

Rate Constant of the OH + HO₂ Reaction from 252 to 420 KU. C. Sridharan, L. X. Qiu,[†] and F. Kaufman*

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The temperature dependence of the OH + HO₂ rate constant was measured in a discharge-flow apparatus using a combination of vacuum UV resonance fluorescence and laser-induced fluorescence (LIF) methods to monitor atom and radical concentrations as described earlier.^{1,2} Seventeen sets of experiments covering the above temperature range showed a negative temperature dependence, $k = (1.7 \pm 0.5) \times 10^{-11} \exp[(416 \pm 86)/T]$ or $(7.2 \times 10^{-11})(T/296)^{-n} \text{ cm}^3 \text{ s}^{-1}$ with $n = 1.30 \pm 0.13$. These findings are compared with published results and discussed in terms of rate theory.

Introduction

The title reaction



has been the subject of many studies because of its importance as a major HO_x removal step in the earth's stratosphere and also because of its unusual rate parameters: (i) a very large rate constant, much larger than either of its symmetrical (OH + OH or HO₂ + HO₂) counterparts, and (ii) a reported pressure dependence.³ Before 1981, published room-temperature values of k_1 ranged from 3×10^{-11} to $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$,⁴⁻¹³ but were based on more or less indirect experimental methods. Three recent, direct, low-pressure (~ 2 torr) studies^{1,14,15} are in very good agreement $k_1 = (6.4-7.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and have also narrowed the gap between this low-pressure value and that at 1 atm of about $1.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.³ Surprisingly, there is very little information available on the temperature dependence of k_1 , and we have therefore extended our rate measurements both to aid atmospheric model calculations and to shed light on the nature of this puzzling reaction.

Experimental Section

The apparatus and method are as described earlier.^{1,2} The removable, coaxial, double injector tube introduces HO₂ into the flow tube where it is mixed with a smaller concentration of OH generated independently in the main 2.54 cm diameter flow tube. HO₂ is produced by $\text{F} + \text{H}_2\text{O}_2$ where F comes from a microwave discharge of a small amount of CF₄ in He in the inner injector and reacts to completion with excess H₂O₂ in the outer injector tube over a distance of 34 cm. OH is produced in the flow tube by the sequence of two reactions, $\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F}$ and $\text{F} + \text{H}_2\text{O} \rightarrow \text{HF} + \text{OH}$, which avoids the use of NO/NO₂ and interference by $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$. [OH] is monitored by laser-induced fluorescence (LIF) at 308.6 nm (Chromatix CMX-4) using a boxcar integrator (PAR 162) in the ratio mode. In later experiments, the data were collected and analyzed by a microcomputer (HP9816). [HO₂] is measured by rapid conversion to OH with excess NO 4.5 cm upstream of the LIF cell. [OH] and [HO₂] are calibrated absolutely by the $\text{H} + \text{NO}_2$ reaction using small excess H and measured NO₂ flow as described earlier.^{1,2}

The 50 cm long section of the flow tube immediately upstream of the LIF cell is surrounded by a copper cooling jacket and a well-insulated heating mantle. Cooling is accomplished by controlled flows of liquid N₂ through the two halves of the copper jacket. Three iron-constantan thermocouples are attached to the outside wall of the flow tube, and their readings are compared with that of a sliding probe thermocouple inside the flow tube. The temperature is uniform to better than ± 2 K throughout the reaction region over the duration of any experiment.

The inhibition of surface effects which had not been a problem in room-temperature experiments became a major obstacle at

higher temperatures. For the Teflon-coated flow tube, the very satisfactory surface recombination rate constant, k_w , of $\sim 6-8 \text{ s}^{-1}$ for OH rose irreversibly to $> 35 \text{ s}^{-1}$ after heating to 420 K. A new batch of Teflon dispersion (Du Pont, FEP 856-200) gave even poorer results, i.e., $k_w \sim 35-40 \text{ s}^{-1}$ at room temperature, and its use had to be abandoned. Early work at $T < 420$ K with the older Teflon dispersion had given acceptably low k_w 's of $< 10 \text{ s}^{-1}$, and these results are included in the data presented below. The later experiments, including those near 400 K as well as several checks at lower T , were done by using halocarbon wax coatings (Halocarbon Products Corp. 15-00). These were prepared following a procedure suggested by L. F. Keyser in which the initial coating was heated to 430 K for about 5 h to let most of the wax drain, resulting in a very thin coating. This surface exhibited satisfactory behavior, i.e., $k_w \sim 8 \text{ s}^{-1}$ at 300 K, $\sim 12 \text{ s}^{-1}$ at 400 K, and $\sim 10 \text{ s}^{-1}$ at 250 K. For HO₂, k_w was about 3 s^{-1} .

