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

1297

OH + CH₂F₂Cl + CH₂F₂Cl + H₂

THERMOCHEMICAL DATA

Thermochemical data for H₂O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 1-chloro,1-difluoromethane and the 2-chloro,2-difluoromethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹, whereas ΔG°₂₉₈ for the reaction is -77 ± 10 kJ mol⁻¹. ΔG°₂₉₈ for the reaction is estimated to be 17.7 ± 5 J mol⁻¹ s⁻¹.

MEASUREMENTS

The reported measurements of kl show considerable scatter, much of which can probably be attributed to impurities. (Paraskevopoulos et al. estimate that the 0.05% C₂F₅Cl₂ impurity could increase the apparent rate coefficient by 35% at room temperature.) Howard and Evenson measured kl at 296 K, using a discharge-flow system to produce the OH radicals by the reaction of H + NO₂, and laser magnetic resonance for OH detection. Their halocarbon was of greater than 99.9% purity. They obtained the lowest reported room temperature value for kl of (1.7 ± 0.25) x 10⁻⁹ L mol⁻¹ s⁻¹. Watson et al. used photolysis of H₂O by an H₂ spark discharge lamp as an OH source and resonance fluorescence for OH detection. Their halocarbon was of stated purity 99.9%. They fitted their data at 273, 298, and 373 K by kl = (6.9 ± 0.9) x 10⁻⁹ exp[(-1748 ± 30)/T] L mol⁻¹ s⁻¹. Handwerk and Zellner produced OH by flash photolysis of H₂O and used resonance absorption to monitor its disappearance. After purification the CH₂F₂Cl contained 0.02-0.1% of other saturated fluorocarbons and unstationed amounts of unsaturated fluorocarbons. They reported kl = (1.08 ± 0.3) x 10⁻⁹ exp[(-1790 ± 150)/T] based on measurements at 293 and 373 K. Clyne and Holt studied the reaction at 5 temperatures between 293 and 477 K, using the H + NO₂ reaction in a discharge flow system to produce OH and resonance fluorescence to monitor its disappearance. The halocarbon was stated to be more than 99.8% pure. They reported log kl = (9.3 ± 0.36) - (780 ± 130)/T in L mol⁻¹ s⁻¹ units, and k(293) = (4.3 ± 0.8) x 10⁻⁹. Paraskevopoulos et al. measured kl at 297 K by flash photolysis-resonance absorption and reported (2.79 ± 1.04) x 10⁻⁹ L mol⁻¹ s⁻¹. Their reagent was 99.9% pure. Cox et al. reported the same result, but their method requires some unproven assumptions about the reaction mechanism. Liu et al. measured kl by flash photolysis-resonance fluorescence at 270 < T/K < 400.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate kl to temperatures above 300 K to test for consistency of the data with data for reactions of other saturated fluorocarbons and unstationed amounts of unsaturated fluorocarbons. They reported kl = (9.3 ± 0.36) - (780 ± 130)/T in L mol⁻¹ s⁻¹ units, and k(293) = (4.3 ± 0.8) x 10⁻⁹. Paraskevopoulos et al. measured kl at 297 K by flash photolysis-resonance absorption and reported (2.79 ± 1.04) x 10⁻⁹ L mol⁻¹ s⁻¹. Their reagent was 99.9% pure. Cox et al. reported the same result, but their method requires some unproven assumptions about the reaction mechanism. Liu et al. measured kl by flash photolysis-resonance fluorescence at 270 < T/K < 400.

DISCUSSION

The TST calculations predict a slightly larger temperature dependence than the results of Ref. 7, which should be the most reliable experiments. We rely on the latter, but assume a preexponential factor of 3.4 x 10⁷ s⁻¹ exp(-1300/T) for 270 < T/K < 2000. This agrees with the data of Ref. 7 within 10%.

References

OH + CH₃CCl₃ → CH₂CCl₂ + H₂O

\[ \Delta H_{298}^{\circ} = -77 \pm 10 \text{kJ mol}^{-1} \] (18.4 kcal mol⁻¹)

\[ \Delta S_{298}^{\circ} = 20.2 \pm 5 \text{J mol}^{-1} \text{K}^{-1} \] (4.8 kcal mol⁻¹ K⁻¹)

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>k₁</th>
<th>k(T)</th>
<th>Range</th>
<th>k(298)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 x 10⁶</td>
<td>( \exp(-1610/T) )</td>
<td>250 - 2000 K</td>
<td>6.3 x 10⁵</td>
<td>L mol⁻¹ s⁻¹</td>
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<tr>
<td>4.0 x 10⁻¹⁵</td>
<td>( \exp(-1610/T) )</td>
<td></td>
<td>1.0 x 10⁻¹⁴</td>
<td>cm³ molecule⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

Uncertainty in log k₁: ±0.2 at 250 - 300 K, increasing to ±0.4 at 2000 K. Expressions for K and k⁻₁ are not given because the reverse reaction is unlikely to be important at any temperature.

