Identification of BrONO as the Major Product in the Gas-Phase Reaction of Br with NO_2

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Products of the gas-phase reaction of Br atoms with NO_2 have been quantitatively determined at temperatures between 215 and 300 K in an environmental chamber interfaced to an FT-IR spectrometer. The major product of the reaction (yield > 75%) was found to be the cis isomer of BrONO, which was identified and quantified by means of its N═O stretching fundamental at 1660 cm^{-1}; this represents the first gas-phase detection of this species. Although rapid thermal decomposition back to Br and NO_2 precludes its detection at room temperature (lifetime < 1 s), BrONO was detected at temperatures at and below 263 K. Isomerization of the BrONO to $BrNO_2$ was found to be an important fate of BrONO at low temperatures. The rate coefficient for this process was found to increase with decreasing pressure, indicative of a heterogeneous process. At 700 Torr, this isomerization rate was $(0.013 \pm 0.003)\ s^{-1}$, independent of temperature over the range 218−243 K. Evidence was also obtained for rapid reactions between Br atoms and both BrONO and $BrNO_2$ ($10^{-10} > k > 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$).

Introduction

Termolecular reactions between halogen atoms and NO_2 have received a great deal of attention,[1−18] both out of fundamental interest and because of their potential importance in the atmosphere. The reaction of Br atoms with NO_2 has been studied in cryogenic matrixes[1,2] and in the gas phase.[3−5] By analogy to the reactions of other halogens with NO_2, the products of the reaction are expected to be BrONO (cis and/or trans isomers) and/or $BrNO_2$:

$$Br + NO_2 + M \rightarrow BrONO + M \quad (1a)$$

$$\rightarrow BrNO_2 + M \quad (1b)$$

In the study of Tevault,[1] $BrNO_2$ was the major product identified from the co-condensation of Br atoms and NO_2 in an Ar matrix, while a similar study by Feuerhahn et al.[2] appears to have led to the production of both $BrNO_2$ and *trans*-BrONO. Early gas-phase studies[3,4] focused on the rate coefficient of the Br + NO_2 reaction, and reaction products were not determined. However, Kreutter et al.[4] observed that the reaction product (believed at the time to be $BrNO_2$, but now thought to be BrONO, see below) was thermally unstable, and that the reverse of reaction 1 occurred with a time constant of order a few milliseconds near 400 K.

Further interest[5,19−25] in the thermodynamics, spectroscopy, and chemistry of $BrNO_2$ has been stimulated, at least in part, by the observation that this species, in addition to being a product of reaction 1, is also a product of some heterogeneous reactions of importance in the Earth's troposphere[19] and stratosphere.[26]

$$N_2O_5(g) + NaBr(s) \rightarrow BrNO_2(g) + NaNO_3(s) \quad (2)$$

$$N_2O_5(g) + HBr(s) \rightarrow BrNO_2(g) + HNO_3(s) \quad (3)$$

Computational studies[21] have shown that $BrNO_2$ is more stable (Br−N bond strength at 298 K of 22.5 kcal/mol) than either the *cis*- or *trans*-BrONO isomer (Br−O bond strengths at 298 K of 16.1 and 12.2 kcal/mol, respectively), but that *cis*-BrONO is sufficiently thermally stable to exist in the atmosphere. Furthermore, the thermal lifetime of $BrNO_2$ has been shown[5,23] to be of order 1 h at room temperature, considerably longer than the predicted[27] lifetime of the Br + NO_2 reaction product observed (indirectly) by Kreutter et al.[4] Thus, it is now believed[5,23] that, although BrONO has yet to be observed in the gas phase, it is the major product of reaction 1 and has eluded detection largely due to its thermal instability (lifetime likely of order 1 s or less near room temperature).[27] By analogy to the ClONO/$ClNO_2$ system,[9,10] the isomerization of BrONO to $BrNO_2$, reaction 4, may also play a role in the inability to detect this species:

$$BrONO + M \rightarrow BrNO_2 + M \quad (4)$$

In this work, products of the reaction of Br with NO_2 were studied by infrared spectroscopy over the range 215−300 K in a static reaction chamber. BrONO was indeed observed at temperatures below ambient, and is shown to be the major product of reaction 1. In addition, rate coefficients for its isomerization and thermal decomposition and for the reaction of Br atoms wtih both BrONO and $BrNO_2$ are estimated over the temperature range studied.

