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Heterogeneous Interconversion Reactions of $BrNO_2$, $ClNO_2$, Br_2, and Cl_2

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The heterogeneous reactions leading to formation and loss of $BrNO_2$ on salt solutions as a model substrate for atmospheric sea salt aerosol are investigated. Further to the reaction of $ClNO_2$ with bromide solutions, the reaction of Br_2 with nitrite solution was found to be a convenient method for the synthesis of $BrNO_2$. We measured the temperature-dependent lifetime of $BrNO_2$ in a quartz cell and obtained the activation energy $E_A = 89 \pm 9$ kJ/mol for the unimolecular decay at atmospheric pressure. The reactive uptake of $BrNO_2$ and $ClNO_2$ on water and aqueous solutions was determined using a wetted-wall flow tube technique. We observed the reactions $Br_2 + NO_2^- \leftrightarrow BrNO_2 + Br^-$, $Cl_2 + NO_2^- \rightarrow ClNO_2 + Cl^-$, and the net reaction $ClNO_2 + Br^- \leftrightarrow BrNO_2 + Cl^-$. $BrNO_2$ and $ClNO_2$ both react with NO_2^- to release NO_2 into the gas phase. Observed concentration profiles in the gas phase and in solution can be described qualitatively by a numerical model of the diffusion and reaction processes in the experimental setup.

Introduction

Halogen species in the marine troposphere had been measured many years ago.[1] Triggered by the observation of ozone depletion events in the Arctic troposphere, increased attention has been drawn to the activation mechanisms of halogens in recent years. Integrated halogen atom concentrations can be inferred from the consumption patterns of light non-methane hydrocarbons such as alkanes, aromatics, and acetylene.[2] The impact of bromine atoms on Arctic tropospheric ozone concentrations has been confirmed by field measurements.[2−6] Chlorine atoms in the marine troposphere are thought to originate mainly from sea salt aerosol, which releases HCl upon acidification,[1] by heterogeneous reactions with nitrogen oxides,[7−9] or photolytic induction.[10,11] Various sources of bromine atoms have been suggested: photolysis of $CHBr_3$ and other brominated methanes,[3] heterogeneous reactions of nitrogen oxides with sea salt aerosol,[12−14] photochemical oxidation of bromide in sea salt aerosol,[15−17] autocatalytic heterogeneous cycling of inorganic bromine species,[18,19] or free radical reactions in aqueous aerosols.[20]

Considering the heterogeneous reactions of nitrogen oxides with sea salt aerosols, nitryl bromide ($BrNO_2$) may play an important role. $BrNO_2$ is known to be formed from heterogeneous reaction of N_2O_5 with solid sodium bromide[13] or with aqueous solutions of chloride and bromide.[14] The infrared and UV/vis absorptions of $BrNO_2$ were measured,[13,21−23,25] and an ab initio calculation was reported.[24] A possible synthesis for $BrNO_2$ from the heterogeneous reaction of $ClNO_2$ with dilute bromide solution has been described recently.[25] In a previous study, an atmospheric lifetime of $BrNO_2$ of a few seconds was extrapolated from the gas phase association reaction of Br atoms with NO_2.[26,27]

In this study we focused our attention on the heterogeneous reactions of nitryl halides with aqueous salt solutions as a model substrate for atmospheric sea salt aerosol.

Experimental Section

Synthesis of $BrNO_2$ and $ClNO_2$. $BrNO_2$ was synthesized by heterogeneous reaction of Br_2 with 0.005 mol/L aqueous $NaNO_2$ solution in a wetted-wall flow tube. The experimental setup is shown in Figure 1. It is similar to the one described in a previous publication,[28] except for the detection scheme, where UV/vis was used instead of FTIR. The left part of Figure 1 shows the synthesis of $BrNO_2$. All transfer lines were PTFE tubing (Teflon, Dupont). A small gas flow of He (14 mL min^{-1}) was fed through a cold trap with solid Br_2 at −25 °C (respectively −35 °C, in some measurements) and diluted with He (140 mL min^{-1}) to obtain a volume mixing ratio of typically 700 ppmv (respectively 300 ppmv). The concentration was determined by UV absorption. The Br_2 was fed to a thermostated flow tube (6 mm i.d.) whose inner walls were covered by a falling film of 0.005 mol/L $NaNO_2$ solution flowing down (0.08−0.09 $cm^3\ s^{-1}$), which was constantly supplied by a peristaltic pump. After a reaction path of 5 cm a yield of typically 190 ppmv $BrNO_2$ was obtained, measured by the UV/vis absorption between 200 and 400 nm.[21] The volume mixing ratio of the remaining Br_2 was below 15 ppmv, and NO_2 was formed on the order of 80 ppmv.[29]

This synthesis from nitrite and Br_2 has several advantages compared to the heterogeneous reaction of $ClNO_2$ with dilute bromide solution[25] (still employed here when we used MI/FTIR detection for $BrNO_2$): The synthesis is only a one step process, which enhances stability of the yield significantly. Br_2 is easier to handle than $ClNO_2$ and readily available. Furthermore, the achieved $BrNO_2$ concentrations in this reaction are about 10-fold higher. Finally, every impurity of chloride species can be excluded.

$ClNO_2$ was synthesized in a wetted-wall flow reactor from N_2O_5(g) and NaCl(aq), as described earlier,[25] or by reaction of Cl_2 with 0.003 mol/L nitrite solution.

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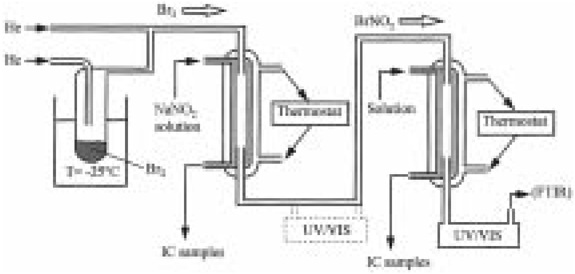

Figure 1. Experimental setup for synthesis of $BrNO_2$ and uptake measurements.

Uptake Measurements. The uptake of $BrNO_2$ and $ClNO_2$ on aqueous solutions was studied in a second wetted-wall flow tube, as shown in the right-hand part of Figure 1. The gas stream containing $BrNO_2$ or $ClNO_2$ was passed through that second wetted-wall flow tube with variable reaction path and then through the detection cells.

The uptake of $ClNO_2$ over nitrite solution was measured in the same flow tube as it was produced from Cl_2 (280 ppmv N_2), except for one experiment where it was produced from N_2O_5. The concentrations of $BrNO_2$, $ClNO_2$, NO_2, Br_2, and Cl_2 were observed by UV/vis and/or FTIR absorption as a function of reaction time. Some uptake measurements were performed employing the matrix-isolation–FTIR technique, described earlier.[25,29] The synthesis of $BrNO_2$ and $ClNO_2$ in those cases follows also the description given there. Samples of the solution pumped out of the flow tube were collected in small batches (10 mL) and analyzed by ion chromatography.

