Nitrate Ion Photolysis in Thin Water Films in the Presence of Bromide Ions

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Supporting Information

ABSTRACT: Nitrate ions commonly coexist with halide ions in aged sea salt particles, as well as in the Arctic snowpack, where NO₃⁻ photochemistry is believed to be an important source of NO_{ν} (NO + NO₂ + HONO + ...). The effects of bromide ions on nitrate ion photochemistry were investigated at 298 \pm 2 K in air using 311 nm photolysis lamps. Reactions were carried out using NaBr/NaNO3 and KBr/KNO3 deposited on the walls of a Teflon chamber. Gas phase halogen products and NO₂ were measured as a function of photolysis time using long path FTIR, NO_{ν} chemiluminescence and atmospheric pressure ionization mass spectrometry (API-MS). Irradiated NaBr/NaNO3 mixtures show an enhancement in the rates of production of NO₂ and Br₂ as the bromide mole fraction (χ_{NaBr}) increased. However, this was not the case for KBr/KNO₃ mixtures where the rates of production of NO₂ and Br₂ remained constant over all values of χ_{KBr} . Molecular dynamics (MD) simulations show that the presence of bro-



mide in the NaBr solutions pulls sodium toward the solution surface, which in turn attracts nitrate to the interfacial region, allowing for more efficient escape of NO_2 than in the absence of halides. However, in the case of KBr/KNO₃, bromide ions do not appreciably affect the distribution of nitrate ions at the interface. Clustering of Br⁻ with NO_3^- and H_2O predicted by MD simulations for sodium salts may facilitate a direct intermolecular reaction, which could also contribute to higher rates of NO_2 production. Enhanced photochemistry in the presence of halide ions may be important for oxides of nitrogen production in field studies such as in polar snowpacks where the use of quantum yields from laboratory studies in the absence of halide ions would lead to a significant underestimate of the photolysis rates of nitrate ions.

INTRODUCTION

Investigations of surface marine air in the Arctic and at lower latitudes have provided compelling evidence that inorganic halogen chemistry can significantly influence the composition of the marine boundary layer (MBL).^{1–13} Sea salt aerosols arising from wave action are a large source of halides that can travel hundreds of kilometers inland and deposit onto surfaces.^{14,15} Bromide ions are oxidized by OH radicals and O₃, and chloride by OH radicals to form gaseous halogen species such as Br₂, Cl₂ and BrCl.^{4,6,8,16–37} Molecular halogens can then be photolyzed by actinic radiation^{38,39} to produce reactive halogen atoms that impact tropospheric chemistry.^{7–9,40–42}

Despite the fact that bromide ions are a minor component of sea salt,⁴³ with one bromide ion for every 650 chloride ions, they are thought to play an important role in MBL chemistry. Particles less than 1 μ m in diameter are often observed to be enriched in bromide ions^{44,45} and Koop et al.⁴⁶ reported that bromide

concentrations are enriched on the Arctic snowpack, with as many as one bromide ion to 188 chloride ions. Bromine has been clearly shown to be involved in processes causing severe tropospheric ozone destruction during polar sunrise^{4–6,41,47,48} and to impact chemistry at midlatitudes as well.^{49–54} The source of atomic and molecular bromine is believed to be the oxidation of Br⁻ in sea salt aerosol and snow likely initiated by reaction with O₃.^{4,6,8,9,19,20,22–24}

The conventional view of simple salt solutions has been that ions are repelled from the air—water interface and prefer bulk solvation.⁵⁵ However, a combination of computational^{56–67,162,163}

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and experimental studies^{18,24,68–82} has shown that Cl⁻, Br⁻ and I⁻ can be present at the air—water interface. Furthermore, with increasing size and polarizability of these anions, the interfacial concentration increases. There is also evidence that both the kinetics and mechanisms of interfacial reactions are different from those in the bulk phase.^{21,69,70,74,83–94} The presence of these halides at the air—water interface suggests their oxidation may take place at the surface without the need for incoming gas molecules to diffuse into the bulk before reaction. Indeed, there is evidence for this in the OH + Cl⁻ and O₃ + Br⁻ reactions.^{70,87,95}

Nitrate ions are typically present in sea salt aerosols and snowpacks as a result of reactions between halide ions and gaseous nitrogen oxides.^{96–108} These reactions result in the conversion of Cl⁻ and Br⁻ to gaseous halogen products, with a concomitant increase in the number of nitrate ions in the condensed phase. Deposition of inorganic nitrate onto snowpack also occurs.^{38,109,110} Calculations of nitrate concentrations on the Arctic snowpack quasi-liquid layer suggest that it could be as high as $0.3 \,\mu$ M.¹¹¹ Nitrate absorbs light in the actinic region above 290 nm and dissociates via two pathways:

$$NO_3^- + h\nu \leftrightarrow NO_2 + O^-$$
 (1a)

$$\Leftrightarrow \mathrm{NO_2}^- + \mathrm{O}(^{3}\mathrm{P}) \tag{1b}$$

$$O^- + H_2 O \rightarrow OH + OH^-$$
(2)

Pathway 1a in bulk aqueous solution at 305 nm and 298 K produces O⁻ and NO₂ with a quantum yield of 0.01.^{112–116} The O⁻ reacts rapidly with water to form the hydroxyl radical (OH), reaction 2.¹¹⁷ Pathway 1b, producing nitrite ion and O(³P), occurs with an overall quantum yield of 0.001. The overall photolysis quantum yields for both pathways are low due to recombination of photoproducts confined by a solvent cage.

