affect the shape or amplitude of the transmitted light vs. time curve.

The values given in Table VI indicate that the contribution of the k_5 term would be about twice as large for TEA as compared to MDEA at similar amine concentrations. The difference may come from the decrease of the k_2 term in the case of TEA, because the reaction takes place in a slightly less basic region. A way of checking the validity of these assumptions would have been to carry out the MDEA reaction in a slightly more acidic range, so as to decrease the contribution of reaction 17 relative to the catalytic term, due to the fact that the more basic hydroxide ion is neutralized before MDEA by a small addition of a strong acid.

We thus tried to decrease the pH at the initial stage of the reaction by adding a small amount of HCl to the amine solution before mixing. Unfortunately, we could not simulate the experimental curve obtained with our program. A possible explanation could be the occurrence of an esterification reaction on the -OH groups of ethanolamine changing the pH prediction. This part of our investigations will be further developed by using tertiary alkylamines (see below).

We have not examined in this paper the eventuality of CO_2 reaction with the -OH groups of ethanolamines postulated by others.^{2,20} Such a situation is in fact very unlikely because we found in preliminary experiments that qualitatively the same behavior is obtained when using triethylamine in place of triethanolamine, as also demonstrated by Nguyen and Donaldson.⁴ On the other hand, this assumption would result in a kinetic law formally analogous to eq 27; indeed, the formation of monoalkyl carbonate from CO_2 and triethanolamine²⁰ can be represented by the following reaction scheme:

(20) E. Jørgensen and C. Faurholt, Acta Chem. Scand., 8, 1141 (1954).
(21) J. Legras, "Méthodes et Techniques de l'Analyse Numérique", Dunod, Paris, 1971.

$$\begin{array}{r} N(R)_2 CH_2 CH_2 OH + CO_2 + OH^- \rightleftharpoons \\ N(R)_2 CH_2 CH_2 CO_3^- + H_2 O \end{array}$$

The corresponding rate equation (analogous to eq 27) has been rejected because of the poor quality of the curve fitting then obtained (see above). In addition, as pointed out by one referee, the kinetics observed in ref 20 took place on a much slower time scale than observed here.

In conclusion, these investigations greatly clarify the mechanism of the reaction of tertiary amines with carbon dioxide in aqueous solution. Previous investigations using solutions of tertiary ethanolamines generally assumed the formation of an alkyl carbonate as a first step. In fact, the present results show that the main contributions to the reaction rate simply arise from the hydration of the CO₂ molecules either by the water molecules or by the hydroxide ions, depending upon the pH, itself governed by the ionization equilibrium of the dissolved amine. Moreover, a specific ("catalytic") effect has been shown to occur with TEA on the basis of mechanism II or III, with a preference for mechanism II. The program which has been developed to calculate the theoretical curve gives the best simulation with a value of 2.85 M⁻¹ s⁻¹ for the catalytic rate constant k_5 at 25 °C, in very good agreement with ref 4, which, however, used a completely different experimental approach. A catalytic effect is also very likely to occur with MDEA, but it is much more difficult to ascertain owing to its relatively weak contribution to the overall reaction rate. In fact, mechanism I, which is the simplest possible, gives an excellent description of the experimental results when the CO_2 concentration is kept well below the saturation limit.

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Absolute Rate Constant of the Reaction $OH + HO_2 \rightarrow H_2O + O_2$

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The absolute rate constant of the reaction $OH + HO_2 \rightarrow H_2O + O_2$ was determined by using the discharge-flow resonance fluorescence technique at 299 K and 1-torr total pressure. Pseudo-first-order conditions were used with HO_2 concentrations in large excess over OH. Secondary reactions of atomic oxygen and atomic hydrogen were shown not to interfere under the conditions used. The result is $(6.4 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ where the error limits are twice the standard deviation. The overall experimental error is estimated to be $\pm 30\%$.

Introduction

Reactions of odd-hydrogen radicals, HO₂ (H, OH, HO₂), play a major role in atmospheric chemistry and combustion processes.¹⁻³ In the stratosphere HO_x species enter into several catalytic cycles which destroy odd oxygen $(0, 0_3)$. They also interact with other radical species such as NO_x and ClO_x . The recombination of OH and HO_2 (eq 1) is an

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{1}$$

important loss of odd-hydrogen species in the upper atmosphere and limits the efficiency with which they destroy odd oxygen.

There have been several previous measurements of the rate constant, k_1 , using various experimental techniques.⁴⁻¹¹

Nicolet, M. Rev. Geophys. Space Phys. 1975, 13, 593;
 Kaufman, F. Annu. Rev. Phys. Chem. 1979, 30, 411.
 Chang, J. S.; Duewer, W. H. Annu. Rev. Phys. Chem. 1979, 30, 443.

⁽⁴⁾ Hochanadel, C. J.; Sworski, T. J.; Ogren, P. T. J. Phys. Chem. 1980, 84, 3274.

⁽⁵⁾ Lii, R. R.; Gorse, R. A., Jr.; Sauer, M. C., Jr.; Gordon, S. J. Phys. Chem. 1980, 84, 819.



Figure 1. Schematic drawing of the discharge-flow resonance fluorescence apparatus.

