Kinetics of the BrO + BrO Reaction

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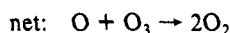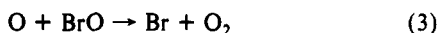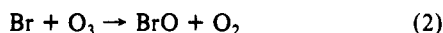
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Discharge flow/mass spectrometry has been used to measure the rate coefficient for the disproportionation reaction of BrO radicals, BrO + BrO → products, at 2-Torr total pressure and over the temperature range 253–400 K. The value of k_1 was found to be $(1.06 \pm 0.20) \times 10^{-12} \exp[(251 \pm 56)/T]$ cm^3 molecules^{-1} s^{-1}, where k_1 is defined by $-d[\text{BrO}]/dt = 2k_1[\text{BrO}]^2$. This is the first direct study of the temperature dependence of the BrO/BrO system that does not rely on the measurement of the absorption cross section of BrO and is in good agreement with previous studies using flash photolysis.

Introduction

The chemistry of halogens has been an essential part of understanding the chemistry of the stratosphere since the work of Stolarski and Cicerone[1] and that of Molina and Rowland[2] showed that chlorine, introduced into the stratosphere by volcanoes or chlorofluorocarbons, could engage in catalytic destruction of ozone. Since then it has been shown that bromine can undergo a similar cycle:[3]

$$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \qquad (2)$$

$$\text{O} + \text{BrO} \rightarrow \text{Br} + \text{O}_2 \qquad (3)$$

$$\text{net: } \text{O} + \text{O}_3 \rightarrow 2\text{O}_2$$

Even though concentrations of stratospheric bromine-containing species are only about 1/100 that of chlorine species, their capability for ozone destruction is significant. This is due to the fact that removal reactions of Br atoms with H_2 and CH_4 to produce HBr are endothermic. Also, reservoir molecules such as HBr and $BrONO_2$ are considerably less stable than their chlorine counterparts.[3] Stratospheric modeling suggests that the predominant form of bromine in the stratosphere is BrO,[4] which as an "active" form of bromine can participate in ozone destruction. This is in contrast to chlorine, which is predominantly present as the reservoir species HCl and $ClONO_2$.

Catalytic ozone destruction cycles such as the one shown above are thought to be less important at lower altitudes in the stratosphere, since O atom concentrations are small. At these altitudes, other reactions become important in converting BrO to Br and continuing the catalytic chain. Reaction with ClO is thought to be the most important of these; however, BrO can also undergo self-disproportionation
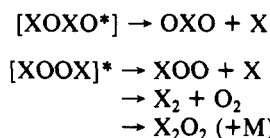
$$\text{BrO} + \text{BrO} \rightarrow \text{BrOO} + \text{Br} \qquad (1a)$$

$$\rightarrow \text{Br}_2 + \text{O}_2 \qquad (1b)$$
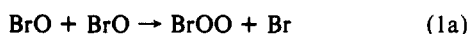
BrOO is unstable and unimolecularly decomposes to form oxygen and a bromine atom. Br_2 is easily photolyzed in the stratosphere to form two bromine atoms; therefore, both channels convert BrO to Br and continue the catalytic cycle for destroying ozone. This reaction sequence is thought to be significant when BrX mixing ratios ($[\text{BrX}] = [\text{Br}] + [\text{BrO}] + [\text{HBr}] + [\text{BrONO}_2]$) exceed

100 ppt.[5] It is estimated that the current growth of chlorofluorocarbons and bromohalocarbons in the atmosphere is ≃5% yr^{-1}.[6,7] Concentrations of bromine radical species such as BrO are thought to be growing proportionately. As [BrO] in the stratosphere increases linearly, the effect of reaction 1 increases as the square of [BrO], suggesting that the BrO disproportionation reaction will play an increasingly important role in stratospheric ozone chemistry in the future.

Reactions of the type XO + XO (X = halogen atom) have been of interest for several years due to their importance in the stratosphere. However, the mechanisms of these reactions have been difficult to elucidate, since the intermediates are often unstable and experimental conditions complex. Presently, it is thought that the reaction proceeds by the formation of a metastable intermediate

$$\text{XO} + \text{XO} \rightarrow [\text{XOOX*}]$$
$$\rightarrow [\text{XOXO*}]$$
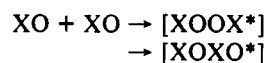
This complex then can decompose unimolecularly along several different pathways or be collisionally stabilized (as in the case of ClO) to form a dimer

$$[\text{XOXO*}] \rightarrow \text{OXO} + \text{X}$$

$$[\text{XOOX}]^* \rightarrow \text{XOO} + \text{X}$$
$$\rightarrow \text{X}_2 + \text{O}_2$$
$$\rightarrow \text{X}_2\text{O}_2 \ (+\text{M})$$

