

Rate Constants for the Reactions of HO₂ with OH and with HO₂

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Hydroperoxyl radicals are generated by the flash photolysis of H₂O vapor in systems containing 2% O₂ and either CO or He. Observation of HO₂ decay kinetics at 220 nm coupled with knowledge of the H₂O dissociation yield permits a direct evaluation of ϵ_{HO_2} , $k_5(\text{HO}_2 + \text{HO}_2)$, and $k_6(\text{HO}_2 + \text{OH})$. For system conditions of 1 atm, 296 K, and 21 torr of H₂O, the results are the following: $\epsilon_{\text{max}} = (1050 \pm 140) \text{ M}^{-1} \text{ cm}^{-1}$ at 205 nm, $k_5 = (4.0 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, and $k_6 = (7.0 \pm 1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Comparisons with other reported values, including our own previous work, are discussed in terms of pressure effects, the effect of H₂O on k_5 , and the possible reaction products of the HO₂ self-reaction.

Introduction

Reactions of the hydroperoxyl radical play an important role in atmospheric chemistry and combustion chemistry, and the reactions of HO₂ with HO₂ or with OH have been studied by several groups using a variety of techniques.¹⁻²¹ It has been established that HO₂ has a broad absorption centered at ~210 nm with $\epsilon_{\text{max}} = 1100\text{--}1200 \text{ M}^{-1} \text{ cm}^{-1}$ and that the rate constant $k_5(\text{HO}_2 + \text{HO}_2) = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A discrepancy between early measurements²⁻³ of k_5 was partially resolved by the work of Hamilton et al.⁴⁻⁶ showing that the presence of water vapor increases the rate constant. This effect has been attributed to a more reactive HO₂·H₂O complex. Recent studies have also shown that k_5 is pressure dependent below ~10 torr^{8,10} and has a negative temperature coefficient,^{8,9} suggesting that the reaction proceeds through an H₂O₄ intermediate rather than by a simple H-atom transfer.

There is less agreement about the rate constant k_6 for OH + HO₂. The measurements which have been reported range over an order of magnitude from 10¹⁰ to 10¹¹ M⁻¹ s⁻¹.^{3,11-21} Although there has been no systematic study of pressure or temperature dependence, a pressure dependence has been suggested¹⁹ based on the observation that the lower values of k_6 have been obtained at pressures of a few torr and the higher values have been obtained in studies of systems at atmospheric pressure. An H₂O₃ intermediate is at least plausible for this reaction.

Several years ago we reported ϵ_{max} , k_5 , and k_6 values³ which were determined in the flash photolysis of H₂ or Ar systems containing water vapor (3%) and O₂ (2%) at ambient temperature and pressure. Absolute values of these parameters were based on measurements of the H₂O₂ produced in reaction 5 and ultraviolet kinetic spectrophotometry of HO₂. Our value for $\epsilon(\text{HO}_2)_{\text{max}}$ was ~50% higher than a value of 1179 M⁻¹ cm⁻¹ published by Paukert and Johnston,² and our value for k_5 was also significantly higher than values reported by others.^{1,2} Our recent study of the flash photolysis of water vapor in methane²² has permitted us to measure the H₂O dissociation yield per flash, and use of this system as an "actinometer" has then allowed us to reexamine our earlier studies, proceeding from a known H₂O dissociation yield during the flash rather than from measured products. We report here results for systems containing an atmosphere of CO or He with 3% H₂O and 2% O₂. In our new measurements, the value for ϵ_{max} is lowered to $(1050 \pm 140) \text{ M}^{-1} \text{ cm}^{-1}$. This value is in good agreement with the earlier value of Paukert

and Johnston and with a recent value of 1111 M⁻¹ cm⁻¹ reported by Cox and Burrows.⁸ Our new value for k_5 is lowered to $(4.0 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (for 1 atm with 21 torr of H₂O at 296 K), in agreement with the results of Hamilton and Lii⁶ which take into account the effect of H₂O on k_5 . Our new value for k_6 is $(7.0 \pm 1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This value is in reasonable agreement with some of the reported values obtained from studies of systems near 1 atm total pressure. Comparison with our earlier work suggests that the measured H₂O₂ is about one-third less than would be expected on the basis of reaction 5. Cox and Burrows discuss a similar observation,⁸ but the reasons for the possible effect are unknown at this time.