The uptake coefficient γ is defined by

$$\gamma = \text{the number of molecules lost through the surface/number of molecules hitting the surface} \quad (1)$$

If there is a loss reaction of first order in the liquid phase, γ is given by[30]

$$1/\gamma = 1/\alpha + c/(4HRT\,(kD_{\mathrm{liq}})^{1/2}) \quad (2)$$

where α is the mass accommodation coefficient, c the thermal velocity of the molecule, H Henry's law constant, k the first order rate constant, and D_{liq} the liquid phase diffusion coefficient. For the experiments described here, where the measured γ are low (see below), it can be assumed that $\alpha \gg \gamma$, and thus $1/\alpha$ is neglected as a consequence. At uptake rates of $\gamma > 5 \times 10^{-4}$ at atmospheric pressure the resistance of gas phase diffusion has to be considered. The gas phase diffusion coefficients were estimated by the method of Fuller et al. as described in the review of Reid et al.[31] In those cases where the loss rate was found to be monoexponential, γ was evaluated using the solution of the diffusion equation for a cylindrical denuder,[32] given by Murphy and Fahey,[33] which was fitted to the measured slope of the concentration versus reaction time with γ as a free parameter.[28] If γ is dependent on reaction time, due to saturation effects or secondary reactions, this solution does not apply. In those cases we used a fit to the initial slope, to get an estimate of an upper or lower bound, respectively.

$Hk^{1/2}$ can be calculated from γ, if the liquid phase diffusion coefficient is known. We used diffusion coefficients estimated by the method of Wilke and Chang or employing the Nernst–Haskell equation (for ions), both described in the review of Reid et al.[31]

Lifetime Study. The lifetime of $BrNO_2$ with respect to thermal dissociation was measured in a cylindrical 10 cm quartz cell. The cell was heated electrically, and the temperature was measured with an Fe/constantan thermocouple. The synthesis of $BrNO_2$ from Br_2 and nitrite was carried out (at 10 °C) as described above. A small stream of pure propene (to scavenge Br atoms) was added through a flow controller to the gas stream from the synthesis flow reactor (resulting in a volume mixing ratio of approximately 3000 ppmv). The gas mixture was fed through the quartz cell, and concentrations were monitored by UV absorption. After a stabilization time of about 10 min, the cell was disconnected from the stream and the lines were closed by stoppers (PTFE-Teflon). Spectra of $BrNO_2$ were taken from 390 to 190 nm with a scan velocity of 100 nm/min. $BrNO_2$ was quantified by its UV absorption around 200 nm. An experimental error is introduced through the limited temperature stability of the cell. Since temperature was controlled only by the heating power, a slight temperature drift occurred in some experiments ($\delta T < 1$ K). The error in the temperature measurement is much smaller than that. The statistical error of the $BrNO_2$ concentration measurement is thought to be represented by the 95% confidence limit of the slopes of the logarithmic decay curves (determined by linear regression).

In some test measurements we measured the lifetime of $BrNO_2$ in different cells by IR absorption (at the temperature of the spectrometer sample compartment, approximately 29 °C). The lifetime in a Teflon cell, equipped with AgCl windows, was on the order of 6–10 min, whereas in the same cell, equipped with Si windows, the lifetime was 60 ± 10 min. This indicates heterogeneous loss of $BrNO_2$ on AgCl in the first case, while in the second case the results are consistent with the measurements in the quartz cell. Additionally we tested NO as a scavenger for Br atoms in the lifetime measurement. In those experiments, the $BrNO_2$ concentration was found to be reduced instantaneously and NOBr appeared. We assume that there is a fast reaction of NO with $BrNO_2$, similar to the reaction of NO with $ClNO_2$.[34,35]

Analytical Techniques. The UV absorption was determined in a 10 cm quartz cell with a double beam spectrometer (Kontron UVIKON 860). In experiments with $ClNO_2$, an IR absorption cell (20 cm Teflon cell, Bruker IFS 113v spectrometer) was added after the UV cell, to support deconvolution of the overlapping UV spectra of $ClNO_2$ and $BrNO_2$. The $ClNO_2$ concentration was determined from its IR absorption and the respective UV absorption subtracted in the UV spectra. The detection limits were for $BrNO_2$ 5×10^{-11} mol/cm^3, for $ClNO_2$ (IR absorption) 10^{-9} mol/cm^3, and for Br_2 (also estimated for BrCl, which did not appear) and NO_2 on the order of 10^{-9} mol/cm^3.

The ion chromatography was performed with a Dionex AS4 column, a CO_3^{2-}/HCO_3^- eluent, and a conductivity detector for the detection of Br^-, Cl^-, NO_2^-, and NO_3^-. If ionic concentrations were higher than approximately 10^{-3} mol/L, the samples had to be diluted with eluent. This analytical procedure is not capable of detecting HOBr in the liquid.

Results

Synthesis of $BrNO_2$ and $ClNO_2$ from Nitrite Solution and Br_2 and Cl_2. The formation of $BrNO_2$ from the reaction of Br_2(g) with dilute (0.005 mol/L) $NaNO_2$ solution was investigated. Figure 2 shows the observed concentration profiles along the flow tube. Br_2 was found to be lost at a high rate, so that the uptake is near the gas phase diffusion limit. Due to the weak absorption of Br_2, its concentration is close to the detection limit, even at the shortest reaction lengths. $BrNO_2$ appears instantaneously (in the time scale of our method) and is then

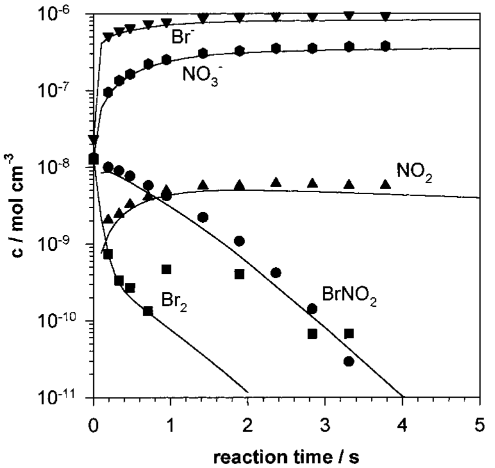

Figure 2. Measured gas and liquid phase concentrations in the reaction of Br_2 with 0.005 mol/L $NaNO_2$ solution (symbols); results of numerical model (lines).

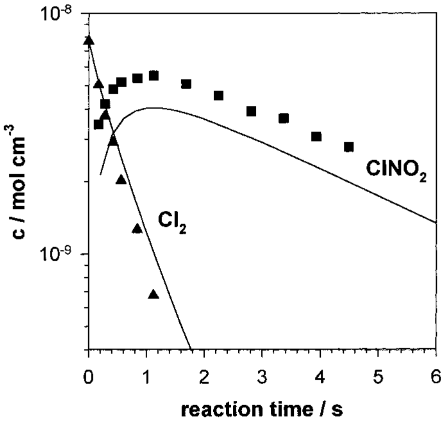

Figure 3. Reactive uptake of Cl_2 on 0.001 mol/L $NaNO_2$ solution. $ClNO_2$ is formed; NO_2 concentrations are below the detection limit: symbols, measured concentrations; lines, results of the numerical model.

lost at an increasing loss rate. Extrapolation of the measured $BrNO_2$ curve to zero reaction time suggests quantitative conversion of Br_2 to $BrNO_2$.