The rates of these reactions and the relative importance of the various channels depend on the rates at which XOOX and XOXO are formed and their stability, as well as on their rates of decomposition. The fact that the relative importance of the bimolecular and termolecular channels depends on the experimental conditions (e.g., pressure, temperature) has led to many discrepancies within the studies of these reactions. The ClO and IO self-reactions have considerable pressure dependences,[8,9] whereas studies have shown that the BrO + BrO reaction does not.[5] The rate coefficient for the bimolecular channels of the ClO reaction also shows a strong positive temperature dependence,[8] whereas the analogous reactions of IO and BrO are thought to have small negative temperature dependences.[5,9] Recent studies

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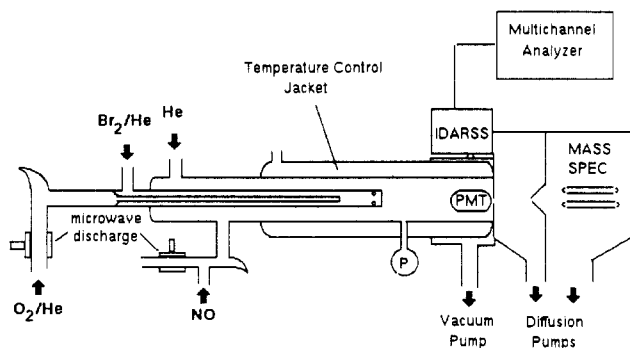
Figure 1. Discharge flow/mass spectrometer system used for studying the BrO + BrO reaction. System also includes the placement of a photomultiplier tube (PMT) and diode array spectrometer (IDARSS) for the monitoring of chemiluminescence.

have also shown that the cross-reaction of ClO + BrO has virtually no temperature dependence[10] or a small negative temperature dependence.[11]

The BrO + BrO reaction has been studied several times with varying results.[5,12-15] Although there is good agreement on the branching ratio into each of the channels,[5,16] there is considerable disagreement on the value of the rate coefficient[5,12-15] and the temperature dependence of the reaction.[5,13,14] In four of the five studies, absorption spectroscopy was used to monitor the BrO radical concentration. The absorption cross section, σ, must also be known in order to accurately measure [BrO] and therefore k_1. Measurements of σ in previous studies have shown considerable variance. The value of σ also has been shown to vary with temperature[5,17] which, if unaccounted for, can affect the measured temperature dependence of k_1. Sander and Watson[5] postulated that the technique used to measure σ in several of these studies was used incorrectly. Therefore, much of the wide variation in the measured rate constants may lie in the measurement of σ. In the present study we have measured the temperature dependence of the rate coefficient of BrO + BrO using the technique of discharge flow/mass spectrometry. An advantage of this technique is that the knowledge of the absorption cross section is unnecessary.

Experimental Section

A diagram of the discharge flow/mass spectrometer system is shown in Figure 1. The discharge flow technique[18] and its coupling to mass spectrometry[19] have been described in detail elsewhere. The main reactor consisted of a 80-cm-long Pyrex tube with an i.d. of 2.51 cm. A large flow of He was introduced into the Pyrex flow tube to establish a known flow rate, pressure, and linear velocity. Radicals can be generated either in the side arm of the flow tube or in a movable dual injector. The dual injector consisted of a 140-cm-long, 1.27-cm-o.d. Pyrex tube, which was concentric with main reactor flow tube. The present experiments used a total flow rate in the range 8–12 (STP) cm^3 s^{-1} and a total pressure of 2 Torr. The flow partitioning between the main reactor and the movable dual injector was such that the flow through the injector made up 5–10% of the total flow. All flows were measured

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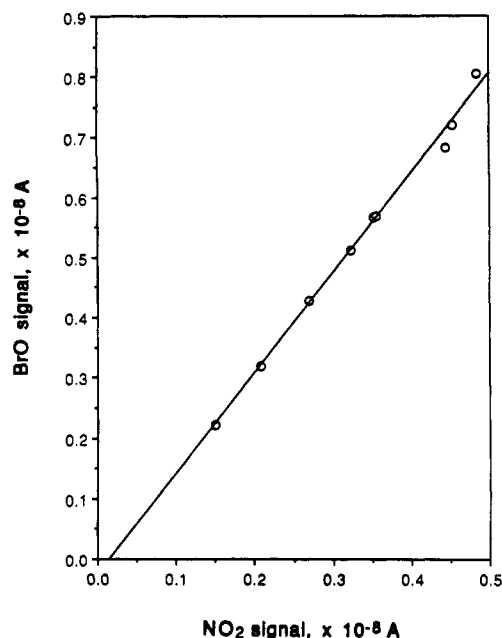
by using calibrated mass flowmeters (Tylan FC260 and FC200, Teledyne-Hastings NALL-100), and the pressure was measured by a capacitance manometer (MKS Baratron Model 170M). Reaction time was varied by translation of the movable injector which varies the distance to the point of detection. Varying the movable injector by 40 cm resulted in reaction times on the order of 40–45 ms. Temperature within the reaction zone was varied between 250 and 400 K by circulating either cooled methanol or heated ethylene glycol through an outer Pyrex jacket. The discharge region, movable injector, and flow tube were all coated with phosphoric acid to reduce wall loss of radical species.

