A Reflection−Absorption Infrared Spectroscopy (RAIRS) Investigation of the Low-Temperature Heterogeneous Hydrolysis of Bromine Nitrate

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Reflection−absorption infrared spectroscopy (RAIRS) has been employed to investigate the heterogeneous hydrolysis of bromine nitrate ($BrONO_2$) in and on thin ice films between 95 and 185 K. Hydrolysis is observed to occur throughout the temperature range with evidence for two competing mechanisms. At the stratospherically relevant temperature of 185 K, the reaction proceeds by an ionic mechanism to give the hypobromous ion, H_2OBr^+, and both nitric acid di- and trihydrate. A molecular mechanism is also operative to give hypobromous acid, HOBr, and hydrated nitric acid ($HNO_3 \cdot (H_2O)_n$). This second route becomes more important under conditions of limited water presence and at lower temperatures. All of the results are compared to analogous studies previously performed on chlorine nitrate ($ClONO_2$).

Introduction

Bromine nitrate is a well-established and major bromine reservoir in the lower stratosphere.[1] The regeneration of active, ozone-destructive bromine species from $BrONO_2$ is therefore of key importance to the chemistry of stratospheric ozone. It is formed in the atmosphere by the reaction of BrO radicals with NO_2 (reaction 1)[2,3] and is destroyed by photolysis (reactions 2 and 3)[4−6] or by hydrolysis (reaction 4).[7−10]

$$BrO + NO_2 \rightarrow BrONO_2 \tag{1}$$

$$BrONO_2 + h\nu \rightarrow Br + NO_3 \tag{2}$$

$$BrONO_2 + h\nu \rightarrow BrO + NO_2 \tag{3}$$

$$BrONO_{2(ads)} + H_2O_{(ads)} \rightarrow HOBr_{(ads\ or\ g)} + HNO_{3(ads)} \tag{4}$$

Although photolysis of $BrONO_2$ can initiate catalytic ozone destruction,[4] it is considered to have little atmospheric significance due to its low abundance. However, the heterogeneous hydrolysis of $BrONO_2$ does directly affect atmospheric ozone concentrations by the primary release of the photochemically labile compound hypobromous acid, HOBr,[11] which is then rapidly converted to active bromine radicals as shown in reaction 5.[12−16]

$$HOBr + h\nu \rightarrow OH + Br \tag{5}$$

In principle, active bromine can also be released from HOBr following its heterogeneous reaction with solvated halide ions:[17−20]

$$HOBr_{(ads)} + Br^-_{(aq)} + H_3O^+_{(aq)} \rightarrow 2H_2O + Br_2 \tag{6}$$

$$HOBr_{(ads)} + Cl^-_{(aq)} + H_3O^+_{(aq)} \rightarrow 2H_2O + BrCl \tag{7}$$

Both of these reactions represent key steps in the chemistry of the so-called "sudden" tropospheric ozone loss phenomenon.[8,21−26] Thus $BrONO_2$ may also play a role in these events, after hydrolysis to HOBr, as long as it adsorbs efficiently to atmospherically relevant interfaces.[21]

In fact the uptake (sticking) coefficients of $BrONO_2$ have been measured for water-ice and sulfuric acid surfaces, with and without added HCl.[19,20,27] For these systems, the results indicate uptake coefficients in the range between 0.2 and 0.5. These values predict hydrolysis reaction probabilities, which are 2 orders of magnitude more than the analogous chlorine nitrate reaction.[27] The hydrolysis products, HOBr and HNO_3, were also identified using mass spectrometry, and the experiments show that BrCl is produced in the presence of HCl.[19,20,27]

The mechanism for the heterogeneous (water-ice) hydrolysis of bromine nitrate would be expected to be analogous to that of its theoretically and experimentally well-studied chlorine nitrate analogue. It has been established for many years that $ClONO_2$ can produce HOCl, nitric acid, and molecular chlorine from water-ice surfaces containing HCl.[28] The nature of the steps involved in the overall process are still subject to some debate. However, recent experimental and theoretical findings are all consistent with the following ionic mechanism, which was initially proposed from the results of a series of reflection−absorption infrared spectroscopy RAIRS experiments performed on surfaces held at 160−180 K:[29−36]

$$ClONO_{2(g)} \rightarrow Cl^+NO_3^-{}_{(ads)} \tag{8}$$

$$Cl^+NO_3^-{}_{(ads)} + H_2O \rightarrow [H_2OCl]^+NO_3^-{}_{(ads)} \tag{9}$$

$$[H_2OCl]^+NO_3^-{}_{(ads)} + nH_2O \rightarrow HOCl + HNO_3 \cdot (H_2O)_n \tag{10}$$

At lower, stratospherically irrelevant temperatures (140 K),

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evidence of a nonionic mechanistic route has recently been presented, which is in agreement with certain theoretical predictions for the system.[37]

Ab initio calculations on the interaction between H_2O and $BrONO_2$ predict, in a fashion analogous to chlorine nitrate hydrolysis, that bonding between the oxygen of the water and the bromine atom occurs.[38] This attraction is likely to initiate the first step in the hydrolysis of bromine nitrate. Therefore, the aim of the current study was to experimentally test the theoretical predictions for bromine nitrate hydrolysis using RAIRS as a probe of the chemical mechanism.

Experimental Section

The experimental arrangement used in this study has been detailed elsewhere.[39] It consists of a temperature-controlled gold foil substrate mounted in an ultrahigh vacuum (UHV) chamber. Background pressures of the differentially pumped vacuum chamber were typically 1×10^{-9} mbar. RAIRS was employed for the analysis of a variety of thin substrate films of varying chemical composition deposited in vacuo. The infrared beam emitted from a Bio-Rad FTS-60A spectrometer was reflected off the gold substrate at a high angle of incidence to the surface normal (ca. 75°) and detected by an external liquid nitrogen cooled MCT detector. RAIR spectra were recorded at 4 cm^{-1} resolution with 256 scans. Based on the exposure rate (1×10^{-6} mbar s^{-1} = 1 Langmuir $\approx$ 0.5 monolayer s^{-1}), the layers were estimated to be approximately 500 nm thick.