Several of these studies were made relative to the rate constant of reaction 2. Others have used computer sim-

$$OH + H_2O_2 \rightarrow HO_2 + H_2O \tag{2}$$

ulations of OH and HO₂ concentrations vs. time to obtain k_1 . The results range from 2×10^{-11} to 1.6×10^{-10} cm³ molecule⁻¹ s⁻¹ near 298 K.

In the present study, the discharge-flow resonance fluorescence technique was used to make an absolute measurement of k_1 under pseudo-first-order conditions $([HO_2] \gg [OH])$. The rate constant was obtained directly from observed decays of OH concentrations vs. time. Simultaneous monitoring of OH and atomic species such as O and H was used to assess the importance of secondary reactions. Computer simulations were used only to confirm that the secondary chemistry was of minor importance.

Experimental Section

The discharge-flow resonance fluorescence system has been described previously.^{12,13} Several modifications have been made for the present measurements, and the apparatus is shown schematically in Figure 1. A movable reactor for generating HO₂ replaced the usual sliding inlet port. A separate fixed reactor for producing OH was added just upstream of the temperature-controlled main reaction zone. To allow simultaneous detection of OH radicals and atomic species such as H or O, a second resonance fluorescence system was added downstream of the reaction zone. All of the present experiments were carried out at 299 K with a 50.6-mm diameter flow tube. Reactor surfaces were coated with a halocarbon wax (Series 15-00, Halocarbon Corp.). With this coating, the measured HO_2 wall loss was $\sim 5 \text{ s}^{-1}$. The wall loss of OH was less than 10 s⁻¹ with an average value near 5 s⁻¹.

OH Sources. For most of these experiments, OH radicals were produced by reacting atomic hydrogen with an excess of F_2 and the resulting atomic fluorine with an excess of H_2^-O (eq 3-5, source A). Atomic hydrogen was

$$H_2 \rightarrow 2H$$
 (3)

$$H + F_2 \rightarrow HF + F \tag{4}$$

$$F + H_2O \rightarrow OH + HF$$
 (5)

- (6) DeMore, W. B. J. Phys. Chem. 1979, 83, 1113.
 (7) DeMore, W. B.; Tschuikow-Roux, E. J. Phys. Chem. 1974, 78, 1447.
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 (9) Hack, W.; Preuss, A. W.; Wagner, H. Gg. Ber. Bunsenges. Phys. Chem. 1021, 902 (1997). Chem. 1978, 82, 1167.
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generated in a microwave discharge of $\sim 4 \times 10^{-3}$ % H₂ in helium. The total flow in the OH source was 0.515 L atm \min^{-1} (293 K) at a pressure of ~1.3 torr. This results in a 12-ms reaction time in the 25-mm i.d. OH source before expansion into the 50.6-mm i.d. main flow tube. Under typical conditions in the source, $[F_2] = 1.4 \times 10^{14} \text{ cm}^{-3}$ and $[H_2O] = 3.6 \times 10^{14} \text{ cm}^{-3}$. After entering the main flow tube, these concentrations are reduced by a factor of ~ 6 . An additional 32 ms of reaction time allowed OH formation to be completed before addition of the HO_2 . This method of generating OH radicals was found to be relatively free of atomic-hydrogen and atomic-oxygen impurities. For example, at $[OH] = 1 \times 10^{11} - 2 \times 10^{11} \text{ cm}^{-3}$, $[H] \le 3 \times 10^{9}$ cm^{-3} and $[O] \le 6 \times 10^9 cm^{-3}$.

Other sources of OH were found to be less suitable for the present measurements because they contained considerably higher concentrations of atomic oxygen. A microwave discharge in dilute mixtures of F_2 in helium followed by reaction of the atomic fluorine with excess H₂O (eq 5, source B) was found to generate $[OH] = 1 \times 10^{11} - 2$ $\times 10^{11} \text{ cm}^{-3} \text{ with } [O] = 1.1 \times 10^{10} \text{ cm}^{-3}$. Reaction of atomic hydrogen with an excess of O_3 (eq 6a, source C) produced

$$H + O_3 \rightarrow OH(v \le 9) + O_2 \tag{6a}$$

OH in the 10^{11} cm⁻³ range with [O] = 1.3×10^{11} cm⁻³. Atomic-oxygen production from the $H + O_3$ reaction has been reported earlier and discussed in terms of a second exothermic channel (eq 6b) which accounted for 20-30%

$$H + O_3 \rightarrow HO_2 + O \tag{6b}$$

of the total reaction.¹⁴ Subsequent studies have reported values of 3-40% for the fraction of the total reaction which goes by channel 6b.¹⁵⁻¹⁷ Vibrationally excited OH produced in reaction 6a is another possible source of the O atoms observed.

$$OH(v \ge 3) + O_3 \rightarrow OH + O_2 + O \tag{7}$$

The reaction between atomic hydrogen and NO_2 (eq 8, source D) generates OH and an equivalent amount of NO.

$$H + NO_2 \rightarrow OH + NO \tag{8}$$

Atomic-hydrogen and atomic-oxygen impurities in this source were found to be less than 1×10^9 cm⁻³. However, reaction of NO with HO_2 to produce OH (eq 9) could

$$HO_2 + NO \rightarrow OH + NO_2$$
 (9)

interfere with the $OH + HO_2$ measurement. Thus, reaction 8 as a source of OH is not entirely suitable for the present study.

