

## LETTERS

### Kinetics of the Reaction $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ at 296 K

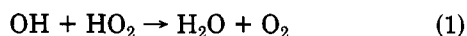
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In Final Form: September 9, 1981)

The rate constant of the title reaction was measured in a discharge-flow reactor by addition of excess  $\text{HO}_2$  from a movable double injector to a gas stream containing small concentrations of  $\text{OH}$ .  $[\text{OH}]$  was measured by laser-induced fluorescence,  $\text{HO}_2$  by conversion to  $\text{OH}$ , and  $\text{H}$  and  $\text{O}$  by vacuum-UV resonance fluorescence. Five sets of experiments, each with different excess  $[\text{HO}_2]$ , gave an average rate constant of  $(7.5 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  where the error limits (single  $\sigma$ ) include uncertainties of all experimental parameters. This result is compared with other findings and is discussed in terms of its importance in stratospheric chemistry and in rate theory.

#### Introduction

The title reaction



$\Delta H^\circ_{298} = -69.6 \text{ kcal/mol}$ , is interesting and important in several ways: it is an efficient removal mechanism for  $\text{HO}_x$  radicals ( $\text{OH}$  and  $\text{HO}_2$ ) and effectively controls the level of  $\text{HO}_x$  concentrations in the upper stratosphere and thereby profoundly influences the chemistry of the natural or perturbed stratosphere;<sup>1,2</sup> it presents a challenging problem to the experimentalist in providing a reasonably direct rate measurement; and it provides a serious test for the application of reaction rate theory to elementary radical reactions. Its rate constant has remained one of the least accurately known parameters of stratospheric models in spite of its rich history of experimental studies. The latter may be broadly subdivided into photolysis

studies<sup>3-7</sup> with results of  $k_1 \sim (1-2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , mostly at 1 atm total pressure with several torr of  $\text{H}_2\text{O}$ , and low-pressure flow reactor studies,<sup>8-10</sup>  $k_1 \sim (3-5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The discrepancy between these results has not yet

- (1) R. D. Hudson and E. I. Reed, *NASA Ref. Publ.*, No. 1049 (1979).
- (2) "Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport", National Academy of Sciences, Washington, DC, 1979.
- (3) C. J. Hochenadel, J. A. Ghormley, and P. J. Ogren, *J. Chem. Phys.*, **56**, 4426 (1972).
- (4) W. B. De More and E. Tschuikow-Roux, *J. Phys. Chem.*, **78**, 1447 (1974).
- (5) W. B. De More, *J. Phys. Chem.*, **83**, 1113 (1979).
- (6) R. R. Lii, R. A. Gorse, Jr., M. C. Sauer, and S. Gordon, *J. Phys. Chem.*, **84**, 819 (1980).
- (7) C. J. Hochenadel, T. J. Sworski, and P. J. Ogren, *J. Phys. Chem.*, **84**, 3274 (1980).
- (8) J. P. Burrows, G. W. Harris, and B. A. Thrush, *Nature (London)*, **267**, 233 (1977); J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush and J. P. T. Wilkinson, *Proc. R. Soc. London, Ser. A*, **368**, 463 (1979).
- (9) W. Hack, A. W. Preuss, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **82**, 1167 (1978).
- (10) J. S. Chang and F. Kaufman, *J. Phys. Chem.*, **82**, 1683 (1978).

