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Temperature Dependence of the Rate Constant and Product Channels for the BrO + ClO Reaction

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We have measured the rate constant for the reactions BrO + ClO → Br + OClO (6a), BrO + ClO → Br + Cl + O_2 (6b), and BrO + ClO → BrCl + O_2 (6c) over the temperature range 241–408 K and found $k_6 = (8.2 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} independent of temperature. Measurement of the individual product branching ratios yielded values for channels 6a, 6b, and 6c equal to 0.55 ± 0.10, 0.45 ± 0.10, and <0.02, respectively. Measurements of ozone in the stratosphere over Antarctica have shown that the springtime ozone column has fallen 40% from 1960 to 1985. The reaction above could account for a large fraction of the springtime "ozone hole" reported recently, provided that at least 20 ppt of total inorganic bromine is present, and it may provide a source of chlorine dioxide of sufficient magnitude to explain the recent measurements of this species in the Antarctic stratosphere.

Introduction

In 1974 Molina and Rowland implicated chlorofluorocarbons released to the atmosphere as a means of catalytic destruction of stratospheric ozone.[1] Chlorofluorocarbons are inert, highly volatile compounds used industrially as solvents, refrigerants, and aerosol spray propellants. They exhibit extreme chemical stability, precluding their chemical degradation and rainout in the lower atmosphere. Their tropospheric lifetimes are thought to be about 100 years.[1] Molina and Rowland pointed out that CFCl$_3$ and CF$_2$Cl$_2$ can diffuse into the stratosphere and be photolyzed, releasing Cl atoms. The photolysis will occur mainly in the 175–200-nm *window* that penetrates into the stratosphere between the intense absorption regions of O$_2$ and O$_3$. The released Cl atoms can then engage in ozone destruction via the catalytic cycle

$$Cl + O_3 \rightarrow ClO + O_2 \tag{1}$$

$$ClO + O \rightarrow O_2 + Cl \tag{2}$$

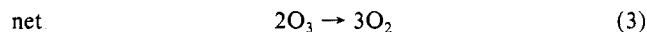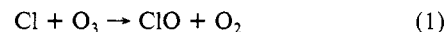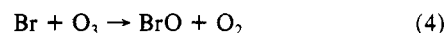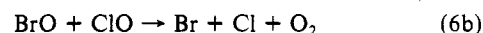net
$$O_3 + O \rightarrow 2O_2 \tag{3}$$
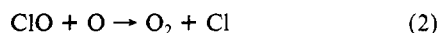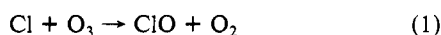
Molina and Rowland estimate that one Cl atom could, on average, catalytically destroy up to 10^5 ozone molecules.

Recent papers[2-4] dealing with atmospheric bromine indicate that bromine engages in catalytic ozone destruction cycles similar to those of chlorine

$$Br + O_3 \rightarrow BrO + O_2 \tag{4}$$

$$BrO + O \rightarrow Br + O_2 \tag{5}$$

net
$$O_3 + O \rightarrow 2O_2 \tag{3}$$
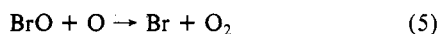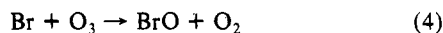
Although the concentration of bromine-containing species in the stratosphere is estimated to be about one-hundredth that of chlorine species, bromine compounds have the potential for large ozone depletion. The reasons for this are several fold. Bromine atoms and BrO are much less easily removed from such cycles than are chlorine species, because Br atoms will not undergo chain termination reactions with CH$_4$ or H$_2$. The Br + CH$_4$ and Br + H$_2$ reactions are both endothermic. Bromine reservoir molecules such as HBr are also more unstable than their chlorine analogues. Therefore, the injection of large amounts of bromine species into the stratosphere is expected to result in even larger catalytic O$_3$ destruction than would the same amount of chlorine species.

Another catalytic ozone destruction cycle has been discovered in which bromine and chlorine species link up synergistically:

$$BrO + ClO \rightarrow Br + Cl + O_2 \tag{6b}$$

$$Br + O_3 \rightarrow BrO + O_2 \tag{4}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{1}$$

net
$$2O_3 \rightarrow 3O_2 \tag{3}$$

Yung et al.[5] and others[4,6] have shown that synergistic coupling of bromine and chlorine chemistry may be an important ozone sink in the lower stratosphere, where the rate of ozone loss due to O + ClO and O + NO$_2$ reactions is small due to the low O atom concentrations.

Reaction sequence 6b, 4, 1 may contribute to the large scale "ozone hole" observed over Antarctica. Recent measurements of ozone in the stratosphere over Antarctica have shown that the springtime ozone column decreased by 40% from 1960 to 1985.[7,8] Both dynamical[9] and chemical theories[10-14] have been advanced to explain the formation of the Antarctic ozone hole. Prominent among these theories is that of McElroy et al.,[11] who speculate that the synergistic interaction between gas-phase BrO and ClO radicals may be responsible for springtime ozone loss.