Similar experiments were perfomed with Cl_2 and $NaNO_2$ solutions (0.001, 0.003, 0.01, 0.03, and 0.1 mol/L). The uptake of Cl_2 could be evaluated only for the lowest nitrite concentration ($\gamma \approx 6.5 \times 10^{-5}$); it was near the diffusion limit in all other cases. Figure 3 shows that $ClNO_2$ is formed at a maximum yield of about 50% and then lost by reaction with the remaining nitrite in solution.

Uptake Measurements. The reactive uptake of $BrNO_2$ on solutions of NaBr (0.005, 0.01, and 0.05 mol/L), on $NaNO_2$ (0.005 mol/L), and on water at 18 °C is shown in Figure 4.

On water we measured the uptake of $BrNO_2$ at four different temperatures (2.4, 10, 18, and 25 °C). The $BrNO_2$ concentration decreased exponentially after approximately 1 s of reaction time. The small offset between the extrapolation of the final slope toward zero reaction time and the measured initial concentration can be interpreted as an effect of solubility. The loss rates after 1 s lead to values of γ in the range of $(2.5-3.5) \times 10^{-6}$, as given in Table 1. Figure 5 shows the resulting values of $Hk^{1/2}$ for the observed loss of $BrNO_2$ on water compared with data for $ClNO_2$ on water (at 4.4, 9, 14.2, and 18.2 °C) and buffered solution (at 18.0 °C). In both cases there appears to be no distinct temperature dependence. The presence of bromine in $BrNO_2$ experiments is a hint at Br^- (the final hydrolysis product of Br_2 and of $BrNO_2$ itself) leading to an enhanced uptake compared to the theoretical value for pure water (see below), so that the measured γ values do not necessarily represent the hydrolysis reaction of $BrNO_2$. This is indicated by the different uptake coefficients at 2 °C, which were measured at very different initial concentrations of $BrNO_2$ and Br_2 (in matrix-isolation–FTIR experiments, $BrNO_2 \approx 2 \times 10^{-9}$, $Br_2 \approx 10^{-9}$ mol/cm^3; in UV/vis experiments, $BrNO_2 \approx 10^{-8}$, $Br_2 \approx 5 \times 10^{-10}$ mol/cm^3).

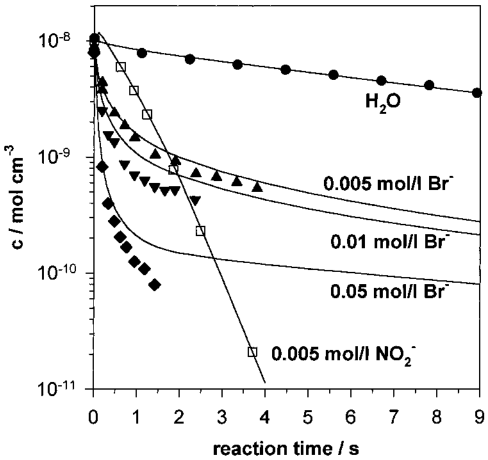

Figure 4. Reactive uptake of $BrNO_2$ on different solutions: symbols, measured $BrNO_2$ concentrations; lines, results of the numerical model.

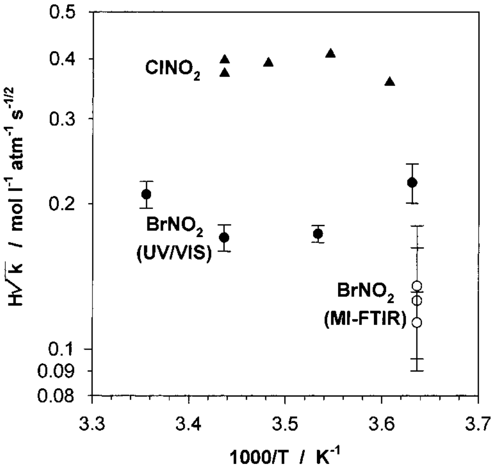

Figure 5. Observed values of $Hk^{1/2}$ for $BrNO_2$ and $ClNO_2$ uptake on water at different temperatures, using gas phase FTIR (triangles), UV/vis (filled circles), and MI-FTIR (open circles) for the analysis. For $BrNO_2$, k should be considered to be controlled by the reaction with NO_2^-(see text).

On bromide solutions, $BrNO_2$ shows a fast initial loss rate. The fact that the initial uptake of $BrNO_2$ on bromide solution is much faster than on water and dependent on bromide concentration indicates the reaction $BrNO_2 + Br^- \rightarrow Br_2 + NO_2^-$. Figure 6 shows that Br_2(g) and NO_2^- and NO_3^- are formed at short reaction times. Toward longer reaction times the system seems to run into a steady state with considerably slower loss in the liquid phase, due to the increasing concentrations of the products Br_2 and NO_2^- in the liquid film along the flow tube. From the initial slopes of the $BrNO_2$ curves, lower bounds for the uptake coefficients γ are estimated and listed in Table 1. Similar results are obtained with buffered solution (2 mol/L KH_2PO_4/K_2HPO_4, pH = 6.2), while on acidic solution the initial slopes are somewhat steeper, so that for 0.01 mol/L HBr the loss rate is at the diffusion limit. This behavior is very different from the uptake of $ClNO_2$ on chloride solutions, where the analogous reaction $ClNO_2 + Cl^- \rightarrow Cl_2 + NO_2^-$ does not

TABLE 1: Measured Uptake Coefficients, γ, for $BrNO_2$ on Different Solutions[a]

solution	concn mol/L	T, °C	γ, 10^{-6}	$H(k^I)^{1/2}$, mol/(L atm $s^{1/2}$)	technique
H_2O	0	2.0	1.26 ± 0.2	0.11 ± 0.02	MI−FTIR[b]
H_2O	0	2.0	1.4 ± 0.4	0.13 ± 0.04	MI−FTIR[b]
H_2O	0	2.0	1.5 ± 0.5	0.14 ± 0.05	MI−FTIR[b]
H_2O	0	2.4	2.46 ± 0.23	0.22 ± 0.02	UV/vis[c]
H_2O	0	10	2.24 ± 0.09	0.17 ± 0.01	UV/vis[c]
H_2O	0	18	2.52 ± 0.16	0.17± 0.01	UV/vis[c]
H_2O	0	25	3.45 ± 0.22	0.21± 0.01	UV/vis[c]
HBr	0.001	18	>22.1	>1.51	UV/vis[c]
NaBr	0.005	18	>121	>8.17	UV/vis[c]
NaBr[d]	0.005	18	>87.7	>5.98	UV/vis[c]
NaBr	0.01	18	>214	>14.5	UV/vis[c]
NaBr[d]	0.01	18	>240	>16.4	UV/vis[c]
HBr	0.01	18	>932	>63.5	UV/vis[c]
NaBr	0.05	18	>659	>44.5	UV/vis[c]
$NaNO_2$	0.005	18	<21.7	<1.28	UV/vis[c]
NaCl	0.5	18	>38	>2.57	UV/vls + FTIR[c]

[a] The given errors represent the 95% confidence interval of the regression and a 5% error in gas-phase diffusion coefficients. A lower limit of $H(k^{II})^{1/2}$ for the reaction with Br^- can be estimated from the measurements of $H(k^I)^{1/2}$. [b] $BrNO_2$ synthesized via $ClNO_2 + Br^-$. [c] $BrNO_2$ synthesized via $Br_2 + NO_2^-$. [d] Buffered with KH_2PO_4/K_2HPO_4.