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CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

OH + CH3CCL3 + CH2CCL3 + H2O

THERMOCHEMICAL DATA

Thermochemical data for H2O and OH are from JANAF Thermochemical Tables, 3rd edition (1985). Data for 2,2,2-trichloroethane are from Chao et al.1 Data for the 2,2,2-trichloroethyl radical are not available. We estimate the C-H bond dissociation energy to be 423 ± 10 kJ mol⁻¹, whence DH°₂₉₈ for the reaction is -77 ± 10 kJ mol⁻¹. DH°₂₉₈ for the reaction is estimated to be 20.2 ± 9 J mol⁻¹ K⁻¹.

MEASUREMENTS

Of the published studies of this reaction,²⁻¹⁰ the first four have been invalidated on the grounds that the methyl chloroform contained significant levels (-0.1%) of CH₂CCL₃, which reacts two to three orders of magnitude more rapidly with OH and therefore gives spuriously large results. The methyl chloroform was produced by pulse radiolysis of H₂O/Ar mixtures and its absorption monitored by resonance fluorescence as a means of OH detection. The two studies are in excellent agreement, the former giving k₁ = (3.25 ± 1.1) x 10⁶ L mol⁻¹ s⁻¹ and the latter, k₁ = (3.3 ± 0.8) x 10⁶ L mol⁻¹ s⁻¹. Both reported a room temperature value very close to 6.4 x 10⁶ L mol⁻¹ s⁻¹. Reference 8 is unreliable because of the indirectness of the method. Nelson et al.⁵,¹⁰ measured k₁ by two separate techniques: at 298 K OH was produced by photolysis of CH₂O/NO₂ mixtures and the rate was measured relative to that for OH + CH₂Cl by monitoring the relative disappearance of CH₂CCL₂ and CH₂Cl.¹⁰ At 359, 376, and 402 K OH was produced by pulse radiolysis of H₂O/Ar mixtures and its absorption monitored by kinetic absorption spectroscopy at 309 nm.¹⁰ The points plotted are from Ref. 10. Though both methods are somewhat indirect, the results are in good agreement with other studies.

CALCULATIONS

Transition-state-theory (TST) calculations were carried out to extrapolate k₁ to temperatures beyond the range of experimental data and to test for consistency of the data with data for reactions of OH with other halocarbons. Log k₁(298) was assumed to be 6.8. The model for the activated complex was based on that used previously for the reaction of OH with CH₄ with appropriate changes for the vibrational frequencies, moments of inertia, etc. The results, in reasonable agreement with the data considering the scatter, could be described by the expression, k₁ = 2.8 x 10⁶ T⁻¹ exp(-1832/T) L mol⁻¹ s⁻¹. For further details, see Ref. 11.

DISCUSSION

After discarding the results of Ref. 3, which were superseded by Ref. 7, those of Ref. 5, which have proven less reliable in the cases of other OH + halocarbon reactions, and Ref. 8, we are left with five presumably reliable measurements of log k₁(298), three near 6.8 and two near 6.95. We accept the lower value because of possible reagent impurities in the other studies. The TST calculations based on this room temperature value are in good agreement with the other data of Refs. 6 and 7 at other temperatures, and we rely on them for our recommended expression. We recommend k₁ = 2.8 x 10⁶ T⁻¹ exp(-1610/T) L mol⁻¹ s⁻¹, with an uncertainty in log k₁ of ±0.2 at 250 - 300 K. Increasing to ±0.3 at 2000 K.

References

N. COHEN AND K. R. WESTBERG

\[ \text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2 \text{O} \]

\[ \Delta G_{\text{deg}} = -94.56 \pm 6 \text{ kJ mol}^{-1} (-10.65 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{\text{deg}} = 7.1 \pm 0.4 \text{ J mol}^{-1} \text{K}^{-1} (1.7 \text{ cal mol}^{-1} \text{K}^{-1}) \]

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

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Ref.</th>
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<tr>
<td>O</td>
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</tr>
<tr>
<td>△</td>
<td>19</td>
</tr>
</tbody>
</table>

**Recommendation Rate Coefficients**

- \( k_1 \)
  - \( 5.0 \times 10^4 \ t^{1.6} \exp(-480/T) \)
  - Range: 225-3000 K
  - \( k(298) = 9.1 \times 10^7 \)
  - Units: L mol\(^{-1}\) s\(^{-1}\)

- \( k_{-1} \)
  - \( 2.5 \times 10^3 \ t^{1.9} \exp(-5720/T) \)
  - Range: 300-3000 K
  - \( k(298) = 0.6 \)
  - Units: L mol\(^{-1}\) s\(^{-1}\)

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

May 1991

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THERMOCHEMICAL DATA

Thermochemical data are taken from the JANAF Thermochimical Tables, 3rd ed. (1985), according to which \( \Delta H_{298}^\circ (NH_2) = -190.9 \pm 5.3 \text{ kJ mol}^{-1} \). The analytic expression chosen for \( K(T) \) matches equilibrium constants calculated from those data to within 5% between 200 and 6000 K.