$BrONO_2$ was prepared by the reaction of BrCl with $ClONO_2$ according to the method of Spencer and Rowland.[40]

$$BrCl + ClONO_2 \rightarrow BrONO_2 + Cl_2 \qquad (11)$$

In this case, 0.1 mol of BrCl was added to an approximately equimolar quantity of $ClONO_2$ (10 g) in a blackened Schlenk tube. The mixture was maintained at −50 °C for 1 week, following which the reaction was quenched by cooling to 195 K. $ClONO_2$ and Cl_2 were removed from the reaction mixture by vacuum distillation at 195 K for 10 h. Br_2 and BrCl could not be easily removed from the $BrONO_2$ due to their similar vapor pressures. The effects of these impurities on the spectroscopic measurements are discussed below.

$BrONO_2$ samples were obtained from the stock material by warming the mixture at room temperature until a sufficient vapor pressure was achieved. By comparison with literature values for the absorption cross section of bromine nitrate,[4] it was estimated that the final product was typically 20% $BrONO_2$ in a mixture of Br_2 and BrCl. Nitric acid impurities were also observed if the glassware had not been conditioned sufficiently prior to addition of $BrONO_2$. Nitrogen dioxide was observed if the $BrONO_2$ was allowed to decompose. However, it was found that $BrONO_2$ could be stored without significant decomposition in a blackened Schlenk tube frozen under vacuum at 77 K.

Results

RAIR Spectra of Thin Films of Neat Bromine Nitrate. Bromine nitrate, $BrONO_2$, was dosed onto the gold substrate held at 80 K for 30 s at a background pressure of 1×10^{-6} mbar to produce a thin-film < 1 μm in depth. The resultant RAIR spectrum is shown as Figure 1b along with the observed room temperature, gas-phase spectrum for comparison (Figure 1a).

A minor impurity in the samples is identified with nitric acid as revealed by gas phase absorption features at 3550, 1325, 886, 762, and 457 cm^{-1} and by adsorbed counterparts at 3230, 1303, 933, and 765 cm^{-1}. Such impurities are produced from the hydrolysis of bromine nitrate by water deposited on the walls of the IR cell and the UHV chamber.

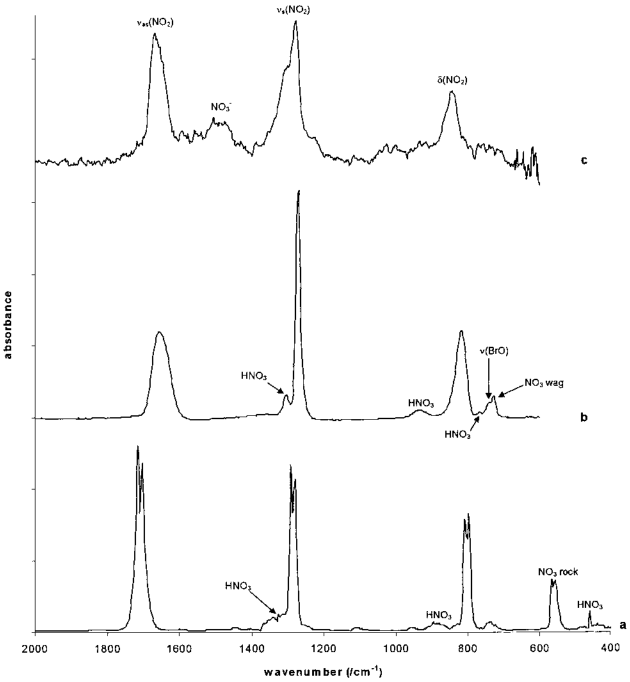


Figure 1. Spectra of $BrONO_2$. Spectra not to scale and offset for clarity. (a) IR spectrum of gas-phase $BrONO_2$ (in Br_2 and BrCl), 20 mbar, 298 K. (b) RAIR spectrum of a thin film of $BrONO_2$ (in Br_2 and BrCl) at 80 K. (c) RAIR spectrum of a thin film of $BrONO_2$ deposited at 160 K.

$BrONO_2$ has a planar, C_s, structure and hence all nine fundamental modes are IR active.[41] The observed vibrational wavenumbers and assignments of bromine nitrate are shown in Table 1. The main spectral differences between gas-phase and adsorbed bromine nitrate are: (i) a red-shifting of the $-NO_2$ stretching mode wavenumbers and (ii) a blue-shifting of the $-NO_2$ deformation mode wavenumber. The bands also change their relative intensities.

For the "pure" adsorbed $BrONO_2$ spectra, measured as part of the current study, the RAIRS bands were observed to be shifted more than might be expected following a simple amorphous condensation process. For example the $\nu_{as}(NO_2)$ band is shifted by ca. 50 cm^{-1}. This phenomenon is due to surface interactions between the bromine nitrate, molecular bromine, and possibly BrCl. The latter two compounds are major impurity components of the thin films as discussed above. In the presence of condensed polar molecules, molecular bromine can be polarized enabling interspecies dipolar bonding to occur. This interaction alters the internal bonding of $BrONO_2$ and hence its vibrational IR spectrum. The effect has been observed previously for thin films of water condensed with Br_2.[42,43] It has also been observed for HNO_3 and $ClONO_2$ condensed with Br_2; here vibrational frequency shifts of up to 30 cm^{-1} were measured relative to pure, Br_2-free films.[44] For bromine nitrate, such an interpretation would require a truly pure sample of the material to be deposited, thereby allowing a spectral comparison to be made. This objective was achieved using the following approach.