However, there is increasing evidence that photolysis of species at various liquid interfaces can have higher quantum yields than those in the bulk.^{89–94,118–123} If the nitrate ion has an incomplete solvent cage, then the photolysis products can more easily escape the condensed phase into the surrounding atmosphere, preventing recombination and resulting in an increased overall quantum yield. This enhancement may play a role in laboratory studies that have shown that NO_y (NO + NO₂ + HONO + ...) and OH are readily released during irradiation of nitrate doped snow and ice.^{100,121,122,124–131} Furthermore, field studies show that nitrate photolysis is a source of OH in the interstitial air within snowpacks and/or the overlying boundary layer.^{132–140}

Studies by Wingen et al.¹⁴¹ have shown that there are enhanced NO₂ yields from photolysis of deliquesced nitrate aerosols containing chloride ions. This was attributed to the presence of Cl⁻ at the solution—air interface, which draws the Na⁺ cation toward the surface. This in turn attracts the nitrate ions closer to the interface where they experience a reduced solvent cage. Both theory and experiment show that bromide ions have a higher propensity for the interface than chloride ions^{58,59,61,64,65,67,69,73} and therefore may be expected to have a similar or even greater effect on nitrate ion photochemistry. Recent high pressure XPS measurements on aqueous mixtures of nitrate and halide ions provide experimental confirmation that these halide ions do indeed draw nitrate ions closer to the interface.¹⁴² This paper

investigates the photochemistry that occurs when nitrate and bromide ions are present together in a thin film of aerosol particles deposited on a Teflon substrate. The implications of this photochemistry are discussed in terms of the role of nitrate ion photolysis in snowpack as a major source of oxides of nitrogen.

EXPERIMENTAL SECTION

Photolysis Experiments. Photolysis experiments were performed in 230 L Teflon reaction chambers constructed using 51 μ m thick FEP Teflon, surface area 2.6 m², and heat sealed along the edges. The Teflon chambers were coated with salt solution particles using a 6-jet Collison nebulizer (BGI Inc., Model CN25) at a backing pressure of 20 psi provided by N_2 gas (Oxygen Service Co., UHP, 99.999%). This process was repeated three times for 15 min each. Suspended aerosol was evacuated each time, leaving a thin layer of aerosol particles coating the walls of the chamber. The approximate thickness of the coating is 0.8 μ m, which was calculated by weighing the reaction chamber dry (no aerosol added) and then weighing after treatment with aerosol. By use of the mass of the aerosol on the chamber walls (2.8 g) and densities of NaNO $_3$ solutions,¹⁴³ the volume of the solution added to the chamber walls could be estimated. Knowing the surface area of the Teflon chamber and the volume of solution added, the average thickness of the coating was calculated, assuming it was uniform. The molal concentration of nitrate ions in the thin films was determined from the measured relative humidity during photolysis experiments (75% RH) and the relationship between water activity and molality of nitrate.¹⁴³ Molarity was calculated from molality on the basis of published data for the density of NaNO₃ solutions.¹⁴⁴ By comparing the initial number of moles of NaNO3 in the film and the number of moles of NO2 produced during photolysis, we determined that approximately 0.03% of the nitrate was photolyzed during the experiment. This value is a lower limit since it does not take into account losses of NO₂, for example, by photolysis.

After being coated with salt, the Teflon reaction chamber was filled with synthetic air (Scott-Marrin, Riverside, CA; $NO_r <$ 0.001 ppm, $SO_2 < 0.001$ ppm) that had passed through a water bubbler to yield air with relative humidities for the NaBr/NaNO₃ experiments in the range of 70-75% RH and for the KBr/KNO3 experiments of 85-90% RH. These relative humidities, which were measured using a relative humidity-temperature probe (Vaisala, HMP 338), are above the mutual deliquescence point of the mixed salts, which is 57.5 \pm 0.6% RH for the sodium salt mixture and 80.4 \pm 0.5% for the potassium salts (Supporting Information). The coated chamber was irradiated with 14 narrow band UVB lamps ($\lambda \sim 311$ nm) that overlap with the lowest electronic absorption band of aqueous nitrate (Figure 1). Each chamber was equipped with Teflon ports for gas sampling. All experiments were conducted at 298 \pm 2 K, and chambers were sampled for a total of 150-400 min.

Measurements of Gas Phase Products. Gaseous NO₂ was measured as a function of time by periodically sampling from the Teflon chamber and analyzing by either a multiple reflection White-type optical system¹⁴⁵ interfaced to a Fourier transform infrared spectrometer (Mattson, Infinity 60AR) or a chemiluminescence nitrogen oxides analyzer (ThermoElectron Corp., Model 42C). The total optical path length for the White cell was 28 m and infrared spectra were recorded at a resolution of 0.5 cm⁻¹ with 1024 coadded scans. Both the nitrogen oxides analyzer and FTIR were calibrated in the range of NO₂ levels



Figure 1. Absorption spectrum of dilute aqueous NaNO₃ (0.4 M, green line) and photolysis lamp spectrum (black line).

detected in the experiments using mixtures of known concentrations of NO_2 in nitrogen (see below). Errors in concentrations are reported as 2s, where s is the sample standard deviation defined as

$$s = \sqrt{\frac{\sum_{i=0}^{N} (x_i - \overline{\mathbf{x}})^2}{N-1}}$$

where N is the number of samples and was 3-5 depending on the measurement.¹⁴⁶

A dual quadrupole mass spectrometer (Perkin-Elmer Sciex, API-300) was used to quantify Br₂ production as a function of photolysis time. The Teflon chamber contents were sampled at \sim 1 L min⁻¹ for 6 min directly into the API-MS source. Monitoring techniques utilized in this study are single quadrupole (Q1) and multiple reaction monitoring (MRM), both in negative ion mode. Q1 scans cover the range m/z 30–500 amu. Molecular bromine has relative peak intensities of 1:2:1 for m/z 158, 160, and 162 due to the natural isotopic abundances of 51% ⁷⁹Br and 49% ⁸¹Br. Increased sensitivity and selectivity can be achieved using MRM in which the first quadrupole is set to transmit m/z160 due to Br_2 and the second quadrupole transmits the ⁷⁹Br fragment generated in the collision cell separating the two quadrupoles. The MRM mode ensures that all fragments of m/z 79 originated from the parent ion of 160 rather than other bromine-containing products. The MRM or Q1 signal intensity is measured during experiments and is calibrated using known concentrations of gaseous Br₂. For each calibration point, a known volume of Br₂ was flowed into a Teflon chamber with a measured volume of air.