The current atmospheric growth rates of chlorofluorocarbons and bromohalocarbons are ≈5%/yr.[15,16] Since radical chlorine and bromine levels are proportional to atmospheric halocarbon concentrations, Br$_x$ and Cl$_x$ species are probably growing at similar rates. As Br$_x$ and Cl$_x$ concentrations grow linearly, the atmospheric effects of reaction 6b increase as the product of the two concentrations; hence (6b) will eventually play a much greater

(1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.
(2) Prather, M. J.; McElroy, M. B.; Wofsy, S. C. *Nature* **1984**, *312*, 227.
(3) Wofsy, S. C.; McElroy, M. B.; Yung, Y. L. *Geophys. Res. Lett.* **1975**, *6*, 215.
(4) Watson, R. T. *The Natural Stratosphere of 1974*; CIAP Monograph 1, DOT-TST-75-51, September 1975, Section 5.7.5.
(5) Yung, Y. L.; Pinto, R. T.; Sander, S. P. *J. Atmos. Sci.* **1980**, *37*, 339.
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(7) Farman, J. C.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.
(8) Stolarshi, R. S.; Krueger, A. J.; Schoeberyl, M. R.; McPeters, R. D.; Newman, P. A.; Alpert, J. C. *Nature* **1986**, *322*, 808.
(9) Mahlman, J. D.; Fels, S. B. *Geophys. Res. Lett.* **1986**, *13*, 1316.
(10) Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.
(11) McElroy, M. B.; Salawitch, R. J.; Wofsy, S. C.; Logan, J. A. *Nature* **1986**, *321*, 759.
(12) Crutzen, P. J.; Arnold, F. *Nature* **1986**, *324*, 651.
(13) Toon, O. B.; Hamill, P.; Turco, R. P.; Pinto, J. *Geophys. Res. Lett.* **1986**, *13*, 1284.
(14) Rodriguez, J. M.; Ko, M. K.; Sze, N. D. *Geophys. Res. Lett.* **1986**, *13*, 1292.
(15) Cronn, D. R.; Bamesberger, W. L.; Menzia, F. A.; Waylett, S. F.; Waylett, A. S.; Rerrara, T. W.; Howard, H. M.; Robinson, E. *Geophys. Res. Lett.* **1986**, *13*, 1272.
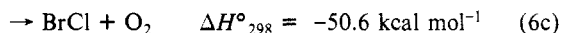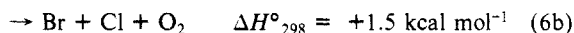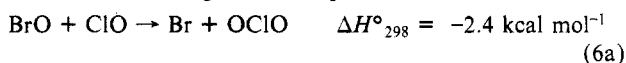(16) World Meteorological Organization Global Ozone Research and Monitoring Project "Atmospheric Ozone"; Report No. 16, Vol. II, p 636, 1985.

†University of Colorado.
‡National Center for Atmospheric Research.

role in control of future stratospheric ozone levels.

Major uncertainties in estimating the effects of reaction sequence 6b, 4, 1 have been the rate constant and product distribution of the BrO + ClO reaction as a function of temperature. There are no prior measurements of the temperature dependence of the BrO + ClO reaction, nor have the product channels been accurately determined. The bimolecular reaction of BrO with ClO has the following accessible product channels:

$$BrO + ClO \rightarrow Br + OClO \quad \Delta H°_{298} = -2.4 \text{ kcal mol}^{-1} \quad (6a)$$

$$\rightarrow Br + Cl + O_2 \quad \Delta H°_{298} = +1.5 \text{ kcal mol}^{-1} \quad (6b)$$

$$\rightarrow BrCl + O_2 \quad \Delta H°_{298} = -50.6 \text{ kcal mol}^{-1} \quad (6c)$$

The sets of products Br + ClOO and BrOO + Cl are also possible, but we do not distinguish these from channel 6b because of the rapid thermal dissociation of ClOO and BrOO to halogen atoms and molecular oxygen, both in our laboratory experiments and in the stratosphere.

Reaction 6 has been investigated twice. The first study was by Basco and Dogra[17] in 1971. They reported a rate constant for reaction 6, $k_6 = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is much smaller than that obtained in the subsequent study of Clyne and Watson,[18] $k_6 = 1.34 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Both of these studies generated the BrO and ClO radicals by reacting large amounts of atomic bromine with OClO

$$Br_{excess} + OClO \rightarrow BrO + ClO \quad (-6a)$$
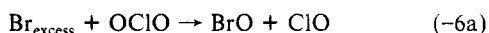
The kinetic behaviors of OClO, BrO, and ClO were monitored either by UV absorption (Basco and Dogra) or mass spectrometry (Clyne and Watson). Since reaction -6a forms BrO and ClO in equal amounts, pseudo-first-order kinetics were not obeyed. This resulted in a complicated reaction scheme involving at least six reactions occurring simultaneously. Modeling techniques were used to extract rate coefficients for several of the reactions. Basco and Dogra[17] report the rate coefficient for reaction 6, $k_6 = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Clyne and Watson[18] report a much larger raw rate coefficient than that of Basco and Dogra, which they attribute to channels 6b + 6c, $k_{6b+6c} = 6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Through additional modeling, taking into account reaction 6a, the reverse of their source reaction, Clyne and Watson arrive at an overall rate constant equal to twice their measured value or $1.34 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These two investigations are reviewed further in the Discussion.

We were interested in studying the BrO + ClO reaction because this rate constant is crucial in evaluating the effectiveness of the ozone destruction cycles involving bromine and chlorine, and because the reaction was poorly understood with respect to overall rate constant, product distribution, and temperature dependence.

In the present investigation, reaction 6 is investigated under true pseudo-first-order conditions, [ClO] >> [BrO], and in the absence of significant chemical interferences. This is achieved through use of a separate source to generate each radical. BrO and ClO are formed individually in a side inlet and movable inlet, respectively, of a discharge flow system coupled to a differentially pumped quadrupole mass spectrometer.

