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Authors
Hills, AJ
Cicerone, RJ
Calvert, JG
et al.

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

Alan J. Hills,*† Ralph J. Cicerone,† Jack G. Calvert,‡ and John W. Birks§

Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 449, University of Colorado, Boulder, Colorado 80309, and National Center for Atmospheric Research (NCAR), P.O. Box 3000, Boulder, Colorado 80307-3000 (Received: July 23, 1987; In Final Form: October 12, 1987)

We have measured the rate constant for the reactions BrO + CIO → Br + OCIO (6a), BrO + CIO → Br + Cl + O2 (6b), and BrO + CIO → BrCl + O2 (6c) over the temperature range 241–408 K and found \( k_6 = (8.2 ± 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) 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 CFC1, and CF2Cl1 can diffuse into the stratosphere and be photolyzed, releasing CI radicals. The photolysis will occur mainly in the 175–200-nm window that penetrates into the stratosphere between the intense absorption regions of O2 and O3. The released CI radicals can then engage in ozone destruction via the catalytic cycle

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]

(1)

\[
\text{ClO} + \text{O} \rightarrow \text{O}_2 + \text{Cl}
\]

(2)

net \( \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \) (3)

Molina and Rowland estimate that one CI atom could, on average, catalytically destroy up to 105 ozone molecules.

Recent papers4–6 dealing with atmospheric bromine indicate that bromine engages in catalytic ozone destruction cycles similar to those of chlorine

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2
\]

(4)

\[
\text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2
\]

(5)

net \( \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \) (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 \( \text{CH}_4 \) or \( \text{H}_2 \). The \( \text{Br} + \text{CH}_4 \) and \( \text{Br} + \text{H}_2 \) 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 O3 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:

\[
\text{BrO} + \text{CIO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2
\]

(6b)

\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2
\]

(4)

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]

(1)

net \( 2\text{O}_3 \rightarrow 3\text{O}_2 \) (3)

Yung et al.1 and others4–6 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 ClO and O + NO2 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 dynamical7 and chemical theories10–14 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, Br2 and Cl2 species are probably growing at similar rates. As Br2 and Cl2 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

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(4) Watson, R. T. The Natural Stratosphere of 1974; CIAP Monograph 1, DOT-TST-75-51, September 1975, Section 5.7.5.
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:

\[ \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO} \quad \Delta H^\circ_{298} = -2.4 \text{ kcal mol}^{-1} \]  
\[ \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \quad \Delta H^\circ_{298} = +1.5 \text{ kcal mol}^{-1} \]  
\[ \rightarrow \text{BrCl} + \text{O}_2 \quad \Delta H^\circ_{298} = -50.6 \text{ kcal mol}^{-1} \]

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 OCIO

\[ \text{Br}_{\text{excess}} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO} \]  

The kinetic behaviors of OCIO, 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 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\(^{19}\) has 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 was used to monitor the concentration of all the important molecules during each experiment. Detection limits (S/N = 2) for BrO, ClO, O3, NO2, OCIO, and BrCl were 1.5 \( \times 10^{11}, 6 \times 10^{10}, 2.5 \times 10^{10}, 1.5 \times 10^{11}, 1.2 \times 10^{10} \text{ molecules cm}^{-3} \), 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 NO2, were removed by passing it through a refrigerated line held at ~85 °C. Bromine was prepared by admitting pure Br2 vapor (from liquid Br2, >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% Br2/He mixtures.

Chlorine dioxide, OCIO, was prepared in real time for these experiments by passing a 10% Cl2/He flow (65 STP cm3/s) through a reactor containing sodium chlorite (NaC1O2, Matheson Chemical) held at >50 °C. In contrast to previous investigations, it was found that oxygen was not required for the production of OCIO. The source produced OCIO in 78% yield, as measured by loss of Cl2 at \( m/e 70 \), as the Cl2 flow was diverted over the sodium chlorite. Note: On two occasions the OCIO source exploded violently during OCIO 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 NaC1O2, obtained from lower in the sodium chlorite bottle, was placed into the source. Any use of the OCIO source should include blast shielding, as was done in this work.

Dichlorine monoxide, C12O, was prepared by passing a 10% Cl2/He flow (0.6 cm3/s) over a heated (=30 °C) bed of H2O (J. T. Baker). The yield of this source was ~50%. Nitrogen dioxide was prepared by reacting nitric oxide with oxygen. The NO2 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 N2O3 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 cm3 s⁻¹) and was used in real time in the kinetics experiments. The O2 to O3 conversion was typically 4%.