Scanning Electron Microscopy (SEM). The morphology and elemental composition of thin films of NaBr/NaNO₃ and NaCl/NaNO₃ were investigated using a Zeiss Evo LS 15 scanning electron microscope equipped with a Thermo Electron Corp. UltraDry Silicon Drift energy dispersive X-ray spectroscopy (EDS) detector. An accelerating electron beam voltage of 8 keV was used. The thin films were prepared on copper stubs (Ted Pella Inc.) placed inside a Teflon reaction chamber and subjected to nine cycles of coating with salt solution particles. SEM images were taken after the last evacuation.

UV/Visible Spectra. The UV absorption spectra of aqueous NaNO₃ (0.5 M), KNO₃ (0.5 M), 8:1 NaBr/NaNO₃ (4 M/ 0.5 M) and 8:1 KBr/KNO₃ (4 M/0.5 M) solutions were obtained using UV-visible grade quartz cells of 1 mm path length and a Cary 50 UV-visible spectrophotometer at 0.5 nm resolution.

Determination of Deliquescence Relative Humidities. Relative humidity measurements on saturated solutions of NaBr/NaNO₃, KBr/KNO₃ and NaCl/NaNO₃ were conducted at 294 \pm 0.5 K as a function of mole fraction of NaBr (i.e., bromide ions), χ_{NaBr} , to determine the mutual deliquescence relative humidity (MDRH) for each mixture. Solutions were placed in a Vaisala humidity calibrator (HMK15) and sampled consecutively with two relative humidity probes. Relative humidity was recorded every hour until three consistent measurements were obtained to ensure equilibration and reproducibility. Saturated solutions of NaBr, NaCl, NaNO₃, MgCl₂, LiCl, KBr and KNO₃, which have well-known deliquescence points, were sampled frequently to test the accuracy of the relative humidity probes. The measured values were within \pm 0.9% RH of published values.

Chemicals and Solution Preparation. Solutions of the salts NaBr (Fluka, >99.5%), NaNO₃ (Fisher, Certified ACS, >99.0%), NaCl (Fluka, >99.5%), KBr (EMD Chemicals, >99.4%) and KNO₃ (Fisher, >99.4%) were made using nanopure water (Barnstead, 18.2 M Ω cm). Experiments on pure NaNO₃ and mixtures of NaBr/NaNO₃ were carried out in two ways (1) varying both Br⁻ and NO₃⁻ concentrations while keeping total molarity and ionic strength constant and (2) varying the bromide concentrations varied from 0.13 to 4 M. Experiments on pure KNO₃ and mixtures of KBr/KNO₃ were performed by varying the bromide concentration.

NO₂ was synthesized for calibrations by mixing NO gas (Matheson, 99.5%), purified by passage through a dry ice acetone bath to remove impurities such as HNO₃, with excess O₂ (Oxygen Services Co., 99.993%) for several hours. The NO₂ product was condensed using a dry ice acetone bath, while excess O₂ was pumped away. The purified NO₂ was stored in the dark at room temperature in a glass bulb. The Br₂ mixture used for calibrations was prepared by collecting the vapor over liquid Br₂ (Acros, 99.8%), which had been purified by three freeze=pump=thaw cycles, and diluting with N₂ and then storing in a glass bulb.

Computations. Molecular dynamics (MD) simulations were performed to investigate ion partitioning and the environment of nitrate at the liquid-vapor interface of aqueous NaNO₃, KNO₃, mixtures of NaBr/NaNO3 and mixtures of KBr/KNO3. The surface of aerosol droplets was simulated using a slab geometry^{118,150} of water and ions with dimensions of 30 Å \times 30 Å \times 100 Å with three-dimensional, periodic boundary conditions.¹⁵¹ Simulations were run in the NVT ensemble with a temperature (300 K) regulated by a Berendsen thermostat.¹⁵² The MD trajectories were generated using Sander in the AMBER 8 suite, ¹⁵³ which has a modified calculation of induced dipole to avoid well-known problems with polarization catastrophe.¹⁵⁴ The time step was 1 fs, and trajectory data were recorded every ps. Particle-mesh Ewald, a method for computing the interaction energies in periodic systems, was used to calculate electrostatic interactions with the real-space part of Ewald sum and the Lennard-Jones interactions truncated at 12 Å. 155,156 The polarizable POL3 water model 157,158 was employed to simulate water molecules. Water bond lengths and angles were constrained using SHAKE algorithm.¹⁵⁸ Nitrate ions were modeled using parameters by Thomas et al.¹⁵⁹ which were modified from Lennard-Jones parameters from Minofar et al.¹⁶⁰ and polarizability parameters by Salvador et al.¹⁶¹ The sodium and bromide parameters were adapted from the work of Berkowitz and co-workers.^{162,163} Potassium parameters were



Figure 2. NO₂ production during photolysis experiments of pure NaNO₃ and mixtures of NaBr/NaNO₃ at 75% RH and 298 K in air, where χ_{NaBr} is the mole fraction of NaBr (a) at a constant total ion concentration, (b) same as (a) but normalized to the initial [NO₃⁻], (c) with constant 0.5 M nitrate ion concentration and increasing amounts of Br⁻. Error bars are 2s of replicate experiments.

taken from Chang et al.¹⁶⁴ Force field parameters are provided in the Supporting Information (Table S1). Solutions of 2M NaBr, 2M NaNO₃, 4 M NaNO₃ and mixed NaBr and NaNO₃ solutions (total 4 M) were simulated using a slab containing 864 water molecules. Each simulation was equilibrated for 3 ns, and an additional 5 ns were used for analysis. The potassium series of simulations was performed at the same concentrations as the sodium series solutions with the exception of the simulation of neat aqueous KNO₃, which was performed at 2 M. The potassium series of simulations was equilibrated for 3 ns and a further 8 ns were used for analysis.