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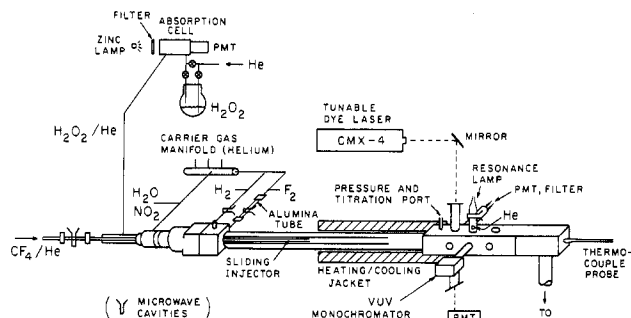


Figure 1. Diagram of apparatus.

been resolved. Two very recent flow tube measurements<sup>11,12</sup> are finding higher values of about  $6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  under more accurately controlled conditions. An indirect flame modeling study<sup>13</sup> has given a range of  $(1.7\text{--}5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for  $k_1$  near 1500 K. In the present work, the decay of OH is measured by laser-induced fluorescence (LIF) in the presence and absence of excess  $\text{HO}_2$  in a discharge-flow reactor under conditions where interfering reactive species such as H and O are monitored and kept far below maximum acceptable concentration levels and where the observed decays are mainly due to reaction 1.

### Experimental Section

The discharge-flow apparatus is shown in Figure 1. It is similar to that used recently to measure the rate of the  $\text{OH} + \text{H}_2\text{O}_2$  reaction,<sup>14</sup> consisting of a 2.5-cm i.d. Pyrex flow tube, 110 cm long, an LIF and vacuum-UV resonance fluorescence (VUVRF) detection cell, and a movable, coaxial double injector for the preparation and addition of  $\text{HO}_2$ . [OH] was monitored by LIF at the  $P_1$ -2 line of its  $^2\Sigma^+ \rightarrow ^2\Pi$ , 0-0 band as described earlier,<sup>1</sup> as were [H] and [O] at 121.6 and 130.2 nm, respectively. Their concentrations were kept below  $2 \times 10^9 \text{ cm}^{-3}$  in rate experiments.

$\text{HO}_2$  was produced by the  $\text{F} + \text{H}_2\text{O}_2$  reaction. F atoms were generated in a microwave discharge of  $\text{CF}_4$  in excess He in an  $\text{Al}_2\text{O}_3$  discharge tube at the upstream end of the inner movable injector tube (7 mm i.d.) and mixed with  $\text{H}_2\text{O}_2$  in the middle tube (10 mm i.d.) produced and monitored as before.<sup>14</sup> Dilute mixtures of  $\text{F}_2$  in He could not be used, because they produced too much atomic oxygen, possibly from  $\text{O}_2$  impurity in  $\text{F}_2$ . A distance of 34 cm between the ends of the inner and middle tube allowed the  $\text{F} + \text{H}_2\text{O}_2$  to go to completion,  $kt \sim 20$ , without excessive losses of  $\text{HO}_2$  due to the  $\text{HO}_2 + \text{HO}_2$  reaction.

[ $\text{HO}_2$ ] was measured by rapid conversion to OH with excess NO 4.5 cm ahead of the LIF cell.<sup>15</sup> The absolute calibration of [ $\text{HO}_2$ ] and [OH] was accomplished by generating known [OH] by the  $\text{H} + \text{NO}_2$  reaction with additions of known [ $\text{NO}_2$ ] 9 cm from the LIF detection cell to excess [H]. Corrections for OH loss at the wall ( $k_w = 8 \text{ s}^{-1}$ ) and for the  $\text{OH} + \text{OH}$  reaction were found to be  $\leq 10\%$  and were included. Such calibrations were performed immediately after each  $\text{OH} + \text{HO}_2$  measurement. [ $\text{HO}_2$ ] was determined before and after each decay and found to be constant to better than 5% during the period of each OH-decay measurement. The calibration plots were reproducible to within  $\pm 6\%$  and were linear to  $\leq 5\%$ .