Experimental Section

Experiments were conducted in a temperature-regulated stainless steel reaction chamber, described in detail previ-

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ously.[28,29] The chamber is 2 m long, with a volume of 47 L, and is interfaced via a set of Hanst-type optics to a Bomem DA3.01 Fourier Transform Spectrometer. The analyzing path length for these measurements was 32.6 m, and spectra were recorded over the range 800−3900 cm^{-1} with a resolution of 1 cm^{-1}. Spectra were obtained from the co-addition of 8−50 interferograms and required 10−60 s total acquisition time. The temperature of the cell was controlled by flowing chilled ethanol from a circulating bath through a jacket surrounding the cell.

Experiments involved the cw photolysis of static mixtures of Br_2 (typically about 2.5×10^{14} molecule cm^{-3}, but varied from $(1-10) \times 10^{14}$ molecule cm^{-3}) and NO_2 ($5-70 \times 10^{14}$ molecule cm^{-3}) in N_2 (700 Torr). At low temperatures, N_2O_4 was also present in some experiments ($[N_2O_4] \leq 7 \times 10^{13}$ molecule cm^{-3}); its presence had no effect on the measurements. Br_2 and NO_2 were swept into the photolysis chamber from calibrated volumes; pressure measurements in the calibrated volumes were used to determine the initial $[Br_2]$ and $[NO_2]$. The photolysis light source was a cw Xe arc lamp, equipped with a water-cooled filter to provide radiation at $\lambda > 410$ nm such that Br_2 was efficiently photolyzed (with a first-order rate coefficient of $(2.2 \pm 0.4) \times 10^{-3}$ s^{-1}), but photolysis of NO_2 did not occur to any measurable extent (photolysis rate coefficient $<2 \times 10^{-5}$ s^{-1}). The Br_2 photolysis rate was measured periodically by monitoring the decay of HCHO in a $Br_2/HCHO/O_2/N_2$ photolysis experiment.

The Br_2 used in these experiments was purchased from Aldrich, and purified by several freeze−pump−thaw cycles before use. NO_2 was synthesized from the addition of excess O_2 to NO (Linde, UHP), followed by removal of the O_2 by pumping at liquid nitrogen temperature. N_2 was obtained from the boil-off from a liquid N_2 dewar (U.S. Welding).

Results and Discussion

Experimental Results. Experiments involved monitoring the temporal profile of NO_2 and reaction products both during and following the photolysis of mixtures of Br_2 ($1-10 \times 10^{14}$ molecule cm^{-3}) and NO_2 ($0.5-10 \times 10^{14}$ molecule cm^{-3}) in 700 Torr N_2. Initial experiments were conducted at relatively low temperature (228 K) and high total pressure (1 atm), since it was thought that these conditions would be optimum for detection of BrONO. Experiments were also conducted at 218, 248, 263, and 298 K. The results discussed below apply to the 228 K experiments unless otherwise specified.

At 228 K, thermal dissociation of both BrONO and $BrNO_2$

$$BrONO + M \rightarrow Br + NO_2 + M \qquad (-1a)$$

$$BrNO_2 + M \rightarrow Br + NO_2 + M \qquad (-1b)$$

should be negligibly slow,[4,5,27] and the chemistry should be controlled by the formation of BrONO and $BrNO_2$ (reaction 1), the possible isomerization of BrONO to $BrNO_2$ (reaction 4), and by the destruction of the BrONO and $BrNO_2$ species by reaction with Br atoms:[3,5]