Experimental Section

Detailed descriptions of the gas-handling system, the flash system, and computational methods are available in previous publications.²²⁻²⁴ CH₄ (Matheson Co. ultrahigh purity grade) and CO (Matheson purity grade) were treated and used as described elsewhere.^{22,23} The He used was very high purity as indicated by mass-spectrometric analysis. Flowing mixtures of CO and O₂ were passed through a water bubbler to saturate the mixture with H₂O vapor at a temperature slightly below the temperature of the optical cell, the latter being $(296 \pm 1) \text{ K}$. Concentrations of the various gas-mixture components were known with an accuracy of ~1%.

The flash-photolysis system produces a flash of ~3 μs duration at half-peak height, which is used to dissociate H₂O into H and OH radicals. The CH₄-H₂O system, in which these radicals are largely converted to measurable CH₃ radicals, serves as a calibration system for determining the H₂O dissociation yield per flash.²² The measured dissociation yield is then used as a fixed parameter in modeling kinetics initiated by H and OH in other systems. A blanket of flowing air is used in the flash housing between the flash lamps and the sample, both to minimize gradients and to prevent the formation of small amounts of O(¹D) atoms via O₂ photodissociation by wavelengths shorter than 176 nm.

Measurements of HO₂ absorbance and kinetics were made at 220 nm with occasional check studies at other wavelengths. The experimental kinetics were matched to optimum values of ϵ_{HO_2} , k_5 , and k_6 by using the method of least squares with the D. W. Marquardt program (NLL2, Share 3094).²⁵ This program was also used to determine the sensitivity of the adjusted variables to changes in as-

TABLE I: Reactions in the H₂O-CO-O₂ and H₂O-He-O₂ Systems

reaction	rate constant	ref
(1) $\text{H}_2\text{O} \xrightarrow{h\nu} \text{H} + \text{OH}$		
(2) $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$	$k_2 = (9.2 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	26
(3) $\text{H} + \text{CO} \xrightarrow{\text{M}} \text{HCO}$		
(a) $\text{M} = \text{CO}$	$k_{3a} = (3.6 \pm 0.9) \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$	23
(b) $\text{M} = \text{O}_2$	$k_{3b} = (3.6 \pm 0.9) \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$	^a
(c) $\text{M} = \text{H}_2\text{O}$	$k_{3c} = (5.8 \pm 0.6) \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$	23
(4) $\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$		
(a) $\text{M} = \text{CO}$	$k_{4a} = 2.0 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	^b
(b) $\text{M} = \text{He}$	$k_{4b} = 6.4 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	27
(c) $\text{M} = \text{O}_2$	$k_{4c} = 2.0 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	27
(d) $\text{M} = \text{H}_2\text{O}$	$k_{4d} = 1.6 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$	27
(5) $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_5 = (4.0 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	this work ^c
(6) $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_6 = (7.0 \pm 1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	this work
(7) $\text{HO}_2 + \text{H} \rightarrow 2\text{OH}$	$k_7 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	28
(8) $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	$k_8 = (1.9 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	17
(9) $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	$k_9 = 3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	27, 29
(10) $\text{HCO} + \text{HCO} \rightarrow \text{products}$	$k_{10} = (1.4 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	23
(11) $\text{HCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}$	$k_{11} = 3.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	30
(12) $\text{HCO} + \text{H} \rightarrow \text{products}$	$k_{12} = (6.9 \pm 1.7) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	23
(13) $\text{HCO} + \text{O} \rightarrow \text{products}$	$k_{13} = 1.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$	29
(14) $\text{HO}_2 + \text{HCO} \rightarrow \text{products}$	$k_{14} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	^d
(15) $\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$	$k_{15} = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	27
(16) $\text{O} + \text{O}_2 \xrightarrow{\text{M}} \text{O}_3$		
(a) $\text{M} = \text{O}_2$	$k_{16a} = 2.2 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$	27
(b) $\text{M} = \text{He}$	$k_{16b} = 1.2 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$	27
(c) $\text{M} = \text{H}_2\text{O}$	$k_{16c} = 19.5 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$	27
(d) $\text{M} = \text{CO}$	$k_{16d} = 2.3 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$	27
(17) $\text{O} + \text{CO} \rightarrow \text{CO}_2$	$k_{17} = 8.3 \times 10^5 \text{ M}^{-2} \text{ s}^{-1} (\text{M} = \text{N}_2)$	31
(18) $\text{H} + \text{H} \xrightarrow{\text{M}} \text{H}_2$		
(a) $\text{M} = \text{CO}$	$k_{18a} = (3.3 \pm 0.2) \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	^e
(b) $\text{M} = \text{He}$	$k_{18b} = 2.5 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	32
(c) $\text{M} = \text{O}_2$	$k_{18c} = 3.3 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	^e
(d) $\text{M} = \text{H}_2\text{O}$	$k_{18d} = (9.0 \pm 2.0) \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	33
(19) $\text{H} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}$		
(a) $\text{M} = \text{CO}$	$k_{19a} = (1.7 \pm 0.6) \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$	^f
(b) $\text{M} = \text{He}$	$k_{19b} = 5.3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	34
(c) $\text{M} = \text{O}_2$	$k_{19c} = 1.7 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$	^f
(d) $\text{M} = \text{H}_2\text{O}$	$k_{19d} = (9.5 \pm 3.5) \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$	35
(20) $\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O} + \text{O}$	$k_{20} = (1.4 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	36-38
(21) $\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$		
(a) $\text{M} = \text{CO}$	$k_{21a} = (6.2 \pm 2.3) \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	^g
(b) $\text{M} = \text{He}$	$k_{21b} = 1.9 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	^g
(c) $\text{M} = \text{O}_2$	$k_{21c} = 6.2 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$	^g
(d) $\text{M} = \text{H}_2\text{O}$	$k_{21d} = (3.4 \pm 1.3) \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$	^g