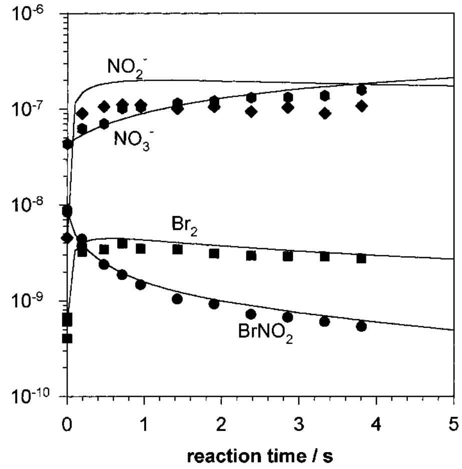

Figure 6. Reactive uptake of $BrNO_2$ on 0.005 mol/L NaBr solution: symbols, measured data, lines, results of numerical model. Background NO_2(g) concentration (about 4 × 10^{-9} mol/cm^3) is not shown for clarity.

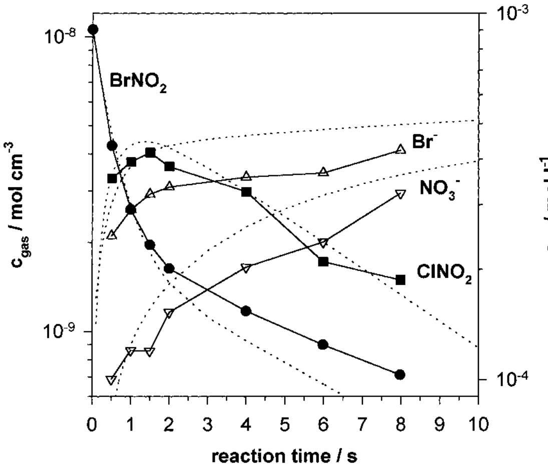

Figure 7. Uptake of $BrNO_2$ on 0.5 mol/L NaCl solution: dashed lines, results of numerical model.

play a role but, in contrast, hydrolysis is slowed strongly with increasing chloride concentration.[28]

The loss of $BrNO_2$ on a 5 × 10^{-3} mol/L nitrite solution was increasing with reaction length, similar to the observation in the $Br_2(g) + NO_2^-(aq)$ experiment. Accordingly, in Table 1 we only give an upper limit, estimated from the initial slope of $BrNO_2$ concentration. The initial uptake of $BrNO_2$ is slower than on an equally concentrated bromide solution, indicating a slower reaction of $BrNO_2$ with nitrite than with bromide. Uptake coefficients for $ClNO_2$ on nitrite solution (given in Table 2) were deduced from the final slope of $ClNO_2$ concentration profiles, where $ClNO_2$ decreases after its production from Cl_2 and nitrite (assuming that no interference of Cl^- in the solution occurs and taking nitrite depletion into account). Nitrite enhances the uptake as it does in the case of $BrNO_2$, but the effect is lower and the uptake showed no reaction time dependence in contrast to $BrNO_2$.

The uptake of $BrNO_2$ on 0.5 mol/L chloride solution was also enhanced in the first part of the flow tube, but then an equilibrium between $ClNO_2$ and $BrNO_2$ appeared to be established, where both nitryl halides decrease with approximately the same rate, somewhat faster than in water; see Figure 7. From the initial slope $\gamma > 3.8 \times 10^{-5}$ was calculated, while at the end of the flow tube we deduce $\gamma \approx 3.6 \times 10^{-6}$.

To get information about the mechanism of the interconversion between $ClNO_2$ and $BrNO_2$, the uptake of $ClNO_2$ on different bromide solutions was measured. The results are given in Table 2. The uptake of $ClNO_2$ on bromide is strongly enhanced compared to that on water, as stated before.[28] Figure 8 shows that the decrease in the flow tube was monoexponential, and $BrNO_2$ and Br_2 were produced. Measurements on buffered and on acidic solution showed similar results.

Lifetime of $BrNO_2$ in the Gas Phase. The decay rates, k, of $BrNO_2$ were measured in eight experiments at six different temperatures in the presence of propene (except one measurement at 27 °C) and are listed in Table 3. The slope of ln k against $1/T$ should be linear for a unimolecular decay. Figure 9 shows that this is not the case, and a simple linear regression yields no acceptable result. We interpret the nonlinearity as a combination of the thermal decay rate and a heterogeneous loss rate. By analogy to the heterogeneous loss rate measured on pure water, we may assume that the wall disappearance is only poorly affected by the temperature. This is also suggested by the variation of the measured decays at low temperature, where the unimolecular decay is probably mostly affected by heterogeneous loss.

A weighted fit of the expression $\ln k = \ln(A \exp(-B/T) + k_{het})$ to the data, using a Marquardt algorithm, yields $A = 1.9 \times 10^{11}$ s^{-1}, $B = 10\,760$ K, and $k_{het} = 2.0 \times 10^{-4}$ s^{-1}. Fitting

TABLE 2: Uptake Coefficients, γ, of $ClNO_2$ on Water, Bromide, and Nitrite Solution[a]

solution	concn, mol/L	T, °C	γ, 10^{-6}	$H(k^{I})^{1/2}$, mol/(L atm $s^{1/2}$)	technique
H_2O	0	4.4	3.41	0.30	FTIR[b]
H_2O	0	9.0	4.27	0.37	FTIR[b]
H_2O	0	14.2	4.48	0.38	FTIR[b]
H_2O	0	18.2	4.84 ± 0.13	0.40	FTIR[b,d]
buffer[e]	0	18.0	4.0 ± 0.1	0.33	FTIR[c]
NaBr	0.0005	2	12.5 ± 2.5	1.37	MI−FTIR[b]
NaBr	0.001	2	14.6 ± 1.5	1.60	MI−FTIR[b]
NaBr	0.001	18	15.1 ± 2.1	1.22	UV + FTIR[b]
NaBr[e]	0.001	18	15 ± 13	1.3	UV + FTIR[c]
HBr	0.001	18	11.3 ± 6.0	0.94	UV + FTIR[c]
NaBr	0.005	2	40.2 + 16/−3	4.40	MI−FTIR[b]
NaBr[e]	0.005	18	38.4 ± 14	3.2	UV + FTIR[c]
HBr	0.005	18	33 ± 8.5	2.8	UV + FTIR[c]
$NaNO_2$[f]	0.0005	18	3.7 ± 0.3	0.31	UV + FTIR[c]
$NaNO_2$[f]	0.0012	18	2.5 + (1/−0.4)	0.2	UV + FTIR[c]
$NaNO_2$[f]	0.01	18	8.0 ± 1.6	0.7	UV + FTIR[c]
$NaNO_2$[f]	0.03	18	16.3 ± 1.6	1.3	UV + FTIR[c]
$NaNO_2$[f]	0.1	18	22.0 ± 3.8	1.8	UV + FTIR[c]
$NaNO_2$	0.2	18	20.0	1.67	FTIR[b]