The majority of the flow was pumped by a mechanical vacuum pump (Sargent-Welch No. 1375). A small fraction of the flow mixture was sampled through a pinhole into a differentially pumped quadrupole mass spectrometer (UTI 100C) operated at an electron impact energy of 60 eV. Ion detection was accomplished by means of a high current Channeltron electron multiplier (Galileo Electrooptics No. 4717) which was maintained at 2300 V. Selected ion monitoring was used to monitor the concentrations of all important species. For our conditions the detection limits (S/N = 2) for BrO (m/e = 95), Br$_2$ (m/e = 160), O$_3$ (m/e = 48), and NO$_2$ (m/e = 46) were 1.2×10^{11}, 1.5×10^{11}, 1.0×10^{11}, and 7.1×10^{10} molecules cm^{-3}, respectively.

The flow tube was also equipped with optical windows oriented at 90° to the direction of flow. Placement of a cooled, red-sensitive photomultiplier tube (EMI, 9659QB) and an intensified diode array rapid scan spectrometer (IDARSS, Tracor-Northern, TN 1720) at these windows allowed for the detection of chemiluminescence and emission spectra simultaneous with mass spectrometric detection.

Cylinder gases used in this work were helium (UHP, >99.999%), oxygen (UHP, >99.97%), and a 9.936% nitric oxide (CP, >99%)/He (UHP) mixture. The NO mixture was first passed through a dry ice/acetone trap to remove impurity NO$_2$. Nitrogen dioxide was prepared by reacting nitric oxide with oxygen. Trap-to-trap distillation was repeated in the presence of excess oxygen until the sample was a white solid at 197 K, free from any bluish N$_2$O$_3$ impurity. Excess oxygen was then removed by pumping on the solid at 197 K. NO$_2$ was then volatilized into a 22-L, blackened Pyrex bulb and diluted with He (1656 Torr). This resulted in mixtures of 0.2–0.5% NO$_2$/He. These mixtures were found to be stable for several weeks by the reproducibility of the mass spectrometric calibration curves. These mixtures were also tested for decomposition of NO$_2$ to NO by observing the NO + O$_3$ chemiluminescent emission. A large excess of ozone was added to the flow tube, and then a flow of the NO$_2$ mixture was added to the movable injector. The chemiluminescence signal could be calibrated by adding known amounts of NO through the movable injector. This method found that NO$_2$ decomposition to NO was never more that 1%.

Ozone was prepared by passing pure oxygen through an electrical discharge and then trapped on silica gel at 197 K. After oxygen had been pumped away, the ozone was allowed to volatilize into a 22-L, blackened, Pyrex bulb and diluted in He ($\cong$1147 Torr). Ozone mixtures were prepared every few days since it decomposed slowly, and ozone concentrations were always measured within the flow tube by NO titration. Bromine was prepared by admitting pure Br$_2$ vapor (from liquid Br$_2$, >99%, J.T. Baker) into an evacuated 35-L stainless steel tank and diluting with He (3692 Torr), resulting in bromine mixtures of 1.0–2.2%.

For generation of BrO radicals, a dilute mixture of O$_2$ (0.5–2.0%) in He was passed through a microwave discharge (2460 MHz, Kiva) to generate O atoms. This was admitted into the inner portion of the movable dual injector. An excess of bromine was then admitted into the outer portion of the movable injector (see Figure 1). The reaction

$$O + Br_2 \rightarrow BrO + Br \qquad (4)$$

could then occur at the end of the dual injector just before entering the flow tube. By use of a large excess of Br$_2$, reaction 4 was forced to completion (>99%) within the 6-ms reaction time within the dual injector. BrO also was generated by reaction of Br atoms

Figure 2. Typical BrO calibration plot of BrO signal (at $m/e = 95$) at $t = 0$ vs NO_2 signal (at $m/e = 46$) from the titration of BrO with excess NO. The NO_2 signal produced from this reaction can then be quantified by calibrating the mass spectrometer with known amounts of NO_2.

(produced by microwave discharge) with excess O_3 via reaction 2. Reaction time within the dual injector source also could be adjusted by varying the distance before entering the flow tube. This aided in compensating for the fact that the Br + O_3 reaction is about an order of magnitude slower than the reaction of O + Br_2 ($k_2 = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_4 = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}),[20,21] and more time could be allowed to produce BrO before entering the flow tube. In some experiments BrO was produced by generating Br atoms within the side arm of the flow tube and adding ozone to the dual injector. In this case the source chemistry and BrO disproportionation were fully coupled.