 HO_2 Source. HO_2 radicals were generated in a movable source by adding atomic fluorine to an excess of H_2O_2 (eq 10 and 11). Fluorine atoms were produced in a microwave

$$F_2 \rightarrow 2F$$
 (10)

$$\mathbf{F} + \mathbf{H}_2 \mathbf{O}_2 \to \mathbf{H} \mathbf{F} + \mathbf{H} \mathbf{O}_2 \tag{11}$$

discharge of $\sim 3 \times 10^{-2}$ % F₂ in He. An alumina discharge tube was used to minimize production of impurities.¹⁸ Dissociation of F_2 was from 60% to 95%, with a value greater than 80% being typical. HO₂ production was optimized by changing the H_2O_2 concentration and the reaction time in the HO_2 source. Concentrations of HO_2 were varied by changing the flow rate of the F_2 in He mixture. Under typical conditions the total flow was 0.64 L atm

- (15) Howard, C. J.; Finlayson-Pitts, B. J. J. Chem. Phys. 1980, 72, 3842.
- (16) Washida, N.; Akimoto, H.; Okuda, M. J. Chem. Phys. 1980, 72, 5781.
- (17) Force, A. P.; Wiesenfeld, J. R. J. Chem. Phys. 1981, 74, 1718. (18) Kolb, C. E.; Kaufman, M. J. Phys. Chem. 1972, 76, 947.

⁽¹⁴⁾ Finlayson-Pitts, B. J.; Kleindienst, T. E. J. Chem. Phys. 1979, 70, 4804.

min⁻¹ (293 K) at a pressure of 1.4 torr. In the 12.6-mm i.d. outer tube of the source, this yielded a flow velocity of 4700 cm s⁻¹. The inner source tube was displaced 27 cm to produce a 5.7-ms reaction time. Concentrations of H_2O_2 in the HO₂ source were ~ 1.6×10^{14} cm⁻³. The ratio of concentrations in the HO₂ source to those in the main OH + HO₂ reaction zone was ~5:1. This source was used to generate HO₂ concentrations in the OH + HO₂ reaction zone between 1 × 10¹² and 2.8 × 10¹² cm⁻³.

Resonance fluorescence analysis showed that concentrations of OH were less than 5×10^9 cm⁻³ with atomic hydrogen less than 1×10^9 cm⁻³ and atomic oxygen less than 2×10^9 cm⁻³. The HO₂ source was also analyzed by using a sensitive mass-spectrometer system¹⁹ for the possible presence of other species such as fluorine oxides. No signals were observed at m/e 51 (O₂F) or at m/e 66 (COF₂). Very small signals were observed at m/e 35 (OF) and at m/e 54 (OF₂). Concentrations of OF were found to be less than 10^{11} cm⁻³ at HO₂ concentrations near 3×10^{12} cm⁻³. The OF signal was calibrated in the absence of HO₂ by adding excess NO to convert the OF to NO₂ $(m/e \ 4\tilde{6})$.²⁰ The mass spectrometer had been previously calibrated at m/e 46 by addition of a known amount of NO₂. A signal was also observed at m/e 36. Contrary to the signals at m/e 35 and 54, this signal did not decrease when the microwave discharge in the HO_2 source was turned off. However, it did decrease when the fluorine flow was turned off. The m/e 36 signal may be due to HOF or possibly HCl.

Detector Calibration. OH was monitored by resonance fluorescence near 308 nm. Fluorescence background signals were determined with the microwave discharges off in both the OH and HO₂ sources. OH signals were calibrated by adding a known amount of NO₂ to an excess of H atoms. To minimize calibration errors, OH and NO concentrations were similar to those used during the rate-constant measurements. Corrections, generally less than 5%, were made for losses due to reaction 12 by using

$$OH + OH \rightarrow H_2O + O \tag{12}$$

 $k_{12} = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Calibration runs were carried out immediately before or after each series of rate-constant measurements. Over a period of several hours, calibrated OH fluorescence sensitivities varied typically by less than 12%. Fluorescence signals were generally 6×10^3 -9 $\times 10^3$ counts s⁻¹ at [OH] = 1 $\times 10^{11}$ cm⁻³ with background signals near 800 counts s⁻¹.

Atomic oxygen and hydrogen were monitored by resonance fluorescence at 130.6 and 121.6 nm, respectively. Oxygen-atom fluorescence was calibrated by adding a known amount of NO to an excess of N atoms (eq 13).

$$N + NO \rightarrow N_2 + O \tag{13}$$

Atomic-hydrogen signals were calibrated by converting the H atoms to OH by adding an excess of NO_2 (eq 8) or by adding F_2 and H_2O (eq 4 and 5). The OH fluorescence had been previously calibrated as described above.

Reagents. Gases used were chromatographic-grade helium (99.9999%), research-grade hydrogen (99.9995%), nitric oxide (CP (99.0%)), and mixtures of fluorine in helium (0.5% and 5%). The nitric oxide was purified by passage through a molecular sieve (Linde 13X) trap at 195 K. Nitrogen dioxide was prepared from nitric oxide by adding a large excess of oxygen. After several hours the oxygen was removed by slowly passing the mixture through a 195 K trap. The nitrogen dioxide was stored at 77 K and distilled to a 195 K trap before use. The fluorine-in-helium mixtures were passed through 77 K traps, and the chromatographic helium was passed through a molecular sieve (Linde 3A) trap at 77 K just before use. Hydrogen peroxide (90%) was obtained from FMC. It was concentrated to greater than 95% by pumping.