$$Br + BrNO_2 \rightarrow Br_2 + NO_2 \qquad (5)$$

$$Br + BrONO \rightarrow Br_2 + NO_2 \qquad (6)$$

Photolysis of the $Br_2/NO_2/N_2$ mixtures resulted in the appearance of two new absorption features, one centered at 1294 cm^{-1} and the other occurring in the region around 1665 cm^{-1}. The intensity of these absorption features increased over the first minute or two of photolysis and then reached a steady-state value, which was maintained for many minutes. A product spectrum obtained at 228 K from the photolysis of Br_2 (2.6×10^{14} molecule cm^{-3}) in the presence of NO_2 (9.2×10^{13} molecule cm^{-3}) in 700 Torr N_2, after steady-state is achieved is shown in Figure 1a (the strong NO_2 absorption centered at 1616 cm^{-1} has been subtracted for clarity). Absorptions of $BrNO_2$ are expected at 1292−1294 and 1667 cm^{-1},[19−23] and clearly this species is present in the product spectrum, as expected.[5] However, close inspection of the feature around 1665 cm^{-1} shows it to be slightly different in location and shape from previously published $BrNO_2$ spectra, and the possibility of the presence of another absorber must be considered. The most likely possibility is the cis isomer of BrONO, which has not previously been observed in the gas phase, but for which an N=O stretching frequency of 1664 cm^{-1} has been calculated.[21] This species has also recently been observed in a matrix-isolation study.[25]

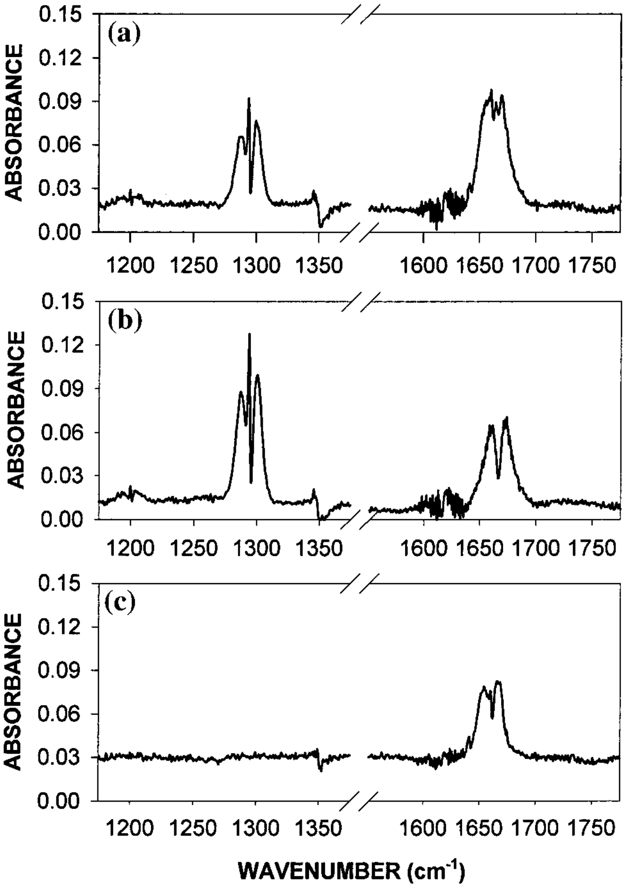

Figure 1. (a) Spectrum recorded following the photolysis of a mixture of Br_2 (2.6×10^{14} molecule cm^{-3}), NO_2 (9.2×10^{13} molecule cm^{-3}), and N_2 (700 Torr) at 228 K. The NO_2 absorption centered at 1616 cm^{-1} has been subtracted for clarity. (b) Spectrum recorded following the dark decay of the gas mixture shown in (a). (c) Residual spectrum obtained by subtraction of the $BrNO_2$ features from the spectrum of (a). This residual spectrum is assigned to *cis*-BrONO, see text for details.

A possible means of confirming the presence of *cis*-BrONO is via the observation of its isomerization to the more stable[21] $BrNO_2$ (reaction 4), a process which is expected on the basis of similar observations in the ClONO/$ClNO_2$ system.[9,10] Thus, following the acquisition of spectra such as that shown in Figure 1a, the photolysis lamp was blocked and the behavior of the gas mixture was monitored for a few minutes. The spectrum shown in Figure 1b, obtained approximately 5 min after cessation of photolysis of the same gas mixture shown in Figure 1a, shows an increase in absorption in the 1294 cm^{-1} band and a change in shape and intensity of the band(s) near 1665 cm^{-1}. This spectrum now corresponds identically with that of $BrNO_2$,[19-23] and clearly indicates that (at least) two species were present initially. Subtraction of the contribution of $BrNO_2$ from the spectrum of Figure 1a (using the spectrum of Figure 1b, from an examination of the 1294 cm^{-1} band) yields the spectrum shown in Figure 1c. Based on a reasonable analysis of the chemistry occurring in the system and the close correspondence of the observed band center with that predicted,[21] we assign this residual absorption feature, centered at 1660 cm^{-1}, to *cis*-BrONO. Further evidence for the assignment of the spectrum of Figure 1c to *cis*-BrONO is obtained from the work of Scheffler et al.,[22,25] who photolyzed $BrNO_2$ in a matrix and reported the conversion of the $BrNO_2$ to BrONO. Although only *trans*-BrONO was thought to be present initially,[22] further work[25] proved the existence of *cis*-BrONO as well, and the existence of the ν_1 fundamental near 1650 cm^{-1} was confirmed.