Calibration of the mass spectrometer for BrO was accomplished by the addition of excess NO (($2-4$) × 10^{14} molecules cm^{-3}) to a flow of BrO radicals which converts BrO to NO_2 rapidly and completely

$$NO + BrO \rightarrow NO_2 + Br \qquad (5)$$

Because BrO decays throughout the flow tube, NO was added upstream of the movable injector so that all BrO exiting the movable injector (reaction time = 0) was rapidly converted to NO_2. Since the point of the earliest measurement within the system is reached at about 3 ms, a signal corresponding to BrO at $t = 0$ was obtained by the intercept of a plot of 1/BrO signal vs time. Calibrations were always made using the O + Br_2 source reaction, since excess ozone from the Br/O_3 source could interfere with the calibration. Figure 2 shows a calibration plot of BrO signal at $t = 0$ vs NO_2 signal generated by the NO titration. The NO_2 signal was converted to a concentration by calibrating the mass spectrometer using known concentrations of NO_2. Ozone concentrations were measured in an analogous way by the reaction

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6)$$
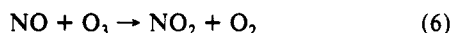
which converts a stoichiometric amount of ozone into NO_2.

Results and Discussion

Results Using the O + Br$_2$ Source. The O + Br_2 source reaction has the advantage that secondary chemistry can be eliminated

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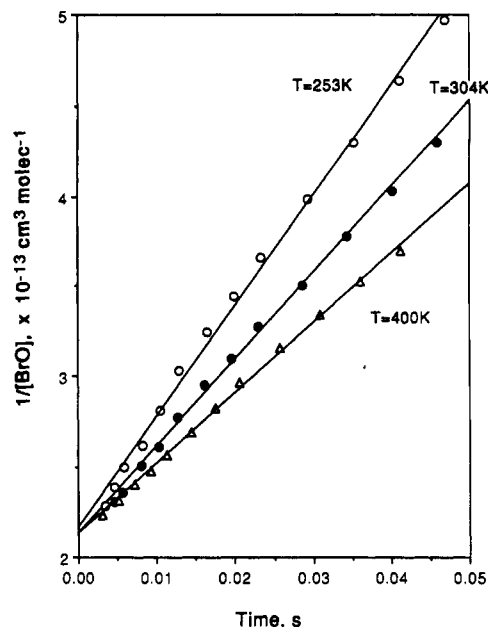
Figure 3. Typical decay curves of 1/BrO vs time observed at the three temperatures studied. $[BrO]_0 \cong 4.6 \times 10^{12}$ molecules cm^{-3}.

TABLE I

technique[a]	temp, K	$k_1 \times 10^{-12}$,[b] cm^3 molecule^{-1} s^{-1}	k_{1b}/k_1	ref
FP/UV	223	3.0 ± 0.6		5
	298	2.2 ± 0.7	0.16 ± 0.03	
	388	1.9 ± 0.6		
DF/MS	298	3.2 ± 0.7		12
MM/UV	298	4.1 ± 1.5		13
				present work
DF/MS	253	2.83 ± 0.34 (21)[c]		using O + Br_2
	304	2.45 ± 0.26 (36)		
	400	1.89 ± 0.24 (18)		
	253	4.57 ± 1.70 (21)		using Br + O_3
	304	2.35 ± 0.72 (16)	0.12 ± 0.04 (5)	
	400	2.05 ± 0.18 (13)		

[a] Technique abbreviations: FP/UV = flash photolysis/UV absorption; DF/MS = discharge flow/mass spectrometry; MM/UV = molecular modulation/UV absorption. [b] Defined as $d[BrO]/dt = -2k_1[BrO]^2$. [c] Errors shown are reported as 2σ. Number of measurements is given in parentheses.

from the reaction zone. By use of a large excess of bromine (>3 × 10^{14} molecules cm^{-3}) within the dual injector source, complete consumption of O atoms occurs within the source region from reaction 4 and the reaction

$$O + BrO \rightarrow Br + O_2 \qquad (7)$$
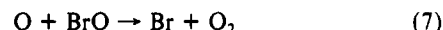
which occurs to a small extent. Concentrations of BrO in the flow tube in the range ($1-11$) × 10^{12} molecules cm^{-3} were generated in this way. Once in the flow tube reaction zone, the only significant loss of BrO radicals is through the gas-phase bimolecular disproportionation. This follows a second-order rate law

$$d[BrO]/dt = -2k_1[BrO]^2$$

which can be integrated to yield

$$\frac{1}{[BrO]_t} = 2k_1 t + \frac{1}{[BrO]_0}$$

Decay plots of 1/$[BrO]_t$ vs time at several temperatures are shown in Figure 3. Decays were linear at all temperatures. The results are summarized and compared with other studies of the BrO + BrO reaction in Table I. The rate coefficient measured shows a small negative activation energy and fits the Arrhenius equation