^a k_{3b} is assumed equal to k_{3a} . ^b k_{4a} is assumed equal to k_{4c} . ^c In the presence of 21 torr of H₂O. ^d Assumed to be the same as k_5 . ^e The values of k_{18} for $\text{M} = \text{CO}$ and O_2 are assumed to be the same as for $\text{M} = \text{N}_2$ (ref 32). ^f The values of k_{19} for $\text{M} = \text{CO}$ and O_2 are assumed to be the same as for $\text{M} = \text{N}_2$ (ref 34). ^g We assume that $k_{21} = 0.36k_{19}$ (ref 35).

summed parameters in the kinetic model ("sensitivity analysis").

Results and Discussion

The CO-H₂O-O₂ System. In a typical study, the CH₄-H₂O system at 1 atm was used to establish a yield of 4×10^{-7} M H₂O dissociated per flash. This value was then used in modeling the experimental results for a system containing 1.0×10^{-3} M H₂O, 0.039 M CO, and 8.0×10^{-4} M O₂. The most important reactions in the system are reactions 1-5 and 9 listed in Table I. The OH radicals convert rapidly to H atoms via reaction 2 ($\tau \sim 0.3 \mu\text{s}$), and the H atoms form HO₂ via reaction 4, or reaction 3 followed by reaction 9, on a time scale of $\sim 5.5 \mu\text{s}$. Thus, most of the initial radicals are converted to HO₂, which reaches a maximum concentration $\sim 15 \mu\text{s}$ after the flash. Over 97% of the HO₂ radicals react with each other; the most significant competing reaction is reaction 7 which accounts for 2% of the HO₂ removed. The only significant reaction

occurring after the flash is reaction 5, and this second-order reaction was followed spectrophotometrically as described elsewhere.³ The H₂O dissociation yield per flash was used along with initial estimates of k_5 and k_6 in the computer model. The computer program then adjusted $\epsilon(\text{HO}_2)$ and k_5 to give a least-squares fit to the experimental data. Since OH reacts very rapidly with the bulk CO, the modeling in this system is not very sensitive to the value of k_6 . Thus it was possible to use an estimate of k_6 to get good values for $\epsilon_{220 \text{ nm}}$ and k_5 . The average values from three different runs are listed in Table II along with the estimates of errors originating from various sources. The value obtained for ϵ_{HO_2} (220 nm) was $889 \pm 110 \text{ M}^{-1} \text{ cm}^{-1}$, and for k_5 ($\text{HO}_2 + \text{HO}_2$) it was $(4.0 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Most of the other reactions in Table I are of minor importance in this system but are included for accuracy and completeness. The O-atom reactions illustrate this point. For the conditions mentioned, $\sim 10^{-8}$ M O atoms are formed by the flash dissociation of some of the O₂ in

TABLE II: Results from the H₂O + CO + O₂ System

no. of expt averaged	10 ⁷ [OH]/ flash, ^a M	ε _{HO₂} (220 nm), M ⁻¹ cm ⁻¹	10 ⁻⁹ k- (HO ₂ + HO ₂), M ⁻¹ s ⁻¹
5	3.928 ± 0.086	956.6 ± 8.6	4.258 ± 0.210
3	4.247 ± 0.151	845.3 ± 5.6	3.341 ± 0.103
4	8.871 ± 0.634	865.1 ± 10.2	4.398 ± 0.276
av value		889.0	3.999 × 10 ⁹
E _r ^b		±48.5	±0.209
E ₁ ^c		±8.4	±0.469
E _g ^d		±98	±0.463
(E _r ² + E ₁ ² + E _g ²) ^{1/2}		±110	±0.691
final value ± std error		889 ± 110	(4.0 ± 0.7) × 10 ⁹

^a Determined from measurements on the H₂O + CH₄ system (each value is an average of three experiments).