Experimental Section

A. Flow Tube Apparatus. The kinetics investigations were performed using the technique of discharge-flow mass spectrometry. Discharge-flow mass spectrometry[19] and the discharge-flow technique in general[20] have been described previously. The system used in these experiments, shown in Figure 1, has also been described in a recent publication.[21] Ion detection was via a high-current Channeltron electron multiplier. Selected ion monitoring

(17) Basco, N.; Dogra, S. K. *Proc. R. Soc. A* **1971**, *323*, 417.
(18) Clyne, M. A. A.; Watson, R. T. *J. Chem. Soc., Faraday Trans. 1* **1977**, *75*, 1169.
(19) Birks, J. W.; Shoemaker, B.; Leck, T. J.; Borders, R. A.; Hart, L. J. *J. Chem. Phys.* **1977**, *66*, 4591.
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(21) Hills, A. J.; Cicerone, R. J.; Calvert, J. G.; Birks, J. W. *J. Phys. Chem.* **1987**, *91*, 1199.
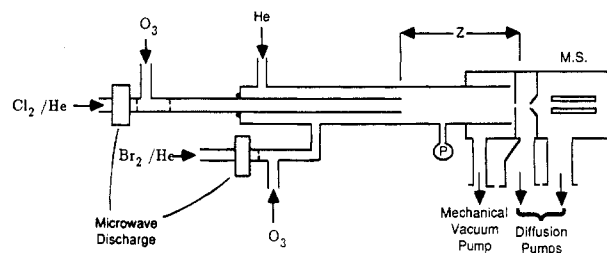

Figure 1. Discharge-flow apparatus as configured for measurement of the rate constant and product distribution of the BrO + ClO reaction. ClO radicals are produced in the movable inlet by microwave discharge of Cl_2 diluted in He followed by reaction of the Cl atoms with O_3. BrO radicals are produced analogously by reaction of Br with O_3 and are introduced to the flow tube via a fixed inlet. Reaction time is varied by moving the ClO source relative to the first sampling orifice of a differentially pumped quadrupole mass spectrometer. Reaction time is computed from this distance, Z, and the velocity of the carrier gas. The latter is established by a mechanical vacuum pump and is calculated from measurements of the total flow rate of gases into the flow tube, the cross-sectional area of the flow tube, and the pressure and temperature of the reaction zone.

was used to monitor the concentration of all the important molecules during each experiment. Detection limits (S/N = 2) for BrO, ClO, O_3, NO_2, OClO, and BrCl were 1.5×10^{11}, 6×10^{10}, 8×10^{10}, 2.5×10^{11}, 1.5×10^{11} and 1.2×10^{11} molecules cm^{-3}, respectively.

B. Reagents. Cylinder gases used in this work were helium (UHP, >99.999%), nitric oxide (CP, >99%), oxygen (UHP, >99.97%), and 10% chlorine (HP >99.5%)/He (UHP) mix. Impurities in the NO, primarily NO_2, were removed by passing it through a refrigerated line held at -85 °C. Bromine was prepared by admitting pure Br_2 vapor (from liquid Br_2, >99.9%, J. T. Baker) into an evacuated 35-L stainless steel tank to pressures of 6-70 Torr. Helium was then added to 60 psi. This resulted in 0.2-2.3% Br_2/He mixtures.
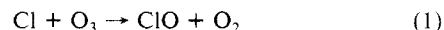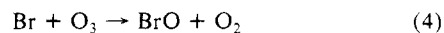
Chlorine dioxide, OClO, was prepared in real time for these experiments by passing a 10% Cl_2/He flow (0.5 STP cm^3/s) through a reactor containing sodium chlorite ($NaClO_2$, Mathieson Chemical) held at ≈50 °C. In contrast to previous investigations, it was found that oxygen was not required for the production of OClO. The source produced OClO in 78% yield, as measured by loss of Cl_2 at m/e 70, as the Cl_2 flow was diverted over the sodium chlorite. Note: On two occasions the OClO source exploded violently during OClO production. The reason for this is not known, but may have involved an impurity in the sodium chlorite, since the source was operated safely for months until new $NaClO_2$, obtained from lower in the sodium chlorite bottle, was placed into the source. Any use of the OClO source should include blast shielding, as was done in this work.

Dichlorine monoxide, Cl_2O, was prepared by passing a 10% Cl_2/He flow (0.6 cm^3/s) over a heated (≈30 °C) bed of HgO (J. T. Baker). The yield of this source was ≈50%. Nitrogen dioxide was prepared by reacting nitric oxide with oxygen. The NO_2 was further purified via trap-to-trap distillation in the presence of excess oxygen until an aliquot was a white solid at 197 K, free of any bluish N_2O_3 impurities. Excess oxygen was then removed by pumping on the solid at 197 K. Ozone was produced by electrical discharge of a slow stream of oxygen (1 STP $cm^3 s^{-1}$) and was used in real time in the kinetics experiments. The O_2 to O_3 conversion was typically 4%.

C. Radical Production. BrO and ClO were produced via microwave discharge of trace Br_2 and Cl_2 in He
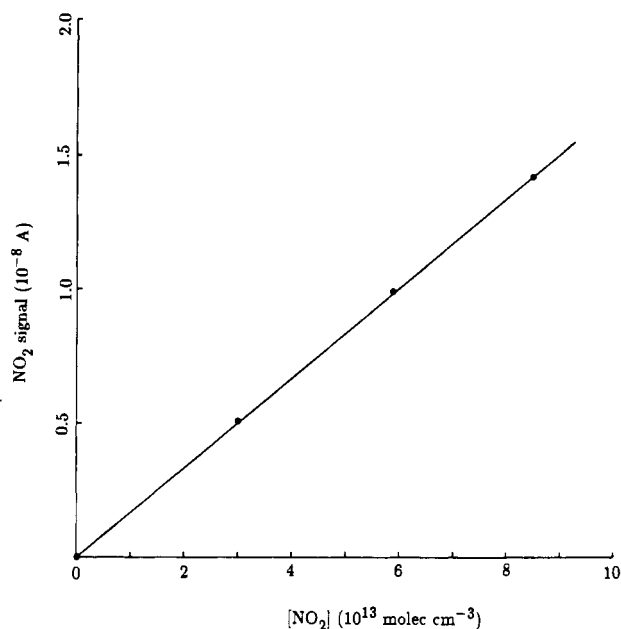
$$Br_2 \rightarrow 2Br \quad (7)$$

$$Cl_2 \rightarrow 2Cl \quad (8)$$

followed by reaction with ozone

$$Br + O_3 \rightarrow BrO + O_2 \quad (4)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

Figure 2. Typical NO_2 calibration plot. $T = 306$ K, $P = 1.27$ Torr, $F_{total} = 415$ cm^3 min^{-1}.