[a] Estimates of $H(k^{II})^{1/2}$ for Reactions with Br^- and NO_2^- can be obtained from the measurements of $H(k^{I})^{1/2}$. [b] $ClNO_2$ synthesized via N_2O_5 + Cl^-. [c] $ClNO_2$ synthesized via Cl_2 + NO_2^-. [d] From Behnke et al.[28] [e] Buffered with 0.02 mol/L KH_2PO_4/K_2HPO_4. [f] From Cl_2 + NO_2^- experiments.

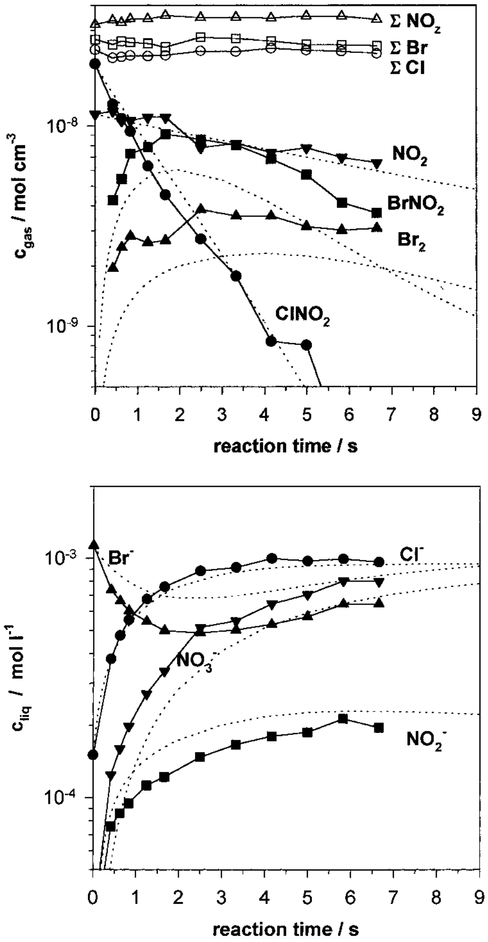

Figure 8. Uptake of $ClNO_2$ on 0.001 mol/L NaBr solution: dashed lines, results of numerical model. (a, top) Gas phase species and the sums of all chlorine, bromine, or nitrogen oxide species, respectively, expressed as gas-phase concentrations. (b, bottom) Liquid phase concentrations.

TABLE 3: Observed Decay Rates of $BrNO_2$

T, °C	k, 10^{-4} s^{-1}	T, °C	k, 10^{-4} s^{-1}
27.0	2.79 ± 0.30	58.0	16.1 ± 0.9
31.0	2.61 ± 0.10	66.3	39.1 ± 6.9
36.0	3.45 ± 0.15	66.4	31.0 ± 3.7
48.6	8.04 ± 0.41	67.0	33.9 ± 6.4

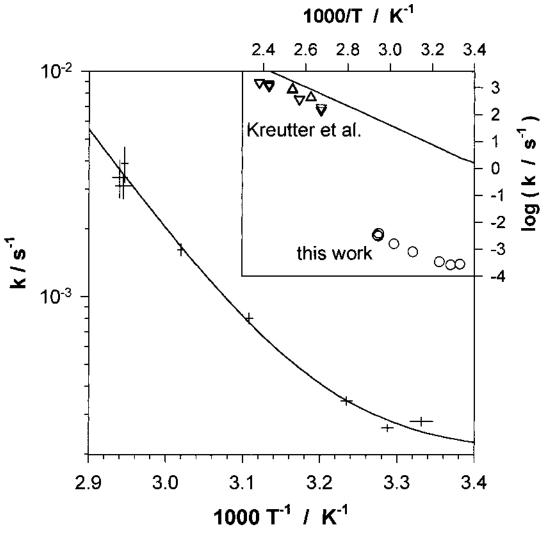

Figure 9. Arrhenius plot of the decay rates of $BrNO_2$ in s^{-1}. The inset compares our data (circles) with those of Kreutter et al. (triangle up, 533 hPa; triangle down, 266 hPa; line, extrapolation to atmospheric pressure). Vertical error bars represent the 95% confidence limits of a least squares fit for each single measurement; horizontal error bars represent the temperature drift of the cell.

A and k_{het} with parameter B fixed at different values the variation of χ^2 gives a 70% confidence limit for B of ±10−15% and an uncertainty of the A factor of about an order of magnitude. Therefore the activation energy for unimolecular decay, E_A, can be given as $E_A = 89 \pm 9$ kJ/mol.

The reverse reaction of Br atoms with NO_2 to form $BrNO_2$ can be neglected, since the lifetime of Br atoms toward other loss processes is too short to be the rate-limiting step of $BrNO_2$ loss. The lifetime for Br + NO_2 at the typical observed NO_2 concentration is $\tau_{NO_2} \approx 8.5 \times 10^{-6}$ s, using the reaction rate constant of Kreutter et al.;[26] the lifetime for the reaction Br + propene at the given propene concentration is $\tau_{propene} = 5.2 \times 10^{-6}$ s ($k_{propene} = 2.7 \times 10^{-12}$ cm^3 s^{-1}).[36] Diffusion of Br to the walls is on the order of seconds. Heterogeneous formation of $BrNO_2$ on the wall from $Br_2 + NO_2$ is not known to be an efficient source of $BrNO_2$, and $BrNO_2$ was not found in test experiments where a gas stream of typical concentrations of Br_2 and NO_2 was mixed in a glass vessel; BrNO and HNO_3 were found if the mixture was illuminated by UV-A light. On the other hand, reaction of Br atoms with $BrNO_2$ should enhance $BrNO_2$ loss, but this process would be second order in $BrNO_2$ and deviation from monoexponential behavior was not detected in the decay curves.

