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Kinetics of the Gas-Phase Reaction of $BrNO_2$ with NO

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$BrNO_2$ was prepared in situ in a static reactor (v = 420 L) by photolyzing $Br_2/NO_2/N_2$ mixtures in the wavelength range 500−700 nm at temperatures between 263 and 294 K. After the lights were switched off, the excess NO was added, and IR and UV spectra were monitored simultaneously as a function of time. From the pseudo-first-order decay of the IR absorption of $BrNO_2$ in the presence of a large excess of NO, the second-order rate constant for reaction 4, $BrNO_2 + NO \Rightarrow BrNO + NO_2$, was determined to be $k_4 = 2.3 \times 10^{-12} \exp[(-17.8 \pm 2.1)\ \mathrm{kJ\ mol^{-1}}/RT]\ \mathrm{cm^3 molecule^{-1} s^{-1}}$ (2σ). The measured yields of BrNO were close to 100% (98 ± 5%). These results suggest that reaction 4 is unimportant as a loss process of $BrNO_2$ under most tropospheric conditions. Additional experiments on the thermal stability of $BrNO_2$ led to an upper limit of $4.0 \times 10^{-4}\ \mathrm{s^{-1}}$ for its thermal gas-phase decomposition rate constant at 298 K in 1 atm of synthetic air. Finally, the mechanism of the Br + NO_2 reaction and the thermochemistry of $BrNO_2$ and BrONO are discussed in light of the results of the present experiments and of previous work from the literature.

1. Introduction

$BrNO_2$ is presently being discussed as a product of the reaction of N_2O_5 with sea salt aerosols (see, e.g., refs 1 and 2). It is difficult to estimate its source strength in the marine atmosphere because the reaction rates of volatile compounds on sea salt are still very uncertain. To assess the bromine balance in the marine troposphere, the rate parameters for the most important loss processes of $BrNO_2$ are also needed. However, the present knowledge on the kinetic properties of $BrNO_2$ is very sparse. Previous work on the thermal gas-phase decomposition of $BrNO_2$[3,4] is not unequivocal, but evidence emerges now (ref 4, this work) that its thermal lifetime around room temperature is on the order of an hour or more. In the troposphere and under sunlight conditions, photolysis is estimated to be faster than thermal deomposition on the basis of the UV absorption cross sections from Scheffler et al.[5] For the conditions July 1, noon, 50 °N, no clouds, the photolysis lifetime of $BrNO_2$ is about 4 min. The reaction of $BrNO_2$ with NO is another possible atmospheric loss process of $BrNO_2$. In the present work, the rate constant of this reaction has been measured as a function of temperature.

2. Experimental Section

The experiments were performed at total pressures close to 1 bar in a temperature-controlled 420 L photochemical reaction chamber from DURAN glass, which was described elsewhere[6] in more detail. $BrNO_2$ was prepared in situ by photolyzing $Br_2/NO_2/N_2$ mixtures with fluorescent lamps radiating in the wavelength range 500−700 nm (Phillips TLD36W/16). In the first 1−2 min of photolysis, the light intensity increased with time until a stationary temperature of the photolysis lamps was achieved. The gas mixtures were analyzed by long-path IR absorption (optical path length 40 m) using an FT-IR spectrometer (NICOLET Magna 550). UV absorption spectra could be measured simultaneously (optical path length 3 m) with a diode array spectrometer, which consists of a diode array detector (EG&G; model 1412) and a modified 25 cm double monochromator (SPEX).

$BrNO_2$ was formed according to the mechanism

$$Br_2 + h\nu \Rightarrow Br + Br \tag{1}$$

$$Br + NO_2\ (+M) \Rightarrow BrNO_2\ (+M) \tag{2a}$$

It was identified by comparison of the photolysis product spectra with published low-temperature matrix and gas-phase IR spectra of $BrNO_2$.[5,7−10] After a certain period of time that depended on the initial NO_2 concentration, the $BrNO_2$ concentration leveled off, probably owing to the loss reaction

$$BrNO_2 + Br \Rightarrow Br_2 + NO_2 \tag{3}$$

After stationary concentrations of $BrNO_2$ were established, the photolysis lamps were switched off. In the dark and with no NO present, the lifetime of $BrNO_2$ in the photoreactor was on the order of 1 h. In the presence of NO (3.2×10^{13}−1.4×10^{14} molecule cm^{-3}), $BrNO_2$ decayed on the time scale of minutes. The decay of $BrNO_2$ and the simultaneous formation of the product BrNO were monitored by their IR absorption. IR absorption coefficients of $BrNO_2$ and BrNO were determined from their simultaneously measured IR and UV absorptions, on the basis of Beer's law and the UV absorption cross sections of Scheffler et al.[5] for $BrNO_2$ and of Houel and van den Bergh[11] for BrNO.