RESULTS AND DISCUSSION

The impact of bromide ions on nitrate ion photolysis was investigated using two approaches: (1) holding the total number of ions constant while varying the relative amounts of bromide and nitrate and (2) using constant initial amounts of nitrate, with increasing amounts of bromide. The first case is analogous to the atmospheric situation where halide ions in sea salt particles are replaced by nitrate during transport in air,^{40,98,99,165} but interpretation of the data requires normalizing due to the differences in nitrate concentrations. The second approach avoids the need for normalization, thus making comparisons more straightforward, but is less representative of atmospheric conditions.

The formation of NO₂ as a function of photolysis time for NaBr/NaNO₃ mixtures at a constant total number of ions is shown in Figure 2a. The production of NO₂ increases as the relative amounts of nitrate ions increase and bromide ions decrease. To compare NO₂ production rates per nitrate ion, the data were normalized to the initial concentration of NO₃⁻ present in the nebulized solution. Figure 2b shows that NaNO₃ ($\chi_{NaBr} = 0$) in the absence of bromide produced the least NO₂ per initial NO₃⁻. The production of NO₂ became more pronounced as χ_{NaBr} increased beyond 0.5. As seen in Figure 2c, results similar to Figure 2b were obtained using constant NO₃⁻ concentrations (0.5 M) and increasing amounts of Br⁻.

Figure 3 shows that the rate of NO₂ production (Figure 3a) using constant [NO₃⁻] (data from Figure 2c) and the corresponding production of gas phase Br₂ (Figure 3b) both increase with χ_{NaBr} . The rate of Br₂ release during photolysis experiments ranged from 0.57 to 1.1 ppb min⁻¹ after the initial induction period. The ratio of Br₂ to NO₂ at the end of the experiments was

measured to be $\Delta Br_2/\Delta NO_2 = 0.25 \pm 0.03$ (2s). A search for other bromine-containing products such as BrNO, BrNO₂, and BrONO₂ was made using long-path FTIR, but no such species were observed. In addition, using Q1 mass spectra the ratio of the fragment at m/z 79 to the parent peak for Br₂ at m/z 160 was consistent with that of an authentic sample of Br₂, suggesting there were no significant amounts of other bromine-containing gaseous products.

The formation of NO₂ is expected from the direct photolysis of NO₃ $\overline{}$:

$$NO_3^- + h\nu \leftrightarrow NO_2 + O^-$$
 (1a)

In aqueous solutions, O^- reacts with water, with a lifetime of ${\sim}0.2~{\rm ns}$:

$$O^- + H_2 O \rightarrow OH + OH^-$$

 $k = 9.3 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 117)}$ (2)

Bromide ions are well-known to be oxidized by OH radicals, generating Br₂:

Br⁻ + OH → BrOH⁻

$$k = 1.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 28)}$$
 (3)

BrOH⁻ + Br⁻
$$\rightarrow$$
 Br₂⁻+OH⁻
 $k = 1.9 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 28)}$ (4)

$$2Br_2^- \rightarrow Br_3^- + Br^-$$

 $k = 2.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 166)}$ (5)

$$Br_3^- \rightarrow Br_2 + Br^-$$

 $k = 5 \times 10^7 \text{ s}^{-1} \text{ (ref 167)}$ (6)

Another possibility is reaction of Br⁻ with O⁻:

Br⁻ + O⁻ → products

$$k = 1.8 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 168)}$$
 (7)

While the products of reaction 7 do not appear to have been identified, they may include O^{2-} + Br, with subsequent reactions of the bromine atoms generating Br₂. Although reaction 7 is not generally considered in bromide oxidation in bulk aqueous



Figure 3. (a) Rates of production of NO₂ as a function of χ_{NaBr} and (b) Br₂ production as a function of time. Symbols correspond to different molar ratios for mixtures of NaBr/NaNO₃ at 70–75% RH at 298 K in air and a constant initial NO₃⁻ concentration of 0.5 M. The open square is for pure NaNO₃. All error bars are 2s.

solutions due to the rapid conversion of O^- to OH, it cannot be discounted a priori at the interface where the effective water concentration transitions from that in the liquid to the gas phase.