**C. Radical Production.** BrO and ClO were produced via microwave discharge of trace Br2 and Cl2 in He

\[ \text{Br}_2 \rightarrow 2\text{Br} \]  
\[ \text{Cl}_2 \rightarrow \text{Cl} \]  

followed by reaction with ozone

\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]  
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]
To determine whether the means of producing C10 influenced the experimental results, C10 was produced in two additional ways, by reaction of chlorine atoms with OClO and with C12O:

\[
\text{Cl + OClO} \rightarrow 2\text{ClO} \quad (9)
\]

\[
\text{Cl + C12O} \rightarrow \text{ClO} + \text{C12} \quad (10)
\]

**D. Calibrations.** Flow rates of the bulk carrier gas, He, and the stable reactant gases, O2, Cl2, Br2, 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 H2O). 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. NO2 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

\[
\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \quad (11)
\]

to substitute a stoichiometric amount of NO2 for O3. The NO2 thus formed was monitored at m/e 46. Dividing this ion current by the slope of an NO2 mass spectrometer signal vs [NO2] plot (Figure 2) yielded the initial concentration of ozone. NO2 calibrations were performed one or two times daily.

The concentrations of C10 and BrO radicals were measured analogously to that of ozone via the reactions

\[
\text{C1O + NO} \rightarrow \text{Cl + NO}_2 \quad (12)
\]

\[
\text{BrO + NO} \rightarrow \text{Br + NO}_2 \quad (13)
\]

A typical C1O \( \rightarrow \) NO2 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. nominal 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 C10 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 + OC10, was measured by first calibrating C10 relative to OC10. The reaction

\[
\text{OC10 + Cl} \rightarrow 2\text{ClO} \quad (14)
\]

was used in these calibrations. Ion currents at m/e 67 and 51 were monitored as the Cl2 discharge (Cl source) was turned on and off. The \( \Delta m/e \) 67 signal was directly proportional to [OC10] changes due to reaction 6. The \( \Delta m/e \) 51 signal was the result of both changes in [ClO] and [OC10] as the Cl source was modulated, because OC10 fragments, \( \approx \) 50%, into ClO. The m/e 51 signal was corrected for OC10 contribution by using the method of Birks et al.23 The branching ratio into channel 6a was measured by monitoring \( \Delta\text{OClO}/\Delta\text{ClO} \) as BrO was turned on and off. The BrO source was modulated either by turning the Br2 discharge on and off, or by leaving it on, but interrupting the flow of Br2 through the discharge.

The branching fraction into channel 6c, BrCl + O2 products, was measured similarly to that of (6a). The value \( \Delta\text{BrCl}/\Delta\text{ClO} \) 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 Br2 or excess O3, was added to a stream of chlorine atoms to produce equal amounts of BrCl or ClO, respectively, according to the reactions

\[
\text{Cl + Br}_2 \rightarrow \text{BrCl} + \text{Br} \quad (15)
\]

\[
\text{Cl + O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (1)
\]

The BrCl/ClO sensitivity ratio was determined over a range of concentration by varying the flow rate of Cl2 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 Br2 (reaction 15). The corresponding reaction of Br with Cl2 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 to not react with BrO, ClO, O3, or OC10, but exhibited a rapid reaction with atomic chlorine.

After it was established that channel 6c was inoperative, the fast secondary reaction of Cl with Br2 (reaction 15, \( k_{15} = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \)) allowed channel 6b to be quantified. By use of a sufficiently large concentration of Br2 (6 \( \times \) 1017 molecules cm-3), reaction 15 was forced to completion, and the branching

---

discrepancy is certainly within the experimental error of the.

invariant with temperature in the range 241-408 K. The 5%
change in BrO signal as a function of increasing BrO
reaction time. C10 levels at a negligible BrO injector surface loss. The lower plot shows the
of the BrO source.