Typical experimental parameters were as follows: pressure ≈ 2.5 torr, average flow velocity $\approx 10-16 \text{ m s}^{-1}$, diluent gas He (Air Products, HP grade) was further purified by passage through heated Cu wool at 700 K and then through a molecular sieve trap at 77 K at 1-atm pressure, $[\text{H}_2\text{O}_2] \sim 1 \times 10^{13} \text{ cm}^{-3}$, $[\text{CF}_4] \sim (1-5) \times 10^{12} \text{ cm}^{-3}$, $[\text{F}_2] \sim (6-30) \times 10^{13} \text{ cm}^{-3}$, $[\text{H}_2\text{O}] \sim 1 \times 10^{14} \text{ cm}^{-2}$, $[\text{HO}_2] \sim (3-19) \times 10^{11} \text{ cm}^{-3}$, $[\text{OH}]_0 \sim 7 \times 10^{10} \text{ cm}^{-3}$.

Results and Discussion

Experiments were performed under pseudo-first-order conditions with $[\text{HO}_2] \gg [\text{OH}]_0$ as described earlier.¹ $[\text{H}_2\text{O}_2]$ was kept constant throughout each experiment, and $[\text{HO}_2]$ was varied by varying the flow of CF₄ through the discharge. Typically, plots of $\ln [\text{OH}]$ vs. injector position were obtained for four to eight different $[\text{HO}_2]$ as well as for $[\text{HO}_2] = 0$, i.e., CF₄ discharge off. The latter represents a combination of the effects of the OH + H₂O₂ reaction¹⁶ and the injector surface effect.^{1,2} As in our earlier work, there was no indication of interference by CF_x radicals by

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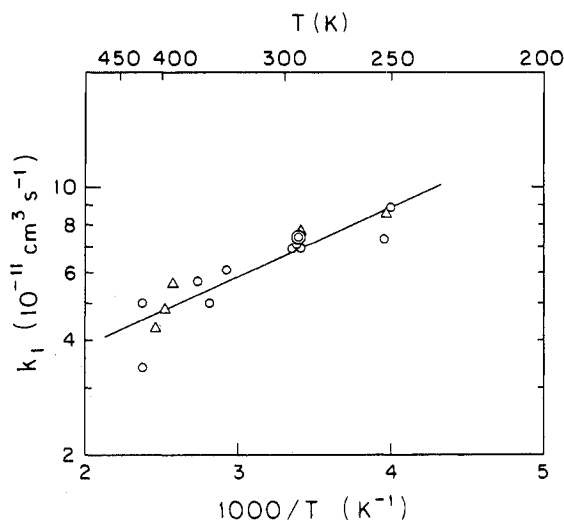
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TABLE I: Rate Constant k_1 for OH + HO₂ Reaction

temp, K	no. of HO ₂ additions	$10^{11} k_1, ^a \text{ cm}^3 \text{ s}^{-1}$
252	7	8.5 ± 1.6^b
253	6	7.3 ± 1.3
259	5	8.8 ± 1.7
295	5	7.4 ± 1.2^c
298	5	6.9 ± 1.1^c
295	5	7.4 ± 1.1^c
294	6	6.9 ± 1.1^c
296	6	7.1 ± 1.1^c
294	4	7.6 ± 1.3^b
341	5	6.1 ± 1.0
355	7	5.0 ± 0.8
365	5	5.7 ± 1.4
389	5	5.6 ± 1.6^b
396	6	4.8 ± 0.9^b
406	5	4.3 ± 0.9^b
420	8	3.4 ± 1.0
420	6	5.0 ± 1.0

^a Reported uncertainties include both random (1 σ) and systematic error of $\pm 15\%$. Teflon-coated flow tube unless otherwise noted. ^b Experiments using halocarbon wax coated flow tube. See text for details. ^c Data reported in ref 1 and Appendix of ref 2.

Figure 1. Arrhenius plot, $\ln k_1$ vs. $1/T$.

rapid reaction with OH. Pseudo-first-order rate constants, k^1 , were obtained from the weighted (σ_i^{-2}) linear least-squares slopes of the above plots multiplied by the average flow velocity, where σ_i is the statistical error. Corrections for axial diffusion (2–6%) were included. Bimolecular rate constants, k_1 , were obtained from the linear least-squares fits of k^1 vs. $[\text{HO}_2]$ plots, where an estimated systematic error of 15% was included with the statistical error of k^1 .