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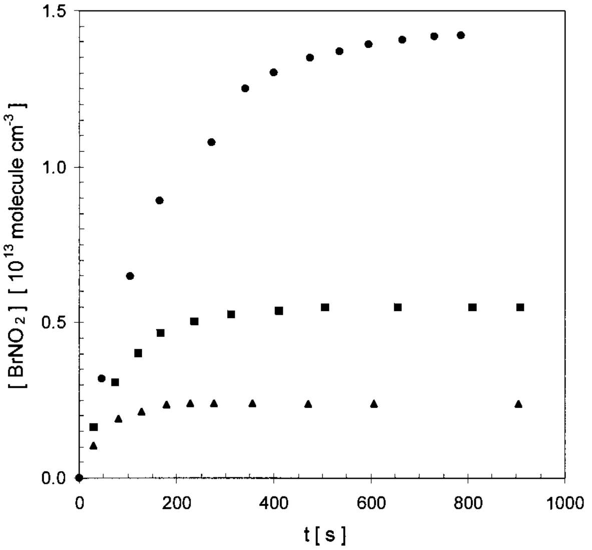

Figure 1. Concentration−time profiles for $BrNO_2$ formation at different initial concentrations of NO_2, $T = 293 \pm 1$ K, $p = 988 \pm 2$ mbar, M = N_2; initial concentrations (in molecule cm^{-3}): triangles, $[Br_2]_0 = 7.1 \times 10^{14}$, $[NO_2]_0 = 1.7 \times 10^{14}$; squares, $[Br_2]_0 = 7.1 \times 10^{14}$, $[NO_2]_0 = 3.5 \times 10^{14}$; circles, $[Br_2]_0 = 8.2 \times 10^{14}$, $[NO_2]_0 = 7.1 \times 10^{14}$.

Known amounts of NO_2, Br_2, and NO were introduced into the reaction chamber using a glass bulb of calibrated volume for NO and gastight syringes for NO_2 and Br_2. NO_2 dimer formation in the syringe was taken into account using the equilibrium constants for $NO_2 + NO_2 \Leftrightarrow N_2O_4$ from Harwood and Jones.[12]

Research grade Br_2 (Aldrich, 99%) and NO_2 (Messer Griesheim, 1.8) were used as supplied. NO, which was present as an impurity in NO_2, was titrated with O_3 in some of the experiments. Pressures were measured using capacitance pressure gauges. The temperature in the reaction chamber was measured with a platinum resistance gauge. The temperature was constant within ±0.5 K during an experiment.

3. Results and Discussion

Stationary State in the Br_2/NO_2 Photolysis. When $Br_2/NO_2/N_2$ mixtures were photolyzed in the wavelength range 500−700 nm, stationary concentrations of $BrNO_2$ were established after certain periods of time (Figure 1). Traces of NO in the NO_2 sample led to a reduced yield of $BrNO_2$ according to the chain reaction

$$BrNO_2 + NO \Rightarrow BrNO + NO_2 \tag{4}$$

$$BrNO + Br \Rightarrow Br_2 + NO \tag{5}$$

($k_{5,298\mathrm{K}} = 3.7 \times 10^{-10}$[13] or 5.2×10^{-12}[14] cm^3 $molecule^{-1}$ s^{-1}). For this reason, NO was titrated with ozone in the $BrNO_2$ lifetime experiments (next section) before the photolysis was started, leading to larger stationary concentrations and longer lifetimes of $BrNO_2$. As a consequence, small amounts of excess ozone led to the formation of N_2O_5 in these experiments; however, there was no experimental evidence for any interference of the equilibrium $N_2O_5 \Leftrightarrow NO_3 + NO_2$ with either the rate of $BrNO_2$ formation or its stationary concentration. The equilibrium concentration of the reactive NO_3 radical was extremely low owing to the large excess of NO_2. An IR spectrum of the reaction mixture during photolysis is shown in Figure 2a, and the residual after subtracting the absorptions from NO_2, N_2O_5, and traces of BrNO and water is displayed in Figure 2b, showing the three IR absorption bands of the photolysis product $BrNO_2$ in the range 1100−1900 cm^{-1}.[5] Whereas ClONO is formed in the photolysis of Cl_2/NO_2 mixtures as the main primary product which is then converted to the more stable isomer $ClNO_2$,[15,16] BrONO could not be identified as a product in the present work. This is in line with previous experimental findings of Yarwood and Niki[17] and consistent with recent theoretical work of Lee,[18] who calculated $BrNO_2$ to be more stable than *cis*- and *trans*-BrONO by 27 and 43 kJ mol^{-1}, respectively. Since the absorption cross sections of $BrNO_2$ are lower by a factor of 10−20 as compared to those of Br_2 in the 500−540 nm range (photolysis threshold of Br_2 ~540 nm, photolysis rate constant of Br_2 in the photoreactor 1×10^{-4} s^{-1}) and lower than 10^{-20} cm^2 $molecule^{-1}$ beyond this wavelength, the photolysis of $BrNO_2$ cannot be important in the present reaction system.