Molecular bromine has been shown previously to desorb from a gold substrate held at 160 K.[42] Thus dosing the $BrONO_2$ sample at 160 K should produce a relatively pure, Br_2-free film

TABLE 1: Vibrational Frequencies of $BrONO_2$[a]

		wavenumber/cm^{-1}					
vibrational mode		gas-phase $BrONO_2$[b,c]	adsorbed amorphous $BrONO_2$[b,c]	$BrONO_{2(ads)}$ dosed at 160 K[b]	adsorbed crystalline $BrONO_2$[b]	gas-phase $BrONO_2$[41]	solid crystalline $BrONO_2$[41]
$\nu_{as}(NO_2)$	ν_1	1709	1655	1669	1614	1714	1616
$\nu_s(NO_2)$	ν_2	1285	1270	1269	1261	1282	1265
$\delta(NO_2)$	ν_3	801	816	842	846	806	839
$\nu(BrO)$	ν_4	736	741		762	750[d]	765
NO_3 ‘wag’	ν_8	723	727		734	733	735
NO_3 ‘rock’	ν_5	560			643	564	642
$2\nu_{as}(NO_2)$	$2\nu_1$	3394			3384	3406	
	$\nu_1 + \nu_2$	2975	2893		2859	2982	
$2\nu_s(NO_2)$	$2\nu_2$	2559	2523		2490	2565	
	$\nu_1 + \nu_5$	2270	2255		2264	2273	
	$\nu_2 + \nu_5$	1820					
$2\delta(NO_2)$	$2\nu_3$	1599				1610	
$2NO_3$ ‘wag’	$2\nu_8$	1443			1467	1449	1468
$2NO_3$ “rock”	$2\nu_5$	1108	1074		1265[e]	1112	1260[f]
	$\nu_5 + \nu_6$	954			1048	958	
$\nu(NO)$	ν_6						400
$\delta(NOBr)$	ν_7						245

[a] Gas-phase frequencies are reported for the absorbance center point. Overtone and combination bands are very weak and may not be visible in the presented spectra. The NO_3 wagging and NO_3 rocking modes are also referred to respectively as the out of plane and in plane deformations of the NO_3 group. [b] This study. [c] Data refers to ca. 20% $BrONO_2$ in Br_2/BrCl. [d] Ne matrix. [e] Observed only as a shoulder on the large $\nu_s(NO_2)$ absorbance. [f] Raman spectrum.

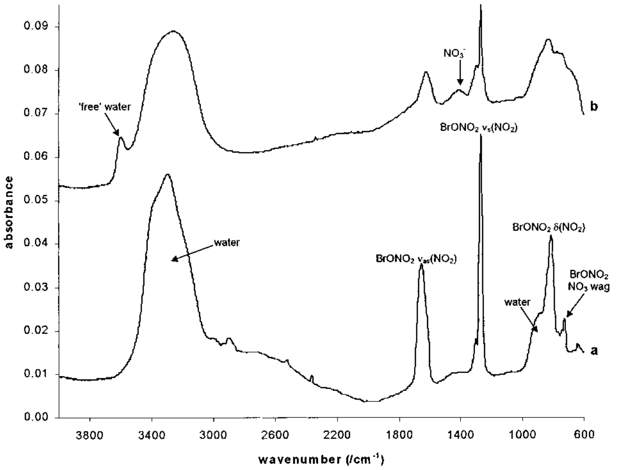


Figure 2. RAIR spectra of $BrONO_2$ (in Br_2) dosed with water. Spectra offset for clarity. (a) $BrONO_2$ dosed onto a water-ice film at 80 K, then annealed to 140 K. (b) $BrONO_2$ co-deposited with water (1:3) at 95 K.

of $BrONO_2$. The RAIR spectrum of such a sample is shown in Figure 1c and the wavenumbers summarized in Table 1. The data show that the $BrONO_2$ vibrational wavenumbers do indeed shift from those obtained after deposition below 160 K.

The gas-phase IR spectra of HNO_3, $ClONO_2$, and $BrONO_2$ exhibited no changes upon the addition of molecular bromine to their respective cells.[44]

After annealing a thin film of $BrONO_2$ previously deposited at 80 K to ca. 150 K, a phase change is observed due to conversion from a disordered (amorphous state) $BrONO_2$ to its crystalline counterpart. The observed vibrational wavenumbers of crystalline $BrONO_2$ obtained in the current study are shown in Table 1. They are in excellent agreement with the previous work of Wilson and Christe.[41] The bands are shifted considerably from the gas-phase counterpart spectrum: for example, the $\nu_{as}(NO_2)$ band is shifted by ca. 100 cm^{-1}. The results suggest that Br_2 interactions have been eliminated by the crystallization process but replaced by other stronger, solid-phase interactions. It is interesting to note that while annealing can induce crystallization of $BrONO_2$, dosing at 160 K appears to form pure but amorphous $BrONO_2$. Why this phenomenon should occur is not clear. However it must be related to the different physical processes associated with the annealing of a preadsorbed, bromine-containing film compared to adsorbing the film directly at 160 K.

The Hydrolysis of Bromine Nitrate. Thin films of bromine nitrate and water-ice were produced by the effusive deposition of each vapor onto the gold substrate using separate dosing lines. Subsequently, the temperature of the material was varied to study its effect upon the heterogeneous hydrolysis of $BrONO_2$.

Figure 2a shows the RAIR spectrum obtained following the warming to 140 K of a thin film of $BrONO_2$. In this case the sample had been deposited on top of a thin film of water-ice. Despite the annealing process, no sign of hydrolysis is observable and the distinctive spectra due to molecular $BrONO_2$ (1655, 1270, 816, and 727 cm^{-1}) and water-ice (3300 and 890 cm^{-1}) are clearly measured.