Results and Discussion

The present experiments were carried out at 299 K at a total pressure of 1.0 torr. Pseudo-first-order conditions were used with HO₂ in large excess over OH. HO₂ concentrations were between 1.0×10^{12} and 2.8×10^{12} cm⁻³. Initial OH concentrations were 0.4×10^{11} – 2.2×10^{11} cm⁻³. Initial stoichiometric ratios, [HO₂]/[OH]₀, were between 7.4 and 58 with a typical value greater than 10. Under these conditions, the loss of OH may be written

$$k_{+}^{I} \equiv -(d \ln [OH]/dt)_{+} = k_{1}[HO_{2}] + k_{2}[H_{2}O_{2}] + k_{L}$$
(14)

where k_+^{1} represents the pseudo-first-order loss of OH with HO₂ present in the system (movable discharge on), k_2 is the rate constant for the reaction of OH with H₂O₂ (eq 2), and $k_{\rm L}$ represents possible first-order losses of OH other than reaction with HO₂ or H₂O₂. The $k_{\rm L}$ term would include, for example, the increased surface loss of OH in the presence of H₂O₂.¹² When HO₂ is not present (movable discharge off), the loss of OH is

$$k_{-}^{I} \equiv -(d \ln [OH]/dt)_{-} = k_{2}[H_{2}O_{2}] + k_{L}$$
 (15)

Small amounts of HO₂ are generated by reaction 2, and strictly speaking a term, $k_1[HO_2]$ from reaction 2, should be added to the right-hand side of eq 15. However, computer simulations show that this term contributes only 2–9% of the total observed OH loss with the movable discharge off. Measured values of k_{-}^{I} were corrected for this added loss. Subtracting eq 15 from eq 14 gives $k_1[HO_2]$

$$k_1[\text{HO}_2] = (k_+^{I} - k_-^{I})$$
 (16)

One experimental run consists of a pair of OH-loss measurements to determine both k_+^{I} and k_-^{I} under identical conditions. Typical results using OH source A are shown in Figure 2. The lines through the data are linear least-squares fits. OH decay plots with HO₂ present generally showed some negative curvature (lower slope) at longer reaction times. Therefore, k_+^{I} was obtained from the initial slope, usually between ca. 4- and 10-ms reaction time. Computer simulations discussed below in more detail suggest that this curvature could be due to regeneration of OH from reactions 17 and 18a even at the rel-

$$0 + HO_2 \rightarrow OH + O_2 \tag{17}$$

$$H + HO_2 \rightarrow OH + OH$$
 (18a)

atively low atomic-oxygen and atomic-hydrogen concentrations observed in OH source A.

The kinetic data using OH source A are summarized in Table I. In the OH + HO₂ reaction zone, $[H_2O_2] = 3.2 \times 10^{13} \text{ cm}^{-3}$, $[H_2O] = 6.3 \times 10^{13} \text{ cm}^{-3}$, and $[F_2] = 1.4 \times 10^{13}-5.3 \times 10^{13} \text{ cm}^{-3}$. Absolute concentrations of HO₂ were determined at the minimum and maximum reaction times used in each run. Observed HO₂ decays due to wall loss, recombination (eq 19), and reaction with OH were gen-

$$\mathrm{HO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{19}$$

erally less than 12%. Average concentrations were used to calculate k_1 and are given in column one of the table.

⁽¹⁹⁾ Sander, S. P.; Ray, G. W.; Watson, R. T. J. Phys. Chem. 1981, 85, 199.

⁽²⁰⁾ Ray, G. W.; Watson, R. T. J. Phys. Chem., submitted for publication.

TABLE I: Kinetic Data for $OH + HO_2 \rightarrow H_2O + O_2$

$10^{-12}[HO_{2}],$	$10^{-11}[OH]_{0},$	<i>b</i> I s ^{−1}	b I s ⁻¹	b I _ b I s ⁻¹	$10^{11}k_1, \text{ cm}^3,$	
 		<i>n</i> ₊ , s		n ₊ n ₋ , 5		
1.03	1.06	115.2	54.3	60.9	5.91	
1.11	1.51	122.5	62.6	59.9	5.40	
1.23	1.36	132.9	66.0	66.9	5.44	
1.37	0.97	153.2	70.6	82.6	6.03	
1.64	1.95	180.2	69.0	111.2	6.78	
1.67	0.75	186.7	71.7	115.0	6.89	
1.68	0.81	192.6	75.7	116.9	6.96	
1.71	0.80	180.7	68.2	112.5	6.58	
1.72	2.03	167.2	64.2	103.0	5.99	
1.78	1.42	196.9	65.5	131.4	7.38	
1.78	1.57	206.3	69.3	137.0	7.70	
1.99	1.70	222.3	64.2	158.1	7.94	
1.99	1.76	223.2	67.0	156.2	7.85	
2.01	1.34	215.5	74.4	141.1	7.02	
2.01	1.74	181.5	67.0	114.5	5.70	
2.04	0.97	215.2	77.7	137.5	6.74	
2.08	1.03	207.9	58.2	149.7	7.20	
2.20	0.85	202.2	71.9	130.3	5.92	
2.24	2.25	218.7	68.4	150.3	6.71	
2.26	0.85	209.8	69.6	140.2	6.20	
2.26	2.00	222.4	69.9	152.5	6.75	
2.28	0.68	223.5	59.8	163.7	7.18	
2.28	1.03	200.4	77.3	123.1	5.40	
2.30	0.36	214.8	58.8	156.0	6.78	
2.34	0.57	197.2	63.3	133.9	5.72	
2.39	2.04	225.5	64.7	160.8	6.73	
2.49	1.80	250.0	73.4	176.6	7.09	
2.60	1.23	214.9	70.9	144.0	5.54	
2.62	1.68	218.7	74.5	144.2	5.50	
2.64	1.72	217.8	68.8	149.0	5.64	
2.72	1.62	233.7	65.4	168.3	6.19	
2.79	1.55	217.4	63.8	153.6	5.50	
					$av = 6.45 \pm 1.53$	