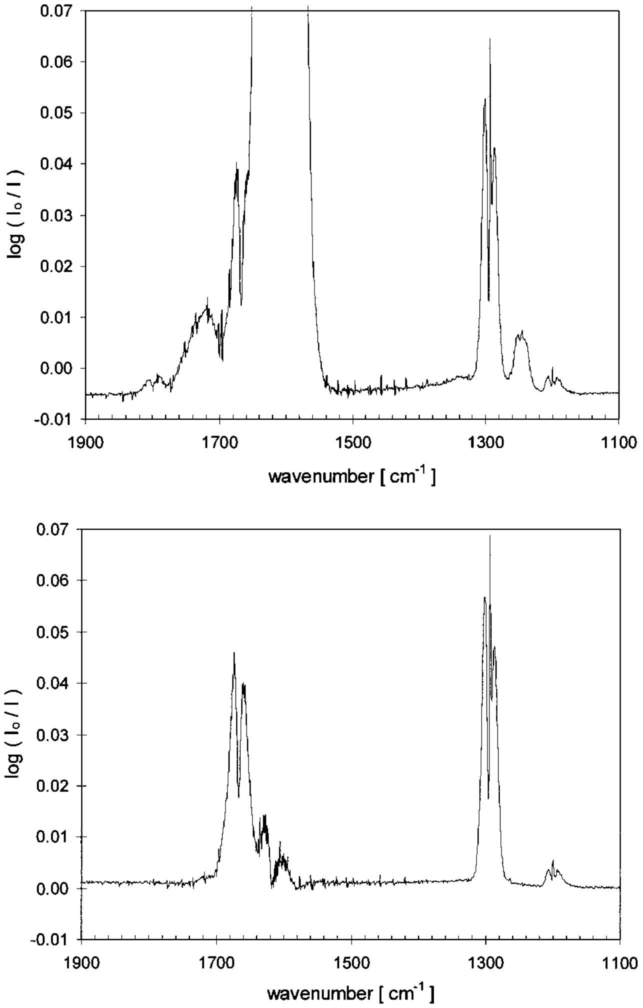

Figure 2. IR spectra during photolysis of a $Br_2/NO_2/N_2$ mixture with 500−700 nm light, photolysis time, 475 s, $T = 292$ K, $p = 989$ mbar, M = N_2, $[Br_2]_0 = 8.2 \times 10^{14}$ molecule cm^{-3}, $[NO_2]_0 = 7.1 \times 10^{14}$ molecule cm^{-3}, water vapor absorption lines have been subtracted from both spectra: (a, top) product spectrum; (b, bottom) absorptions from NO_2, N_2O_5, and traces of BrNO subtracted from spectrum a, showing the IR absorptions of $BrNO_2$ centered at 1200, 1292, and 1667 cm^{-1}; between 1580 and 1640 cm^{-1} there is residual absorption from the nearly saturated NO_2 band.

Provided that reactions 2a and 3 are the only source and loss processes, respectively, for $BrNO_2$, the stationary concentration of $BrNO_2$ is given by

$$[\mathrm{BrNO_2}]_{\mathrm{ss}} = (k_{2a}/k_3)[\mathrm{NO_2}]_0 \qquad \mathrm{(I)}$$

since the NO_2 concentration is in excess and nearly constant during photolysis. For this reason, $[BrNO_2]_{ss}$ is expected to be proportional to $[NO_2]_0$. It turns out, however, that $[BrNO_2]_{ss}$ is proportional to $([NO_2]_0)^{1.3}$, indicating that the mechanism of reactions 1−3 is not complete (see below). The time constant of the approach of the $BrNO_2$ concentration to its stationary state depends on the initial concentration of NO_2 (see Figure 1 for comparison) and should also depend on the initial Br_2 concentration, which, however, was only slightly varied in the present work. With $[Br_2]_0 = 8.2 \times 10^{14}$ molecule cm^{-3} and $[NO_2]_0 = 7.1 \times 10^{14}$ molecule cm^{-3}, for example, a relatively high stationary concentration of $BrNO_2$ is formed after a relatively long time. Contrary to this, at lower initial concentrations of NO_2 (e.g., $[Br]_0 = 7.1 \times 10^{14}$ molecule cm^{-3}, $[NO_2]_0 = 1.7 \times 10^{14}$ molecule cm^{-3}), the stationary concentration of $BrNO_2$ is much smaller, and the stationary state is established in a much shorter time. This time behavior is rationalized by the fact that the stationary Br atom concentration increases with decreasing NO_2 concentration such that the initial $BrNO_2$ formation rate remains unaffected whereas the rate of reaction 3 increases, thus reducing the stationary $BrNO_2$ concentration. Semiquantitatively, the concentration−time profiles of $BrNO_2$ in Figure 1 can be reproduced by computer simulation of a simple mechanism consisting of reactions 1, 2a, and 3, i.e., assuming $BrNO_2$ to be stable on the time scale of the experiments, in agreement with the experimental findings (see below). Using the kinetic simulation program LARKIN[19] and applying the measured photolysis rate rate constant for Br_2, the best fits of the concentration−time profiles of Figure 1 were obtained by selecting the ratio k_{2a}/k_3 to be about 0.016. With this ratio and $k_{3,298K} = 2.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [20] from Mellouki et al.,[21] $k_{2a} = 3.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} is calculated, which is lower by a factor of 13 as compared to $k_{2a} = 4.9 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for $M = N_2$ derived from the work of Kreutter et al.[3] Assuming the k_3 value of Mellouki et al. to be correct, the present result on k_{2a}/k_3 is consistent with the work of Kreutter et al. only if one assumes that BrONO is the main primary product of reaction 2 and only a small fraction (∼ 8%) leads to $BrNO_2$:

$$\mathrm{Br} + \mathrm{NO_2}\,(+\mathrm{M}) \Rightarrow \mathrm{BrNO_2}\,(+\mathrm{M}) \quad \text{(minor product)} \qquad \text{(2a)}$$

$$\mathrm{Br} + \mathrm{NO_2}\,(+\mathrm{M}) \Rightarrow \mathrm{BrONO}\,(+\mathrm{M}) \quad \text{(major product)} \qquad \text{(2b)}$$

In the next section, evidence will be given to support this assumption. This being true, BrONO must also be the isomer primarily formed in the work of Mellouki et al.,[21] and the rate constant for reaction 3 determined by these authors has to be assigned to the reaction

$$\mathrm{Br} + \mathrm{BrONO} \Rightarrow \mathrm{Br_2} + \mathrm{NO_2} \qquad (6)$$

rather than reaction 3. On the basis of the preceding discussion, it is concluded that both isomers $BrNO_2$ and BrONO are involved in the mechanism, and k_{2a}/k_{2b}, k_3, and k_{-2a} are important but unknown parameters that are needed to fully describe the Br + NO_2 recombination/dissociation system. It is difficult to unravel these rate parameters from the present experiments, in particular since k_6 is also not well-known and the time resolution in the present work is poor at the beginning of the photolysis phase owing to the time dependence of the light intensity.

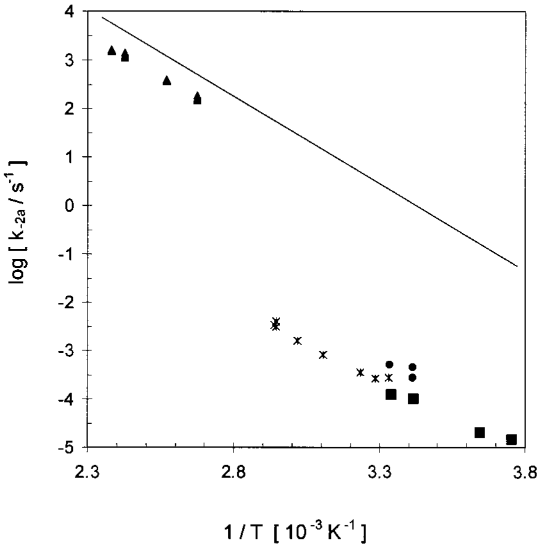

Figure 3. Thermal decay rate constants of $BrNO_2$ (BrONO): triangles, from ref 3, $p = 267$ mbar, $M = N_2$, isomer assumed to be $BrNO_2$; straight line, calculated from ref 3 for $p = 1$ bar; crosses, ref 4, isomer $BrNO_2$, $p = 1000$ mbar, M = He, propene added in order to scavenge Br atoms; full squares, this work, isomer $BrNO_2$, $p = 988 \pm 2$ mbar, M = synthetic air, *trans*-2-butene added in order to scavenge Br atoms; full circles, 293/300 K, 805 ± 5 mbar, M = synthetic air, $[Br_2]_0 = 7.8 \times 10^{14}$ molecule cm^{-3}, $[NO_2]_0 = 1.6 \times 10^{14}$ molecule cm^{-3}, excess CH_3CHO (3.5×10^{15} molecule cm^{-3}) added in order to scavenge Br atoms.

The nonlinear increase of $[BrNO_2]_{ss}$ with increasing $[NO_2]_0$ ($[BrNO_2]_{ss} \propto [NO_2]_0^{1.3}$) is difficult to rationalize. The most reasonable explanation is to assume a reaction between BrONO and NO_2

$$\mathrm{BrONO} + \mathrm{NO_2} \Rightarrow \mathrm{BrNO_2} + \mathrm{NO_2} \qquad (7)$$

i.e. an NO_2-catalyzed isomerization of BrONO. A value of about 2×10^{-16} cm^3 $molecule^{-1}$ s^{-1} for k_7 is able to reproduce the observed 1.3th power dependence of $[BrNO_2]_{ss}$ on the initial NO_2 concentration as shown in Figure 1. The uncertainty about the existence of reaction 7 does not affect the rate data on the reaction of $BrNO_2$ with NO since BrONO is thermally too unstable ($\tau = 1.2$ s at 298 K, 1 bar of N_2[3]) to accumulate to nonnegligible concentrations on the time scale of the present experiments.