MEASUREMENTS

Since the 1972 review by Baulch et al., the following studies have been published. At low temperatures (<700 K), \( k_1 \) has been measured by discharge flow-mass spectrometry at 298 K, UV photolysis-resonance fluorescence (298 K),1 pulsed radiolysis-resonance absorption (418 K),2 flash photolysis-resonance fluorescence (298 K, 297-447 K),3 discharge flow-IR (298-669 K),4 flash photolysis resonance absorption (228-472 K),5 pulsed radiolysis-computer modeling (300 K),6 and discharge flow-resonance fluorescence (297-364 K)7 and 299-1075 K.8 There have been 5 shock tube studies: a combined flash photolysis-shock tube experiment (1080-1695 K),9 an induction time measurement (1390-1920 K),10 a shock tube-laser absorption study11 (1750-2500 K); a similar study but using resonance absorption15 (1600-2000 K); and one16 that obtained only an upper limit to the value of \( k_1 \) (not shown on the graph). More recently a laser photolysis-laser induced fluorescence study (840-1425 K),17 a flame study (2600-2360 K),18 and a flash photolysis laser-induced fluorescence study (273-433 K)19 have appeared.

CALCULATIONS

Transition-state theory (TST) calculations were carried out for several activated complex configurations to test which of the high-temperature measurements could be consistent with the low-temperature results. The \( N+H_2+O \) bond angles were assumed to be 165 and 110° respectively; the \( N-H \) and \( N-O \) bond lengths were assumed only slightly lengthened from their normal lengths. The \( N-H \) symmetric stretching and the two \( N-H \) bending frequencies were assumed to be 2500 and 1000 cm\(^{-1} \), respectively. The \( N-H \) and \( H-O \) bending frequencies were varied between 800 and 900 cm\(^{-1} \). The two internal rotations were assumed either free or with low barriers of 4.2 and 8.4 kJ/mole. With the varied vibrational frequencies taken to be 900 cm\(^{-1} \) and free internal rotation, the calculations agreed with the data of Refs. 3, 6, 8, 10, and 17, and could be fitted over the temperature range of 250 to 3000 K by \( k_1 = 5.0 \times 10^9 \text{ s}^{-1} \). None of the models allowed the data of Ref. 13 to be consistent with a room temperature value of \( k_1 \) of \( 9 \times 10^9 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1} \), which all the reliable room temperature data suggest. The calculations also imply that the results of Ref. 12 are too low by a factor of 3-5. The calculations suggest values of log \( k_1 \) at 2000 K of 9.7 - 10.0. Another TST calculation17 gave nearly identical results at \( T > 400 \text{ K} \), but slightly larger at lower temperatures (500 at 250 K).

DISCUSSION

The shock tube study of Fujii et al.13 has been criticized14 for the over-simplified data analysis and the indirect dependence of \( k_1 \) on the induction time. Ref. 15, which corroborated the results of Ref. 13, may have been misled by the erroneous choice for the rate coefficient for the \( O + NH_2 \) reaction. The value of \( k_1 \) deduced in Ref. 12 depends on computer modeling and may be sensitive to assumed values for some other rate coefficients. The much larger values of \( k_1 \) deduced in Ref. 14 were obtained by a more direct experimental procedure; the flame study results of Ref. 17 agree with these. The recently reported larger values for the rate coefficient for the \( N + NH_2 \) reaction will lower the deduced value of \( k_1 \) in both of these studies -- possibly by 50%. Refs. 3, 6, 8, 10, and 11 all agree on a value for log \( k_1 \) of 7.95 ± 0.10 at 295-300 K. Between 500 and 1500 K there is at least a factor of 2 uncertainty in the data. We recommend the expression for \( k_1 \) based on the TST calculation described above: \( k_1 = 5.0 \times 10^9 \text{ cm}^3 \text{ s}^{-1} \exp(-460/T \text{ K}) \). This gives agreement with the lowest temperature experimental data6,10,11,19 and the highest14,18, within experimental error (taking into account the necessary lowering of \( k_1 \), because of the revised value for the \( N+NH_2 \) rate coefficient). The uncertainty in log \( k_1 \) is ±0.1 at 300 K, increasing to ±0.3 at 2000 K.

References

\( \Delta H_{298} = -119.3 \pm 12 \text{ kJ mol}^{-1} \) \( (-28.5 \text{ kcal mol}^{-1}) \)

\( \Delta S_{298} = -6.3 \pm 0.4 \text{ J mol}^{-1} \text{K}^{-1} \) \( (-2.0 \text{ cal mol}^{-1} \text{K}^{-1}) \)

\[ K(T) = 0.73 + 0.1 \exp(14320/T) \]

The uncertainty in \( \log K(T) \) is \( \pm 3.1 \) at 200 K, decreasing to \( \pm 2.1 \) at 298 K and \( \pm 0.24 \) at 3000 K.