There is no evidence for the presence of the *trans*-BrONO species (N═O stretching frequency 1725 cm^{-1}) in any of our gas-phase spectra. Lee[21] has calculated a difference in energy between the cis and trans isomers of 3.7 kcal/mol, meaning that the cis isomer would be favored by a factor of 500 at equilibrium. Thus, although the trans isomer may also be formed initially in reaction 1, it seems reasonable to assume that rapid interconversion of the two isomers is possible, thus explaining the absence of the trans isomer in the observed spectra. Similar energy differences have been calculated for the *cis*- and *trans*-ClONO isomers,[12] and only the cis species is observed in this case as well.[9,10]

The data of Figure 1 can be used to estimate the IR absorption cross sections for both $BrNO_2$ and *cis*-BrONO, by means of mass balance arguments (i.e., by assuming that the loss of NO_2 in a given $Br_2/NO_2/N_2$ photolysis experiment is always equal to the sum of the $BrNO_2$ and BrONO present), and by assuming a 1:1 conversion of BrONO to $BrNO_2$ following the cessation of photolysis. The determination of the absorption cross sections for $BrNO_2$ can be made by equating the final $BrNO_2$ concentration after the dark decay period (i.e., after total conversion of BrONO to $BrNO_2$) with the change in the NO_2 concentration from the beginning to the end of the experiment. Multiple experiments, conducted over a range of Br_2 and NO_2 concentrations at 228 K, yielded absorption cross sections of 2.0, 3.0, and 2.3×10^{-18} cm^2 $molecule^{-1}$ for the peaks of the P, Q, and R branches near 1294 cm^{-1}, and 1.5 and 1.7×10^{-18} cm^2 $molecule^{-1}$ for the peaks of the P and R branches near 1667 cm^{-1}, with uncertainties (including precision and possible systematic uncertainties) for all values of ±20%. Integrated band intensities were also obtained, and were found to be $(4.3 \pm 0.6) \times 10^{-17}$ cm^2 $molecule^{-1}$ cm^{-1} and $(3.7 \pm 0.5) \times 10^{-17}$ cm^2 $molecule^{-1}$ cm^{-1} for the 1296 and 1667 cm^{-1} bands, respectively.

Gas-phase IR absorption cross sections for $BrNO_2$ have previously been reported by Frenzel et al.[20] and Scheffler et al.,[22] who generated $BrNO_2$ from the reaction of gas-phase $ClNO_2$ with Br^- ions. Our measured peak absorption cross sections appear to be about 10% higher than the room-temperature absorption cross sections reported by Frenzel et al.,[20] and about 20% higher than the low resolution spectrum of Scheffler et al.[22] The higher values obtained in our work are likely due, at least in part, to the lower temperature employed herein compared with the previous work. Integrated absorption intensities are not reported in these previous studies for comparison. The integrated absorption intensities reported for both absorption bands in the ab initio study of Lee[21] are 50% higher than the values obtained in our work.