The data in Figure 3b show an induction time for the appearance of Br_2 in the gas phase. This is attributed to the sensitivity to pH of the cycling of bromine compounds between the gas and aqueous phases.⁹ The generation of hydroxide ions in reaction 2 provides a mechanism for hydrolysis of Br_2 and the deprotonation of HOBr in the aqueous phase to BrO^- :

Br₂ + OH⁻ → HOBr + Br⁻

$$k = 7.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 169)}$$
 (8)

 $HOBr + OH^- \leftrightarrow BrO^- + H_2O$ $pk_a = 8.8 \text{ (ref 26)} (9)$

HOBr + Br⁻ + H⁺ ↔ Br₂ + H₂O

$$k = 1.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \text{ (ref 169)}$$
 (10)

The further oxidation of some NO₂ by OH in the film and secondary heterogeneous chemistry involving water¹⁷⁰ generates HNO₃, causing acidification of the film, the conversion of BrO⁻ to HOBr and the generation of Br₂ via reaction 10. The delay in production of gas phase Br2 reflects the time to acidify the film from the initial pH of 5.5 to the point that Br₂ is formed. This was confirmed by experiments in which the pH of the nebulizing solution was lowered from 5.5 to 3 by addition of HNO₃, which showed no delay in bromine production. As seen in Figure 2b,c, NO₂ is generated faster for the larger mole fractions of Br⁻, leading to more rapid acidification and generation of Br₂. The measured yield of Br₂ relative to NO₂ is half that expected if every photolysis event via (1a) led to Br₂. This is likely due to retention of bromine products in the film, e.g., BrO⁻. Gas phase HOBr cannot be detected as its parent ion by API-MS, but any HOBr remaining in the film could also contribute to the lack of mass balance for the bromine products.

Similar experiments were carried out for mixtures of KBr and KNO₃ at relative humidities between 85 and 90%. These were above the MDRH of 80.4 \pm 0.5% (Supporting Information) so the mixtures should be deliquesced, which was confirmed by visual inspection. Figure 4a shows the initial rate of NO₂ production as a function of χ_{KBr} . In contrast to the NaBr/NaNO₃ mixtures, the rate of NO₂ production is independent of the bromide mole fraction. In this experimental system, it was difficult to



Figure 4. (a) Rates of production of NO₂ as function of χ_{KBr} and (b) Br₂ production as a function of time. Symbols correspond to different molar ratios for mixtures of KBr/KNO₃ at 85–90% RH at 298 K in air and a constant initial NO₃⁻ concentration of 0.5 M. The open squares are for pure KNO₃ at 85% RH. All error bars are 2s.



Figure 5. UV/visible spectra of 0.5 M NaNO₃ (red dashed line), 0.5 M KNO₃ (blue line), 4 M NaBr/0.5 M NaNO₃ (yellow line), and 4 M KBr/0.5 KNO₃ (green line). Errors are 2s.

obtain reproducible and stable water vapor concentrations above 90% RH, so the data point for pure KNO₃ in Figure 4a (open squares) was obtained at 85% RH, below the KNO₃ deliquescence relative humidity of 92.2 \pm 0.4%. The rate of NO₂ production from solid KNO₃ will be less than that for the deliquesced salt since surface passivation will occur, ^{171,172} and hence, the rate of NO₂ production for $\chi_{KBr} = 0$ in Figure 4a is lower than expected for deliquesced KNO₃. Figure 4b shows that the formation of gaseous Br₂ is also independent of χ_{KBr} . In short, there does not appear to be a significant impact of added bromide ions on either NO₂ or Br₂ production for the potassium salts, in contrast to the sodium salts.

One possible source of the difference between the sodium and potassium salts is a difference in the UV absorption spectra that results in more rapid photolysis for KNO₃. Hudson et al.¹⁷³ showed that as nitrate solutions of calcium, magnesium and sodium salts became more concentrated, the lowest electronic absorption peak ($n \rightarrow \pi^*$) shifted to higher energies and also decreased in intensity as a function of nitrate concentration and the nature of the cation. On the other hand, Wingen et al.¹⁴¹ reported no noticeable shift in the absorption spectra of the 9:1 NaCl/NaNO₃ mixture ($\chi_{NaCl} = 0.9$) over that of pure NaNO₃. However, to probe this possibility, the UV-visible absorption spectra of aqueous solutions of NaBr/NaNO₃ and KBr/KNO₃ were recorded. Figure 5 shows the molar absorptivities (base 10)

Table 1. Composition of MD Simulations (864 Water Molecules)

$\chi_{ m Br^-}$	no. of Br ⁻	no. of NO_3^-	no. of Na^+ or K^+
0 (2 M)		36	36
0 (4 M)		72	72
0.1	7	65	72
0.5	36	36	72
0.75	54	18	72
0.9	65	7	72

for 0.5 M NaNO₃ (red line), 0.5 M KNO₃ (blue line), 4 M NaBr/ 0.5 M NaNO₃ mixture (yellow line), and 4 M KBr/0.5 M KNO₃ (green line) in the region of the $n \rightarrow \pi^*$ transition. Both NaNO₃ and KNO3 have molar absorptivities centered at 302 nm. The $4 \text{ M NaBr}/0.5 \text{ M NaNO}_3 (\chi_{\text{NaBr}} = 0.9)$ shows a 2 nm shift toward the blue (300 nm) while the 4 M KBr/0.5 M KNO₃ ($\chi_{KBr} = 0.9$) shows no significant shift. The absolute values of the molar absorptivities are slightly smaller, but still within 10%, of those of the dilute solutions. These small changes clearly cannot be responsible for increased production of NO₂ from NaNO₃ in the presence of bromide.

There are some differences in the aqueous concentrations for the KBr/KNO3 and NaBr/NaNO3 mixtures. The MDRH for NaBr/NaNO₃ was measured to be 57.5 \pm 0.6% RH (Supporting Information) and experiments were carried out well above this at 70-75% RH. However, the MDRH for KBr/KNO₃ mixture was measured to be $80.4 \pm 0.5\%$ RH (Supporting Information), and experiments were able to be carried out reproducibly at 85-90% RH. Because the KBr/KNO₃ experiments were carried out at a RH approaching the MDRH, the KBr/KNO3 mixtures were more concentrated relative to the NaBr/NaNO₃ mixtures. This may have contributed to the somewhat higher rate of gas phase NO₂ generation from the KBr/KNO₃ solutions (Figure 4a compared to Figure 3a) and the lack of an induction time for Br₂ production (Figure 4b) since acidification of the thin film will be faster as well. However, these differences do not account for increasing production of NO₂ as χ_{NaBr} increased.