**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>Rate Constant ( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 9.0 \times 10^5 \exp(230/T) )</td>
<td>250-3000 K</td>
<td>( 1.0 \times 10^9 )</td>
<td>( L \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 1.5 \times 10^{-16} \exp(230/T) )</td>
<td></td>
<td>( 1.7 \times 10^{-12} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{-1} )</td>
<td>( 1.2 \times 10^5 \exp(-14090/T) )</td>
<td>600-5000 K</td>
<td>( 6.6 \times 10^4 )</td>
<td>( L \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 2.0 \times 10^{-16} \exp(-14090/T) )</td>
<td></td>
<td>( 1.2 \times 10^{-12} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>

Uncertainty in \( \log k_1 \): \( \pm 0.7 \) throughout range of 250-3000 K. Uncertainty in \( \log k_{-1} \): \( \pm 1.3 \) at 600 K, decreasing to \( \pm 0.8 \) at 3000 K. \( k_{-1} \) has not been studied directly. Its uncertainty reflects those of both \( k_1 \) and \( K(T) \).
CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

1303

OH + NH$_2$ \rightarrow NH + H$_2$O

THERMOCHEMICAL DATA

Thermochemical data (except for $\Delta H_{\text{f}}$ (NH$_2)$ are taken from the JANAF Thermochemical Tables, 3rd ed., according to which $\Delta H_{\text{f}}$ (NH$_2$) = 190.3 ± 6.3 kJ mol$^{-1}$; $\Delta H_{\text{f}}$ (NH) = 376.6 ± 16 kJ mol$^{-1}$. More recently, Piper$^1$ reanalyzed experimental data for $\Delta H_{\text{f}}$ (NH) and recommended 352 ± 10 kJ mol$^{-1}$; we use this value. The analytic expression chosen for $K(T)$ matches equilibrium constants calculated from those data to within 3% between 200 and 600 K.

MEASUREMENTS

There are no direct measurements of this reaction. Dean et al.$^2$ found the kinetics of NH$_3$ oxidation at 1279 to 1323 K to be sensitive to $k_1$, and that their model was consistent with experiments if they assumed $k_1 = 3 \times 10^7$ T$^{-0.66}$ exp(-600/T) L mol$^{-1}$s$^{-1}$, an expression taken from Tunder et al.$^3$; this gives values of approximately 2.5 x 10$^9$ in their temperature range. Kimball-Linne and Hanson$^4$ modeled experiments in a combustion-driven flow reactor in which NO and NH$_3$ were reacted at 1050 - 1450 K. They optimized fits to data when $k_1$ was taken to be 6 x 10$^5$. Branch, Kee and Miller$^5$ modeled NH$_3$ reduction by NO near 1200 K and found they needed to have $k_1 = 4.5 \times 10^9$ exp(-1100/T) to predict NO behavior correctly. This gives $k_1 = 1.8 \times 10^9$ at 1200 K and is slightly smaller than the value they earlier assumed$^6$ because of the revised value for the NH$_2$ + NO reaction rate coefficient. Niemitz et al.$^7$ required a value of 5 x 10$^9$ at 1350 K to model their experiments on the OH + NH$_3$ reaction studied by flash photolysis of shock heated mixtures of NH$_3$, H$_2$O and Ar.

CALCULATIONS

We have used transition-state theory to calculate values of $k_1$, assuming a model for the transition state very similar to that used in a successful TST calculation for the OH + NH$_3$ rate coefficient (see data sheet for that reaction). (This model implicitly assumes the reactor proceeds directly by H atom abstraction, rather than by formation of an OH···NH$_2$ complex that subsequently rearranges.) The principal differences in the transition state properties for the OH + NH$_3$ reaction are in the electronic degeneracies (NH$_2$OH$^*$ is assumed to be a triplet state, whereas NH$_3$OH$^*$ was assumed to be a doublet) and in the symmetry changes. With an assumed value of $k_1(298)$ of 1 x 10$^5$, the calculated values could be fitted by the expression, $k_1 = 5.0 \times 10^4$ T$^{1.5}$ exp(230/T), which gives k$_1$(1300) = 5 x 10$^9$, in reasonable agreement with the modeling requirements.

DISCUSSION

In the absence of direct measurements we recommend the above TST calculated values for $k_1$: $8.6 \times 10^8$ T$^{-1.5}$ exp(230/T), with an uncertainty of a factor of 5 throughout the range of 250 to 3000 K. This large uncertainty allows for the possibility that the reaction proceeds via two parallel pathways: direct abstraction (modeled by the TST calculations) and addition followed by rearrangement of an OH···NH$_2$ complex.