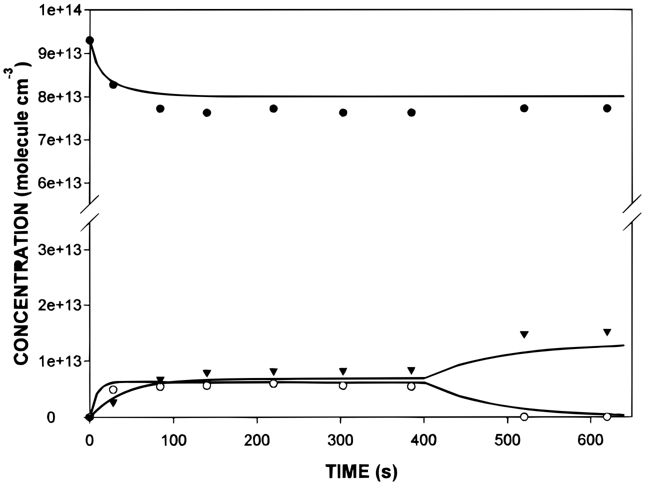

Figure 2. Time profile of the concentrations of NO_2 (solid circles), $BrNO_2$ (inverted triangles), and BrONO (open circles) following the photolysis (0−380 s) and subsequent dark decay (380−620 s) of a mixture of Br_2 (2.6×10^{14} molecule cm^{-3}), NO_2 (9.2×10^{13} molecule cm^{-3}), and N_2 (700 Torr) at 228 K. Solid lines represent model calculations, using the rate coefficients given in the text.

Absorption cross sections for BrONO were then obtained from an analysis of the dark decay period in the 228 K experiments, in which the isomerization of the BrONO to $BrNO_2$ occurred. Assuming 1:1 interconversion, an absorption cross section of $(1.7 \pm 0.6) \times 10^{-18}$ cm^2 $molecule^{-1}$ at the peak of the P and R branches near 1660 cm^{-1} is obtained for BrONO with an integrated band intensity of $(3.7 \pm 1.3) \times 10^{-17}$ cm^2 $molecule^{-1}$. Strictly, these values should be treated as upper limits, since it is possible that the BrONO is not stoichiometrically converted to $BrNO_2$. However, no significant change in $[NO_2]$ was noted during the dark decay period in almost all experiments carried out at 228 K and no other species were detected, indicating the likelihood of near-stoichiometric conversion. Furthermore, the agreement between our $BrNO_2$ absorption cross sections and previous values also argues against significant loss of BrONO to other than $BrNO_2$. Thermal dissociation can be ruled out as a loss process for BrONO at 228 K from a consideration of the available data on its thermal properties.[4,27] Although no previous observations are available for comparison, the cross section value reported here for the BrONO absorption feature is broadly consistent with the findings of Lee,[21] who calculated the integrated band strength of the 1660 cm^{-1} band in *cis*-BrONO to be 4.2×10^{-17} cm^2 $molecule^{-1}$. In addition, the corresponding bands in $ClNO_2$ and ClONO appear to be of very similar intensities to each other,[9,10] and to their bromine-containing counterparts.

With the determination of the absorption cross sections for both the $BrNO_2$ and BrONO species, full concentration versus time profiles for these species during the light and dark phase of an experiment can be obtained, as shown in Figure 2. A number of conclusions can be drawn from these data. Most importantly, it is apparent that BrONO is the major product of reaction 1, as can be seen from the product yields observed at the onset of photolysis. In the first data point of Figure 2, the concentration of BrONO exceeds that of $BrNO_2$ by a factor of 2. Because of the rapid reaction of both species with Br atoms (with k_6 probably greater than k_5, see later) and because of the isomerization of BrONO to $BrNO_2$, our experiments do not provide sufficient time resolution to directly measure the initial $[BrONO]/[BrNO_2]$ ratio. Additional experiments were conducted, at temperatures of 218, 228, and 248 K, in which spectra