However, hydrolysis does occur when $BrONO_2$ and water are *simultaneously* co-deposited at low temperatures to produce a mixed film. Figure 2b reveals that, at 95 K, a partial solvation of $BrONO_2$ occurs. IR bands due to water-ice and molecular bromine nitrate are observed in addition to readily assigned features arising from the nitrate ion, NO_3^- (1411, 1298, 1039 cm^{-1}) and free, non-hydrogen bonded water (3598 cm^{-1}). The latter band originates from individual water molecules becoming trapped in a matrix of bromine or bromine nitrate. A band at ca. 1650 cm^{-1} is also apparent.

Complete hydrolysis of $BrONO_2$ occurs when it is co-deposited with water at higher substrate temperatures (> ca. 140 K). Figure 3 shows a series of RAIR spectra recorded following the co-deposition of $BrONO_2$ (in Br_2) and H_2O in a 1:2 ratio as a function of temperature. At 140 K a small amount of nonreacted molecular $BrONO_2$ is apparent from observation of the $\nu_{s(NO2)}$ mode at 1260 cm^{-1}. The major product of hydrolysis at 140 K (and the sole species observed with hydrolysis at 155 and 170 K) is amorphous nitric acid dihydrate and/or trihydrate.[45−48]

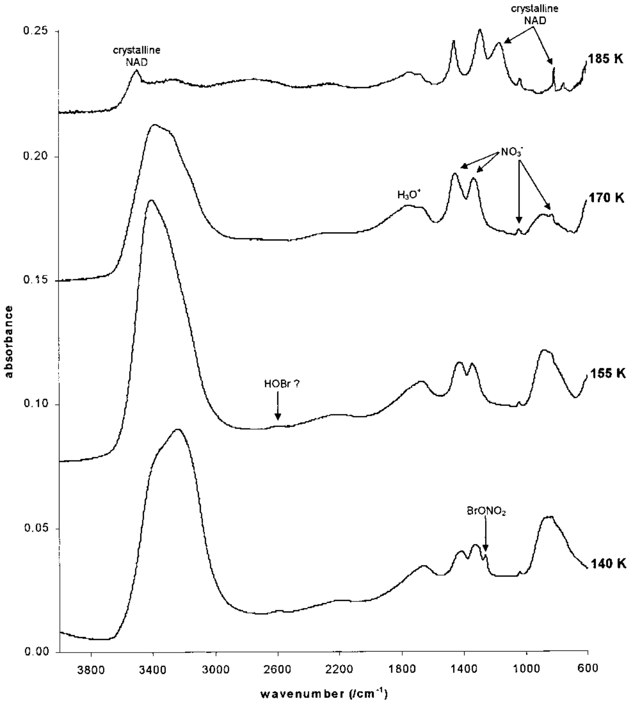


Figure 3. RAIR spectra of $BrONO_2$ co-deposited with water in a 1:2 ratio between 140 and 185 K. Spectra offset for clarity. 185 K spectrum magnified 5 times.

Absorption features due to water-ice (3300, 2230, 1650, and 880 cm^{-1}) are measured at deposition temperatures between 140 and 170 K. A peak at 2596 cm^{-1} is also observed, which can be assigned to HOBr, as discussed below.

At 185 K the temperature is too high for adsorption of either molecular water or molecular bromine nitrate, and thus only a small quantity of ionized products is observed. The main product, which is crystalline nitric acid dihydrate (NAD), has a characteristic RAIR spectrum and consists of IR bands at 3498, 1163, and 810 cm^{-1}, whereas amorphous NAD is also revealed by peaks at 1755, 1462, and 1296 cm^{-1}.[47]

The hydrolysis mechanism of bromine nitrate was further investigated in a series of experiments in which $BrONO_2$ and water were co-deposited at different ratios onto the gold substrate held at 185 K. The resultant RAIR spectra obtained under conditions of (i) limited water; (ii) excess water; (iii) "intermediate" water are shown in Figure 4. The vibrational wavenumbers observed are listed in Table 2. It is important to reiterate that molecular bromine does not adsorb at this temperature, and therefore films condensed at 185 K are considered to be free of Br_2 (and BrCl) contamination.

The Hydrolysis of Ionic Bromine Nitrate. Ionic bromine nitrate, $Br^+NO_3^-$, was isolated by dosing $BrONO_2$ onto the gold substrate held at 185 K. By analogy with ionic chlorine nitrate, $Br^+NO_3^-$ is characterized by the NO_3^- group vibrational modes at 1535($\nu_{(N=O)}$), 1326 ($\nu_{as(NO2)}$), 1039($\nu_{s(NO2)}$), and 797($\nu_{(NO2)}$) cm^{-1}.[29] As observed for chlorine nitrate, the ionization of bromine nitrate produces a C_{2v} nitrate ion, possibly interacting with the countercation via two oxygen atoms, i.e., in the current study, $O{=}NO_2{-}Br^+$. The RAIR spectrum of $Br^+NO_3^-$ is shown in Figure 5a and its vibrational wavenumbers are summarized in Table 2. Weak vibrations due to H_2O are also observed at 3400 and 1650 cm^{-1}. This contamination arises most likely from background water inside the UHV chamber. As molecular water cannot absorb directly onto the substrate at 185 K, the water must be associated with $Br^+NO_3^-$, either as water of hydration or H_2OBr^+.