Behavior of $BrNO_2$ in the Dark. After the lights were switched off, $BrNO_2$ disappeared according to a first-order rate law with a time constant between ≈1 and several hours. This is in line with the work of Frenzel et al.,[4] who suggested that the room-temperature value of k_{-2a},

$$\mathrm{BrNO_2}\,(+\mathrm{M}) \Rightarrow \mathrm{Br} + \mathrm{NO_2}\,(+\mathrm{M}) \qquad (-2a)$$

is smaller by several orders of magnitude than the value derived from the work of Kreutter et al.[3] (see Figure 3). To elucidate these discrepancies, experiments similar to those of Frenzel et al. (ref 4, 10 cm quartz cell) were performed in our 420 L photoreactor, i.e., at considerably larger volume:surface ratios. The measured first-order loss rate constants can be either larger than k_{-2a} owing to wall loss or smaller owing to regeneration of Br atoms and thus of $BrNO_2$ via reaction 2a. To avoid the re-formation of $BrNO_2$, excess *trans*-2-butene (8.6×10^{14} molecule cm^{-3}) was added to the reaction mixture as a Br atom scavenger in several experiments (k_{298}(Br + *trans*-2-butene) $= 9.3 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [22]). Synthetic air was used as a buffer gas in these experiments in order to scavenge the olefin−Br addition product by addition of O_2. There was no difference in the lifetime of $BrNO_2$ whether *trans*-2-butene was present or not. Since the Br atoms scavenged by *trans*-2-butene could have been reliberated in the course of the bromine atom initiated degradation of *trans*-2-butene, acetaldehyde (3.5×10^{15} molecule cm^{-3}) was added in place of *trans*-2-butene in three experiments since Br atoms are irreversibly converted to HBr by the reaction with acetaldehyde

$$Br + CH_3CHO \Rightarrow HBr + CH_3CO \qquad (8)$$

($k_{8,298} = 3.9 \times 10^{-12}$ cm^3 molecule $^{-1}$ s^{-1}[23]). In these experiments, synthetic air was used as a buffer gas in order to scavenge the acetyl radicals formed in reaction 8 and to prevent them from regeneration of Br atoms via the reaction

$$CH_3CO + Br_2 \Rightarrow CH_3C(O)Br + Br \qquad (9)$$

($k_{9,298} = 1.08 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}[24]). In the presence of synthetic air, the acetyl radicals react via the reactions

$$CH_3CO + O_2\ (+M) \Rightarrow CH_3C(O)O_2\ (+M) \qquad (10)$$

$$CH_3C(O)O_2 + NO_2\ (+M) \Rightarrow CH_3C(O)O_2NO_2\ (+M) \qquad (11)$$

Since the first-order loss rate constants of $BrNO_2$ at identical reaction conditions varied within a factor of 2−3, these experiments were conducted in such a way that the excess of acetaldehyde was added in the middle of a long observation period. There were indications for a slight increase of the first-order loss rate constant after the addition of CH_3CHO by a factor of ≤ 2; however, this effect was difficult to quantify. Since it was considered to be safe that the scavenging of Br atoms by acetaldehyde is irreversible, these latter experiments were used to derive a rigorous upper limit for k_{-2a} at 298 K and atmospheric pressure (M = synthetic air) of $k_{-2a} \leq 4.0 \times 10^{-4}$ s^{-1} (full circles in Figure 3).