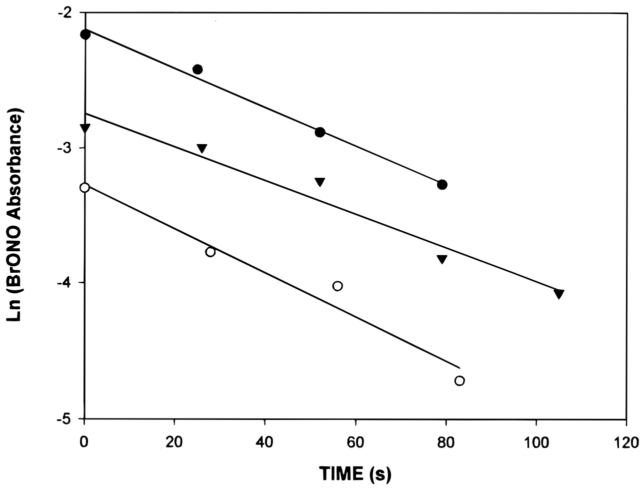

Figure 3. Sample plots of ln(BrONO absorbance) vs time in the dark under a variety of conditions, to obtain the first-order rate of BrONO isomerization to $BrNO_2$. Filled triangles: 216 K, 700 Torr total pressure, $[NO_2]_o = 3.6 \times 10^{14}$ molecule cm^{-3}, $k_4 = 0.012$ s^{-1}; open circles: 228 K, 700 Torr total pressure, $[NO_2]_o = 1.2 \times 10^{14}$ molecule cm^{-3}, $k_4 = 0.016$ s^{-1}; filled circles: 228 K, 700 Torr total pressure, $[NO_2]_o = 7.5 \times 10^{14}$ molecule cm^{-3}, $k_4 = 0.014$ s^{-1}.

were acquired as early as possible (over the first 10 s) following the start of the photolysis. In all cases, [BrONO] exceeded $[BrNO_2]$, usually by a factor of 3 or 4, very similar to observations made in studies of the reaction of Cl with NO_2.[9,10,30] Thus, BrONO must account for at least 75% of the reaction product at these temperatures. However, modeling studies (using the measured Br_2 photolysis rate and estimated values for k_4, k_5, and k_6, see details below) indicate that some $BrNO_2$ (probably about 5−20%) is very likely formed directly in reaction 1, since the isomerization of BrONO to $BrNO_2$ is too slow to account for all of the $BrNO_2$ observed early in the photolysis period. This point will be discussed in more detail later.

Data such as those shown in Figure 2 can also be used to determine approximate rate coefficients for reactions 4−6. Values for k_4 were determined by monitoring the conversion of BrONO to $BrNO_2$ during the dark period over a range of conditions (see Figure 3). At 228 K, the isomerization rate coefficient, k_4, was found to increase with decreasing pressure, from a value of 0.011 ± 0.003 s^{-1} at 1000 Torr to 0.023 ± 0.003 s^{-1} at 150 Torr. This inverse pressure dependence provides strong evidence for the influence of the cell walls in the isomerization process. The isomerization rate was found to be independent of the NO_2 concentration (varied from 6×10^{13} to 60×10^{13} molecule cm^{-3}), and N_2O_4 concentration (from $< 1 \times 10^{13}$ to 7×10^{13} molecule cm^{-3}). Isomerization rates at 218 K were similar to those found at 228 K. Studies at higher temperature do not provide clean measurements of k_4 due to the increased importance of thermal dissociation of BrONO (reaction −1a), but no large change in the isomerization rate coefficient was evident at 248 K. Isomerization of ClONO to $ClNO_2$ has also been reported to be influenced by heterogeneous processes.[9,10]

Rate coefficients for reactions 5 and 6 could then be estimated by examining the steady-state levels of $BrNO_2$ and BrONO, using a box model (run with the Acuchem software package[31]) to simulate the reaction system. For the low-temperature experiments ($T = 218$ and 228 K), thermal decomposition of BrONO and $BrNO_2$, reactions (−1a) and (−1b), are both sufficiently slow to be ignored. Thus, the model consisted of only the photolysis of Br_2 ($k = 2.2 \times 10^{-3}$ s^{-1}, measured by monitoring the disappearance of CH_2O in the photolysis of $Br_2/CH_2O/O_2/N_2$ mixtures), and reactions 1, 4, 5, and 6. The total k_1 was obtained from previously published data,[3,4] and the value of k_4 was fixed to the 700 Torr value of 0.013 s^{-1} determined above. The branching ratio for k_1, and the values for k_5 and k_6 were then varied to achieve the best fit to a number of experiments obtained over a range of temperatures and $[NO_2]_o$. Averages of these fitted rate coefficient data are as follows: $k_{1a}/k_1 = 0.85 \pm 0.08$, $k_6 = (7 \pm 3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and $k_5 = (3 \pm 2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. A fit to a single experiment using these rate coefficients is shown in Figure 2. Previous estimates[3,5] of k_5 and k_6 are in reasonable accord with our results. In the flow tube study of Mellouki et al.[3], the product of reaction 1, probably BrONO, was found to react with Br with a rate coefficient of order $10^{-11}-10^{-10}$, while Broske and Zabel used a value for k_5 of 2.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} to model their $BrNO_2$ temporal profiles in room-temperature Br_2/NO_2 static photolysis experiments. It should be stressed that the rate coefficients and branching values determined above are estimates only, since their values are somewhat dependent on each other. More accurate values for the branching ratio to reaction 1 will require experiments conducted with a better time resolution than is possible with the FT-IR system used here. Direct measurements of k_5 would also be useful in better quantifying the rate parameters describing this chemical system.