Discussion

Heterogeneous Chemistry of $BrNO_2$ and $ClNO_2$. The oxidation of nitrite by bromine and chlorine (or HOCl respectively) has been investigated in stopped flow experiments by different authors,[37−40] who all agree on the postulated formation of a nitryl halide as an intermediate step:

$$Cl_2 + NO_2^- \leftrightarrow ClNO_2 + Cl^- \qquad (k_1, k_{-1})$$

$$Br_2 + NO_2^- \leftrightarrow BrNO_2 + Br^- \qquad (k_2, k_{-2})$$

This formation of both nitryl halides has now been proved by our observations. $ClNO_2$ dissociates in water and hydrolyzes via the short-lived intermediate NO_2^+; [28] analogous reactions for $BrNO_2$ were expected:

$$ClNO_2 \leftrightarrow Cl^- + NO_2^+ \qquad (k_3, k_{-3})$$

$$BrNO_2 \leftrightarrow Br^- + NO_2^+ \qquad (k_4, k_{-4})$$

$$NO_2^+ + H_2O \rightarrow NO_3^- + 2H^+ \qquad (k_5)$$

The heterogeneous loss of $ClNO_2$ on chloride solution is much slower than on water, indicating that the main loss process, k_3 followed by k_5, is suppressed by k_{-3} in the presence of Cl^- [28] and that reaction k_{-1} must be inefficient, even at high chloride concentrations. Our results show that, in contrast, the reaction of $BrNO_2$ with Br^-, k_{-2}, must be fast, while the dissociation of $BrNO_2$ in water (k_4) is even slower than that of $ClNO_2$ (k_3).

Enhanced uptake of $ClNO_2$ and $BrNO_2$ on nitrite solutions and formation of NO_2 indicates further reactions, as already suggested by Pendlebury and Smith:[37,38]

$$ClNO_2 + NO_2^- \leftrightarrow Cl^- + N_2O_4 \qquad (k_6, k_{-6})$$

$$BrNO_2 + NO_2^- \leftrightarrow Br^- + N_2O_4 \qquad (k_7, k_{-7})$$

followed by:

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad (k_8)$$

Because of the low solubility of NO_2, the reaction

$$N_2O_4 \leftrightarrow NO_2 + NO_2 \qquad (k_9, k_{-9})$$

in the liquid phase leads to a release of NO_2 into the gas phase in our experiments. The observed increasing loss rate of $BrNO_2$ on nitrite solution cannot be explained by k_7 as the only effective loss reaction. Pendlebury and Smith suggested a complex reaction mechanism which can describe pH- and bromide-dependent reaction rates. Figure 10 shows a simplified reaction scheme.

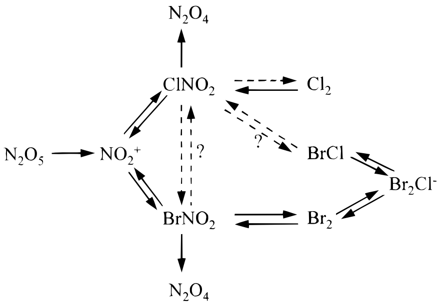

Figure 10. Simplified reaction scheme of N_2O_5 (NO_2^+) and the nitryl halides, where the reactants NO_2^-, Cl^-, and Br^- are omitted for clarity.

TABLE 4: Diffusion Coefficients Used in the Numerical Model of the Wetted-Wall Flow Tube for the Liquid Phase, D_l, and the Gas Phase (He + H_2O), D_g, at Atmospheric Pressure and 291 K

species	$D_l/10^{-5}$ cm^2 s^{-1}	D_g,[f] cm^2 s^{-1} [f]
Br^-	1.59[a]	
Cl^-	1.57[a]	
NO_2^-	1.53[b]	
NO_3^-	1.53[a]	
H^+	3.26[c]	
NO_2	1.76[b]	0.66
N_2O_4	1.16[d]	e
HONO	1.80[d]	0.62
Br_2	1.27[d]	0.33
BrCl	1.31[d]	0.42
Cl_2	1.35[d]	0.45
$BrNO_2$	1.15[d]	0.44
$ClNO_2$	1.20[d]	0.49
HOBr	1.42[d]	0.50

[a] Na salt after Nernst−Haskell.[31] [b] Estimated as equal to D_l of nitrate. [c] HCl after Nernst−Haskell.[31] [d] After Schroeder, LeBas, and Wilke, and Chang.[31] [e] The model assumes that N_2O_4 decays in the gas phase instantaneously into 2 NO_2. [f] After Fuller et al.[31]

TABLE 5: Henry's Law Constants Used in the Model (291 K)

species	H, mol/(L atm)	species	H, mol/(L atm)
Br_2	1.08[a]	HONO	49 [f]
BrCl	0.59[b]	HOBr	6.1×10^3 [g]
Cl_2	0.105[c]	$BrNO_2$	0.3[h]
NO_2	1.45×10^{-2} [d]	$ClNO_2$	4.6×10^{-2} [h]
N_2O_4	1.4[e]		

[a] Gmelin Handbook, Brom Supplement, Vol. A, p 432. [b] Estimated as the mean of H_{Br_2} and H_{Cl_2}. [c] From Wilhelm et al.[46] [d] After NBS.[47] [e] From Schwartz and White,[48] 298 K. [f] From Park and Lee,[49] 298 K. [g] Estimated from data for the Gibbs energy from McGrath and Rowland[50] and Gmelin Handbook, Brom Supplement, Vol. B2, p 177. [h] Estimated by fitting the model to the data; see text.

We tried to simulate the observed concentrations in the flow tube by a numerical model, similar to that described earlier.[28] The one-dimensional model (in cylindrical coordinates), written in the FACSIMILE language, includes radial diffusion in the gas and liquid phases and chemical reactions in the liquid phase. Axial diffusion is neglected, and axial transport is described by the progress of time. Concentration profiles are therefore assumed to be flat in the gas phase. The diffusion coefficients, Henry's law constants, and reaction rates used in the model are listed in Tables 4−6.

Some unknown parameters can be estimated the following way: the initial slopes of $BrNO_2$ uptake on bromide or nitrite solution give the values of $H_{BrNO_2}k^{1/2}$, with $k = k_{-2}[Br^-]$ or k $= k_7[NO_2^-]$, respectively. From the $BrNO_2$ and Br_2 concentra-