Figure 2. In I(OH) vs. reaction time with and without added HO₂. The lines are least-squares fits. The difference between the slopes gives the pseudo-first-order rate constant for reaction 1.

The data have been corrected for axial and radial diffusion²¹ and for the viscous pressure drop between the reaction zone and the pressure measurement port located downstream.²² A value of 0.97 atm $\rm cm^2 \, s^{-1}$ was used for $av = 6.45 \pm 1.53$

the diffusion coefficient of OH in helium at 299 K. Pressure corrections to k_1 were less than 10%. Diffusion corrections were 3–11% and in a direction opposite to the pressure corrections so that net corrections were less than 7%. As discussed above, corrections of 2-9% were applied to k_{-}^{I} for HO₂ generated by reaction 2.

The last column in Table I gives the bimolecular rate constant, k_1 , determined from $(k_1 - k_1)/[HO_2]$. The average value is $(6.4 \pm 1.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the error limits are twice the standard deviation. Overall experimental error is estimated to be $\pm 30\%$. A plot of (k_{+}^{I}) $-k_{-}^{I}$ vs. [HO₂] is shown in Figure 3. The slope of a linear least-squares fit gives $k_1 = (5.7 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ mole-}$ cule⁻¹ s⁻¹ with an intercept of 15 ± 26 s⁻¹. There is no significant difference between the values of k_1 obtained by these two methods of analysis since they are well within two standard deviations. The average value of 6.4×10^{-11} cm³ molecule⁻¹ s⁻¹ is reported here.

From the fourth column of Table I, an average value of $68 \pm 11 \text{ s}^{-1}$ is obtained for k_{-}^{I} . Using $[\text{H}_2\text{O}_2] = 3.2 \times 10^{13} \text{ cm}^{-3}$ yields $k_2 = (2.1 \pm 0.3) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹. This is in good agreement with the previously reported¹² average value of $(1.8 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ and shows that the $k_{\rm L}$ term in eq 14 and 15 is small.

Secondary Reactions. Observation of slight curvature in the OH decay plots at reaction times greater than 10–15 ms suggests that secondary reactions such as reactions 17 and 18a may not have been completely eliminated. Calculations of k_1 using data at short reaction times where the decay appears to be first order should minimize interference. As shown in Table I, no significant variation in k_1 was observed for $[OH]_0$ between 4×10^{10} and 2×10^{11} cm⁻³. This is evidence that secondary reactions do not interfere under the conditions used.

As an additional test for the importance of secondary chemistry, computer simulations of the present experi-

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Figure 3. Pseudo-first-order rate constant vs. [HO₂]. The line represents the average value of $(6.4 \pm 1.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for k_1 . A least-squares analysis gives $k_1 = (5.7 \pm 1.2) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ with an intercept of 15 ± 26 s⁻¹. The errors are twice the standard deviation.

TABLE II: Reactions Used in Computer Simulations

	reaction	rate constant at 298 K ^a
(1)	$OH + HO_2 \rightarrow H_2O + O_2$	$6.4 imes 10^{-11} b$
(2)	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$1.7 imes 10^{-12}$
(17)	$O + HO_2 \rightarrow OH + O_2$	$3.1 imes 10^{-11}$
(18a)	$H + HO_{2} \rightarrow OH + OH$	$3.2 imes 10^{-11}$
(18b)	$H + HO_{2} \rightarrow H_{1} + O_{2}$	$1.4 imes 10^{-11}$
(20)	$O + OH \rightarrow O, + H$	$3.8 imes 10^{-11}$
(12)	$OH + OH \rightarrow H, O + O$	$1.8 imes 10^{-12}$
(19)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 imes 10^{-12}$
(9)	$HO_{2} + NO \rightarrow OH + NO_{2}$	$8.0 imes 10^{-12}$
(21)	$OH + NO + He \rightarrow HONO + He$	$3.6 imes 10^{-31} c$
(22)	$O + NO_2 \rightarrow NO + O_2$	$9.3 imes 10^{-12}$
(8)	$H + NO_{2} \rightarrow OH + NO$	$1.3 imes 10^{-10}$
(23)	$OH + wall \rightarrow products$	<10 s ^{-1 b}
(24)	$HO_2 + wall \rightarrow products$	$5 s^{-1} b$

^a Unless otherwise indicated, units are cm³ molecule⁻¹ s⁻¹ and values were obtained from ref 26-28. ^b Measured. c cm⁶ molecule⁻² s⁻¹.

ments were run by using the first eight reactions plus reaction 24 given in Table II. Reaction 23 was not included since the OH radicals were added at a fixed distance from the detector. Under these conditions a first-order wall loss does not enter into the kinetic analysis.²³⁻²⁵ Initial concentrations of HO₂ and OH were similar to those