At higher temperatures (248, 263, and 298 K), the steady-state [BrONO] was significantly reduced compared to lower temperature measurements under similar conditions, and, in fact, no BrONO was observed at all at 298 K. This observation is very likely the result of the increasing importance of thermal decomposition (reaction −1a) of the BrONO with increasing temperature. Modeling studies (with rate parameters fixed at the central values reported above) indicated that the thermal decomposition of BrONO was occurring with a rate coefficient $k_{-1a} \approx 0.02$ s^{-1} at 248 K, $k_{-1a} \approx 0.1$ s^{-1} at 263 K, and $k_{-1a} \geq 2$ s^{-1} at 298 K. Again, these k_{-1a} values should be considered only as estimates, given that they depend on the actual values of k_5, k_6, and k_{1a}/k_{1b}, which are quite uncertain and could vary with temperature, but are quite consistent with values obtained from an extrapolation[27] of the data of Kreutter et al.[4]

The lack of the observation of BrONO at room temperature is consistent with a previous study[5] of this reaction system. However, the observation of $BrNO_2$ in our room temperature experiments and in those conducted previously[5] provides the strongest evidence for its direct production (albeit in low yield) from reaction 1. With isomerization of BrONO considerably slower than its thermal decomposition (by about a factor of 100, based on the Kreutter et al.[4] thermal decomposition data), $BrNO_2$ formation via this process is quite inefficient and, without direct formation of $BrNO_2$ from reaction 1, steady-state levels of $BrNO_2$ would be smaller than observed. We estimate that at least a 6% branch to $BrNO_2$ formation is required to explain the observed $BrNO_2$ levels, with a most likely value of about 15%. This point was originally made by Broske and Zabel,[5] who used the rate of approach to steady-state in the photolysis of Br_2/NO_2 mixtures at 298 K to estimate k_{1a}/k_{1b}. With reasonable assumptions about the values for k_5 and k_6 and a knowledge of their Br_2 photolysis rate, they showed that the approach to steady-state was about 10 times slower than expected, based on measured values[3,4] of the total k_1. They then reasoned that BrONO thermal decomposition was sufficiently rapid that they were only observing k_{1b}, which then must account for about 10% of the total reaction.

Reevaluation of Thermodynamic and Theoretical Aspects of k_1. Based on the evidence available at that time, Kreutter et al.[4] assumed that $BrNO_2$ was the major product of reaction 1; this fact was then used in both a "third law" analysis of the equilibrium constant for reactions 1 and -1 and in RRKM-based calculations of the strong-collision rate coefficient for reaction 1, k_o^{SC}. With our present knowledge that BrONO is the major product of reaction 1, and with the availability of high-level ab initio thermochemical and spectroscopic data for $BrNO_2$ and the cis and trans isomers of BrONO,[21] we thought it worthwhile to re-consider the calculations of Kreutter et al.[4]

Kreutter et al.[4] conducted both a "second law" and "third law" analysis of their data on the equilibrium system involving reactions 1 and -1, and found that the derived ΔH and ΔS values were only in fair agreement. With the assumption that *cis*-BrONO is the major product of reaction 1, and using a value for S(BrONO) calculated using the spectroscopic data of Lee,[21] a reevaluation of the third law calculation of Kreutter et al. leads to values of $\Delta S(401\ \text{K}) = -30.5$ cal/mole/K and $\Delta H(401\ \text{K}) = -20.07$ kcal/mol, in somewhat better agreement with their original second law data. Averaging the original second law values with the revised third law data gives $\Delta S(401\ \text{K}) = -28.5$ cal/mol/K and $\Delta H(401\ \text{K}) = -19.35$ kcal/mol. In fact, because the calculated entropies for $BrNO_2$ and *cis*-BrONO are quite similar using current[21] spectroscopic and structural information, the third law values are not strongly dependent on the products of reaction 1.