Previous molecular dynamics simulations of the NaCl/NaNO3 system¹⁴¹ suggested that enhanced NO₂ production was attributable at least in part to interfacial Cl⁻ attracting Na⁺, which in turn drew nitrate ions closer to the interface. In this region, enhanced photochemistry can result from the incomplete solvent shell around NO_3^{-} , which enhances loss of NO_2 to the gas phase and makes its recombination with O⁻ less efficient. To explore such interactions in the systems studied here, MD simulations of mixtures of NaNO3 and NaBr were performed with the same ratio of corresponding ions as in experimental results for the constant total ion experiments shown in Table 1. Each density profile was normalized so the area under each curve is 0.5, and then shifted along the z-axis so that the water Gibbs dividing surface (GDS) is located at z = 0 Å. Figure 6a shows that in the absence of Br⁻, nitrate ions prefer bulk solvation as reported earlier.^{61,159,160,174,175} However, as bromide ions are added (Figure 6b,c), nitrate ions are drawn closer to the interface into a region of reduced solvent cage through a double-layer effect similar to that for the NaCl/NaNO3 system.¹⁴¹ Recent high pressure XPS experiments on liquid jets containing nitrate and halide ions confirm this effect.¹⁴²

Figure 6 shows the results of MD simulations for pure KNO₃ (Figure 6d) and the KBr/KNO₃ mixtures (Figure 6e,f). Figure 6e,f



Z (Å)

Z (Å)

-10

0

0.05

ρ (arbitrary units)

0.05

 ρ (arbitrary units)

0.1

Figure 6. Density profiles for MD simulations of the air-water interface of (a) 4 M NaNO3 and mixed aqueous solutions of NaBr/NaNO3 for mole fractions of (b) $\chi_{\text{NaBr}} = 0.5$ and (c) $\chi_{\text{NaBr}} = 0.9$, (d) 2 M KNO₃ and 4 M mixed aqueous solutions of KBr/KNO3 for mole fractions of (e) $\chi_{\text{KBr}} = 0.5$ and (f) $\chi_{\text{KBr}} = 0.9$.

0.05

 ρ (arbitrary units)

0.1 0

0

0.1



Figure 7. Density profiles for NO_3^- ions in 4 M mixtures of (a) KBr/ KNO₃ and (b) NaBr/NaNO₃ as a function of χ_{Br^-} from 0.1 to 0.9.

shows that when bromide ions are added, nitrate ions are only minimally drawn closer to the interface. The saturation concentration of pure KNO₃ is 3.3 M;¹⁷⁶ thus MD simulations for pure KNO₃ were conducted at 2 M, rather than 4 M for as for NaNO₃. In neat NaNO₃ simulations at 2 M (data not shown) approximately 8% of nitrate ions were within 1 ± 0.5 nm compared to 5% for the 4 M solutions. Thus, if a 4 M KNO₃ solution could be simulated, the concentration of nitrate ions at the interface would likely be smaller than that in Figure 6.

Figure 7 compares the density profiles for NO₃⁻ in mixtures of KBr/KNO₃ and NaBr/NaNO₃, respectively, for which χ_{Br^-} = 0.1-0.9. In contrast to the sodium salts, the addition of bromide ions to KNO₃ is predicted to have a relatively small impact on the nitrate ion distribution. This is consistent with our experimental results where addition of Br had no significant effect on the nitrate ion photochemistry for the potassium salts, but in the case of the sodium salts, the generation of the photoproducts NO₂ and Br₂ increased. Considerably more contact-ion-pairing was observed (with no solvent molecules between ions) for the sodium nitrate $(3 \text{ Na}^+ \text{ per NO}_3^-)$ versus potassium nitrate $(2 \text{ K}^+ \text{ per NO}_3^-)$. This results from the smaller radius of Na⁺ causing stronger electrostatic attractions.

The lack of dependence of the rates of NO₂ and Br₂ production on χ_{KBr} for the potassium salts is due to most of the photolysis occurring in the bulk where there is efficient trapping of OH/O^{-} by Br⁻ and the production of NO₂ and Br₂ is limited by the rate of photolysis of NO₃⁻. Note that the film is sufficiently thin, average thickness 0.8 μ m, that the entire film is irradiated and photolysis is not limited by strong nitrate ion absorption as in studies of bulk systems.^{177,178} In the case of the sodium salts, however, nitrate is drawn toward the interface much more strongly (Figures 6b,c and 7b) where trapping by the solvent cage becomes incomplete. In short, the experimental and theoretical data argue for a significant contribution of enhanced overall quantum yields due to bromide ions at the interface in the case of the sodium salts.

Previous studies of the photolysis of *bulk* nitrate—bromide solutions reported that generation of gas phase bromine products (likely Br₂) was independent of the bromide ion concentration above a ratio of Br⁻/NO₃⁻ of 0.02.¹⁷⁷ Similar results for the production of nitrite ions were observed by Das et al.¹⁷⁹ who argued that bromide ions actually scavenge OH inside the solvent shell. Abbatt et al.¹⁷⁸ measured the Br₂ yields from the photolysis of ice containing mixtures of bromide, chloride and nitrate and reported that the Br₂ production was independent of the initial bromide ion concentration. All of these studies were on bulk solutions or ice, consistent with our KBr/KNO₃ experiments where bulk chemistry predominates.