Figure 3. Typical ClO → NO_2 calibration plot. Slope = 0.537, ClO:NO_2 ratio = 1.86.

To determine whether the means of producing ClO influenced the experimental results, ClO was produced in two additional ways, by reaction of chlorine atoms with OClO and with Cl_2O:

$$Cl + OClO \rightarrow 2ClO \qquad (9)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2 \qquad (10)$$
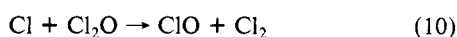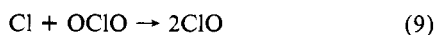
D. Calibrations. Flow rates of the bulk carrier gas, He, and the stable reactant gases, O_2, Cl_2, Br_2, and NO, were measured and controlled by using mass flow controllers (Tylan FC 260 and FC 200 and Teledyne Hastings NALL-100). The meters were referenced by using water displacement vs time flows (correcting for vapor pressure of H_2O). They were further checked by intercalibration tests where identical He flows through the flow meters (as monitored by equal flow tube pressures) were compared to the displayed flow rate. Two factory-calibrated Tylan FC 260 flow meters served as primary flow rate standards with the latter method. NO_2 flow rates were measured by the technique of differential pressure change over time in a calibrated glass volume.[22]

Ozone concentrations were measured by reaction with excess NO

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (11)$$

to substitute a stoichiometric amount of NO_2 for O_3. The NO_2 thus formed was monitored at m/e 46. Dividing this ion current by the slope of an NO_2 mass spectrometer signal vs [NO_2] plot (Figure 2) yielded the initial concentration of ozone. NO_2 calibrations were performed one or two times daily.

The concentrations of ClO and BrO radicals were measured analogously to that of ozone via the reactions

$$ClO + NO \rightarrow Cl + NO_2 \qquad (12)$$

$$BrO + NO \rightarrow Br + NO_2 \qquad (13)$$
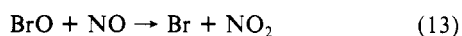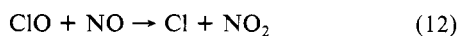
A typical ClO → NO_2 calibration plot is shown in Figure 3.

Flow tube pressure was monitored with a capacitance manometer (MKS Baratron Model 170M). This was calibrated by referencing to an identical Baratron which was factory calibrated during this study. Temperatures were measured by using copper/constantan thermocouples referenced to 0 °C (ice water). The 1-in. nomin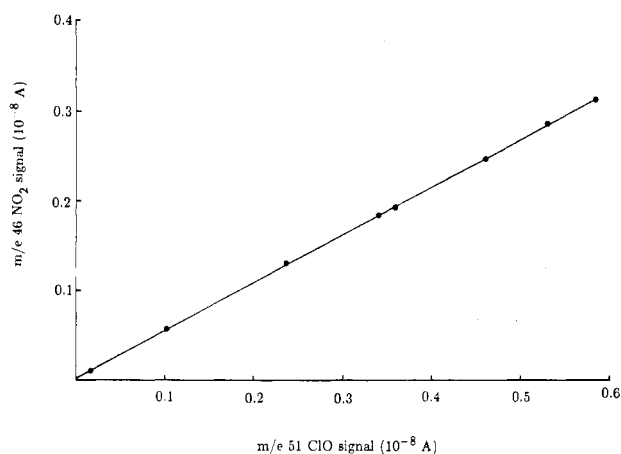al Pyrex flow tube was measured internally at several points using a telescoping micrometer. The average internal diameter was found to be 0.987 in. (2.51 cm). The flow tube and both outer and inner surfaces of the movable injector were coated with phosphoric acid to reduce wall losses of reactive species. First-order wall losses of ClO and BrO on the flow tube surface were measured at various times during this work and were found to be negligible (<2 s^{-1}).

The branching ratio into channel 6a, Br + OClO, was measured by first calibrating ClO relative to OClO. The reaction

$$OClO + Cl \rightarrow 2ClO \qquad (14)$$
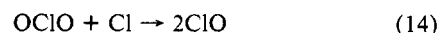
was used in these calibrations. Ion currents at m/e 67 and 51 were monitored as the Cl_2 discharge (Cl source) was turned on and off. The $\Delta m/e$ 67 signal was directly proportional to [OClO] changes due to reaction 6. The $\Delta m/e$ 51 signal was the result of both changes in [ClO] and [OClO] as the Cl source was modulated, because OClO fragments, ≈50% into ClO. The m/e 51 signal was corrected for OClO contribution by using the method of Birks et al.[19] The branching ratio into channel 6a was measured by monitoring ΔOClO/ΔClO as BrO was turned on and off. The BrO source was modulated either by turning the Br_2 discharge on and off, or by leaving it on, but interrupting the flow of Br_2 through the discharge.