TABLE III: Results of Test for Secondary Reactions Using Computer Simulations^a

$10^{-12} \times [HO_2]_0, cm^{-3}$	10 ⁻¹¹ × [OH] ₀ , cm ⁻³	10 ⁻⁹ × [H] ₀ , cm ⁻³	10 ⁻⁹ × [O] ₀ , cm ⁻³	$10^{11}k_1$ (calcd), ^b cm ³ molecule ⁻¹ s ⁻¹	k_1 - (model)/ k_1 - (calcd) ^c
2.0 1.0 2.0 2.0 3.0	2.0 1.0 1.0 2.0 2.0	$0.0 \\ 4.0 \\ 4.0 \\ 4.0 \\ 4.0 \\ 4.0$	0.0 8.0 8.0 8.0 8.0 8.0	6.40 5.55 5.44 5.87 5.76	1.00 1.15 1.18 1.09 1.11

^a First eight reactions plus reaction 24 of Table II. [H_2O_2] = 3.2×10^{13} cm⁻³. ^b k_1 (calcd) is obtained from slope of computer-generated ln [OH] vs. time plots for reaction times between 4 and 10 ms. c_{k_1} (model) = 6.4 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

used in the experimental runs. Concentrations of H atoms and O atoms were at the upper limits observed from the HO_2 source plus OH source A. A value of 6.4×10^{-11} cm³ molecule⁻¹ s⁻¹ was used for k_1 in the model. The results are summarized in Table III. The value of k_1 (calcd) was obtained from the computer-generated ln [OH] vs. time plots for reaction times between 4 and 10 ms. This simulates the procedure used to obtain k_1 from actual experimental data. The last column gives the ratio of k_1 used in the model to k_1 calculated. The results show that use of the initial slope should limit interference from secondary reactions to less than 20% at the maximum concentrations of atomic species observed when using OH source A. When initial O- and H-atom concentrations were set equal to zero (row 1 of Table III), no curvature was observed in the simulation. This suggests that reactions 17 and 18a are responsible for the slight curvature observed in the experimental data. In these simulations no attempt was made to quantitatively fit computed curves with observed OH decays. The only purpose was to estimate the maximum interference from secondary reactions.

Reactions of fluorine-containing species were not included in these simulations because of the lack of information on many of the rate coefficients and reaction products. As a test for possible fluorine secondary chemistry, [F₂] from the OH source was varied from 1.4×10^{13} to 5.3×10^{13} cm⁻³. No significant change was observed in k_1, k_1 , or the loss of HO₂. In addition, mass-spectrometric analysis of the HO_2 source (see Experimental Section) showed that only small amounts of OF_2 and OF ($\leq 10^{11}$ cm^{-3}) were present and, thus, should not interfere with the measurement. The species responsible for the signal at m/e 36 (possibly HOF) should not interfere since its presence is independent of whether the HO₂ source discharge is on or off. Any loss of OH due to reaction with this species would be included in k_{+}^{I} and k_{-}^{I} . Absolute HO₂ Concentrations. HO₂ was determined

after quantitatively converting it to OH by adding a large excess of NO (eq 9) 2-3 ms upstream of the OH detector. To increase mixing efficiency, we added the NO at the center of the flow-tube cross section. Signal intensities of OH generated from HO₂ varied less than 5% for $2.2 \times 10^{14} \le [\text{NO}] \le 5.9 \times 10^{14} \text{ cm}^{-3}$. During the present experiments, $[\text{NO}] = 4.7 \times 10^{14} \text{ cm}^{-3}$. Absolute HO₂ concentrations were then calculated from the calibrated OH signals. The calibration procedure has been described in the Experimental Section.

Background OH fluorescence signals (microwave discharges in both the HO_2 and OH sources off) were observed to increase when NO was added to reaction mixtures containing F_2 and H_2O or F_2 and H_2O_2 . The magnitude of the background enhancement was proportional to the

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TABLE IV: Effect of F, on OH Fluorescence Signals^a

10^{-13} [F ₂], cm ⁻³	$10^{-3}(I_{B+} - I_{B-}),$ counts s ⁻¹	$(I_{\rm F} - I_{\rm B})_{+}/(I_{\rm F} - I_{\rm B})_{-}$
$0.50 \\ 0.71 \\ 2.60$	$4.98 \\ 7.42 \\ 21.7$	0.99 1.00 0.95
4.47	34,0	1.00

 $^{a}I_{B}$ = background fluorescence signal (microwave discharges in OH and HO₂ sources off). I_{F} = total fluorescence signal. The + and – subscripts indicate the presence or absence of added F_{2} .

amount of F_2 present. At $[F_2] = 2.6 \times 10^{13} \text{ cm}^{-3}$ the signal corresponded to an OH concentration near $2.5 \times 10^{11} \text{ cm}^{-3}$ downstream of the NO addition port. Reaction 25 followed

$$F_2 + NO \rightarrow FNO + F$$
 (25)

by reaction 5 or by reactions 11 and 9 is a possible source of this background OH. Reaction 25 has been used in chemical laser systems and k_{25} has been reported to be 1.8 $\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 300 K.²⁹ Estimates using this value for k_{25} indicate that, under the conditions used in the present experiments, background OH concentrations in the 10^{11} cm⁻³ range could be produced in the 2–3-ms reaction time following NO addition.