Results
A. Overall Rate Constant. All of the kinetics measurements were made under pseudo-first-order conditions |ClO| >> [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 → products (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 → products (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

\[ k = k_6/|\text{ClO}| \] (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 II: Summary of Product Distribution Experiments

<table>
<thead>
<tr>
<th>T, K</th>
<th>no. of expts</th>
<th>reaction no.</th>
<th>reaction products</th>
<th>branching ratio (±σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>18</td>
<td>6a</td>
<td>Br + OCIO</td>
<td>0.53 ± 0.04</td>
</tr>
<tr>
<td>241</td>
<td>7</td>
<td>6a</td>
<td>Br + OCIO</td>
<td>0.50 ± 0.01</td>
</tr>
<tr>
<td>305</td>
<td>9</td>
<td>6b</td>
<td>Br + Cl + O₂</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>241</td>
<td>10</td>
<td>6b</td>
<td>Br + Cl + O₂</td>
<td>0.42 ± 0.05</td>
</tr>
<tr>
<td>305</td>
<td>4</td>
<td>6c</td>
<td>BrCl + O₂</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Pressure range 1.25-1.59 Torr. * Error shown is one standard deviation (precision only). Average value = (8.2 ± 1.0) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ where the uncertainty corresponds to the 95% confidence level and includes both random and possible systematic errors.

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 cm³ 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 (±2%), pressure (±2%), ClO source chemistry (±3%), reaction distance (±3%), and ClO concentration (±10%). These errors yield a total systematic uncertainty of ±13%. 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 cm³ 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 cm³ molecule⁻¹ s⁻¹ for \( k_6 \). This is 45% smaller than the value of 6.7 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ measured by Clyne and Watson and used in recent model calculations. 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 cm³ molecule⁻¹ s⁻¹)

\[
\begin{align*}
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \quad (1.1 \times 10^{-12}) \\
\text{BrO} + \text{BrO} & \rightarrow \text{2Br} + \text{O}_2 \quad (2.3 \times 10^{-12}) \\
\text{BrO} + \text{BrO} & \rightarrow \text{Br}_2 + \text{O}_2 \quad (4.4 \times 10^{-13}) \\
\text{ClO} + \text{ClO} & \rightarrow \text{2Cl} + \text{O}_2 \quad (2.4 \times 10^{-14}) \\
\text{Br} + \text{OCIO} & \rightarrow \text{BrO} + \text{ClO} \quad (4.2 \times 10^{-12}) \\
\text{Cl} + \text{BrO} & \rightarrow \text{BrCl} + \text{O} \quad (2 \times 10^{-10}) \\
\text{Cl} + \text{Br}_2 & \rightarrow \text{BrCl} + \text{Br} \quad (1.9 \times 10^{-10})
\end{align*}
\]

Reactions 4, 18, 20, and 21 represent possible chemical complications, interfering 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 $k_{5}$, 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 $k_{1} < 2.2$ 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 $\times$ 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, the actual ClO entering the reaction zone was always measured with the calibrated mass spectrometer. Rate constant 5 of reformation of BrO in the reaction zone, since [Br] < 0.1$\times$ 10$^{12}$ 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], $\approx 5 \times 10^{12}$ molecules cm$^{-3}$, and (b) the presence of Br2 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 used the technique of low-pressure discharge-flow mass spectrometry (DF-MS). Like Basco and Dogra's study, however, Clyne and Watson's study was not a direct measurement of the rate constant for the reaction BrO + ClO $\rightarrow$ products. Their chemical system involved at least six reactions occurring simultaneously. The rate constants, $k_{6a}$ and $k_{obs}$, were extracted separately from an analysis of the fairly complex chemical scheme shown below. ClO and BrO were produced simultaneously by the reaction

$$\text{BrO}_{\text{excess}} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO} \quad (\text{-6a})$$

The subsequent chemical profiles of BrO, ClO and OCIO were monitored by using mass spectrometry. Besides the source reaction, the following reactions were observed in this system:

$$\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + O_{2} \quad (\text{18})$$
$$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + O_{2} \quad (\text{6a})$$
$$\rightarrow \text{BrCl} + O_{2} \quad (\text{6b})$$
$$\rightarrow \text{BrCl} + O_{2} \quad (\text{6c})$$

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 the 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 $[-\text{ClO}]^{-1} \text{d in } [\text{BrO}] / \text{dt}$ was measured and was interpreted as the rate constant to channels 6b + 6c. Two large corrections were applied to the raw $-\text{d in } [\text{BrO}] / \text{dt}$ value in order to arrive at a rate coefficient. The first of these dealt with the radical producing reaction

$$\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO} \quad (\text{-6a})$$

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 $-\text{d in } [\text{BrO}] / \text{dt}$ for each experiment by 10-44%. A second interfering reaction in this study was the bimolecular disproportionation reaction

$$\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + O_{2} \quad (\text{18})$$