The branching fraction into channel 6c, BrCl + O_2 products, was measured similarly to that of (6a). The value ΔBrCl/ΔClO was measured as BrO was modulated. In order to measure the relative sensitivities of BrCl at m/e 116 and ClO at m/e 51, either excess Br_2 or excess O_3, was added to a stream of chlorine atoms to produce equal amounts of BrCl or ClO, respectively, according to the reactions

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (15)$$

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$
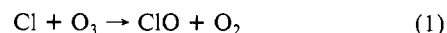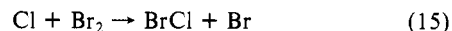
The BrCl/ClO sensitivity ratio was determined over a range of concentration by varying the flow rate of Cl_2 through the microwave discharge. Modulation of the BrO source in the presence of excess ClO was found to result in a large modulation in the BrCl ion current at m/e 116. However, this was found to be due to a secondary reaction of Cl atoms produced in channel 6b with Br_2 (reaction 15). The corresponding reaction of Br with Cl_2 is endothermic by 5.7 kcal mol^{-1} and thus does not contribute to the BrCl signal. Addition of isobutane to the flow tube allowed Cl atoms to be removed from the reactions system. Under these conditions, no BrCl product could be detected. Tests were made to ensure that isobutane was not altering the chemistry of the BrO + ClO system. Isobutane was found not to react with BrO, ClO, O_3, or OClO, but exhibited a rapid reaction with atomic chlorine.

After it was established that channel 6c was inoperative, the fast secondary reaction of Cl with Br_2 (reaction 15, $k_{15} = 1.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) allowed channel 6b to be quantified. By use of a sufficiently large concentration of Br_2 (6 × 10^{13} molecules cm^{-3}), reaction 15 was forced to completion, and the branching

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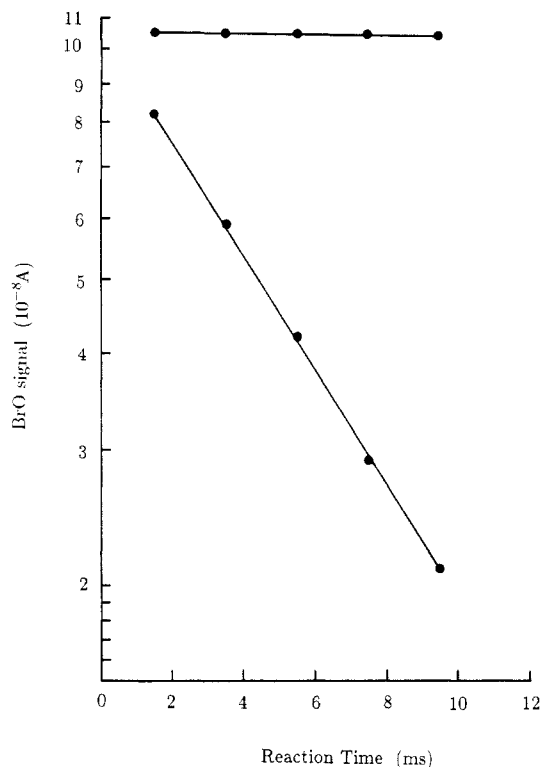(22) Hills, A. J.; Howard, C. J. *J. Chem. Phys.* **1984**, *81*, 4458.

Figure 4. Typical kinetics data for the BrO + ClO reaction. The upper plot is the variation in BrO ion current as a function of movable inlet position with the ClO source turned off. The lower plot shows the decrease in BrO signal as a function of injector position in the presence of excess ClO. Reaction conditions: P = 1.30 Torr, T = 241 K, [ClO] = 2.27 × 10^{13} molecules cm^{-3}. The measured value of k_6^I = 167 s^{-1} gives the result k_6 = 7.4 × 10^{-12} cm^3 molecule^{-1} s^{-1} for this particular run.

ratio into channel 6b was given by $\Delta BrCl/\Delta ClO$ upon modulation of the BrO source.

Results

A. Overall Rate Constant. All of the kinetics measurements were made under pseudo-first-order conditions [ClO] ≫ [BrO]$_0$([ClO] ≥ 16[BrO]). This condition was checked via measurement of the ClO and BrO concentrations and verified by observing the linearity of pseudo-first-order decay plots. A typical decay plot for the reaction

$$ClO + BrO \rightarrow products \quad (6)$$
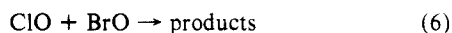
is shown in Figure 4. The reaction distance was varied 20 cm. Over this distance the [BrO] decreased by a factor of 2–8 depending on conditions. The upper plot shows BrO measurements taken with the ClO discharge turned off. This blank is performed to account for any BrO destruction due to

$$BrO + injector\ surface \rightarrow products \quad (16)$$
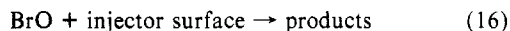
At all temperatures the slope of this plot was <1 s^{-1}, indicating a negligible BrO injector surface loss. The lower plot shows the change in BrO signal as a function of increasing BrO + ClO reaction time. ClO levels at m/e 51 were measured after each kinetics run. After conversion of the ClO signal into a [ClO], the bimolecular rate constant was extracted by using the equation

$$k = k^I/[ClO] \quad (17)$$

Table I summarizes the results of 114 measurements of the rate constant for reaction 6 made in the temperature range 241–408 K. Within experimental error, the overall rate constant did not vary with temperature.