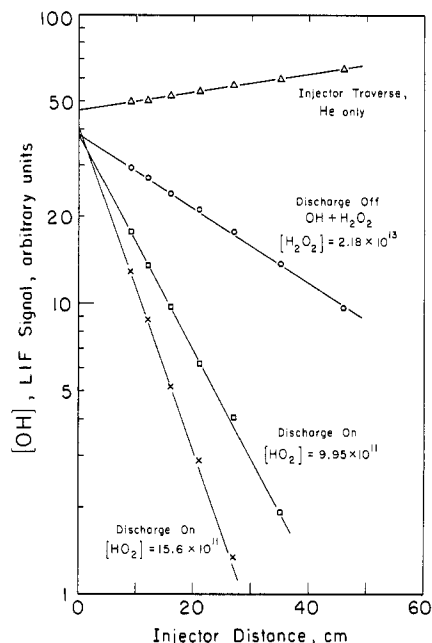


Figure 2. OH decay plots for reaction with  $\text{H}_2\text{O}_2$  and with  $\text{HO}_2$ .

The [ $\text{HO}_2$ ] thus obtained was further corrected for the following effects: (1) wall loss of OH after the conversion of  $\text{HO}_2$  to OH which increased [ $\text{HO}_2$ ] by about 3%; (2) production of  $\text{HO}_2$  in the  $\text{OH} + \text{H}_2\text{O}_2$  reaction which increased [ $\text{HO}_2$ ] an average of 1.5%; and (3) wall loss of  $\text{HO}_2$  which decreased [ $\text{HO}_2$ ] about 2%.

OH was produced in the main flow tube at initial concentrations of  $\sim 5 \times 10^{10} \text{ cm}^{-3}$  by the sequence of reactions,  $\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F}$  and  $\text{F} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{HF}$ , in order to avoid the presence of NO (due to  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ ) which would generate OH by reaction with the excess  $\text{HO}_2$ .

Flow tube and injector surfaces were coated with Teflon or halocarbon wax as before. These coatings were remarkably stable and noncatalytic giving reproducible surface recombination rate constants of  $8 \text{ s}^{-1}$  for OH and  $2.5 \text{ s}^{-1}$  for  $\text{HO}_2$  as verified repeatedly by movable injector experiments.

Typical experimental parameters were as follows: pressure,  $\sim 3$  torr; average flow velocity in the main tube,  $\sim 1150 \text{ cm s}^{-1}$ , and in the intermediate tube,  $\sim 970 \text{ cm s}^{-1}$ ; [ $\text{HO}_2$ ]  $\sim (2\text{--}19) \times 10^{11} \text{ cm}^{-3}$ ; [ $\text{OH}$ ]<sub>0</sub> =  $(4\text{--}6) \times 10^{10} \text{ cm}^{-3}$ ; [ $\text{H}_2\text{O}_2$ ]  $\sim (6\text{--}26) \times 10^{12} \text{ cm}^{-3}$ ; [ $\text{F}_2$ ]  $\sim 6 \times 10^{13} \text{ cm}^{-3}$ ; [ $\text{H}_2\text{O}$ ]  $\sim 5 \times 10^{13} \text{ cm}^{-3}$ .

### Results and Discussion

Matched pairs of semilog OH decays with the  $\text{CF}_4$  discharge on and off as function of injector position were obtained as shown in Figure 2. Traverses of the injector with He along gave the expected slight rise of LIF signal with increasing distance due to the reduced injector surface.<sup>14</sup> The subtraction of the discharge-off from the discharge-on plot gives the effective first-order rate constant,  $k^1 = k_1[\text{HO}_2]$ , on the assumptions of sufficiently large  $\text{HO}_2$  excess to assure first-order OH kinetics and of negligible reduction of [ $\text{H}_2\text{O}_2$ ] by the  $\text{F} + \text{H}_2\text{O}_2$  reaction. This latter point was actually corrected by reducing the contribution of the  $\text{OH} + \text{H}_2\text{O}_2$  reaction slightly, i.e., by decreasing [ $\text{H}_2\text{O}_2$ ] by [ $\text{HO}_2$ ]. This corresponds to the smallest effect that the  $\text{F} + \text{H}_2\text{O}_2$  reaction can have, but considering the magnitude of [ $\text{HO}_2$ ] in the injector and its residence time, there cannot be a much larger reduction of [ $\text{H}_2\text{O}_2$ ] than that corresponding to the [ $\text{HO}_2$ ] produced. In the pseudo-first-order approximation, [ $\text{HO}_2$ ] was taken as the

(11) F. Temps and H. Gg. Wagner, Bericht 18A/1980, Max Planck Institut für Strömungsforschung, Göttingen, 1980.