References

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

CH + OH \rightarrow H + HNO
\rightarrow N + H_2O

THERMOCHEMICAL DATA

Thermochemical data are taken from the JANAF Thermochemical Tables, 3rd ed. More recently, Piper\(^1\) reanalyzed experimental data for (NH\(_2\)(NH) and recommended \(352 \pm 10\) kJ mol\(^{-1}\); we use this value. The analytic expressions chosen for \(K_1(T)\) and \(K_2(T)\) match equilibrium constants calculated from those data to within 10% from 200 to 6000 K.

MEASUREMENTS

There are no direct measurements of either \(k_1\) or \(k_2\) or their sum. Dean and coworkers\(^2\) used \(k_1 = 5 \times 10^8 \exp(-1000/T)\) L mol\(^{-1}\) s\(^{-1}\) in their mechanism for NH\(_3\) oxidation near 2000 K, but provided no comment on the sensitivity of the modeling results to these values.

CALCULATIONS

\(k_2\) can be estimated using the analogous reaction of 2OH \rightarrow H\(_2\)O + O as a guide. The rate coefficient for that reaction is well-described by \(k = 2.1 \times 10^5 \exp(200/T)\) L mol\(^{-1}\) s\(^{-1}\). If we use this expression, augmented by a factor of 16/9 because of the different electronic degeneracies (assuming the activated complex is a quartet state), and converted to a two-parameter expression (a third seems unnecessary considering the approximations involved), the resulting expression is \(k_2 = 2 \times 10^6 \exp(-1000/T)\) L mol\(^{-1}\) s\(^{-1}\).

\(k_1\) can be estimated by comparison with \(k_2\), the rate coefficient for the reaction 2OH \rightarrow H\(_2\)O. The reverse reaction rate coefficient is \(4.4 \times 10^5\) L mol\(^{-1}\) s\(^{-1}\), with formation of 2OH occurring 81% of the time.\(^3\) This implies an intrinsic activation energy barrier of approximately 4 kJ mol\(^{-1}\) if \(g^\ddagger = 1\) and approximately 1 kJ mol\(^{-1}\) if \(g^\ddagger = 3\). Assuming the transition state is a \(^2\Sigma\) state, then \(g^\ddagger\) for Reaction (1) is 2, and the maximum value \(k_1\) can have (if there is no activation energy) is approximately \(5 \times 10^{10}\) L mol\(^{-1}\) s\(^{-1}\). If the activation energy is as large as 4 kJ mol\(^{-1}\), then \(k_1\) will be only \(1 \times 10^{10}\). Since both reactions 2 and 4 pass through addition complexes, we would expect very small, if any, activation barriers. We estimate \(k_1(298) = 2 \times 10^{10}\), with an uncertainty of a factor of 2.5.

DISCUSSION

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

Two other reactions between OH and NH can be written:

CH + NH \rightarrow H + HNO
CH + NH \rightarrow N + H\(_2\)O

The first of these, though exothermic, is a four-center reaction and, like the analogous reaction of 2OH \rightarrow H\(_2\)O + O, would be expected to have a large activation energy. It would therefore not compete with reactions (1) and (2), even at fairly high temperatures. The second reaction is slightly endothermic, and is discussed in the reverse direction in the data sheet for O + NH\(_2\) reactions.

References


N. COHEN AND K. R. WESTBERG

\[ \text{OH} + \text{NH}_2 = \text{O} + \text{NH}_3 \]

\[ \Delta H_{298}^0 = -26.1 \pm 6 \text{ kJ mol}^{-1} (-6.2 \text{ kcal mol}^{-1}) \]

\[ \Delta S_{298}^0 = -24.6 \pm 0.4 \text{ J mol}^{-1} \text{K}^{-1} (-5.9 \text{ cal mol}^{-1} \text{K}^{-1}) \]

\[ k(T) = 1 \times 10^{-3} T^{0.5} \exp(3440/T) \]

The uncertainty in log \( k(T) \) is ±1.1 at 298 K, decreasing to ±0.1 at 3000 K.

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**Recommended Rate Coefficients**

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k(T) )</th>
<th>Range</th>
<th>( k(298) )</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 1.1 \times 10^{2.6} \exp(870/T) )</td>
<td>298-2000 K</td>
<td>( 5.5 \times 10^7 )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 1.8 \times 10^{-11} \times 10^{2.6} \exp(870/T) )</td>
<td></td>
<td>( 9.2 \times 10^{-14} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.1 \times 10^{3.2} \exp(-2620/T) )</td>
<td>298-2000 K</td>
<td>( 2.6 \times 10^5 )</td>
<td>( \text{L mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td></td>
<td>( 1.8 \times 10^{-18} \times 10^{3.2} \exp(-2620/T) )</td>
<td></td>
<td>( 4.3 \times 10^{-17} )</td>
<td>( \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>

Uncertainty in log \( k_1 \): ±0.3 from 298 to 2000 K. Uncertainty in log \( k_2 \): ±1.2 at 298 K, decreasing to ±0.4 at 2000 K. \( k_1 \) is calculated from \( k_{-1} \) and \( k(T) \); its uncertainty reflects the uncertainties in both of those quantities.