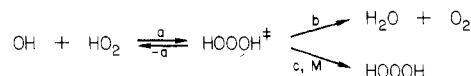
Experimental values of k_1 are shown in Table I. The six room-temperature values, adjusted to $T = 296$ K, give an average of $7.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ compared with our earlier 7.1×10^{-11} based on five of the six experiments. All k_1 's are plotted in Arrhenius form in Figure 1. The two expressions, $k_1 = (1.7 \pm 0.5) \times 10^{-11} \exp[(416 \pm 86)/T] = (7.2 \times 10^{-11})(T/296)^{(-1.30 \pm 0.13)} \text{ cm}^3 \text{ s}^{-1}$, obtained from nonlinear least-squares fits, clearly indicate the rate constant's negative temperature dependence but should not be used for extrapolation far beyond the experimental temperature range.

In the only published temperature dependence study of k_1 , Burrows et al.¹³ reported $(6.2_{-2.0}^{+4.0}) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, independent of T over the small range 288–348 K from modulated photolysis experiments of the $\text{O}_3\text{--H}_2\text{O}$ system at 1-atm pressure.

A rationalization of the reaction process in terms of its likely intermediate and dynamics must account for its very large rate constant and negative temperature dependence as well as discuss its reported pressure dependence. In agreement with DeMore,³ we rule out direct H-atom transfer as being too slow to account

for more than about 10–15% of the measured rate constants, if such a process would proceed via a tight transition state. It should then also exhibit a positive temperature dependence, contrary to our experimental results. If dipole–dipole attraction is assumed to be responsible for the large rate constant for OH + HO₂, it seems strange that this mechanism is not applicable in the much slower HO₂ + HO₂ reaction where the dipole–dipole interaction is larger. The formation of a bound H₂O₃ complex is therefore indicated whose rearrangement to H₂O + O₂, redissociation to reactants, or collisional stabilization controls the observed rate.

Benson¹⁷ has estimated the enthalpy of formation of H₂O₃ to be -17.7 kcal/mol by a combination of bond strength interpolation and group additivity assumptions. This makes the formation of HOOH intermediate about 30 kcal/mol exothermic (a matter of somewhat circular reasoning, since this value is essentially assumed to be the arithmetic mean of the weak HO₂–O₂H bond ($<10 \text{ kcal/mol}$) and the strong HO–OH bond ($\sim 50 \text{ kcal/mol}$). If we accept this value, the large k_1 suggests that the internal barrier for H₂O + O₂ formation is considerably lower than 30 kcal/mol, probably $<20 \text{ kcal/mol}$, since the product (H₂O + O₂) formation rate would otherwise become too small a fraction of the initial rate of adduct formation. In the usual formalism



neglecting direct H-atom transfer

$$k_1 = k_a(k_b + \beta k_c[M]) / (k_{-a} + k_b + \beta k_c[M])$$

in the Lindemann approximation. Here β is the weak collision factor, of order 0.1 for M = He. It is clear that k_b and k_{-a} are strong functions of energy and should be evaluated in the RRKM formalism, but the present discussion will only deal with qualitative estimates.

The magnitude of $\beta k_c[M]$ is readily estimated, i.e., $\beta k_c \approx 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, and the effective energy-transfer rate constant is $\sim 3 \times 10^6 \text{ s}^{-1}$ at 2.5 torr and $\sim 1 \times 10^9 \text{ s}^{-1}$ at 1 atm. An increase of k_1 from $7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at low pressure to 12×10^{-11} at 1 atm therefore requires (i) that $k_{-a} > k_b$, since there is no [M] dependence if $k_b \gg k_{-a}$, i.e., the rate of the process is then given by k_a even though the product distribution is a function of [M], and (ii) that the magnitudes of k_{-a} and k_b be comparable with the energy-transfer rate. Assuming, for example, that $k_{-a} = k_b$, its value has to be $2 \times 10^8 \text{ s}^{-1}$ in order to provide the above rise of k_1 with increasing pressure. This seems much too small. Tsang¹⁸ has done RRKM calculations for several models of H₂O₃ thermochemistry and transition-state configurations and reported k_{-a} and k_b to be in the range $10^{10}\text{--}10^{12} \text{ s}^{-1}$, much too large to accommodate such a pressure dependence.

Since k_1 is so large, it is unlikely that k_a can be very much larger, i.e., $k_a < 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, and the temperature dependence of k_1 should be governed, in large part, by that of the high-pressure recombination rate constant, k_a . The measured $T^{-1.3}$ dependence seems reasonable in this context. Similar processes that are slower and more under control of the redissociation step, $-a$, often exhibit a more strongly negative temperature dependence, e.g., HO₂ + HO₂ or OH + NO₃.

This is not to say, of course, that the book is closed on our understanding of this and other "simple" reactions, including the two mentioned above. Nagging doubt remains that something fundamental may be missing, but the inherent reasonableness and success of reaction rate theory compel us to search for both theoretical and experimental explanations.

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Registry No. Hydroxyl, 3352-57-6; perhydroxyl, 3170-83-0.

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