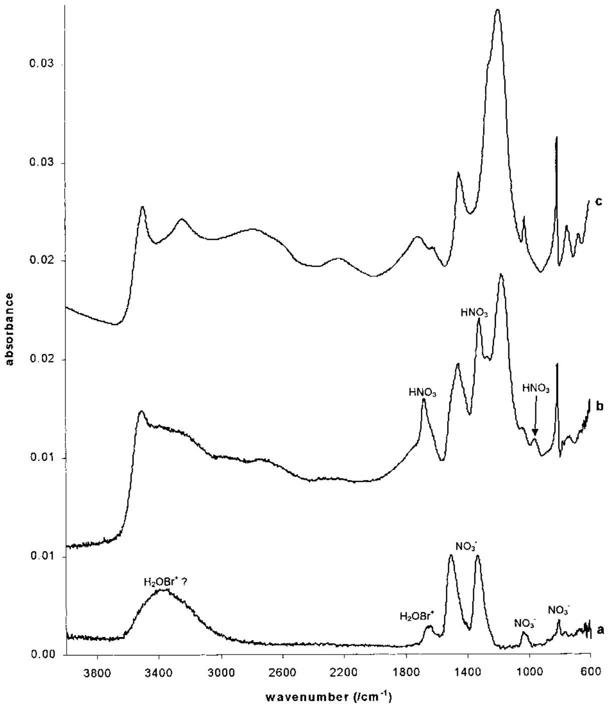


Figure 4. RAIR spectra showing $BrONO_2$ (in Br_2) co-deposited with water at 185 K. Spectra offset for clarity. (a) $BrONO_2/H_2O = 50{:}1$. (b) $BrONO_2/H_2O = 10{:}1$. (c) $BrONO_2/H_2O = 1{:}4$ − crystalline NAD.

TABLE 2: Vibrational Frequencies of Ionic Species Observed during This Study[a]

vibrational mode		vibrational frequency (wavenumber/cm^{-1})			
		$Br^+NO_3^-$	$H_2OBr^+NO_3^-$	NAD[47]	NAT[47]
$\nu_{as,s}(H_2O)$	$\nu_{1,3}$		3380 br	3490 vs	3440 vs
				3230 m	3220 m
				2814 br	2900 br
$\nu_{as,s}(H_3O^+)$	$\nu_{1,3}$			2300 br	
$\delta_{as}(H_3O^+)$	ν_4			1750 vw	1750 vw
$\delta(H_2O)$	ν_2		1650 m		
$\nu(N{=}O)$	ν_1	1531 s	1508 s	1457 m	1364 m
$\nu_{as}(NO_2)$	ν_4	1329 s	1335 s	1267 m	
$\delta_s(H_3O^+)$	ν_2			1182 vs	1136 s
$\nu_s(NO_2)$	ν_1	1039 m	1035 m	1023 vw	
$\delta(NO_2)$	ν_3	797 m	806 m	808 s	821 vs

[a] The nitrate ion is assigned as C_{2v} symmetry, however, it is of D_{3h} symmetry in NAT. For NAT, the asymmetric stretch of NO_3 is doubly degenerate and the symmetric stretch is IR inactive.

On dosing a limited amount of water onto the adsorbed $Br^+NO_3^-$ at 185 K, partial hydrolysis is observed, the associated spectrum is shown in Figure 5b. This spectrum is similar to Figure 4a, albeit with additional water deposited by a different method. The nitrate band features correspond to $H_2OBr^+NO_3^-$ and/or amorphous nitric acid trihydrate, NAT.[45−48] Also observed is molecular nitric acid, which has distinct absorption peaks at 1676, 956, and 779 cm^{-1}.[37] The $\nu_{as}(NO_3)$ band of molecular nitric acid (at 1320 cm^{-1}) is obscured by the $\nu_{as}(NO_3)$ bands of $H_2OBr^+NO_3^-$ and amorphous NAT.

Complete hydrolysis of $Br^+NO_3^-$ is observed on dosing excess water onto adsorbed $Br^+NO_3^-$ at 185 K. Figure 5c shows the products of the complete hydrolysis, namely crystalline and amorphous NAT.[45,47,48] The vibrational wavenumbers and assignments of NAT, which has a nitrate ion of D_{3h} symmetry are shown in Table 2. The existence of non-D_{3h} nitrate is revealed by absorption peaks at 1050 ($\nu_s(NO_2)$) and 1418 ($\nu(N{=}O)$ or $\nu_{as}(NO_2)$). Under "high temperature" experimental conditions, NAT desorbs from the gold foil after several

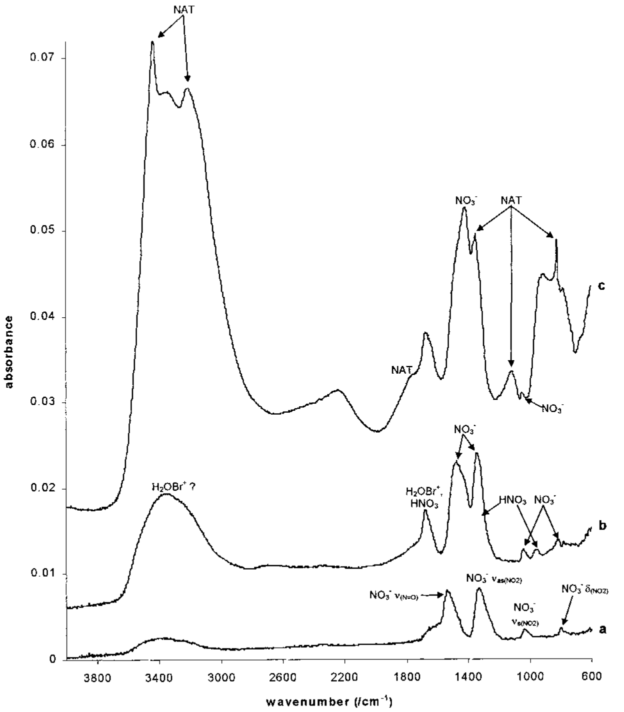


Figure 5. RAIR spectra showing the effect of dosing water onto a thin film of neat $Br^+NO_3^-$ at 185 K. Spectra are offset for clarity. (a) Neat $Br^+NO_3^-$ (with minor H_2O contamination). (b) Limited water dosing. (c) Excess water dosing.

minutes: the resultant RAIR spectrum is identical to that shown in Figure 5b. It follows that this film comprises of $H_2OBr^+NO_3^-$ and molecular nitric acid, which is presumably strongly bound to the surface.