$$k_1 = (1.06 \pm 0.20) \times$$
$$10^{-12} \exp[(251 \pm 56)/T] \quad \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 253–400 K. The negative activation
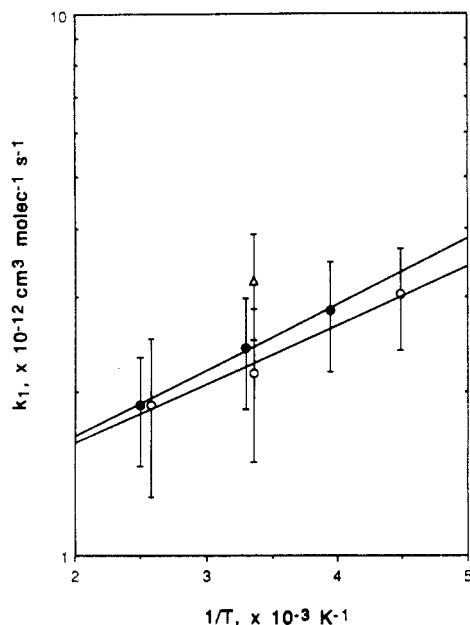
Figure 4. Arrhenius plot showing the temperature dependence of k_1 observed in the present study ($\bullet$), ref 5 (O), and ref 12 ($\triangle$).

energy found in this study is consistent with other studies involving radical–radical reactions of this nature.[11,22] Present theory explains this by the formation of a metastable intermediate complex, although the species Br_2O_2 has never been directly observed. Presumably, lower temperatures facilitate its formation and/or lifetime thereby increasing the observed reaction rate. The major pathway for destruction of this complex is through decomposition, forming either $BrOO + Br$ or $Br_2 + O_2$.

Previous studies of this reaction have produced widely varying results. Studies by Brown and Burns[23] and by Clyne and Cruse[14] have reported positive activation energies for the BrO disproportionation. Both of these studies employed UV-absorption spectroscopy to monitor the BrO radical and are thus affected by measurements of the absorption cross section. Brown and Burns were unable to measure σ and thus could only measure the temperature dependence of k_1/σ. Clyne and Watson[12] have discussed the possible errors involved in the study of Clyne and Cruse,[14] as well as the incorrect mechanistic interpretation of the study of Basco and Dogra.[15] The presently recommended rate constant for reaction 1 is from the combination of two studies.[21] The value of k_1 at 298 K is taken from the average of studies by Sander and Watson[5] and by Clyne and Watson.[12] Of these two studies, only Sander and Watson measured the temperature dependence, reporting $E/R = 225 \pm 195$. This is in excellent agreement with the present study ($E/R = 251 \pm 56$). An Arrhenius plot is shown in Figure 4 with data from the present work, that of Sander and Watson, and that of Clyne and Watson. As can be seen from the figure, agreement of the present work and that of Sander and Watson is excellent, whereas the value of Clyne and Watson is about 25–30% higher at 298 K.

Results Using the Br + O₃ Source. To determine whether the radical source chemistry could affect the kinetics of the BrO + BrO reaction, the rate constant was also determined by using the reaction

$$Br + O_3 \rightarrow BrO + O_2 \qquad (2)$$
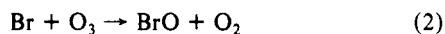
However, due to the relatively slow source reaction, we were unable to produce a large enough bromine atom concentration within the flow tube to completely consume O_3 within a short reaction time. Therefore, the source reaction and the BrO disproportionation were completely coupled. Figure 5 is a typical plot showing the concentration of BrO and O_3 vs time within the flow tube reaction zone. To extract the value of k_1, the method
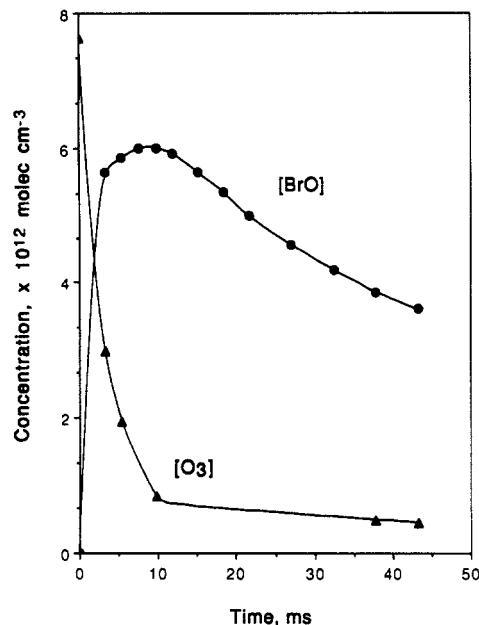
(22) Howard, C. J. *J. Chem. Phys.* **1979**, *71*, 2352.
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Figure 5. Typical plot of [O_3] and [BrO] vs time in the Br + O_3 system (data shown is taken at $T = 400$ K). Bromine atoms were generated in the side arm of the flow tube by microwave discharge, and O_3 was added through the movable injector.
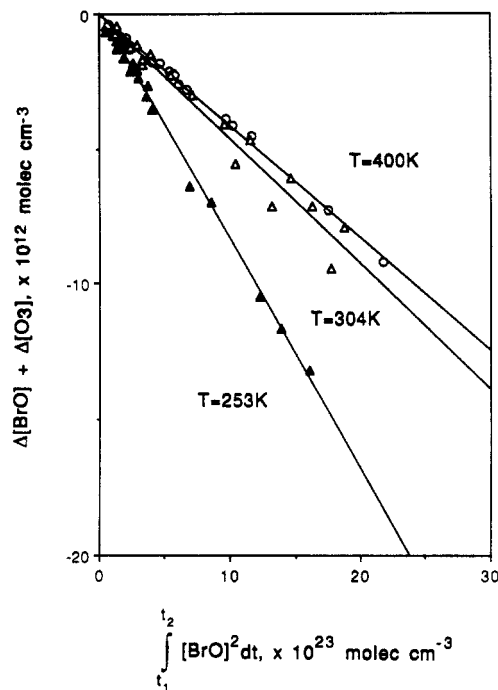