The results of the present work on the thermal lifetime of $BrNO_2$ are shown in Figure 3, together with the results of Kreutter et al.[3] and Frenzel et al.[4] The first-order decay rate constants of $BrNO_2$ from the present work are consistent with the results of Frenzel et al.[4] and extend their temperature range to lower temperatures. At present the origin of the discrepancies between these low upper limits of k_{-2a} and the high values derived from the work of Kreutter et al. is not completely clear. Probably, the BrONO isomer was primarily formed in the reaction system of Kreutter et al.,[3] as was already suggested by Frenzel et al. BrONO was then thermally stable on the short time scale of their experiments below 350 K, and regeneration of Br atoms occurred above 350 K owing to thermal decomposition of BrONO. The much longer lifetime of $BrNO_2$ as determined in the work of Frenzel et al. and the present work can then be explained by the larger bond energy of $BrNO_2$ as compared to BrONO, which is also suggested by the theoretical work of Lee.[18] This being true, the value for the enthalpy of formation of $BrNO_2$ derived by Kreutter et al.[3] and adopted by the most recent JPL[25] and IUPAC[23] reviews should be assigned to BrONO rather than $BrNO_2$ (after reevaluation of the entropy contribution). The most direct thermochemical result of Kreutter et al., which is largely independent of the correct isomer assignment, is the second-law value for the reaction enthalpy of reaction 2 ($\Delta H^\circ_{r,298} \sim \Delta H^\circ_{r,401} = 78 \pm 3$ kJ mol^{-1}, see Figure 5 of ref 3). If this value is assigned to the formation of BrONO rather than $BrNO_2$, $\Delta H^\circ_{f,298}(BrONO) = (67 \pm 3)$ kJ mol^{-1} results. From the rate parameters presented in their paper, $k_{-2b,298K} = 1.2$ s^{-1} can be derived for 298 K and M = N_2.[3] Frenzel et al. analyzed their data on the thermal decay of $BrNO_2$ at different temperatures as a superposition of homogeneous and heterogeneous decomposition, characterized by different activation energies. By fitting their data with a sum of exponential terms, they arrived at an Arrhenius expression for the homogeneous decomposition for 1 bar, M = He, yielding $k_{-2a} = 4 \times 10^{-5}$ s^{-1} at 298 K. From the falloff curves of Kreutter et al. for the reverse reaction, $k_{2a}(N_2)/k_{2a}(He) = k_{-2a}(N_2)/k_{-2a}(He) = 1.6$ can be derived. Combining this ratio with k_{-2a} (M = He) from Frenzel et al., k_{-2a} (M = N_2) = 6.4×10^{-5} s^{-1} results. The difference of the rate constants derived above for k_{-2b} and k_{-2a} is considered to reflect the difference in bond energies in BrONO and $BrNO_2$. This conclusion relies on the assumption that both reactions have a similar preexponential factor of the high-pressure rate constant and a comparable falloff at atmospheric pressure. Setting $\ln(k_{-2b}/k_{-2a}) = \ln(1.2/6.4 \times 10^{-5}) = -\Delta(\Delta H^\circ_{r,298})/RT$, $\Delta H^\circ_{r,298}(Br-NO_2) - \Delta H^\circ_{r,298}(Br-ONO) = \Delta H^\circ_{f,298}(BrONO) - \Delta H^\circ_{f,298}(BrNO_2) \sim (24 \pm 3)$ kJ mol^{-1} is derived. This value compares favorably with the ab initio value of (27 ± 4) kJ mol^{-1} calculated by Lee[18] for the difference of the heats of formation of *trans*-BrONO and $BrNO_2$. From this difference of bond energies and the above value for the heat of formation of BrONO, $\Delta H^\circ_{f,298}(BrNO_2) = (43 \pm 6)$ kJ mol^{-1} is calculated. According to the previous discussion, the findings of the experimental studies of Kreutter et al., Frenzel et al., Mellouki et al., and the present work on the Br + NO_2 system are consistent with each other and with the theoretical work of Lee provided that the main product of the Br + NO_2 recombination is the isomer BrONO and that $BrNO_2$ is thermally much more stable than BrONO.

The lifetimes of $BrNO_2$ in our reaction chamber are larger by 2 orders of magnitude as compared to the observation times applied in the experiments for the reaction of $BrNO_2$ with NO; i.e., the loss of $BrNO_2$ in the presence of NO is due to the reaction of $BrNO_2$ with NO and not to the reaction sequence

$$BrNO_2\ (+M) \Rightarrow Br + NO_2\ (+M) \qquad (-2a)$$

$$Br + NO\ (+M) \Rightarrow BrNO\ (+M). \qquad (12)$$

Another possible loss process of $BrNO_2$ is the self-reaction of $BrNO_2$:

$$BrNO_2 + BrNO_2 \Rightarrow Br_2 + 2NO_2 \qquad (13)$$

Such a reaction is known for INO_2 ($k_{298K}(INO_2 + INO_2 \Rightarrow I_2 + 2NO_2) = 4.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}[23,26]) but not for $ClNO_2$. However, reaction 13 must be of second order in $BrNO_2$, different from the first-order rate law observed in the present work. In addition, the long lifetime of $BrNO_2$ in the dark shows that reaction 13 cannot be important on the time scale of the present experiments.

Behavior of $BrNO_2$ in the Presence of NO. The following conclusions are drawn from the two previous sections:

(i) Probably, only a small fraction of the Br + NO_2 recombination leads, at room temperature, to the isomer $BrNO_2$. Assigning the thermal decomposition rate constants of $BrNO_2$ derived by Kreutter et al.[3] to the isomer BrONO, BrONO would be too unstable in the present reaction system to accumulate to nonnegligible concentrations; i.e., the only important species to react with NO is the isomer $BrNO_2$.

(ii) $BrNO_2$ is thermally stable under the conditions of the present experiments, i.e., the loss of $BrNO_2$ in the presence of NO can be assigned to its bimolecular reaction with NO.