^b Reproducibility error. ^c Error for least-squares fit to the data. ^d Error generated from sensitivity analysis. The principal contribution is from the ±14% uncertainty in [OH] flash.²²

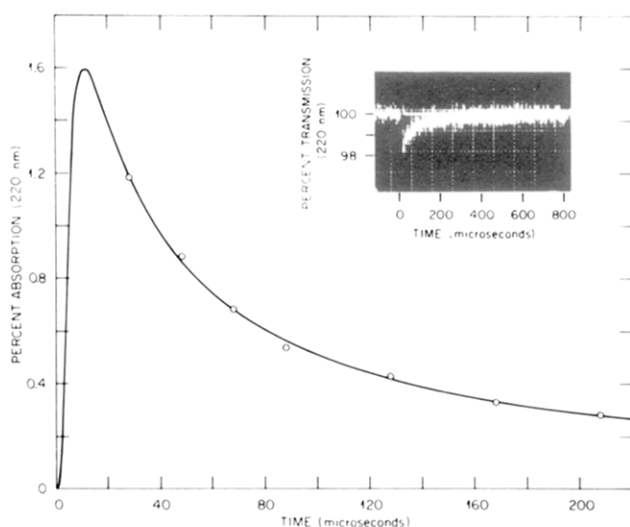


Figure 1. Typical data showing the decay of HO₂ in the flash photolysis of H₂O (3%) in He + 2% O₂ at atmospheric pressure. The solid curve is a computer fit to the data. Most of the decay is due to the reaction of HO₂ with OH.

the system. Although some O(¹D) could be produced by the flash,³ the filtering effect of water vapor in the system and air in the reflector housing prevents this, and only the reactions of ground state O(³P) are included in the table. If these reactions are left out of the modeling, the ε_{max} and k₅ values change by only 2%.

The He-H₂O-O₂ System. In the system composed of H₂O (1.0 × 10⁻³ M), He (0.039 M), and O₂ (8.0 × 10⁻⁴ M), the predominant reactions are reactions 4–6 and 21. Oxygen converts the H to HO₂, and the HO₂ then decays primarily by reaction with OH (reaction 6). Reaction 6 is very important in this system because there is no process comparable to reaction 2 for removing OH. The time scale shown in Figure 1 for HO₂ removal is much shorter than for systems where only reaction 5 occurs, indicating that reaction 6 is a much faster reaction. Figure 1 shows a typical computer fit using ε_{HO₂} and k₆ as adjustable parameters. At the end of the 220-μs period shown, the simulation indicated that 77.6% of the HO₂ had reacted with OH, 8.5% with HO₂, 0.6% with H, and 13.2% remained. The average values of ε_{HO₂} and k₆ from three different runs are listed in Table III along with the estimates of errors originating from various sources. The value obtained for ε_{HO₂} (220 nm) was 916 ± 124 M⁻¹ cm⁻¹, and

TABLE III: Results from the H₂O-He-O₂ System

no. of expt averaged	10 ⁷ [OH]/ flash, ^a M	ε _{HO₂} (220 nm), M ⁻¹ cm ⁻¹	10 ⁻¹⁰ k(HO ₂ + OH), M ⁻¹ s ⁻¹
4	3.928 ± 0.086	984.49 ± 25.00	6.706 ± 0.600
3	4.247 ± 0.151	872.23 ± 37.16	6.882 ± 1.075
4	8.871 ± 0.634	891.18 ± 62.43	7.321 ± 1.412
av value		916.0	6.970 × 10 ¹⁰
E _r ^a		±49.1	±0.259
E ₁ ^b		±44.6	±1.082
E _g ^c		±104.6	±0.918
(E _r ² + E ₁ ² + E _g ²) ^{1/2}		±124	±1.44
final value ± std error		916 ± 124	(7.0 ± 1.5) × 10 ¹⁰

^a Determined from measurements on the H₂O + CH₄ system (each value is an average of three experiments).