B. Branching Ratio Measurement. The measured branching ratios are summarized in Table II. Independent measurements of channels 6a, 6b, and 6c added to 95% and were found to be invariant with temperature in the range 241–408 K. The 5% discrepancy is certainly within the experimental error of the

TABLE I: Data Summary for the Rate Coefficient Measurements[a]

no. of measurements	T, K	[ClO], 10^{13} molecules cm^{-3}	k,[b] 10^{-12} cm^3 molecule^{-1} s^{-1}
32	241	1.57–2.51	8.0 ± 1.1
69	305	1.25–2.01	8.4 ± 1.0
13	408	0.95–1.43	8.3 ± 0.8

[a] Pressure range 1.25–1.59 Torr. [b] Error shown is one standard deviation (precision only). Average value = (8.2 ± 1.0) × 10^{-12} cm^3 molecule^{-1} s^{-1} where the uncertainty corresponds to the 95% confidence level and includes both random and possible systematic errors.

TABLE II: Summary of Product Distribution Experiments

T, K	no. of expts	reaction no.	reaction products	branching ratio ($\pm\sigma$)[a]
305	18	6a	Br + OClO	0.53 ± 0.04
241	7	6a	Br + OClO	0.50 ± 0.01
305	9	6b	Br + Cl + O$_2$	0.44 ± 0.02
241	10	6b	Br + Cl + O$_2$	0.42 ± 0.05
305	4	6c	BrCl + O$_2$	0.00

[a] Temperature-averaged sum of (6a) + (6b) + (6c) = 0.95. Temperature-averaged BR's, normalized to 1.00: Br + OClO, 0.55 ± 0.10; Br + Cl + O$_2$, 0.45 ± 0.10; BrCl + O$_2$; ≤0.02 (uncertainty includes σ and an estimate of possible systematic errors).
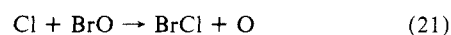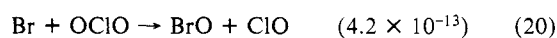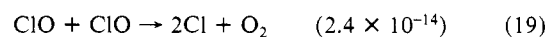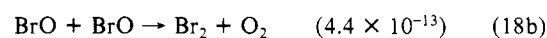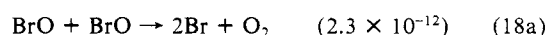
measurements. We attribute all of the products to channels 6a and 6b and recommend a branching ratio of 0.55 ± 0.10 for channel 6a and 0.45 ± 0.10 for channel 6b. Possible effects of ClO source chemistry were tested by use of the three different ClO source reactions, reactions 1, 9, and 10. It was found that the product distribution values were independent of the ClO source used.

Discussion

An estimate of the accuracy of the rate constant measurement is derived from a consideration of both random errors associated with the raw data and possible systematic errors. The statistical error in the data for BrO + ClO, reported as the standard error of the mean, at the 95% confidence level is 0.2 × 10^{-12} cm^3 molecule^{-1} s^{-1}. Possible systematic errors are also incorporated into the overall uncertainty associated with k_6. These consist of measurement of gas flow rates (±3%), temperature (±1%), pressure (±2%), flow tube area (±2%), reaction distance (±3%), and ClO concentration (±10%). These errors yield a total systematic uncertainty of ±11.3%. Combining this with the statistical error, as the square root of the sum of the squares, we obtained a total uncertainty of 12.2% or 1.0 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

Combining the results of the measurements of the overall rate constant with those of the branching ratio for channel 6b gives a value of 3.7 × 10^{-12} cm^3 molecule^{-1} s^{-1} for k_{6b}. This is 45% smaller than the value of 6.7 × 10^{-12} cm^3 molecule^{-1} s^{-1} measured by Clyne and Watson[18] and used in recent model calculations.[11,13]

Analysis of Possible Interfering Reactions. The following interfering reactions occur to varying extents in the BrO + ClO reaction system (the values in parentheses are rate constants, in cm^3 molecule^{-1} s^{-1})

$$Br + O_3 \rightarrow BrO + O_2 \quad (1.1 \times 10^{-12}) \quad (4)$$

$$BrO + BrO \rightarrow 2Br + O_2 \quad (2.3 \times 10^{-12}) \quad (18a)$$

$$BrO + BrO \rightarrow Br_2 + O_2 \quad (4.4 \times 10^{-13}) \quad (18b)$$

$$ClO + ClO \rightarrow 2Cl + O_2 \quad (2.4 \times 10^{-14}) \quad (19)$$

$$Br + OClO \rightarrow BrO + ClO \quad (4.2 \times 10^{-13}) \quad (20)$$

$$Cl + BrO \rightarrow BrCl + O \quad (21)$$

$$Cl + Br_2 \rightarrow BrCl + Br \quad (1.9 \times 10^{-10}) \quad (15)$$

Reactions 4, 18, 20, and 21 represent possible chemical complications, interfereing with the measurement of the rate constant, k_6, by either increasing or decreasing the measured decay of BrO. Reaction 4, the BrO source reaction, can be an interference if it

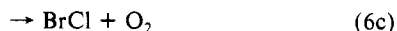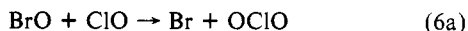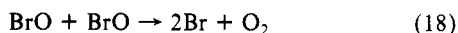occurs to an appreciable extent within the BrO + ClO reaction zone.

BrO formation within the BrO + ClO reaction zone could lead to an underestimate of k_6, since measured BrO decay would be decreased. This potential error was effectively eliminated by keeping the ozone concentration in the reaction zone to $<2 \times 10^{12}$ molecules cm^{-3}, resulting in a pseudo-first-order rate constant for BrO formation of $k_4^{I} < 2.2$ s^{-1}. This represents an upper limit to the perturbation in the measured BrO + ClO pseudo-first-order rate constants of 2%. In all experiments ozone concentrations were monitored at m/e 48 to be certain that this potential interference in the measurement of the rate constant was insignificant.