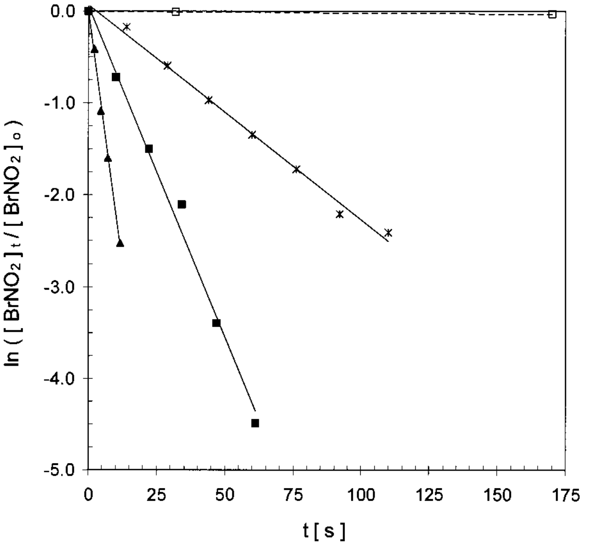

Figure 4. Decay of $BrNO_2$ with time for different excess NO concentrations, $T = 294$ K, added NO (units of molecule cm^{-3}): open squares, no NO added; crosses, 1.78×10^{13}, full squares, 3.85×10^{13}, triangles, 1.42×10^{14}.

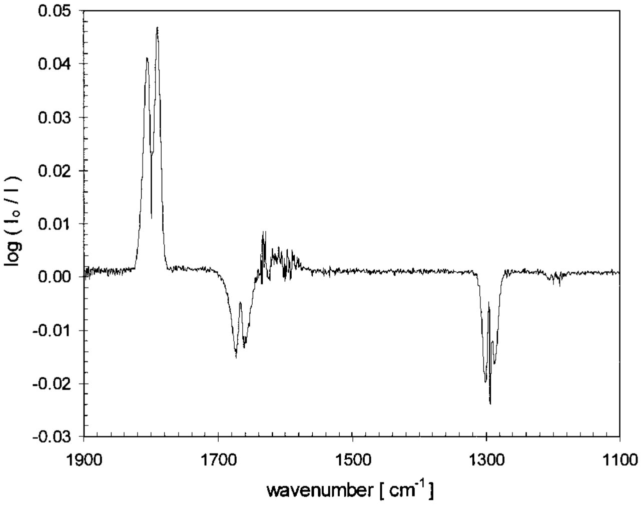

Figure 5. Difference spectrum of a $BrNO_2/NO/N_2$ mixture in the dark obtained by subtracting a spectrum before NO addition from a spectrum after NO addition; $T = 283$ K, $p = 988$ mbar, $M = N_2$, reaction time in the presence of NO ~86 s; absorption at 1800 cm^{-1}: BrNO, absorptions at 1667 and 1292 cm^{-1}: $BrNO_2$.

(iii) The increase of the stationary $BrNO_2$ concentrations in the photolysis experiments with the NO_2 concentration according to a power larger than 1 can possibly be explained by reaction 7. In the present study on the rate of reaction 4, however, this reaction is unimportant owing to the absence of BrONO in the dark.

In the presence of a large excess of NO, $BrNO_2$ disappeared according to a first-order rate law, the apparent first-order rate constant being proportional to the NO concentration. This is shown in Figure 4 for three different excess NO concentrations and for $[NO]_0 = 0$ at 294 K. Simultaneous to the decay of $BrNO_2$, the formation of BrNO was observed by both its IR[27] and UV[11] absorptions. Absolute concentrations of $BrNO_2$ and BrNO were derived by using the UV absorption cross sections of Scheffler et al.[5] and Houel and van den Bergh,[11] respectively. BrNO was the only product apparent in the product IR spectrum (Figure 5). The time constants for the decay of $BrNO_2$ and the formation of BrNO were the same (Figure 6).

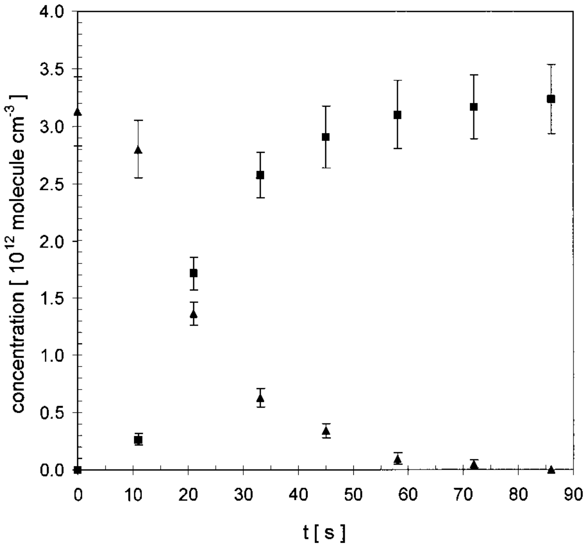

Figure 6. Concentration–time profiles of $BrNO_2$ (triangles) and BrNO (squares) in the dark; reaction conditions same as in Figure 5. During the initial 10 s, the time behavior deviates from first order owing to the finite mixing time of the added NO. In Figure 4, the time of the second data point of each profile is set equal to zero.