Figure 6. Plots of {$\Delta[BrO] + \Delta[O_3]$} vs the integral over time of $[BrO]^2$ at the three temperatures studied.

employed by Clyne and Cruse[14] was used. The differential equations governing the behavior of both BrO and O_3 are

$$d[BrO]/dt = -2k_1[BrO]^2 + k_2[Br][O_3]$$

$$d[O_3]/dt = -k_2[Br][O_3]$$

Addition of these two equations leads to

$$\frac{d[BrO]}{dt} + \frac{d[O_3]}{dt} = -2k_1[BrO]^2$$

Integration over the time regime studied yields

$$\Delta[BrO] + \Delta[O_3] = -2k_1 \int_{t_1}^{t_2} [BrO]^2 \, dt$$

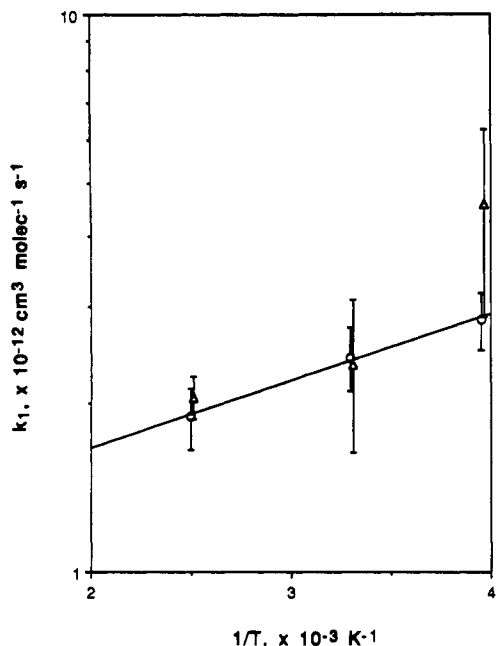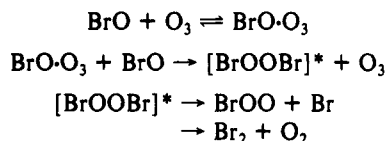where $\Delta[BrO] = [BrO]_{t_2} - [BrO]_{t_1}$ and $\Delta[O_3] = [O_3]_{t_2} - [O_3]_{t_1}$.

Figure 7. Arrhenius plot showing the temperature dependence of k_1 in the present study using both the O + Br$_2$ source (O) and the Br + O$_3$ source ($\triangle$).

The integral on the right side of the equation is evaluated by fitting data of [BrO] vs time with a cubic spline and integrating numerically. Graphing of Δ[BrO] + Δ[O$_3$] vs the integral of the right side of the above equation should yield a straight line with an intercept of zero and a slope equal to $-2k_1$. Figure 6 shows examples of such plots at the three temperatures studied. Errors introduced into the Clyne and Cruse study using this analysis probably resulted largely from the determination of the absorption cross section, σ. Mass spectrometric detection circumvents this source of error. Computer simulations using various initial conditions of Br and O$_3$ indicate that the value of k_1 put into the model can be successfully regenerated by the above data analysis.