While the combination of our experimental data and the MD simulations is consistent with an important role for interface photochemistry, it also suggests that bromide ions can impact bulk phase chemistry as well. Thus, the ratio of the rate of NO₂ production in the presence of bromide ions ($R_{Br^-}^{NO_2}$) to that in its absence ($R_{NO_3^-}^{NO_2}$) can be expressed as a combination of contributions from the interface region and the bulk:

$$\frac{R_{Br^-}^{NO_2}}{R_{NO_3^-}^{NO_2^-}} = \frac{[\phi_{Br^-}^{\text{int}} N_{Br^-}^{\text{int}} + \phi_{Br^-}^{b} N_{Br^-}^{b}]}{[\phi_{NO_3^-}^{b} N_{NO_3^-}^{b}]}$$
(I)

In eq I, ϕ^{int} and ϕ^{b} are the quantum yields for nitrate photolysis in the interface region and the bulk respectively, and N^{int} and N^{b} are the number of available nitrate ions in each region. The numerator refers to the solutions where Br⁻ is present and the denominator to pure NaNO₃ solutions. It is assumed that the interface region does not contribute significantly to the production of NO₂ in the absence of bromide compared to the bulk because of the relatively small concentrations of nitrate ions near the interface (Figure 6a). For the χ_{NaBr} = 0.9, the experimentally measured increase in NO₂ production was a factor of 2.4 \pm 0.2 (2s) higher than that for $\chi_{N_{aBr}} = 0$. Taking the quantum yield in the bulk solution to be 0.011 \pm 0.001,¹¹²⁻¹¹⁶ the thickness of the film to be 800 nm and that of the interface region to be 1 nm (\pm 0.5 nm with respect to the GDS), a quantum yield at the interface of 10-13 would be required to generate the measured increase in NO2 if the nitrate ion concentration was the same in the bulk and at the interface. However, the MD simulations suggest that the concentration of nitrate ions in the interface is a factor of 7 \pm 3 (2s) higher for $\chi_{\text{NaBr}} = 0.9$ mixtures than for pure NaNO₃. This factor arises from the integrated density profile area of nitrate ions within \pm 0.5 nm of the GDS, which is 31 \pm 6% and 4.7 \pm 1.4% (2s) of the total nitrate ions for $\chi_{\text{NaBr}} = 0.9$ and $\chi_{\text{NaBr}} = 0$, respectively. Taking this increase in concentration in the interface region into account, the calculated quantum yield at the interface drops to 1.7 ± 0.9 . This is within experimental error of 1, which is the maximum allowed by definition.³⁹

However, these data do not rule out an enhancement of photochemistry in the bulk as well, as suggested by Das et al.¹⁷⁹



Figure 8. Top view of a snapshot of a $Br^--NO_3^-$ ion pair in a mixture with $\chi_{NaBr} = 0.9$. Key: green = Na⁺, orange = Br⁻, purple = NO₃⁻, blue = O_{water} , white = H_{water} .

The MD simulations also provide insight into potential impacts bromide ions on the bulk phase photochemistry. The calculations show that in the mixture with $\chi_{\text{NaBr}} = 0.9$, 20% of the nitrate ions in the simulation have a bromide ion within 3.8 Å of NO₃⁻. Figure 8 shows a typical top-view snapshot of the nitrate—bromide ion coordination in this mixture. Clustering of NO₃⁻ with Br⁻ and H₂O is evident and occurs both in the bulk and near the interface. A concerted process in which the excited NO₃⁻ transfers an O⁻ to adjacent water which simultaneously transfers the remaining OH radical to Br⁻ seems reasonable under these conditions.

If indeed a concerted process occurs, our experimental data and the MD simulations can be used to estimate enhancement in the bulk phase photochemistry, given reasonable assumptions about the interface. Thus, the solvation environment around nitrate ions was investigated for the χ_{NaBr} = 0.9 mixture by calculating the number of water molecules around NO₃⁻ in the presence of bromide as function of depth into the slab. The solvent cage at the interface was reduced by approximately half, with 12 water molecules at the GDS compared to 22 water molecules surrounding nitrate in the bulk. Therefore, using a quantum yield at the interface of 0.5, a bulk phase quantum yield of 0.02 in the presence of bromide ions is needed to obtain an overall enhancement in NO₂ production of 2.4 ± 0.2 (2s) that was measured experimentally. This represents a doubling of the bulk phase quantum yield compared to the value of 0.01 reported for bulk aqueous phase photochemistry of nitrate ions due to the presence of bromide. Thus the combined experimental and theoretical data suggest that bromide ions markedly impact nitrate photochemistry at the interface via reduced solvent cage effects and increased interfacial nitrate concentrations. Further impacts that result from ion coordination may also play a role in the photochemistry in the bulk and at the interface as well.¹¹²⁻¹¹⁶ If the interface region is taken as 1.0-1.5 nm and the quantum yield in this region as being in the range 0.25-1.0, then the

interface contributes approximately 12-46% to the enhancement in NO₂ production.

In contrast, the bromide ions in the KBr/KNO₃ MD simulations (Figure 7a) do not affect the distribution of nitrate ions at the interface nearly as dramatically as for the NaBr/NaNO₃ system. Also, calculations in Table 2 show that ion coordination is much less important for the potassium salts as expected for the larger cation, thus the concerted mechanism involving ion pairs in the bulk does not appear to be significant. As a result, the rate of nitrate photolysis remains unaffected by the presence of bromide ions for K⁺ solutions (Figure 4a).