To check whether species formed in reactions leading to the enhanced OH background interfere with the absolute HO_2 concentration measurements, we added HO_2 to various amounts of F_2 ; 10 ms downstream of the HO_2 addition point, excess NO was added as described above. During these runs, the concentrations of H_2O , H_2O_2 , and NO were similar to those used in the rate-constant measurements. The results are summarized in Table IV. The second column shows the background enhancement at various F_2 concentrations. The third column gives the ratio of OH fluorescence signal minus background with F_2 present to signal minus background without added F_2 . No corrections have been made for the small amounts of F_2 (<1.1 × 10^{12} cm⁻³) from the HO₂ source. The results show that at $[F_2]$ used in the present study, absolute $[HO_2]$ measurements are unaffected by the enhanced background and that no HO_2 is lost by direct reaction with F_2 .

During the conversion of HO_2 to OH, some loss of radicals is expected to occur mainly by reactions 1 and 12. To estimate the magnitude of this loss, we ran computer simulations by using the reactions in Table II. Reaction 25 and subsequent reactions of atomic fluorine were not included in this simulation because the main effect of these reactions is to shift the OH background without any loss of OH signal (see Table IV). Initial concentrations were set to simulate actual experimental runs with $1 \times 10^{12} \le [HO_2]_0 \le 3 \times 10^{12} \text{ cm}^{-3}$, $1 \times 10^{11} \le [OH]_0 \le 2 \times 10^{11} \text{ cm}^{-3}$, $[H]_0 = 2 \times 10^9 \text{ cm}^{-3}$, and $[O]_0 = 4 \times 10^9 \text{ cm}^{-3}$. The concentrations of O atoms and H atoms are similar to those observed ~ 10 ms after adding HO₂ to OH. The results are summarized in Table V. The third column gives the calculated [OH] 2.5 ms after NO addition. The fourth column gives the ratio of initial $[HO_2]_0 + [OH]_0$ to [OH]at 2.5-ms reaction time. Loss of OH is seen to be less than 15%. The effect of OH loss during the HO₂-to-OH conversion is to increase the observed value of k_1 an estimated 7-13%. However, the effect of secondary reactions is in the opposite direction an estimated 9–18% (see Table III). No corrections for either effect have been made to the values of k_1 given in Table I.

Results Using Other Sources of OH. The previous discussion summarized the results obtained by using OH

TABLE V: Results of Computer Simulations of the HO₂-to-OH Conversion^a

$10^{-12} \times [HO_2]_0, cm^{-3}$	$10^{-11} \times [OH]_{0}, cm^{-3}$	$ \begin{array}{c} 10^{-12} \times \\ [OH]_{2.5 \text{ ms}}, b \\ cm^{-3} \end{array} $	([HO ₂] ₀ + [OH] ₀)/ [OH] _{2.5 ms}
1.0 2.0 2.0	$1.0 \\ 1.0 \\ 2.0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	1.03 1.91 2.00	1.07 1.10 1.10

^a $[H]_0 = 2 \times 10^9 \text{ cm}^{-3}$, $[O]_0 = 4 \times 10^9 \text{ cm}^{-3}$, $[H_2O_2] = 3.2 \times 10^{13} \text{ cm}^{-3}$, $[NO] = 4.7 \times 10^{14} \text{ cm}^{-3}$. ^b $[OH]_{2.5 \text{ ms}}$ is the calculated concentration of OH 2.5 ms after NO addition.

TABLE VI: Results Using Several Sources of OH

OH source ^a	runs	10 ⁻ ° × [O], cm ⁻³	10 ⁻⁹ × [H], cm ⁻³	$ \begin{array}{r} 10^{11}k_{1}, {}^{b} \\ cm^{3} \\ molecule^{-1} \\ s^{-1} \end{array} $
A	32	6	3	$\begin{array}{c} 6.4 \pm 1.5 \\ 4.7 \pm 0.5 \\ 3.1 \pm 0.9 \\ 4.5 \pm 1.5 \end{array}$
B	3	11	6	
C	3	130	1	
D	6	1	1	

^a (A) H + F₂ \rightarrow HF + F; H₂O + F \rightarrow HF + OH. (B) F + H₂O \rightarrow HF + OH. (C) H + O₃ \rightarrow O₂ + OH. (D) H + NO₂ \rightarrow NO + OH. ^b The average value of k_1 is given. Errors are twice the standard deviation.

source A. Three other less-suitable sources of OH were used to obtain limited rate data, and the results are given in Table VI. The decrease in the observed value of k_1 at higher concentrations of O atoms and H atoms illustrates the necessity of monitoring these species. The low value using source D is due to OH regeneration by reaction 9. The results using OH source A have been shown to be substantially free of interference from secondary reactions, and only this value is reported here.

Comparison with Previous Results. Measurements of k_1 near room temperature are summarized in Tables VII and VIII. Three of the low-pressure studies were made relative to or depend on the value of the OH + H₂O₂ rate constant, k_2 . Using the recently published results^{12,30} for k_2 changes the originally reported values of k_1 dramatically. The value reported by Burrows et al.⁸ increases from 5.1 $\times 10^{-11}$ to 10.2×10^{-11} cm³ molecule⁻¹ s⁻¹ while the values reported by Hack et al.⁹ become internally inconsistent.