BrO disproportionation (reaction 18) was negligible and did not contribute to BrO decay, since the [BrO] was always less than 5×10^{11} molecules cm^{-3}. Although ClO disproportionation is slow ($k_{19} = 2.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}), it would be expected to occur somewhat in the movable inlet. Calculations show that up to 25% of the ClO formed in the top of the movable inlet can be lost via reaction 19 enroute down the inlet tube. For this reason, and because of prior experience with this phenomenon,[22] the actual [ClO] entering the reaction zone was always measured with the calibrated mass spectrometer. Reaction 20 could not significantly reform BrO in the reaction zone, since [Br] $<4 \times 10^{11}$ molecules cm^{-3}, and because reaction 20 is very slow, $k_{20} = 4.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The destruction of BrO due to reaction with atomic chlorine, reaction 21, was not significant due to (a) a low [Cl], $\approx 5 \times 10^{12}$ molecule cm^{-3}, and (b) the presence of Br$_2$ which rapidly consumes Cl atoms in the nearly gas-kinetic reaction, reaction 15. Therefore, it was unnecessary to apply corrections to any of the kinetics data reported here.

Previous Work. In an earlier study of reaction 6, Clyne and Watson[18] used the technique of low-pressure discharge-flow mass spectrometry (DF-MS). Like Basco and Dogra's work,[17] however, Clyne and Watson's study was not a direct measurement of the rate constant for the reaction BrO + ClO → products. Their chemical system involved at least six reactions occurring simultaneously. The rate constants, k_{6a} and k_{6b+6c}, were extracted separately from an analysis of the fairly complex chemical scheme shown below. ClO and BrO were produced simultaneously by the reaction

$$Br_{excess} + OClO \rightarrow BrO + ClO \qquad (-6a)$$
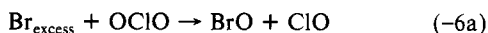
The subsequent chemical profiles of BrO, ClO and OClO were monitored by using mass spectrometry. Besides the source reaction, the following reactions were observed in this system:

$$BrO + BrO \rightarrow 2Br + O_2 \qquad (18)$$

$$BrO + ClO \rightarrow Br + OClO \qquad (6a)$$

$$\rightarrow Br + Cl + O_2 \qquad (6b)$$

$$\rightarrow BrCl + O_2 \qquad (6c)$$

They observed various time regimes where different chemistry was dominant. In the first time period, 0–15 ms, the reactants BrO and ClO were generated in reaction −6a. From 20–55 ms reaction time, [BrO] fell a factor of 5 and [ClO] decreased by 1.5. A region was chosen, 20–55 ms, where [ClO] > [BrO] and pseudo-first-order kinetics were roughly followed. In this region $-[ClO]^{-1}$ d ln [BrO]/dt was measured and was interpreted as the rate constant to channels 6b + 6c. Two large corrections were applied to the raw −d ln [BrO]/dt value in order to arrive at a rate coefficient. The first of these dealt with the radical producing reaction
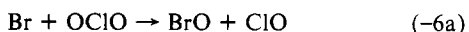
$$Br + OClO \rightarrow BrO + ClO \qquad (-6a)$$

This reaction produced some BrO concurrent with the decay of BrO due to BrO + ClO. Clyne and Watson applied a correction to each BrO decay to account for reaction −6a. This correction served to boost their measured value of −d ln [BrO]/dt for each experiment by 10–44%. A second interfering reaction in this study was the bimolecular disproportionation reaction

$$BrO + BrO \rightarrow 2Br + O_2 \qquad (18)$$
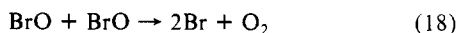
($k_{18} = 2.7 \times 10^{-12}$).[18] Since the BrO concentration was appreciable, reaction 18 contributed to the observed BrO decay. Therefore a second correction had to be applied to −d ln [BrO]/dt. This correction ranged from −3 to −30%. It should be pointed out that these corrections have the potential to introduce significant errors since they are large, $\approx 35\%$ average total correction, and rely upon a knowledge of the absolute [BrO] and [Br] as well as the rate constants for reactions −6a and 18. A third approximation was that true pseudo-first-order reaction conditions did not exist in their study. [ClO] was seen to decay during the BrO observation time by a factor of >1.5, and the investigators were forced to select an average value for [ClO]. A final complication in this study is that the *overall* rate constant, $k_6 = k_{6a} + k_{6b} + k_{6c}$, was not measured due to the interfering reactant source chemistry. Because atomic Br in large amounts ($\approx 10^{15}$ molecules cm^{-3}) was used to produce BrO and ClO via reaction −6a, [Br] remained very high throughout the experiments and served to convert any OClO formed in reaction 6a back into BrO and ClO. The authors maintain that channel 6a and −6a were in equilibrium and that the BrO decay they measured was only that proceeding into channels 6b + 6c. To arrive at the rate constant for channel 6a, they used their own measurement of the rate constant for (−6a), and the concentrations of Br, OClO, BrO, and ClO, to calculate k_{6a} from

$$k_{6a} = \frac{[Br][OClO]}{[BrO][ClO]} k_{-6a} \qquad (22)$$

After applying the corrections mentioned here, Clyne and Watson ultimately report a value for the overall rate constant for BrO + ClO equal to twice their measured value or $k_6 = 1.34 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This method of extracting k_{6a} is indirect, prone to the uncertainties mentioned, and should be considered approximate.

In summary, it can be state that previous studies of reaction 6 suffered from chemical complications. Clyne and Watson have shown from nonlinearity effects in their study of reaction −6a that the reverse reaction, channel 6a, is significant. Basco and Dogra's neglect of this channel is a major concern and, as pointed out by Clyne and Watson, explains why their value for k_6 ($k_6 = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) is much lower than Clyne and Watson's. Clyne and Watson cleverly selected a time regime for extracting k_{6b+6c}. The decay of BrO in this time interval was complicated, however, by reaction −6a which regenerated BrO and by the rapid BrO disproportionation reaction which removed BrO. Their extraction of k_{6a} was necessarily indirect and was dependent on an accurate knowledge of the five variables shown in eq 22. Considering the complications in the earlier work, we feel that the qualitative agreement of our work with that of Clyne and Watson is satisfactory.