(12) L. F. Keyser, *J. Phys. Chem.*, in press.

(13) G. Dixon-Lewis, J. B. Greenberg, and F. A. Goldsworthy, *Symp. (Int.) Combust. [Proc.]*, 15th, 717 (1974).

(14) U. C. Sridharan, B. Reimann, and F. Kaufman, *J. Chem. Phys.*, 73, 1286 (1980).

(15) C. J. Howard, *J. Am. Chem. Soc.*, 102, 6937 (1980).

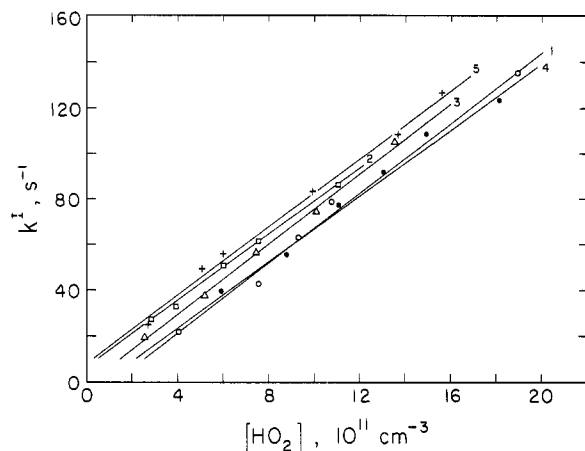


Figure 3. Plot of pseudo-first-order rate constant for OH + HO<sub>2</sub> vs. HO<sub>2</sub> concentration. Lines 1–5 show best fits for separate experiments.

average of its initial and final value in each decay. Finally, each  $k^1$  was corrected ( $\leq 1.5\%$ ) for axial diffusion ( $k^1 D / \bar{v}^2$ ).

The discharge-off decay, corrected for the small injector effect, constitutes a remeasurement of the OH + H<sub>2</sub>O<sub>2</sub> reaction whose rate constant,  $k_2$ , is now well established.<sup>14,16</sup> The agreement with the published value of  $1.65 \times 10^{-12}$  to  $1.70 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> was very good in all cases reported here, i.e., 15 experiments gave a rate constant of  $1.8 \times 10^{-12}$  for the OH + H<sub>2</sub>O<sub>2</sub> reaction.

Figure 3 shows the  $k^1$  vs. [HO<sub>2</sub>] plots whose slopes give the desired rate constant,  $k_1$ . The five sets of experiments are plotted separately, each consisting of five to six independent measurements of  $k^1$  for different [HO<sub>2</sub>]. Since these plots gave very high correlations and small, variable intercepts, it is more reasonable to report the average of these five experimental values  $(7.5 \pm 0.3) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, than a single linear fit to all 27 points which gives  $(7.1 \pm 0.3) \times 10^{-11}$ , but with poorer correlation.

The above error estimates (single standard deviation) include the precision of each of the five sets of experiments plus the spread of their values from the mean. When estimates of the uncertainties of flows, pressure, semilog decays, and HO<sub>2</sub> calibration are included, the result becomes  $(7.5 \pm 1.2) \times 10^{-11}$  (single  $\sigma$ ). The five separate values of  $k_1$  were  $(7.8 \pm 0.4) \times 10^{-11}$ ,  $(7.3 \pm 0.2) \times 10^{-11}$ ,  $(7.8 \pm 0.2) \times 10^{-11}$ ,  $(7.3 \pm 0.5) \times 10^{-11}$ , and  $(7.5 \pm 0.3) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