Discussion

Production of the Hypobromous Acidium Ion. The hypobromous acidium ion, H_2OBr^+, has long been implicated in the hydrolysis of bromine,[49] although it has been identified only recently during studies of the heterogeneous interactions between water and bromine at 170 K.[42,43] The chlorine analogue, H_2OCl^+, has been observed as an intermediate product during the heterogeneous hydrolysis of $ClONO_2$ on water-ice.[32,29] Therefore the H_2OBr^+ ion might also be expected to form in the current study.

The identification of H_2OBr^+ in the observed spectra can be made primarily on the assignment of the distinct ν(HOH) vibration (1650 cm^{-1}). However, the coexistence of “perturbed” nitrate absorption features also suggests that an ion pairing exists, which can be identified with $[H_2OBr]^+[NO_3]^-$. In fact, the ν(HOH) vibrational wavenumber value and peak intensity compares favorably with that of the $[H_2OBr]^+[(H_2O)_nBr]^-$ pair observed in a previously published RAIRS experiment. This latter feature was measured at 1605 cm^{-1} and predicted, by ab initio methods, to appear at ca. 1632 cm^{-1}.[42,43] The blue-shift of the ν(HOH) absorption band for $[H_2OBr]^+$ observed in this study originates presumably with the different nature of the counterion. Indeed, a similar blue-shift is observed for the ν(HOH) feature when the spectra of the $[H_2OCl]^+[NO_3]^-$ ion (1650 cm^{-1}) and the $[H_2OCl]^+[(H_2O)_nCl]^-$ ion (1612 cm^{-1}) are compared.[32,42]

The assignment of H_2OBr^+ is somewhat controversial due to the scarcity of experimental observations of H_2OBr^+ (and H_2OCl^+). The obvious alternative to the H_2OBr^+ assignment (Figure 4a) is molecular nitric acid, which absorbs at 1676 cm^{-1}.[37] However, this can be dismissed due to the lack of other RAIRS peaks of HNO_3, particularly the distinctive peak around 960 cm^{-1}. The same is true for crystalline nitric acid monohydrate (NAM), which has a large peak at 1674 cm^{-1} but also an absorption at 1279 cm^{-1} that is not observed in the current study.[45] The other nitric acid hydrates bear even less similarity to the measured spectra of H_2OBr^+.[45,47,48,50]

Another alternative to account for the 1650 cm^{-1} peak is the deformation mode of water. The associated vibration at 890 cm^{-1} (Figures 2 and 3) is not expected to be observed for nonbulk water. Furthermore, under UHV conditions at 185 K molecular water is highly unlikely to adsorb to the substrate. It follows that if the band at 1650 cm^{-1} is due to water, then the molecules must either be trapped in a matrix or bound to other condensed species on the substrate. The same is true for the peak observed at 3380 cm^{-1}, which could be due to water of solvation rather than the postulated H_2OBr^+ species.

The debate on the intermediacy of hypohalous ions in water-ice chemistry is still clearly active, and further experimental techniques and computational methods are currently being employed in a variety of laboratories to help provide definitive conclusions.

Production of Hypobromous Acid, HOBr. The hydrolysis of $BrONO_2$ has been shown previously to produce nitric acid and HOBr, both in the gas phase and from heterogeneous reactions:[19,27,20]

$$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr \tag{4}$$

Therefore it is reasonable to assume that the production of HOBr should be observed in conjunction with HNO_3 in the current study. On co-deposition of $BrONO_2$ with water at 140 and 155 K, a weak absorption band at 2596 cm^{-1} is observed, which can tentatively be assigned to the $\nu_{(OH)}$ stretch of HOBr; the spectrum is displayed in Figure 3. This peak is not observed at 170 K, which is consistent with the expectation that molecular HOBr would desorb at this temperature.

The vibrational assignment is made by comparison with the wavenumber obtained for HOBr produced by the heterogeneous hydrolysis of Br_2O[44] ($\nu_{(OH)} = 2435$ cm^{-1}) and also that for adsorbed HOCl ($\nu_{(OH)} = 2700$ cm^{-1}).[31,37,51,52] The range of wavenumbers observed arises from the effect of the environments in which the HOX species is produced. Hence, HOBr formed by different methods and complexed to different numbers of neighboring water and bromine molecules would be expected to vibrate at somewhat different frequencies.

The most likely alternative to the assignment of HOBr is the ν_{as} or a combination mode of H_3O^+ associated with hydrated nitric acid. For the study shown in Figure 3, amorphous NAD and/or NAT is produced. This has been measured previously both by careful preparation of thin films and also during the hydrolysis of $ClONO_2$.[45−48,53] Although these studies do not show obvious H_3O^+ peaks at 2600 cm^{-1}, the hydrated nitric acid spectra are characterized by a series of broad bands between 2000 and 3000 cm^{-1}. Furthermore, it is also possible that the interaction of molecular bromine could shift the measured vibrational frequency of H_3O^+.