Rate constants derived from the BrO disproportionation using the Br + O$_3$ source reaction are reported at the bottom of Table I, and a comparison with the data obtained using the O + Br$_2$ source is shown in the Arrhenius plot of Figure 7. Values of the rate constant k_1 at T = 304 and 400 K are in quite good agreement with those obtained with the O + Br$_2$ source. However, at the lower temperature of 253 K, the measured rate coefficient was significantly higher with the Br + O$_3$ source. The reason for this is unknown at present. However, the reaction systems in the present study contained a relatively high concentration of ozone ((1–3) × 10^{13} molecules cm^{-3}) at 253 K. It may be possible that O$_3$ forms a weak adduct with BrO radicals which can then aid in the stabilization of the metathesis intermediate, BrOOBr:

$$BrO + O_3 \rightleftharpoons BrO{\cdot}O_3$$

$$BrO{\cdot}O_3 + BrO \rightarrow [BrOOBr]^* + O_3$$

$$[BrOOBr]^* \rightarrow BrOO + Br$$

$$\rightarrow Br_2 + O_2$$

In this hypothesis, ozone may act as a "chaperone" to help stabilize the BrOOBr intermediate. Since the rate of overall reaction is determined by this stability, large excesses of ozone may enhance the reaction rate. Low temperature should help favor formation of larger amounts of the BrO·O$_3$ adduct, therefore causing a greater influence on the overall rate observed.

Another possible explanation for the enhanced reaction rate is that some higher energy species (e.g., vibrationally or spin–orbit excited BrO radicals) is formed in the Br/O$_3$ system and may affect the overall kinetics. Burkholder et al.[24] have recently

observed the production of vibrationally excited XO from X + O$_3$ reactions. At lower temperatures, collisional deactivation of this species would become less effective and the observed reaction rate could increase due to a faster reaction of the excited species. The study of Sander and Watson[5] used both BrO sources and reported excellent agreement for the measurement of k_1. However, the conditions used in their study were such that ozone was rapidly depleted by a large excess of Br atoms which would have inhibited formation of a BrO·O$_3$ adduct. The relatively high pressures used in their flash photolysis system may have resulted in the rapid thermalization of any excited-state molecules within their system, as opposed to the present low-pressure, flow tube study. Clyne and Watson[12] also used the Br + O$_3$ reaction as a source of BrO at 298 K using the same technique as the present study. Their reported measurements of k_1 using Br + O$_3$ were slightly lower than are those obtained by using O + Br$_2$, although these differences were within the experimental error. The present study also yields a slightly lower value of k_1 using Br + O$_3$ at room temperature, which is also well within the experimental uncertainty.

Measurements of the branching ratio at 304 K were accomplished by using a large excess of O$_3$ relative to Br ([O$_3$] $\geq$ 100[Br]), similar to the method used by Sander and Watson.[5] Ozone concentrations in the range of (1–5) × 10^{14} molecules cm^{-3} were added to the flow tube. Under these conditions the only pathway for decay of BrO radicals is through channel 1b, producing Br$_2$ and O$_2$. Bromine atoms generated in channel 1a are quickly consumed by the excess ozone to regenerate BrO. Under these conditions BrO decay is described by

$$\frac{1}{[BrO]_t} = 2k_{1b}t + \frac{1}{[BrO]_0}$$

Plots of 1/[BrO] vs time were linear after about 6 ms. The initial decay time is most likely due to the time needed to establish the equilibrium between reactions 2 and 1a. Only five measurements using this method were carried out; however, these give a branching ratio ($k_{1b}/k_{1b} + k_{1a}$) = 0.12 ± 0.04 for channel 1b, in reasonable agreement with the value of 0.16 ± 0.03 and 0.16 ± 0.02 obtained by Sander and Watson[5] and Jaffe and Mainquist,[16] respectively.

Workers in the previous studies have all inferred that channel 1b resulted in production of Br$_2$, although Br$_2$ has never been detected directly. The major premise for this hypothesis is that all other possible bromine-containing species are unstable and would decompose to form Br atoms. Emission from electronically excited Br$_2$ (A$^3\Pi_{1u}$, B$^3\Pi_{0u^+} \rightarrow$ X$^1\Sigma_g^+$) has also been detected from the reaction of BrO + BrO.[14,26] We observed an increase in [Br$_2$] with reaction time in the BrO + BrO reaction. Using the Br + O$_3$ source at 304 K, ion currents at m/e = 160 were monitored with reaction time and showed small but reproducible increases. However, because of the large concentrations of Br$_2$ ((1–2) × 10^{13} molecules cm^{-3}) which remained undissociated in the microwave discharge, quantitation of the small increases in [Br$_2$] was not possible; thus, an accurate measurement of the branching ratio based on the direct measurement of Br$_2$ production was not obtained. However, our results support the hypothesis that channel 1b does produce molecular bromine, analogous to production of Cl$_2$ and I$_2$ in the ClO and IO self-disproportionation reactions.[8,9] Previous work in our lab has shown that when excess ozone is used to generate either ClO[25] or BrO,[26] large enhancements in the chemiluminescence emission from Cl$_2$* and Br$_2$*, respectively, are observed. This may indicate that the presence of ozone affects the branching ratio for molecular halogen products. This may occur by a mechanism similar to that described by Toohey and Anderson[27] for the effect of Br$_2$ on the formation of BrCl in the BrO + ClO reaction. Work investigating this possibility is currently underway.