TABLE 6: Reactions Included in the Numerical Model of the Flow Tube (Where Only Equilibrium Constants Are Given, Fast Reaction Rates Are Used To Ensure Rapid Equilibria)

reaction			k or K_{eq}
$BrNO_2$ (aq)	$\rightarrow$	$Br^- + NO_2^+$	$k_4 = (0.06/H_{BrNO_2})^2\ s^{-1}$ [a]
	$\leftarrow$		$k_{-4} = 2.5 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$
$BrNO_2 + Br^-$	$\rightarrow$	$Br_2 + NO_2^-$	$k_{-2} = (2.53 \times 10^2/H_{BrNO_2})^2\ L\ mol^{-1}\ s^{-1}$ [a]
	$\leftarrow$		$k_2 = 2.6k_{-2}$
$BrNO_2 + NO_2^-$	$\rightarrow$	$Br^- + N_2O_4$	$k_7 = 3.3 \times 10^4\ k_{-2}/k_2\ L\ mol^{-1}\ s^{-1}$ [b]
$NO_2^+ + H_2O$	$\rightarrow$	$NO_3^- + 2H^+$	$k_5 = 1.66 \times 10^9\ s^{-1}$ [c]
Br_2 (aq)	$\rightarrow$	$HOBr + Br^- + H^+$	$k = 1.1 \times 10^2\ s^{-1}$ [d]
	$\leftarrow$		$k = 1.6 \times 10^{10}\ L^2\ mol^{-2}\ s^{-1}$ [d]
$Br_2 + Br^-$	$\leftrightarrow$	Br_3^-	$K_{Br_3} = 16.4\ L\ mol^{-1}$ [e]
$N_2O_4 + H_2O$	$\rightarrow$	$NO_3^- + NO_2^- + 2H^+$	$k_8 = 10^3\ s^{-1}$ [f]
N_2O_4 (aq)	$\rightarrow$	$2\ NO_2$	$k_9 = 6.9 \times 10^3\ s^{-1}$ [f]
	$\leftarrow$		$k_{-9} = 4.5 \times 10^8\ L\ mol^{-1}\ s^{-1}$ [f]
HONO	$\leftrightarrow$	$NO_2^- + H^+$	$K_{HONO} = 5.3 \times 10^{-4}\ mol\ L^{-1}$ [g]
H_2O	$\leftrightarrow$	$OH^- + H^+$	$K_{H_2O} = 6.3 \times 10^{-15}\ mol^2\ L^{-2}$
$NO_2^- + HONO$	$\rightarrow$	$HN_2O_4^-$	$k_{20} = 2.0 \times 10^3\ L\ mol^{-1}\ s^{-1}$ [b]
	$\leftarrow$		$k_{-20} = 10\ s^{-1}$ [b]
$HN_2O_4^- + H^+ + Br_2$	$\rightarrow$	$N_2O_3Br^+ + Br^- + H_2O$	$k_{22} = 7.5 \times 10^{11} + k_{-20}\ L^2\ mol^{-2}$ [b]
	$\leftarrow$		$k_{-22} = 10^7\ L\ mol^{-1}\ s^{-1}$ [b]
$N_2O_3Br^+ + 2\ H_2O$	$\rightarrow$	$NO_3^- + HONO + 3H^+ + Br^-$	$k_{23} = 4.16 \times 10^7\ L\ mol^{-1}$ [b]

[a] Values of $Hk^{1/2}$ used in the model, where the units of H_{BrNO_2} are moles per liter•atmosphere. [b] These reactions are supposed to model the mechanism suggested by Pendlebury and Smith[37] reaction rates are "best guess" to fit the data without further justification. [c] Estimated from $k(NO_2^+ + Cl^-)/k(NO_2^+ + H_2O) = 836 \pm 32$ from Behnke et al.[28] [d] Gmelin Handbook, Brom Supplement, Vol. A, p 440. [e] Reference 51. [f] Reference 52. [g] Reference 49.

tions in the gas phase over bromide solution at maximum reaction time, one can estimate $H_{BrNO_2}k_{-2}/k_2$ from

$$H_{BrNO_2}[BrNO_2]_{gas}[Br^-]k_{-2} = H_{Br_2}[Br_2]_{gas}[NO_2^-]\ k_2 \quad (3)$$

assuming a fast equilibrium between Br_2 and $BrNO_2$ and neglecting other loss processes. An estimate for H_{BrNO_2}, which has to be considered to give only the order of magnitude, is obtained by comparison of the modeled $BrNO_2$ concentration with the data for $BrNO_2$ uptake on water. The parameters were refined only by qualitative adjustment of the model to the experimental data. The parameters for the model results shown in Figures 2, 4, and 5 are given in Tables 4−6. The reaction mechanism given above describes the experimental data for $BrNO_2$ uptake on water and on bromide solution (within a factor of 2, in most cases even better) but cannot explain the observed increasing uptake of $BrNO_2$ on nitrite solution. No simple mechanism could be found to model the latter, so we included parts of the complex mechanism suggested Pendlebury and Smith (lower part of Table 6). The latter was found to be able to describe the concentration profiles of $BrNO_2$ over nitrite solution and over 0.01 M HBr, without influencing the model at other conditions, but due to the large number of free parameters no firm conclusion on the correctness of this mechanism can be drawn.

The model shows that the hydrolysis of $BrNO_2$ via k_4 and k_5 has to be slow, and the reaction with nitrite, k_7,was found to dominate the loss of $BrNO_2$ on water under our experimental conditions. Therefore the model results remain unchanged if an alternative hydrolysis reaction like

$$BrNO_2 + H_2O \rightarrow HOBr + HONO \qquad (k_{4a})$$

is included in the model instead of k_4. The reaction sequence k_4 and k_{-4} has been written by analogy to the chemistry of nitryl chloride,[28] where the uptake kinetics on NaCl solutions were suggestive for a the reaction scheme k_3, k_{-3}, and k_5. However, it should be noted that the structures of nitryl chloride and nitryl bromide may be slightly different. In fact, the atomic charge distribution in these nitryl compounds is strongly affected by the nature of the halogen. Theoretical calculations[24] showed that bromine exhibits a larger positive partial charge, indicating that the Br−N bond is more ionic than Cl−N (which is almost purely covalent). These simulations would be in agreement with the alternative hydrolysis pathway given in reaction k_{4a}. However, the same calculations showed that in $BrNO_2$ both Br and N are positively charged which could be in favor of NO_2^+-formation. From this observation it simply appears that the reactivity of $BrNO_2$ may be different from the one reported for $ClNO_2$. However, our uptake studies are not able to distinguish between the two possible hydrolysis pathways, since the already mentioned disappearance in the aqueous phase was governed by NO_2^- during our experiments.

For the experiments including chlorine species, the model was extended by the reactions given in Table 7. The reaction of $ClNO_2$ with nitrite solution does not show any indications for a complex mechanism like for $BrNO_2/Br_2$. The values of $Hk_6^{1/2}$ obtained from the measured uptake coefficients differ from 3.7 to 13.8 $mol^{1/2}\ L^{-1/2}\ atm^{-1}\ s^{-1/2}$. The value used in the model corresponds to the lowest measured value. The difference shown in Figure 3 between experimentally measured concentrations and those simulated by the model simply depicts the uncertainty of the fitted parameters (and especially the Henry's law constant for $ClNO_2$). It should be, however, noted that the difference is less than 50%, which is acceptabe with regard to the complexity of the chemistry occurring here.