Atmospheric Implications. The ClO + BrO reaction is of potential significance to the Antarctic stratosphere in that (1) it could provide a rapid means of ozone depletion if both ClO and BrO radicals are present there, and (2) it could possibly explain the recent observations of OClO in this region of the atmosphere.[23] In general, our results show that the reaction between ClO and BrO is indeed fast, although somewhat slower than originally reported, and that a major product channel is OClO. As no other atmospheric reaction is known to produce significant amounts of OClO, the recent observation of OClO in the stratosphere coupled with our laboratory findings is consistent with the theory that both ClO and BrO radicals are present in the springtime Antarctic stratosphere and that channel 6b of this reaction contributes to the observed ozone loss. These atmospheric implications are further discussed in a recent article by the present authors.[24]

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Photodissociation of the Hydrogen-Bonded Heterodimer Ion [C₆H₅OH–NH₃]⁺

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Photodissociation of the hydrogen-bonded heterodimer ion [C₆H₅OH–NH₃]⁺ has been studied following the selective photoionization of the jet-cooled dimer via its S_1 state by using two-color multiphoton ionization technique. From the mass-selected photoionization yield spectrum for generation of the dimer ion, the adiabatic ionization potential of C₆H₅OH–NH₃ was found to be 62 200 ± 100 cm⁻¹ (ca. 7.71 eV). It was found that the fragment ion C₆H₅OH⁺ is generated by the photoionization of the dimer with the ionization energy higher than a threshold at 70 400 cm⁻¹, whereas only the dimer ion is generated with the photoionization energy lower than the threshold. Dissociation energy of the dimer ion due to [C₆H₅OH–NH₃]⁺ → C₆H₅OH⁺ + NH₃ was found to be 8200 ± 150 cm⁻¹. No NH₄⁺ production was found even when the photoionization energy exceeded the expected threshold for the NH₄⁺ generation. The selective dissociation producing the phenol ion is discussed in relation to the structure of the dimer ion.

Introduction

Photodissociation of the hydrogen bond represents an important class of unimolecular photochemical processes in hydrogen-bonded dimers or clusters in the gas phase. The dissociation of cations of hydrogen-bonded dimers is of particular interest concerning proton transfer. In this respect, the dissociation of a dimer cation, $[AH]_2^+$, is expected to occur in two ways: one is to generate the protonated fragment ion AH_2^+ and the other produces the unprotonated fragment ion AH^+. Both fragment ions are frequently observed in photoionization mass spectroscopic studies of the hydrogen-bonded clusters.[1-7] These extensive studies show that the protonated ion is originated from the photoionized clusters. The dissociation accompanied by the proton transfer occurring in cluster ions results in efficient production of the protonated ion. Several studies on ion–molecule reactions within cluster ions have recently been done, showing a variety of reaction products.[8,9] On the other hand, the origin of the unprotonated ion has not been well understood. Since ordinary cluster sources such as molecular beams or supersonic free expansions necessarily contain a large number of monomer molecules, a mixture of clusters and the monomer AH are subject to the photoionization. In most cases of photoionization mass spectroscopic studies of the clusters, the photoionization is performed by using vacuum-UV light whose photon energy is sufficiently larger than the ionization potential

(IP) of AH. A large number of AH⁺ ions generated directly from AH, then, are indistinguishable from the same ionic species produced by the dissociation of the cluster ions if it occurs. Therefore, the identification of the dissociation process producing the unprotonated AH⁺ ion is quite difficult with this photoionization method.

In this paper, we report a photodissociation study of the cation of the hydrogen-bonded complex of phenol with ammonia under an isolated molecular condition prepared in a supersonic free expansion. We have employed the stepwise photoionization method using the two-color multiphoton ionization technique,[10] where the complex is initially excited to its first singlet S_1 excited state and subsequently photoionized to its cation state. Since the formation energy of the hydrogen bond of the complex in the S_1 state is generally different from that in the ground S_0 state, the $S_1 \leftarrow S_0$ excitation energy of the complex differs from the corresponding energy of other species. In the stepwise photoionization via the S_1 state, therefore, the selective ionization of the complex is allowed without ionizing other species which are included in the free expansion.

The complex of C₆H₅OH–NH₃ is a hydrogen-bonded heterodimer, whose cation may dissociate in one of three ways:

$$[C_6H_5OH-NH_3]^+ \rightarrow C_6H_5OH^+ + NH_3 \qquad (1)$$

$$\rightarrow C_6H_5O + NH_4^+ \qquad (2)$$

$$\rightarrow C_6H_5OH + NH_3^+ \qquad (3)$$
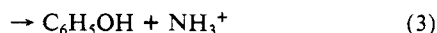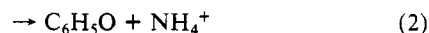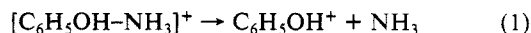
The purpose of this work is to find the major dissociation pathway of the dimer ion among the three dissociation channels above when we put excess energies into the dimer ion during the photoionization. Especially we are interested in the problem of whether the dissociation is accompanied by the proton transfer or not. In a previous work,[11] we reported a photodissociation study of the jet-cooled phenol–trimethylamine dimer ion, [C₆H₅OH–N(CH₃)₃]⁺, which was found to dissociate efficiently into C₆H₅O

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