(August 1987)

CHEMICAL KINETIC DATA SHEETS FOR HIGH-TEMPERATURE REACTIONS

THERMOCHEMICAL DATA

Thermochemical data are taken from JANAF Thermochemo Tables, 3rd ed., according to which ΔHf\textsubscript{298}(\text{NH}_3) = -19.0 ± 6.3 kJ/mol. The analytic expression chosen for K(T) matches equilibrium constants calculated from these data to within 8% from 298 to 6000 K.

MEASUREMENTS

There are no direct measurements of k\textsubscript{1}. k\textsubscript{1} has been measured at moderate temperatures (300-850 K) in flowing\textsuperscript{1-9} and static\textsuperscript{10} systems and at high (>1000 K) temperatures in flames\textsuperscript{11} and in shock tubes.\textsuperscript{12-15} The most precise study is that of Perry,\textsuperscript{5} who used laser photolysis/NO\textsubscript{2} chemiluminescence to follow the reaction at 488 - 841 K. By maintaining a very large excess of NH\textsubscript{3}, he minimized the effects of secondary reactions. He obtained log k\textsubscript{1} = 5.98 and 8.01 (L mol\textsuperscript{-1} s\textsuperscript{-1} units) at 448 and 841 K, respectively. The most reliable high-temperature study is that of Salimian et al.,\textsuperscript{13} who shock heated mixtures of NH\textsubscript{3} and H\textsubscript{2}O to 1750-2060 K and monitored OH absorption in the UV with a ring dye laser, obtaining log k\textsubscript{1} = 9.3 ± 0.3 at 2000 K. Earlier studies near 300 K\textsuperscript{16} indicated values of log k\textsubscript{1} of 4.8 - 5.5. Baulch et al.\textsuperscript{9} studied the reverse reaction at 350 K in a discharge-flow diffusion-stirred reactor. By measuring the NO yields with and without added NO reagent, they concluded that the experimental results were not consistent with a computer simulation in which the initial step produced NH\textsubscript{2}, deciding therefore that 0 + NH\textsubscript{2} must form an NH\textsubscript{2}O addition complex.

CALCULATIONS

Transition-state theory (TST) calculations of k\textsubscript{1} have been described by Salimian et al.\textsuperscript{13} and by Cohen.\textsuperscript{16} The latter obtained good agreement with the data of Refs. 8 and 13 by assuming log k\textsubscript{1}(300) = 4.5, which is a factor of 2 or more lower than the experiments near that temperature indicate.\textsuperscript{2-4} These calculations are fitted by the expression k\textsubscript{1} = 1.1 × 10\textsuperscript{3} T\textsuperscript{2.1} exp(-2620/T) L mol\textsuperscript{-1} s\textsuperscript{-1} for 248 < T < 3000 K. Calculations by Hert\textsuperscript{17} and Melius\textsuperscript{18} indicate than an NH\textsubscript{2}O addition complex would not be stable.

DISCUSSION

The literature through 1969 was reviewed by Cohen and Heicklen\textsuperscript{15} and by Baulch et al.,\textsuperscript{5} both of whom concluded that most of the early studies were unreliable. Detailed computer calculations\textsuperscript{16} carried out to simulate the experimental conditions of Refs. 3, 4, and 9 showed that, notwithstanding the results of Ref. 9, the H-abstraction mechanism could not be unambiguously ruled out. However, a satisfactory explanation for values of k\textsubscript{1} factors of 2-3 larger than the TST calculations obtained in some experimental studies at 298 - 350 K could not be found. Accordingly, we regard the mechanism and the rate coefficient at low temperatures, to be uncertain at present. Provisionally, we recommend the results of the TST calculations of Ref. 16, which are in good agreement with the data of Refs. 8 and 13, but a factor of 2 lower than the lowest experimental results at 298-350 K: k\textsubscript{1} = 1.1 × 10\textsuperscript{3} T\textsuperscript{2.1} exp(-2620/T) L mol\textsuperscript{-1} s\textsuperscript{-1}, with an uncertainty in log k\textsubscript{1} of ±0.3 throughout the temperature range of 298 - 2000 K. The uncertainty in log k\textsubscript{1}(298) is considerably larger, reflecting the uncertainty in ΔHf\textsubscript{298}(\text{NH}_3) and, thereby, in K(T).

References

18. C. F. Melius, unpublished calculations.
O + NH₂ ↔ NH + OH & O + NH₂ = H + HNO & O + NH₂ → H₂ + NO

The uncertainty in log $k_1(T)$ is ±3.1 at 200 K, decreasing to ±2.1 at 298 K and ±0.3 at 3000 K. The corresponding uncertainties in log $k_2(T)$ are ±1.8, ±1.2, and ±0.25, respectively. Those for log $k_3(T)$ are ±1.5, ±1.0, and ±0.2, respectively.