The observation of an enhancement in NO₂ production mainly at χ_{NaBr} above 0.6 is in contrast to previous measurements for NaCl:NaNO₃ mixtures where a 40% enhancement in NO₂ was observed even at a χ_{NaCl} of 0.1.¹⁴¹ The predicted enrichment of bromide ions at the interface compared to chloride ions⁵⁸⁻⁶¹

Table 2. Percentage of NO_3^- Coordinated with Br⁻ within 3.8 Å

$\chi_{ m Br^-}$	$\%~{\rm NO_3}^-$ in contact ion pairs with ${\rm Br}^-$	
	$\chi_{ m NaBr}$	
0.1	1.3	
0.5	9.2	
0.75	13	
0.9	20	
	$\chi_{ m KBr}$	
0.1	0.8	
0.5	4.1	
0.75	6.7	
0.9	7.4	

suggests that bromide ions should enhance the photochemistry at small mole fractions as well. One potential source of the discrepancy is the segregation of bromide and nitrate salts during the preparation of the thin films. If nitrate and bromide segregate during preparation of the thin film and do not remix during the final rehumidification step, bromide would not be available in the vicinity of OH generation, and the NO₂ production would be similar to that for pure NaNO₃. As described above, the chamber was filled with nebulized particles three times, with pumping of the chamber contents after the first three treatments. As the relative humidity in a film with two salt species is lowered below the MDRH, the salt with a concentration above the eutonic point composition will become saturated and a crystalline phase can form, leaving a shell of eutonic point composition surrounding a core.^{180–183}

To probe for possible segregation of bromide and nitrate ions, SEM images were acquired on samples prepared in a manner described above and similar to that used in the NO₂ experiments. Figure 9 shows the element maps for bromine and nitrogen for $\chi_{\rm NaBr}$ 0.5 and 0.9. Segregation of the bromide and nitrate is clearly seen for χ_{NaBr} = 0.5 but not for χ_{NaBr} = 0.9. This is consistent with the eutonic point composition for NaBr/NaNO3 which was measured in the present studies to correspond to $\chi_{\text{NaBr}} = 0.95$ (Supporting Information). Drying of a solution with a composition similar to that of the eutonic composition will not lead to segregation of the salts, as confirmed by the SEM of the χ_{NaBr} = 0.9. However, for the χ_{NaBr} = 0.5, NaNO₃ would crystallize out first because the nitrate ion concentration is much higher than its eutonic point composition. As drying continues, a salt mixture with χ_{NaBr} = 0.95 will be formed, leading to regions of NaNO₃ segregated from a mixed salt with high Br⁻ content, consistent with the element images in Figure 9. It is noteworthy that the eutonic point composition for NaCl/NaNO3



Figure 9. Element maps for mixtures of NaBr/NaNO₃: (a) $\chi_{NaBr} = 0.5$, (b) $\chi_{NaBr} = 0.9$. The left side is Br, and the right side is N.

is $\chi_{\rm NaCl} = 0.4$ at 67% RH (Supporting Information and ref 183). Thus the previous studies of NaCl/NaNO₃ mixtures¹⁴¹ were carried out under conditions that were not far removed from the eutonic point where segregation of the halide and nitrate is not significant. This was confirmed by SEM (data not shown). Thus, the lack of significant enhancement in the NO₂ production at $\chi_{\rm NaBr} < 0.6$ is likely due to incomplete mixing of the nitrate and bromide salts. However, at $\chi_{\rm NaBr}$ approaching the eutonic composition, segregation does not occur and humidification above the MDRH gives a well mixed solution of bromide, nitrate, and sodium ions. Under conditions where the salts do not become segregated such as the atmosphere, it is expected that bromide ions will lead to enhanced nitrate ion photochemistry over the full range of halide ion concentrations as was observed for chloride ions.¹⁴¹

In summary, these data show that the overall quantum yields for nitrate ion photolysis in thin aqueous films containing sodium bromide are enhanced compared to those without sodium bromide. The increased rate of photolysis is a combination of reduced solvent cage effects and increased interfacial concentrations of nitrate, as well as a likely contribution from a concerted process in the bulk and at the interface due to ion coordination which brings NO₃⁻ and Br⁻ into close proximity. A similar enhancement in NO₂ production was observed in earlier studies of NaCl/NaNO3 mixtures and attributed to double layer formation in which interfacial chloride attracted sodium closer to the solution surface, which in turn pulled nitrate toward the surface.¹⁴¹ Whether a concerted mechanism involving ion coordination also contributed in the case of the chloride salts is currently under investigation. Interestingly, these effects are not observed for KBr/KNO3 where nitrate ions reside predominantly in the bulk and there is less ion coordination.

ATMOSPHERIC IMPLICATIONS

Sea salt aerosols deposited on a snowpack are concentrated in a quasi-liquid layer on the surface^{46,111,131,184–186} and in frost flowers.^{41,187,188} Given the large concentrations of Na⁺ in seawater, 0.5 mol per kg compared to only 0.01 mol K⁺ per kg,^{43,189} it seems likely that nitrate photochemistry will be strongly controlled by sodium ions and hence have enhanced production of nitrogen oxides, OH and Br₂. Use of photochemical data for NO₃⁻ in the absence of the halide ions could underestimate the rate of photolysis by a factor of 2 or more. This will particularly impact regions with low NO_y levels, such as the Arctic. For example, measurements at Summit, Greenland, show that concentrations of NO_y are much larger in the interstitial air of the sunlit snowpack than in the overlying atmosphere.^{8,132,135–140,190–192} Other regions where this chemistry could be important include particles from alkaline lakes,^{53,54,193} such as the Dead Sea in Israel and the Great Salt Lake in the U.S.A. and sea salt particles in midlatitudes where halogen chemistry has been shown to play a significant role.^{2,10–13,49–53,194}

ASSOCIATED CONTENT

Supporting Information. Discussion of the mutual deliquescence relative humidity point measurements. Figures showing eutonic point curves. Table of MD force field parameters. This material is available free of charge via the Internet at http:// pubs.acs.org.

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