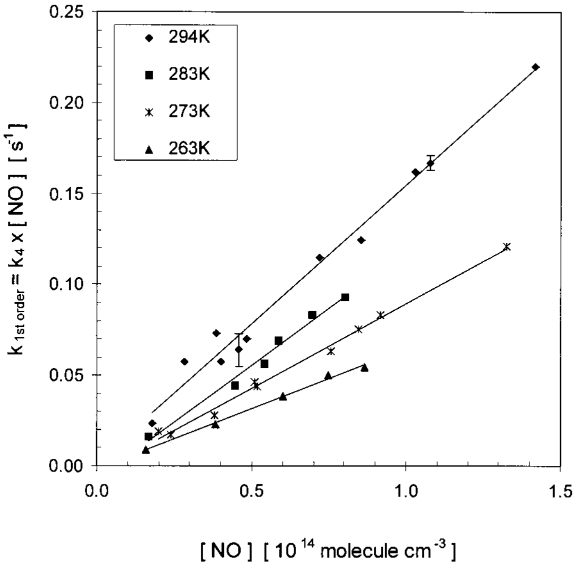

Figure 7. Pseudo-first-order rate constants of $BrNO_2$ loss as a function of [NO] at different temperatures.

The pseudo-first-order rate constants for $BrNO_2$ loss, $k_{\text{first order}} = k_4[NO]$, are presented in Figure 7 as a function of [NO] at 294, 283, 273, and 263 K. The slopes of the straight lines represent k_4. An Arrhenius plot of k_4 is shown in Figure 8. The temperature dependence of k_4 is represented by $k_4 = 2.3 \times 10^{-12} \exp[(-17.8 \pm 2.1)\ \text{kJ mol}^{-1}/RT]$ cm^3 $molecule^{-1}$ s^{-1} (2σ). In Table 1, the Arrhenius parameters are compared with those of related reactions. To the best of our knowledge, rate constants for the reaction of NO with FNO_2 and INO_2 are not available. However, for $ClNO_2$ an Arrhenius expression with a very similar preexponential factor but a higher activation energy has been determined by Wilkins et al.[28] and in this laboratory.[29] The latter work shows that the reaction of ClONO with NO is faster than the reaction with $ClNO_2$ by more than an order of magnitude. Similarly, the rate constant for the reaction of NO with BrONO

$$BrONO + NO \Rightarrow BrNO + NO_2 \qquad (14)$$

might be expected to be larger than k_4.

TABLE 1: Kinetic Data on Reactions $XNO_2 + NO \Rightarrow XNO + NO_2$ (X = halogen)

NO + ...	$\Delta H°_{r,298}$ (kJ mol^{-1})	k_{298} (cm^3 molecule^{-1} s^{-1})	A (s^{-1})	E_a (kJ mol^{-1})	ref
FNO_2					
$ClNO_2$	−17.85 (ref 23)	2.1×10^{-17}	2.3×10^{-12}	28.8	28
$BrNO_2$	−18 ± 6 (ref 23)[a]	1.7×10^{-15}	2.3×10^{-12}	17.8 ± 2.1 (2σ)	this work
INO_2					

[a] See text for $\Delta H°_{f,298}(BrNO_2)$.

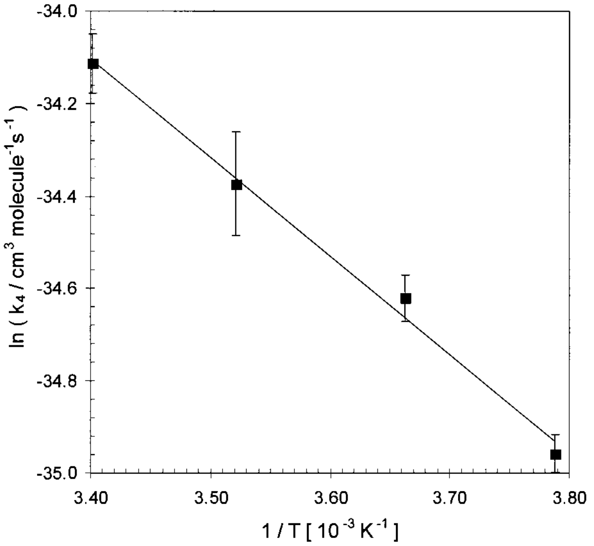

Figure 8. Arrhenius plot for k_4.

4. Conclusion

Analysis of the kinetic data on $BrNO_2$/BrONO from the literature and the present work suggests that $BrNO_2$ is more stable than BrONO by about 23 kJ mol^{-1} and that the major primary product in the recombination of Br atoms with NO_2 is BrONO. $BrNO_2$ is thermally quite stable, with a thermal lifetime of about 1 h or more at 298 K. This kinetic behavior is analogeous to $ClNO_2$/ClONO.

In the lower troposphere and for the presence of 1 ppb NO, the lifetime of $BrNO_2$ with respect to reaction with NO is 6.5 h; i.e., at low solar radiation and relatively high mixing ratios of NO, the reaction with NO could be a nonnegligible loss process of $BrNO_2$. However, in those areas (the marine troposphere) where the mixing ratio of $BrNO_2$ can be expected to be relatively high, the mixing ratio of NO is considerably smaller than 1 ppb, and, for most tropospheric conditions, thermal decomposition and, in particular, photolysis are probably the major loss processes of $BrNO_2$.

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