O + H2 + 1/2 NH2 + OH
O + H2 + H + HNO
O + NH2 + N2 + NO

THERMOCHEMICAL DATA

Thermochromical data for NH2 radicals are taken from the JANAF Thermochemical Tables, 3rd ed., according to ΔHf°(NH2) = -100.4 ± 6; ΔHf°(NH) = 93.6; NH2(0) = 298(100) = 376.1 ± 16 kJ/mol. More recently, Piper² reanalyzed experimental data for ΔHf°(NH2) and recommended 332 ± 10 kJ/mol; we use this value. The analytic expressions chosen for k1(T), k2(T), and k3(T) match equilibrium constants calculated from those data to within 7%, respectively, between 200 and 5000 K.

MEASUREMENTS

Dransfeld et al.² studied these and other reactions of NH2 radicals in a discharge-flow system at 296 K. NH2 radicals were produced by the reaction between F atoms (produced by a microwave discharge through F2) and NH3 and were detected by laser-induced fluorescence (LIF) or laser magnetic resonance (LMR). Other results of Albers et al.⁴ for reaction (3) and the other via direct H atom abstraction, with very little activation energy (approximately 1 x 10⁻¹⁰ L mol⁻¹s⁻¹). Other possible reaction channels (yielding NO + H2, or N + H2O) could be eliminated in both experiments, either on thermochromical grounds or on the basis of product concentration profiles. Their calculations indicate two possible paths to form NH and NO, with activation energy approximately 25 times larger than earlier reported by Gehring et al.³

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

O + NH2 + HNO + H + NH2
O + NH2 + HNO + H2
O + NH2 + HNO + H + H2

They concluded that reaction 2 would dominate, with a smaller contribution from 1, and even less from reaction 3. We have carried out transition-state theory (TST) calculations for k1b using a model for the transition state very similar to that used for the OH + NO reaction (see data sheet for that reaction) but assuming that k1b = (1.4 x 10⁻⁵ T)²/₄ (kJ(298))²/₈ exp(5330/T).

CALCULATIONS

Melvin and Bialek⁶ used fourth-order Walter-Pleasent perturbation theory with bond additivity corrections to investigate the reaction. Their calculations indicate two possible paths to form NH + OH, one via two successive complexes:

O + NH2 + H2O + H + NO₂ + H + OH
O + NH2 + H2O + H + NO + H2

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

O + NH2 + HNO + H + NH2
O + NH2 + HNO + H2 + H2
O + NH2 + HNO + H + H2

They concluded that reaction 2 would dominate, with a smaller contribution from 1, and even less from reaction 3. We have carried out transition-state theory (TST) calculations for k1b using a model for the transition state very similar to that used for the 0 + NH3 reaction (see data sheet for that reaction) but assuming that k1b = (1.4 x 10⁻⁵ T)²/₄ (kJ(298))²/₈ exp(5330/T).

DISCUSSION

The experimental results of Ref. 2 for k3, k4, and k5 are reasonable, but provide only room temperature values. The sensitivities of the separate values for k3 and k5 to details of the computational model assumed were not discussed. The TST calculations described above indicate that if k1b(298) is as large as 7 x 10²⁰ L mol⁻¹s⁻¹ (see Ref. 2), then the barrier height is less than 1 kJ/mol, which seems too small (cf. Ref. 6). Consequently, a considerable contribution to k1 should come from k1b if the results of Albers et al.⁴ are correct. The TST calculations indicate that k1b varies by less than a factor of 2 from 200 to 3000 K. The association process (k1b) should have little-or even negative-temperature dependence. Thus, in any case k1 should have a very weak temperature dependence. The same is true for k2. If the relative enthalpies of the intermediates HNO and HNOH calculated in Ref. 6 are correct (though we don't expect both the barriers to form HNO + H to be so large), then HNO + H2 > HNO + H, except at the highest temperatures. Simple unimolecular reaction theory suggests k2 > k3 > k4, whereas k2 > k3 > k4 > k5. The entropy of activation for reaction 1b is 13-17 J mol⁻¹K⁻¹ larger than for the other four reaction paths. If it has an activation energy — even as small as 10 kJ/mol (Ref. 6 calculates 20), k1b will not dominate until T > 1000 K. Thus, we would expect k1 > k2 > k3 at moderate and low temperatures and k1 > k2 > k3 at high temperatures. The experimental evidence suggests k3 < k2 and k1b, which means the relative barriers heights are incorrect. But even so, k2 may not be negligible.

We rely on Ref. 2, noting that the total value k1 is more reliable than the individual values of k1 and k2. We recommend k1 = 7 x 10¹⁰ and k2 = 4.5 x 10¹⁰ for 298 to 3000 K, with a factor of 2 uncertainty in each. We estimate, on theoretical grounds, that k2 should not be less than 5 x 10⁷, although there is no supporting experimental evidence at present.