This result should be compared mainly with those of other low-pressure experiments,<sup>8–12</sup> since the question of a possible pressure and [H<sub>2</sub>O] dependence at higher pressures is still unsettled experimentally. The results of ref 8 and 9 are based on ratios using an incorrect lower

value of  $k_2$  and are therefore suspect. The earlier estimate from our own laboratory<sup>10</sup> was based on fitting [OH] and [HO<sub>2</sub>] vs.  $t$  plots for the OH + O<sub>3</sub> reaction system to computer calculations of a 12-reaction mechanism for various chosen values of  $k_1$ . Best agreement was found for  $k_1 < 3 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, but such an analysis cannot of course, choose sharply between, say  $3 \times 10^{-11}$  and  $6 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. In fact, the fit for  $k_1 = 5 \times 10^{-11}$  was only marginally poorer, and the small differences between measured and modeled OH and HO<sub>2</sub> concentrations (ref 10, Figure 2) may be further reduced by changes in some of the other rate constants. With the two most recent, as yet unpublished, direct measurements,<sup>11,12</sup> the agreement is very good, i.e.,  $k_1 = 6.5 \pm 2.5 \times 10^{-11}$  (ref 11),  $6.4 \pm 1.5 \times 10^{-11}$  (ref 12), and our  $(7.5 \pm 1.2) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

Above about 35 km, reaction 1 is the principal loss mechanism for HO<sub>x</sub>. The present convergence of laboratory results on a somewhat larger value of  $k_1$  brings about a reduction of calculated HO<sub>x</sub> concentrations and thereby a lowering of the efficiencies of both the HO<sub>x</sub> and the ClO<sub>x</sub> catalytic cycles for O<sub>3</sub> destruction, the latter because of a lowered rate of regeneration of Cl from HCl via OH + HCl → H<sub>2</sub>O + Cl. This also tends to reduce the calculated ozone reduction due to anthropogenic halocarbon release, but less so than reactions such as OH + HNO<sub>3</sub> → H<sub>2</sub>O + NO<sub>3</sub> and OH + HNO<sub>4</sub> → H<sub>2</sub>O + NO<sub>2</sub> + O<sub>2</sub> whose effect is greatest in the lower stratosphere. Further work is now in progress, both on the temperature dependence of reaction 1 and on an extension of these measurements to include the O + HO<sub>2</sub> and H + HO<sub>2</sub> reactions.

A thorough application of reaction rate theory must await the results of the temperature dependence. It is interesting to note that  $k_1$ , the rate constant for the unsymmetrical HO<sub>x</sub> + HO<sub>x</sub> reaction, is much larger than those of its two symmetrical counterparts, OH + OH → H<sub>2</sub>O + O,  $k_3 \approx 1.8 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>,  $\Delta H^\circ_{298} = -16.8$  kcal/mol, and HO<sub>2</sub> + HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>,  $k_4 \approx 3 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>,  $\Delta H^\circ_{298} = -37.6$  kcal/mol. All three reactions are fast, two-body, H-transfer steps, although a concurrent three-body recombination channel is well-known for (3), and uncertain pressure and temperature dependence effects limit our understanding of (4). Still, the factors of about 20–40, by which  $k_1$  is now seen to be larger than  $k_4$  or  $k_3$ , seem real and require explanation.  $k_1$  is unusually large and corresponds to a very loose transition state covering a wide range of geometries. This may be a reflection of its greater exothermicity. It is surprising that reaction 1 appears to be faster than O + HO<sub>2</sub> or Cl + HO<sub>2</sub>, but a detailed comparison must await the remeasurement of all these rates and of their temperature dependence.

**Acknowledgment.** This work was supported by the National Aeronautics and Space Administration under Grant NGR 39 011 161.

(16) L. F. Keyser, *J. Phys. Chem.*, **84**, 1659 (1980).