Mechanism for the Hydrolysis of $BrONO_2$ at 185 K. The heterogeneous (surface) hydrolysis of $BrONO_2$ produces the hypobromous acidium ion, H_2OBr^+, at the stratospherically relevant temperature of 185 K, under water-limited conditions. The production of the observed H_2OBr^+ by the gas-phase reaction of premixing $BrONO_2$ and H_2O has been discounted, as the ion is also readily observed following the subsequent dosing of water onto a $Br^+NO_3^-$ surface. Furthermore, the process is unlikely to occur via molecular intermediates as, under the experimental conditions employed, molecular water and $BrONO_2$ have very short residence times upon the gold substrate. Thus, it is probable that the formation of H_2OBr^+ occurs in a single direct reaction: the nucleophillic attack of water onto the positively charged bromine atom of $BrONO_2$.[38] This mechanistic step may occur either directly or following the partial ionization of $BrONO_2$. The actual process of surface adsorption (as suggested for the analogous hydrolysis of chlorine nitrate) would drive the latter possibility

$$H_2O^{\delta-} + {}^{\delta+}Br{-}ONO_2 \rightarrow H_2OBr^+ + NO_3^- \qquad (12)$$

or

$$BrONO_{2(g)} \rightarrow Br^+_{(ads)} + NO_3^-{}_{(ads)} \qquad (13)$$

$$H_2O + Br^+_{(ads)} \rightarrow H_2OBr^+_{(ads)} \qquad (14)$$

The measured wavenumbers for the nitrate ion absorption bands vary widely with the amount of water present in the system. For example the series of Figures 5a, 4a, and 5b show ionized bromine nitrate films associated with increasing amounts of water. The spectrum obtained for $H_2OBr^+NO_3^-$, as shown in Figure 4a, resembles the RAIR spectrum of nonhydrated $Br^+NO_3^-$ (Figure 5a). In comparison, the spectrum for $H_2OBr^+NO_3^-$ shown in Figure 5b, which has more water content than for Figure 4a, exhibits nitrate absorption features much closer to those observed for amorphous NAD.

The recently published computational study of Ramondo et al. shows that the counterion of H_2OBr^+ is stabilized significantly by solvation and that the ion pair is stable only when water molecules are located between the two ions.[43] It has been shown previously that certain ion pairs can be stabilized when layers of water molecules are inserted between them.[54] Pertinently, this is the case for $H_2OCl^+NO_3^-$.[35] If these findings are applied to the current study, then the calculations imply that $H_2OBr^+NO_3^-$ would actually exist as $H_2OBr^+(H_2O)_nNO_3^-$ (where n, the number of solvating water molecules, depends largely upon the water availability). The species $(H_2O)_nNO_3^-$ is also the anion of hydrated nitric acid, and therefore the similarities observed in the current study for the nitrate absorption bands of $H_2OBr^+NO_3^-$ and amorphous hydrated nitric acid are to be expected.

It is proposed that the fully ionic form of bromine nitrate, $Br^+NO_3^-$, and the nitric acid hydrates observed in the IR spectra obtained in this study represent the two extremes of a continuum of nitrates interacting with different amounts of water. Hence n, the number of water molecules, need not be an integer in process 15.

$$BrONO_2 + nH_2O \rightarrow H_2OBr^+(H_2O)_nNO_3^- \qquad (15)$$

The production of crystalline nitric acid hydrates requires that the oxonium ion, H_3O^+, be formed. It is likely that crystalline NAT and NAD production occurs with the ejection of the HOBr from $H_2OBr^+(H_2O)_nNO_3^-$, which in turn is controlled by the amount of water in the system. The *net* reactions are

$$H_2OBr^+(H_2O)_2NO_3^- \rightarrow HOBr + H_3O^+(H_2O)NO_3^- \qquad (16)$$

$$H_2OBr^+(H_2O)_3NO_3^- \rightarrow HOBr + H_3O^+(H_2O)_2NO_3^- \qquad (17)$$

A study of the analogous surface hydrolysis process for $ClONO_2$ at 185 K reveals that when NAT is produced, HOCl is indeed ejected into the gas phase.[31]

The production of molecular nitric acid under limited-water conditions, as shown in Figures 4b and 5b, can be caused by one of three mechanisms: ionic, molecular, or ionic−molecular. In the first case, the production would result from the decomposition of $H_2OBr^+NO_3^-$:

$$H_2OBr^+NO_3^- \rightarrow HOBr + HNO_3 \qquad (18)$$

Such a step would be expected to occur in water-limited conditions because the H_2OBr^+ ion has been computed to be relatively unstable when not hydrated.[43] Alternatively, if sufficient water is present then proton donation from a water molecule to either molecular or ionic bromine nitrate may occur. A nonionic mechanism for the heterogeneous hydrolysis of chlorine nitrate at 140 K has previously been suggested, which contrasts with the totally ionic mechanism operative at 180 K.[37] However, in the case of bromine nitrate it appears that the molecular mechanism may also occur at temperatures up to 185 K.

A curiosity observed in the present experiments is the fact that when excess water is present (i.e., more stratospherically relevant conditions) the hydrolysis at 185 K of *co-deposited* $BrONO_2$ with water produces NAD (Figure 4c). However, hydrolysis of adsorbed $BrONO_2$ by *subsequent dosing* of water yields nitric acid trihydrate (Figure 5c). NAT is the thermochemically more stable hydrate, but when excess water is dosed onto the NAD, further hydration is not observed in the thin film. The formation of the different hydrated products from the two systems must therefore be dependent upon the sequence in which the reactants are adsorbed. The implication of these observations is that the diffusion kinetics associated with nitric acid hydrate/water surface chemistry is a controlling feature. The possible mechanisms can be envisioned to operate as follows.

Dosing water onto a $Br^+NO_3^-$ film results in an immediate reaction. In the highly mobile surface region, the product formed is likely to be the most energetically stable, hydrated species (NAT). However, under co-deposition conditions, actual adsorption (and therefore partial ionization) of the bromine nitrate is required prior to hydrolysis. This circumstance results in reaction between ${}^{\delta+}BrONO_2$ and adsorbed water (as opposed to $Br^+NO_3^-$ and adsorbing water). Consequently, the hydrolysis will occur within a less mobile environment where only nearby water molecules are available for hydration. The result is the production of NAD.