^b Reproducibility error. ^c Error for least-squares fit to the data. ^d Error generated from sensitivity analysis. The principal contribution is from the ±14% uncertainty in [OH] flash.²²

TABLE IV: Literature Values for k(HO₂ + OH)^a

values from systems near 1 atm		values from low-pressure systems ^b	
k ₆ , M ⁻¹ s ⁻¹	ref	k ₆ , M ⁻¹ s ⁻¹	ref
1.2 × 10 ¹¹	3	1.2 × 10 ¹⁰	15
		(est)	
9.6 × 10 ¹⁰	14	1.8 × 10 ¹⁰	12
		(1300–1600 K)	
1.1 × 10 ¹¹	19	1.8 × 10 ¹⁰	18
6.0 × 10 ¹⁰	21, c		
7.0 × 10 ¹⁰	this work	1.5 × 10 ¹⁰	20
		3.1 × 10 ¹⁰	16, 17

^a Unless stated, T = 300 ± 8 K. ^b A few torr. ^c 1200 torr.

for k₆ (HO₂ + OH) it was (7.0 ± 1.5) × 10¹⁰ M⁻¹ s⁻¹. For the final value of ε_{HO₂} (220 nm), we took the average from the two systems of 902 ± 117 M⁻¹ cm⁻¹. This value for ε (220 nm) corresponds to ε_{max} = 1050 ± 140 M⁻¹ cm⁻¹ at 205 nm based on our earlier determination of the absorbance band shape.³ Sensitivity analysis showed that ε, k₅, and k₆ are most sensitive to possible errors in the value of OH per flash used in modeling.

Comparison with Previous Studies. Our new values for ε_{max}, k₅, and k₆ are based on kinetic measurements coupled with an "actinometer" procedure which has yielded several other rate constants which are consistent with the available literature.^{22,23} The values are in reasonable agreement with values for ε_{max} and k₅ obtained in other groups and agree with some of the reported values for k₆ (cf. Table IV). In an earlier paper, we reported significantly higher values for all three parameters based on the measured H₂O₂ yields from reaction 5. If the measured H₂O₂ yield were lower than predicted by reaction 5, this would imply that the concentration of HO₂ giving rise to an observed adsorbance had been underestimated. A corrected value of the HO₂ concentration would then lead to lower values of Δ_{max} and consequently k₅ and k₆. An apparent lowering of the H₂O₂ yield from reaction 5 has been noted in the molecular modulation studies of Cox and Burrows,⁷ although they were unable to account for the observation. It might be possible for the H₂O₄ intermediate suggested for reaction 5 to decompose either to H₂O₂ + O₂ or to H₂ + 2O₂, but this has not been tested experimentally. At present, both the magnitude and the details of possible alternatives to reaction 5 remain speculative.

Hamilton was the first to note that H₂O vapor increases the rate of reaction 5 and to suggest that this is related

to the formation of a more reactive $\text{HO}_2\cdot\text{H}_2\text{O}$ complex. The water vapor effect has been verified by several others, and, in addition, pressure and temperature studies of reaction 5 have suggested that the reaction proceeds through an H_2O_4 intermediate.⁸⁻¹⁰ Our value for k_5 is obtained at a total pressure of 1 atm, a temperature of 296 K, and in the presence of 21 torr of H_2O . This k_5 value compares very well with other values obtained under similar conditions.⁶

Our value of k_6 may be compared with the summary of recent values in Table IV. There is reasonable agreement, given the error limitations, with the high-pressure values listed, but poor agreement with the low-pressure values. Water vapor has no effect on reaction 6.^{19,21} The possibility of a pressure dependence has been suggested by DeMore, and a reaction mechanism paralleling the details of reaction 5 with H_2O_3 as an intermediate is plausible.³⁹ A study of pressure and temperature effects on reaction 6 would clearly be desirable.

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Bromine Photosensitized Decomposition of Ozone

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Quantum yields are reported for the bromine photosensitized decomposition of ozone as a function of O_3 , Br_2 , O_2 , N_2 , and SF_6 and as a function of temperature between -15 and 60°C . The quantum yields are independent of the ozone concentration at high ozone-to-Br ratios, but they decrease with increasing Br_2 or O_2 . The quantum yields are not a function of third-body pressures with either N_2 or SF_6 . In general, quantum yields are high, ranging from ~ 19 to 12 , indicating a Br atom chain process.

Introduction

Gaseous bromine compounds are suspected of contributing to the depletion of ozone in the stratosphere in a manner analogous to that of chlorine compounds. While a great deal of work has been carried out in the study of the stratospheric reactions of chlorine,^{1,2} much less has been carried out to understand the role of bromine in the stratosphere. Wofsy et al.³ have estimated that a total of

1.1×10^6 ton/yr of bromine compounds may be available to participate in the entire atmospheric and stratospheric process. Ten percent is believed to be derived from methyl bromide, an agricultural fumigant, ten percent from the combustion of leaded gasoline in automobiles, and the remainder from marine aerosols.

The role of bromine compounds in the photochemistry of the stratosphere has been examined in some detail by