Possible difficulities with these measurements have been discussed previously.³⁰ Experimental conditions are not given in sufficient detail to do an analysis of the Burrows et al.⁸ experiments. It is possible that either a true steady state in HO was not reached or that secondary reactions such as reaction 17 interfered since atomic species were not monitored in these experiments.

The good agreement between the present result and the recalculated first measurement of Hack et al. may be fortuitous. HO₂ was generated by the reaction of OH with H₂O₂. For a true steady state to be reached requires that $[OH]_0 \approx 10k_2[H_2O_2]/k_1$.³¹ Using $k_1 = 6.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, $k_2 = 1.64 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, and the $[H_2O_2]$ listed in their Table I gives $[OH]_0 = 1.0 \times 10^{12}$ -3.2 $\times 10^{13}$ cm⁻³ with a typical value greater than 10^{13} cm⁻³. At these initial OH concentrations secondary reactions such as reactions 12, 17, 18, and 20 become important. Also, in these studies radical wall losses were high and enter directly into the measurement of k_1 . Although the wall

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total

TABLE VII: Summary of k_1 Measurements at Low Pressure and $T = 296 \pm 3$ K

$10^{11}k_1, \text{ cm}^3$ molecule ⁻¹ s ⁻¹	press., torr	method ^b	comments	ref	
$\begin{array}{c} 6.4 \pm 1.5 \\ 10.2 \ (5.1 \pm 1.7)^a \\ 7.1 \ (2.3 \pm 1)^a \\ 2.2 \ (3.0 \pm 1)^a \\ 2-3 \end{array}$	$1.0 \\ 2.0 \\ 1.3-2.4 \\ 1.0-2.3 \\ 2.1-3.7$	DFRF DFLMR DFLMR DFLMR DFRF	absolute measurement using pseudo-first-order conditions relative to k_2 , steady-state HO ₂ relative to k_2 , steady-state HO ₂ measurement depends on k_2 , nonlinear OH decays computer simulations of [OH] and [HO ₂] vs. time	present results 8 9 9 10	

^a Corrected for recently reported value of k_2 . The numbers in parentheses are the originally reported values of k_1 . ^b DFRF = discharge-flow resonance fluorescence; DFLMR = discharge-flow laser magnetic resonance.

TABLE VIII: Summary of k_1 Measurements at High Pressure and $T = 302 \pm 6$ K

$10^{11}k_1, \text{ cm}^3$ molecule ⁻¹ s ⁻¹	press., torr	H ₂ O, torr	method ^a	comments	ref
$ \begin{array}{c} 11.6 \pm 2.5 \\ 9.9 \pm 1.2 \\ 12-16^{b} \\ 12^{b} \\ 6 2^{+4} \end{array} $	752 1200 755 700 760	$ 18.4 \\ 1.8-15 \\ 4.6 \\ 3 \\ 4-15 $	FP-UVA PR-UVA SP-UVA SP-UVA MP-UVA	computer simulations of $[HO_2]$ vs. time computer simulations of $[HO_2]$ and $[OH]$ vs. time relative measurement relative measurement	4 5 6 7

^a FP = flash photolysis; UVA = ultraviolet absorption; PR = pulse radiolysis, SP = steady photolysis; MP = modulated photolysis. ^b Recalculated by using recently recommended rate constants (ref 26-28).

loss was determined for each run in separate experiments, this could be a serious source of difficulty since the surface conditions may not be identical. Since atomic species were not monitored in these experiments, it is impossible to assess the importance of secondary reactions in both of the Hack et al. measurements.

In the study of Chang and Kaufman, HO₂ was produced by reacting OH with O_3 . Initial OH concentrations ranged from 2×10^{11} to 3×10^{12} cm⁻³ with an average value of 1.2 \times 10¹² cm⁻³. At the point where half of the initial OH is converted to HO₂, the loss of OH due to reaction 1 was 6-96 s⁻¹ with an average value of 38 s⁻¹. This assumes k_1 = 6.4×10^{-11} cm³ molecule⁻¹ s⁻¹. Surface loss of OH entered directly into the determination of k_1 and was measured in separate experiments. Values ranged from 11 to 24 s⁻¹ with a typical value of 11 s^{-1} . If the surface loss during the actual measurement of k_1 were lower than that determined in separate experiments, the computer simulations could result in a low value of k_1 . This applies especially to those experiments where loss of OH by reaction 1 is comparable to surface loss. At this time, however, it is not clear that this is the reason for the disagreement between the present results and those of Chang and Kaufman.

Except for the recent measurements by Burrows et al.,¹¹ agreement among the high-pressure studies is reasonably good. The results center about a value of 12×10^{-11} cm³ molecule⁻¹ s⁻¹ and appear to be independent of $[H_2O]$. The possibility that reaction 1 is pressure dependent has been suggested previously^{6,32} and may account for the difference between the present measurements at 1 torr and the results obtained at greater than 700 torr.

Very little information is available on the temperature dependence of reaction 1. Burrows et al.¹¹ report k_1 independent of temperature between 288 and 348 K. A shock-tube study at 1255–1810 K and ~1000 torr gave $k_1 = (5 \pm 2) \times 10^{-11}$ cm³ molecule⁻¹ s^{-1.33} Analyses of [OH] vs. time profiles in lean flames yielded $k_1 = (3.3 \pm 1.7) \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹ at 1500 K and 1 atm.^{34,35} Further work is clearly needed to establish both the temperature and pressure dependence of this reaction.

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