The Low-Temperature Hydrolysis of $BrONO_2$. The heterogeneous hydrolysis of $BrONO_2$ certainly occurs between 140 and 170 K (Figure 3), and possibly at temperatures as low as 95 K (Figure 2b). In an analogous study of the hydrolysis of $ClONO_2$ at 140 K, Horn et al. suggested that the hydrolysis mechanism followed a molecular route at low temperatures as opposed to the ionic hydrolysis observed at 185 K.[37] The net reaction under conditions of reduced water was observed to be

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (19)$$

In the experiments, both molecular nitric acid and HOCl were observed by RAIRS. The change of mechanism, from fully ionic to molecular, was attributed to the inability of $ClONO_2$ to preionize, as a consequence of the lower temperature adsorption process. Calculations have shown that limited water also prevents the predissociation of $ClONO_2$, in which case only a nonionic reaction pathway is available for hydrolysis.[35]

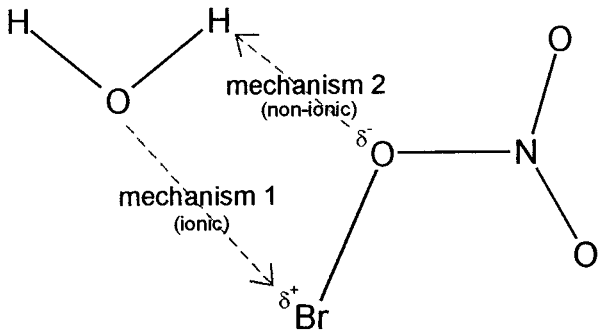


Figure 6. Diagram to illustrate the first step in competing mechanisms proposed for the heterogeneous hydrolysis of $BrONO_2$.

In the current study on bromine nitrate, in the nonlimited water experiments, only hydrated nitric acid production would be expected at high temperatures if the process was fully analogous to the published chlorine nitrate results. However, molecular nitric acid is also produced in the hydrolysis experiments performed at 185 K. Evidence indicating a dual ionic and molecular mechanism is also provided by study of the temperature-controlled dosing of $BrONO_2$. Hence, when it is dosed at 160 K, bromine nitrate adsorbs as *both* $Br^+NO_3^-$ and molecular $BrONO_2$ (Figure 1c). Upon dosing at 140 K it deposits in only the molecular form.

Finally, from the spectra measured in the 140 and 155 K experiments (Figure 3), the IR absorption band observed at 2596 cm^{-1}, which is tentatively assigned to HOBr, provides support for the involvement of a molecular mechanism.

The above results taken together imply that the change from a nonionic to an ionic hydrolysis mechanism occurs at a higher temperature for $BrONO_2$ compared to $ClONO_2$. In turn, this suggests that $ClONO_2$ is more readily ionized on a surface than is $BrONO_2$. Recent calculations on the atomic charge distributions of $ClONO_2$ and $BrONO_2$ are not in agreement with this experimental finding because they predict that unperturbed $BrONO_2$ is more ionic than $ClONO_2$.[55] However, the computational models did not include or account for water molecule interactions and may therefore be of limited applicability to the results obtained in the current study.

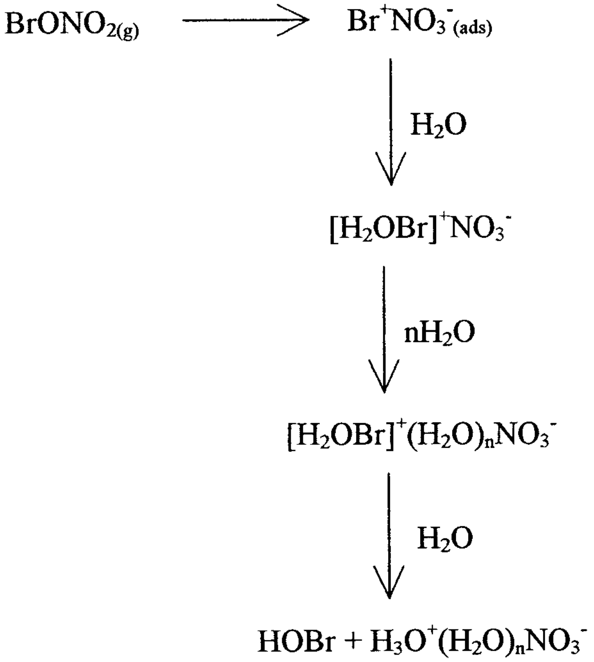
As a final caveat, it should be noted that the observed thin-film ionization of $BrONO_2$ at 160 K is not entirely comparable to the published chlorine nitrate results due to the presence of molecular halogen in the thin films. Complexation between $BrONO_2$ and molecular bromine has been evidenced by the change of the observed RAIRS vibrational frequencies, and therefore this competitive effect may stabilize the molecular $BrONO_2$ and hinder its ionization.

In summary, a nonionic mechanism for the low-temperature heterogeneous hydrolysis of $BrONO_2$ is probable, although the participation of an ionic reaction is not ruled out. Whatever the relative importance, the observations do demonstrate the importance of temperature upon surface reaction mechanisms on ice films. Figure 6 illustrates the proposed competitive mechanisms.

Conclusion

This study has provided the first in situ experimental evidence to show that bromine nitrate ionizes on a surface at the stratospherically relevant temperature of 185 K. The process represents a key step in its heterogeneous hydrolysis to nitric acid. Additional water molecules appear to play an important role in stabilizing the ionic products. Under conditions of limited water a competitive, nonionic mechanism occurs, which becomes more important at lower temperatures.

The following reaction sequence is proposed:



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