Finally, Kreutter et al.[4] calculated the low-pressure limiting value for reaction 1 in the "strong collision" limit, k_o^{SC}, using methods developed by Troe.[32-34] Typically, k_o^{SC} exceeds measured values of k_o in N_2 by about a factor of 3.[34] Kreutter et al. showed that the calculated k_o^{SC} for reaction 1, 2.0×10^{-31} cm^6 molecule^{-2} s^{-1}, was in fact considerably smaller than the measured value, 4.6×10^{-31} cm^6 molecule^{-2} s^{-1}, and suggested the possibility of BrONO formation or the involvement of excited states of $BrNO_2$ in the reaction. We have recalculated the k_o^{SC} for reaction 1, including the formation of $BrNO_2$ and *cis*- and *trans*-BrONO. For these calculations, the Lennard–Jones parameters of Kreutter et al. were used in conjunction with vibrational frequencies, rotational constants, and critical energies from Lee.[21] Values of k_o^{SC} for $BrNO_2$, *cis*-BrONO, and *trans*-BrONO (all in units of 10^{-31} cm^6 molecule^{-2} s^{-1}) of 2.1, 1.3, and 0.6 are obtained, which gives total k_o^{SC} of 4.0×10^{-31} cm^6 molecule^{-2} s^{-1}, still below the measured value of 4.6×10^{-31} cm^6 molecule^{-2} s^{-1} and well below the expected value (defined as about 3 times the measured k_o)[34] of $k_o^{SC} \approx 13 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}. Thus, the full consideration of all isomers does improve the agreement between measured and caluculated k_o values, but is still not sufficient to bring the calculations into accord with the measured values of k_o.

Atmospheric Significance. The BrONO and $BrNO_2$ species likely play only a minor role in atmospheric chemistry, since under most conditions they will photolyze rapidly,[22] and thus act as only temporary reservoirs for bromine. Nonetheless, it is at least of some interest to consider the fate of these species in the atmosphere following their formation from reaction 1 or, in the case of $BrNO_2$, from heterogeneous chemical reactions. At temperatures near 300 K (for example, in the low- to mid-latitude marine boundary layer where halogen chemistry may be of importance), BrONO loss will be dominated by thermal decomposition (lifetime < 1 s).[4,27] In fact, because of the instability of BrONO at these temperatures and because it is the major product of reaction 1, the effective rate coefficient for reaction 1 will be reduced by a factor of 4 or more from the measured[4] and currently recommended[35] value. In colder regions (in the lower stratosphere, or in polar surface ozone depletion events where Br chemistry is known to play a role[36]), the BrONO loss will be controlled either by its isomerization to $BrNO_2$ (if this process occurs in the gas phase) or by photolysis. Preliminary results[37] suggest a photolysis time constant of <30 s for BrONO. The enhanced thermal stability of BrONO means that the effective rate coefficient for reaction 1 will be equal to the measured[4] values at these lower temperatures. The dominant atmospheric loss process for $BrNO_2$ under most atmospheric conditions is likely photolysis (lifetime ≈ 5 min for typical tropospheric actinic fluxes[22]). However, reaction with Br atoms could also be of importance during surface O_3 depletion events, where Br atom levels of order 10^7 molecule cm^{-3} have been inferred.[38] In fact, reactions 1, 4, and 5 could provide a mechanism for Br atom loss during these events.

Conclusions

The species BrONO has been detected for the first time in the gas phase, and has been shown to be the major product (yield $\geq 75\%$) obtained from the reaction of Br with NO_2 over the temperature range studied (218–300 K). Only the cis isomer of BrONO is observed (as characterized by the observation of its N=O stretching fundamental at 1660 cm^{-1}), consistent with the relative stability of the cis and trans isomers.[21] The loss of BrONO at low temperatures is controlled by its isomerization to $BrNO_2$, a reaction which occurs (at least in part) at the cell walls. Evidence for rapid reactions of both BrONO and $BrNO_2$ with Br atoms ($10^{-10} > k > 10^{-11}$ cm^3 molecule^{-1} s^{-1}) has also been presented.

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