$k_{18} = 2.7 \times 10^{12}$, $k_{18}$ Since the BrO concentration was appreciable, reaction 18 contributed to the observed BrO decay. Therefore a second correction had to be applied to $-\text{d in } [\text{BrO}] / \text{dt}$. 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, ~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 the 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, $k_{6a} = k_{6a} + k_{obs}$ was not measured due to the interfering reactant source chemistry. Because atomic Br in large amounts ($\approx 10^{12}$ 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 OCIO 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, OCIO, BrO, and ClO, to calculate $k_{6a}$ from

$$k_{6a} = \frac{[\text{BrO}][\text{OCIO}]}{[\text{BrO}][\text{ClO}]} k_{-6a} \quad (\text{22})$$

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 $k_{6a} = 1.34 \times 10^{-11}$ 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 $k_{6a} = 2.5 \times 10^{-12}$ cm$^{3}$ molecule$^{-1}$ s$^{-1}$ is much lower than Clyne and Watson's. Clyne and Watson cleverly selected a time regime for extracting $k_{6a}$. The decay of BrO in this time interval was complicated, however, by reaction -6a which regenerated BrO and by the transient 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 some of the recent observations of OCIO in this region of the atmosphere. In general, our results show that the reaction between ClO and BrO is indeed fast, although somewhat slower than originally considered. Our laboratory results are consistent with the theory that both ClO and BrO radicals are present there, and (2) it could possibly explain some of the recent observations of OCIO in this region of the atmosphere.

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Photodissociation of the Hydrogen-Bonded Heterodimer Ion \([\text{C}_6\text{H}_5\text{OH} - \text{NH}_3]^+\)

Naohiko Mikami,∗ Akihiro Okabe, and Itaru Suzuki

(Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan)

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Photodissociation of the hydrogen-bonded heterodimer ion \([\text{C}_6\text{H}_5\text{OH} - \text{NH}_3]^+\) has been studied following the selective photopionization of the jet-cooled dimer via its \(S_1\) state by using two-color multiphoton ionization technique. From the mass-selected photopionization yield spectrum for generation of the dimer ion, the adiabatic ionization potential of \(\text{C}_6\text{H}_5\text{OH} - \text{NH}_3\) was found to be \(62200 \pm 100 \text{ cm}^{-1}\) (ca. 7.71 eV). It was found that the fragment ion \(\text{C}_6\text{H}_5\text{OH}^+\) is generated by the photopionization of the dimer with the ionization energy higher than a threshold at \(70400 \text{ cm}^{-1}\), whereas only the dimer ion is generated with the photopionization energy lower than the threshold. Dissociation energy of the dimer ion due to \([\text{C}_6\text{H}_5\text{OH} - \text{NH}_3]^+ - \text{C}_6\text{H}_5\text{OH}^+ + \text{NH}_3\) was found to be \(8200 \pm 150 \text{ cm}^{-1}\). No \(\text{NH}_4^+\) production was found even when the photopionization energy exceeded the expected threshold for the \(\text{NH}_4^+\) 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, \([\text{AH}]_2^+\), is expected to occur in two ways: one is to generate the protonated fragment ion \(\text{AH}^+\) and the other produces the unprotonated fragment ion \(\text{AH}^+\). Both fragment ions are frequently observed in photoionization mass spectroscopic studies of the hydrogen-bonded clusters. These extensive studies show that the protonated cation is originated from the photoionized clusters. The photodissociation 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. 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 \(\text{AH}\) 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 \(\text{AH}^+\) 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 \(\text{AH}^+\) 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, 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 \(S_1 - S_0\) 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 \(\text{C}_6\text{H}_5\text{OH} - \text{NH}_3\) is a hydrogen-bonded heterodimer, whose cation may dissociate in one of three ways:

\[
\begin{align*}
\text{[C}_6\text{H}_5\text{OH} - \text{NH}_3]^+ \rightarrow & \text{C}_6\text{H}_5\text{OH}^+ + \text{NH}_3 \quad (1) \\
& \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{NH}_4^+ \quad (2) \\
& \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{NH}_3^+ \quad (3)
\end{align*}
\]

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, we reported a photodissociation study of the jet-cooled phenol–trimethylamine dimer ion, \([\text{C}_6\text{H}_5\text{OH} - (\text{CH}_3)_3]^+\), which was found to dissociate efficiently into \(\text{C}_6\text{H}_5\text{OH}^+