References

\[ O + NH \rightarrow H + NO \quad \text{and} \quad O + NH \rightleftharpoons N + OH \]

\[ \Delta H^\circ_{298} = -292.8 \pm 10 \text{ kJ mol}^{-1} \quad (-70.0 \text{ kcal mol}^{-1}) \]
\[ \Delta S^\circ_{298} = -16.8 \pm 0.1 \text{ J mol}^{-1} \text{K}^{-1} \quad (-4.0 \text{ cal mol}^{-1} \text{K}^{-1}) \]

\[ K_1(T) = 7.1 \times 10^{-2} \exp(35220/T) \]

\[ \Delta H^\circ_{298} = -89.4 \pm 10 \text{ kJ mol}^{-1} \quad (-21.4 \text{ kcal mol}^{-1}) \]
\[ \Delta S^\circ_{298} = -5.3 \pm 0.1 \text{ J mol}^{-1} \text{K}^{-1} \quad (-1.3 \text{ cal mol}^{-1} \text{K}^{-1}) \]

\[ K_2(T) = 1.1 \times 10^{-1} \exp(10700/T) \]

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

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The uncertainties in \( \log K_1(T) \) and \( \log K_2(T) \) reflect those of both the respective forward rate coefficients and equilibrium constants.

(August 1987)
O + NH \rightarrow H + NO
\rightarrow N + OH

**THERMOCHEMICAL DATA**

Thermochemical data taken from the JANAF Thermochemical Tables, 3rd edition. More recently, Piper reanalyzed experimental data for NH\textsubscript{3}(NH) and recommended 350 \pm 10 kJ mol\textsuperscript{-1}. We use this value. The analytical expressions chosen for \(k_1(T)\) and \(k_2(T)\) match equilibrium constant calculated from those data to within 5\% and 3\%, respectively, between 200 to 6000 K.

**EXPERIMENTAL DATA**

There are no direct measurements of either \(k_1\), \(k_2\), or \(k_2 = k_1 \cdot k_2\). Dransfeld et al.\textsuperscript{2} best fitted their room temperature flow tube data on the \(0 + \text{NH}_3\) reaction system by assuming \(k_2 = (5 \pm 2) \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}\). Dean et al.\textsuperscript{3} assumed \(k_1 = 6.3 \times 10^8 \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}\) and \(k_2 = 6.8 \times 10^8 \text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}\) in their modeling of \(\text{NH}_3\) flames near 2000 K. Neither gave any indication of the sensitivity of their model to these assumed values. Cohen\textsuperscript{8} found much better agreement with experimental data on the \(0 + \text{NH}_3\) reaction by assuming \(k_1 \gg k_2\).

**CALCULATIONS**

Melius and Binkley\textsuperscript{5} carried out fourth-order Möller-Plesset perturbation theory calculations with bond additivity corrections. They found three pathways leading to \(H\) and two leading to \(N + OH\):

\begin{align*}
O + \text{NH} & \rightarrow \text{HNO} + H \rightarrow \text{H} + \text{NO} \\
O + \text{NH} & \rightarrow \text{HNO} + H \rightarrow \text{H} + \text{NO} \\
& \rightarrow \text{HCN} + \text{H} + \text{NO} \\
& \rightarrow \text{HCN} + \text{N} + \text{OH} \\
& \rightarrow \text{NH} + [5\text{e}] + \text{N} + \text{OH}
\end{align*}

(1a) (1b) (1c) (2a) (2b)

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

An approximate lower limit for \(k_1\) can be calculated by assuming that reaction (1) occurs only via path (1a); that the only energy barrier is the so-called centrifugal barrier imposed by conservation of angular momentum; and that all trajectories that cross this barrier lead to reaction. The average position of the barrier as a function of \(T\) can be calculated from data given by Chase et al.\textsuperscript{6} and a formula given by Benson.\textsuperscript{7} The collision frequency thus calculated must be corrected for electronic degeneracies by multiplying by \(\frac{\partial^2}{\partial Q_0^2}\), where \(Q_0\) and \(Q_{\text{NH}}\) are assumed to be 1 and 3, respectively. \(k_{1a}\) thus obtained is \((1.4 \pm 0.2) \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1}\) for 200 < \(T/K\) < 2000. Above 2000 K, the calculated centrifugal barrier lies inside the sum of Van der Waals radii for the reagents, and consequently there may be some steric restrictions, leading to a decrease in \(k_{1a}\). An upper limit for \(k_1\) can be calculated by assuming that all reactions on the \(3\pi^*\) surface also lead to \(H + NO\) (via 1b and 1c), so that \(k_2 = k_1\). Using the same procedure, \(k_{1b} + k_{1c}\) is calculated to be \(\leq 4.1 \times 10^{10}\), so that \(k_1 = (3 \pm 2) \times 10^{10}\) for 200 < \(T/K\) < 2000. A similar procedure was used to calculate the rate coefficient for the analogous reaction between \(O\) and \(OH\), and gave good agreement with the experimental value of \(2.4 \times 10^{10}\) at 298 K.

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

**DISCUSSION**

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

**References**