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Conclusions

We present the first direct study of the temperature dependence of the self-disproportionation of BrO radicals that does not depend upon the measurement of the absorption cross section. Our results are in excellent agreement with the previous flash photolysis work of Sander and Watson. The slight negative activation energy observed lends support to a mechanism involving a metastable intermediate complex:

$$BrO + BrO \rightarrow [BrOOBr^*]$$

$$[BrOOBr^*] \rightarrow BrOO + Br$$

$$\rightarrow Br_2 + O_2$$

$$BrOO \rightarrow Br + O_2$$
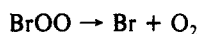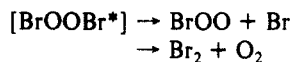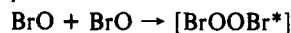
This is similar to the mechanism that has been proposed in the analogous ClO self-reaction. Although the intermediate species Br_2O_2 and BrOO were not identified, their lifetimes under the experimental conditions are expected to be extremely short due to their weak bond strengths. Direct detection of the product Br_2 was observed as well, adding further support to this mechanism. Although the branching ratio was not thoroughly investigated in this study, our observations indicate that about 12% of the reaction produces molecular bromine at room temperature, with bromine atoms being the only other stable bromine-containing product. However, stratospheric chemistry is not sensitive to the branching ratio of the BrO + BrO reaction, since Br_2 is easily photolyzed to produce two Br atoms; therefore, both channels result in a net production of Br. Channel 1b does provide a possible means of sequestering bromine in the polar night of the Arctic and Antarctic regions.

Data obtained at room temperature and above show no dependence on the source of the BrO radical. However, an unexplained enhancement in the rate coefficient occurs at low temperatures ($T = 253$ K) when BrO is generated by the reaction of bromine atoms with ozone. At present, we are unable to explain the observed enhancement; however, it may be due to a $BrO \cdot O_3$ adduct formation at lower temperatures or involve vibrationally or spin-orbit excited BrO radicals which are not efficiently quenched at lower temperatures.

Collision-Theory Calculations of Rate Constants for Some Atmospheric Radical Reactions over the Temperature Range 10-600 K

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Rate constants have been calculated for a number of bimolecular reactions of HO_2, OH, H, ClO, BrO, SO, $O(^3P)$, $O(^1D)$, NO, and NO_2, over the temperature range 10-600 K. For half of the reactions studied so far, calculated capture rates agree with listed experimental rate constants at 300 K to within the stated uncertainties, and calculated temperature coefficients are also consistent with experimental data. Three of the rate constants have not been measured experimentally. For the remaining reactions the calculated value is greater than the measured value and the difference can normally be attributed to the presence of an exit channel barrier, in which case it is possible to predict the form of the temperature dependence to be expected as T tends to zero.

Introduction

Experimental rate constant values, of somewhat variable accuracy, are now available for the majority of homogeneous, gas-phase radical reactions that are of interest to modelers of planetary atmospheres.[1,2] However, because of the experimental difficulty of studying many of these reactions, the available values are mostly restricted to a rather narrow range of temperatures near room temperature and their temperature dependences are correspondingly uncertain. The low-temperature range, between about 10 and 200 K, which is particularly difficult experimentally, is also a range of special relevance to the atmospheres of several planets and massive satellites. Rates of radical reactions at the bottom end of this temperature range may be important in relation to processes occurring in interstellar clouds. Most of these reactions lack any significant activation barrier, so that their rate constants outside the range of measurements cannot be predicted simply on the basis of an Arrhenius-type expression. Thus it is of interest to find a reliable means of predicting the temperature dependence of radical reactions at low temperatures. The present paper gives the results of calculations which yield values of rate constants which are in excellent agreement with room-temperature experimental data for many reactions, without the use of adjustable parameters, and also agree well with available data at other temperatures. Unlike the exeriments, these calculations are as easy to perform for a temperature of 10 K as for 300 K. Where the results of the calculations are not in agreement with experimental data, the calculated values are invariably larger, and the difference between observed and calculated results can provide an indication of the importance of such factors as exit-channel barriers or the requirements of electronic angular momentum conservation. Also, when there is an exit channel barrier, the calculations can still predict the likely form of the temperature dependence in the low-temperature range.

Calculation of ion-molecule reaction rates from the classical rate of crossing the centrifugal barrier in an ion-dipole + ion-quadrupole + ion-induced dipole potential has been a standard practice for many years.[3] Clary[4] used analogous quantum-scattering calculations of the barrier-crossing rate to obtain rate

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