For interconversion of $BrNO_2$ and $ClNO_2$ an additional problem arises: the dissociation reactions of both species (k_3, k_4) are too slow to explain the interconversion via the intermediate NO_2^+, following reactions k_3, k_{-4} or k_4, k_{-3}, respectively. From the enhanced uptake of $ClNO_2$ on bromide solution it is clear that a fast reaction of $ClNO_2$ with Br^- exists, but two reaction products, BrCl or $BrNO_2$, are possible in principle. Wang et al.[41] measured the equilibrium constants between BrCl, Br_2Cl^-, and Br_2 and stated that these equilibria are very fast. From our data also the Br_2−$BrNO_2$ equilibrium was found to be fast; therefore, it is possible to explain $ClNO_2$ to $BrNO_2$ conversion either by direct halogen X^- exchange

$$ClNO_2 + Br^- \leftrightarrow BrNO_2 + Cl^- \qquad (k_{10}, k_{-10})$$

TABLE 7: Reactions of Chlorine Species Included in the Numerical Model of the Flow Tube

reaction			k or K_{eq}
$ClNO_2$	$\rightarrow$	$Cl^- + NO_2^+$	$k_3 = (0.44/H_{ClNO_2})^2$ s^{-1} [a,c]
	$\leftarrow$		$k_{-3} = 2.5 \times 10^{10}$ L mol^{-1} s^{-1}
$ClNO_2 + NO_2^-$	$\rightarrow$	$Cl^- + N_2O_4$	$k_6 = (4.11/H_{ClNO_2})^2$ L mol^{-1} s^{-1} [c]
$Cl_2 + NO_2^-$	$\rightarrow$	$ClNO_2 + Cl^-$	$k_1 = 2.5 \times 10^6$ L mol^{-1} s^{-1}
$BrCl$	$\leftrightarrow$	$HOBr + Cl^- + H^+$	$K_{BrCl} = 1.3 \times 10^{-9}$ mol^2 L^{-2} [b]
$BrCl + Br^-$	$\leftrightarrow$	Br_2Cl^-	$K = 1.8 \times 10^4$ L/mol [b]
Br_2Cl^-	$\leftrightarrow$	$Br_2 + Cl^-$	$K = 1.3$ L/mol [b]
$ClNO_2 + Br^-$	$\rightarrow$	$BrNO_2 + Cl^-$	$k_{10} = (50.0/H_{ClNO_2})^2$ L mol^{-1} s^{-1} [c]
	$\leftarrow$		$k_{-10} = 3 \times 10^2$ L mol^{-1} s^{-1}
alternative reaction path:			
$ClNO_2 + Br^-$	$\rightarrow$	$BrCl + NO_2^-$	$k_{10a} = (50.0/H_{ClNO_2})^2$ L mol^{-1} s^{-1} [c]
	$\leftarrow$		$k_{-10a} = 10^7$ L mol^{-1} s^{-1}

[a] After Behnke et al.[28] [b] After Wang et al.[41] [c] Values of $Hk^{1/2}$ used in the model, where the units of H_{ClNO_2} are liters per mole·atmosphere.

or via the Br_2–BrCl equilibrium. In the latter case a reaction

$$ClNO_2 + Br^- \leftrightarrow BrCl + NO_2^- \qquad (k_{10a}, k_{-10a})$$

has to be assumed. Since BrCl is known to hydrolyze into HOBr and HCl, one may object to the Cl^+ transfer (not a Br^+ transfer) in reaction −10a. In addition, the formation of BrCl in reaction 10a would be in analogy to the interpretation of the reaction of $ClNO_2$ with iodide as a fast nucleophilic attack with Cl^+ transfer.[42]

Unimolecular Decay of $BrNO_2$ in the Gas Phase. In our decay experiments, the lifetime of $BrNO_2$ in the UV cell (and also in the IR cells) at 300 K appears to be limited by heterogeneous wall loss. Using the fitted parameters for the unimolecular decay, a gas phase lifetime of about 7 h at 298 K is found. This lifetime, and also that directly observed in our experiments, is clearly inconsistent with the earlier results reported by Kreutter and Wine.[26,27] The differences are far outside experimental error (and cannot be explained by any assumption on the temperature dependence of the heterogeneous contribution) so that it must be assumed that a different reaction was observed. $BrNO_2$ was identified in our measurements by its IR absorption spectrum without doubt,[21] and its stability at room temperature was observed in many experiments under different conditions. Since Kreutter and Wine did not observe the reaction product of Br atoms with NO_2, we assume that the BrONO isomer of nitryl bromide was formed in their experiment. This would follow the analogous reaction Cl + NO_2 which is known to form ClONO,[43,44] that can isomerize to $ClNO_2$, probably heterogeneously.[45] Accordingly BrONO is thought to be less stable than $BrNO_2$, which is confirmed by a recent ab initio study.[24] This ab initio study reports an enthalpy for $BrNO_2$ decay into Br and NO_2 of 94.2 kJ/mol. Compared with our experimental activation energy for unimolecular decay of 89 ± 9 kJ/mol, this is consistent within the range of error if the transition state is not more than about 4 kJ/mol higher than the enthalpy of the products.

Conclusions

$ClNO_2$ is known to be released by the heterogeneous reaction of N_2O_5 with chloride solution at high yield.[28] In the presence of bromide also $BrNO_2$ and Br_2 are released.[14,25] In this work we found that $BrNO_2$ and Br_2 are coupled by a fast reversible liquid phase reaction. Also the (net) reaction of $ClNO_2$ to form $BrNO_2$ is reversible. A model of diffusion and reaction processes in the experimental setup shows that the proposed reaction mechanism can explain the measured concentration profiles. Rough estimates of Henry's law constants and of different reaction rate constants in the scheme are obtained by fitting the model to the data. It must be emphasized that these estimated constants are highly uncertain; reliable values can only be given for the uptake coefficients γ and the products $Hk^{1/2}$ calculated thereof.

The reactions of $ClNO_2$ and $BrNO_2$ with bromide can be regarded as conversion reactions which do not lead to an effective loss of total halogen species from the gas phase. The loss in the liquid phase is governed by the slow hydrolysis reactions of $ClNO_2$ and $BrNO_2$ and by their reactions with nitrite. The latter lead partly to the release of NO_2 to the gas phase, thereby decreasing the efficiency of NO_y loss to the liquid phase.

In the presence of nitrogen oxides and ozone, $ClNO_2$, $BrNO_2$, and Br_2 may be released at night from heterogeneous reactions on sea salt aerosol in the marine troposphere. All three species are easily photolyzed in the morning to yield halogen atoms. In contrast to previous reports, $BrNO_2$ can survive for several hours to yield Br atoms by photolysis in the morning. In the case in which the reaction of N_2O_5 with sea salt aerosol is a major path for halogen release, the above described interconversion reactions might influence the resulting Cl/Br atom ratio at sunrise.

Note Added in Proof. Very recently, R. Bröske and F. Zabel (University of Wuppertal) determined lifetimes of $BrNO_2$ (obtained by photolysis of Br_2 and NO_2, using yellow light and removing inherent traces of NO afterwards by adding O_3) between 266 and 299 K in 1 atm of N_2 in a 420 L chamber. The observed lifetimes between 2 and 18 h (independent of the presence or absence of *trans*-2-butene as a scavenger of atomic Br) are consistent with our data and continue the Arrhenius plot of Figure 9 to lower temperatures. Communication of these data to us prior to publication is gratefully acknowledged.

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