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Parahalogenated Phenols Accelerate the Photochemical Release of Nitrogen Oxides from Frozen Solutions Containing Nitrate

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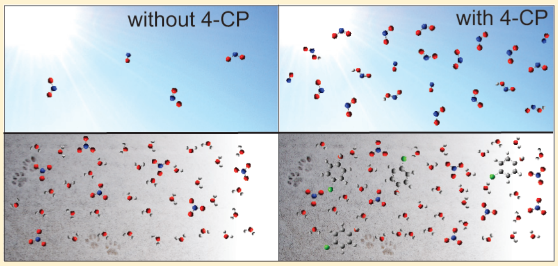
Supporting Information



ABSTRACT: The photolysis of nitrate anion (NO_3^-) contained in surface ice and snow can be a regionally significant source of gas-phase nitrogen oxides and affect the composition of the planetary boundary layer. In this study, the photochemical release of nitrogen oxides from frozen solutions containing NO_3^- in the presence of organic compounds was investigated. Gas-phase nitrogen oxides were quantified primarily by NO−O_3 chemiluminescence detection of NO and NO_y (=NO + NO_2 + HONO + HNO_3 + ∑PAN + ∑AN ...) and cavity ring-down spectroscopy of NO_2 and total alkyl nitrates (∑AN). The photochemical production of gas-phase NO_y was suppressed by the presence of formate, methanesulfonate, toluene, or phenol. In contrast, *para*-halogenated phenols (in the order of Cl > Br > F) promoted the conversion of NO_3^- to gas-phase NO_y, rationalized by acidification of the ice surface.

1. INTRODUCTION

Atmospheric chemistry is driven to a very large part by photochemical reactions in the gas phase. Important photochemical reactions also take place on surfaces,[1−3] in liquids such as clouds,[4] and in terrestrial snow and ice,[5−7] where photochemically initiated transformations of inorganic and organic substances can have a profound influence on the composition of the planetary boundary layer.[8−12] The nitrate anion (NO_3^-) is one of the major anions present in the polar snowpack,[13] and its photolysis is of particular importance to the polar boundary layer. It is generally accepted that photolysis of NO_3^- in ice occurs mainly in a thin liquid-like surface layer;[7] hence, its photochemistry closely resembles that encountered in aqueous solutions where photolysis of NO_3^- in the relatively weak n → π* band proceeds via two main channels.[14,15]

$$NO_3^- + h\nu \rightarrow NO_2 + O^- \qquad O^- + H^+ \rightarrow OH \qquad (1)$$

$$NO_3^- + h\nu \rightarrow NO_2^- + O(^3P) \qquad (2)$$

In ice, the quantum yields of reactions 1 and 2 are of similar magnitude (e.g., at 263 K, $\Phi_1 \approx 0.0040$ and $\Phi_2 \approx 0.0015$).[7] The nitrite anion (NO_2^-), produced by reaction 2, readily photodissociates to produce NO.

$$NO_2^- + h\nu \rightarrow NO + O^- \qquad O^- + H^+ \rightarrow OH \qquad (3)$$

The photolysis of NO_3^- in ice is of interest for several reasons. First, the nitrogen oxide photoproducts (i.e., NO_x = NO + NO_2 and, under acidic conditions,[16] HONO) are volatile and partition to the gas phase. There, NO_x catalyzes the photochemical production of ozone,[11] an important greenhouse gas, and ultimately changes the oxidative balance of the polar boundary layer.[17−19] Second, photolysis of NO_3^- removes it from snow and ice and thus needs to be considered in the interpretation of polar ice core data, in particular because this chemistry is accompanied by isotopic fractionation.[20,21] Third, photolysis of NO_3^-, NO_2^-, and HONO yields the hydroxyl radical (OH), the most important oxidant in the atmosphere. Production of OH from NO_3^- photolysis in the condensed phase has consequences on, among others, the breakdown of persistent organic pollutants and has been shown to lead to photonitration of aromatic compounds to generate toxic and carcinogenic nitroaromatics in both the liquid[22−31] and ice[32] phases. Further, OH radicals produced from NO_3^- photolysis can release active halogens from the condensed phase.[33]

Because of its importance to atmospheric chemistry, photolysis of NO_3^- in ice has been the subject of numerous laboratory studies.[34−49] Many factors are known to affect the yield of nitrogen oxides in the gas phase, including temperature, ionic strength, and acidity. For example, in a previous study in our laboratory, we found the production of gas-phase nitrogen oxides to be promoted by acidic conditions.[49] To explain higher yields of gas-phase NO_2 at low pH, we suggested that peroxynitric acid (HOONO), formed in a minor channel in the reaction of OH with NO_2, acts as a volatile intermediate under acidic conditions.[48,49] Furthermore, the extent of accumulation of NO_3^- ions and other ice solute molecules in either a liquid or quasi-liquid phase on the ice surface and/or in so-called micropockets or microveins upon freezing is undoubtedly an important factor.[50−52]

Surprisingly, there have been relatively few studies investigating how the presence of organic impurities might

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affect the production of nitrogen oxides from photolysis of NO_3^- in ice. For example, Dubowski et al.[36] and Minero et al.[47] have shown that the yield of NO_2^- from NO_3^- photolysis can be increased up to 5-fold by the presence of organic compounds such as formate, but we are not aware of a study investigating how the presence of organic compounds affects the yield of nitrogen oxides in the gas phase.

In this study, we investigated the production of gas-phase nitrogen oxides from NO_3^- photolysis in ice under actinic conditions (i.e., $\lambda > 300$ nm) in the presence of the organic compounds formate ($HCOO^-$), methanesulfonate (MSA^-, $CH_3SO_3^-$), methanesulfonic acid (MSA, CH_3SO_3H), the neutral aromatic compounds toluene and phenol, and *para*-halogenated phenols (4-XP) such as 4-chlorophenol (4-CP). Chlorinated phenols are ubiquitous in the environment as they are introduced by a multitude of anthropogenic activities, such as water disinfection, waste incineration, use of pesticides and herbicides, and the bleaching of paper pulp with chlorine.[53] Further, a considerable amount of literature exists on both the direct[54−60] and indirect photodegradation of 4-CP, for example, by OH produced from NO_3^- photolysis in aqueous solution,[23] from H_2O_2 photolysis in ice,[61] or from NO_2^- photolysis in ice,[62,63] making it a suitable model organic compound to include in this study.

2. EXPERIMENTAL METHODS

2.1. Chemicals. All reagents were of the purest commercially available grade and used as received. Sodium nitrate, phenol (4-HP), 4-fluorophenol (4-FP), 4-bromophenol (4-BP), 4-CP, sodium MSA^-, MSA, sodium formate ($HCOO^-$), toluene, and isopropanol were obtained from Sigma-Aldrich. All aqueous solutions were prepared with deionized water (Barnstead Easypure II, 18 MΩ cm). The pH of the solutions was measured prior to freezing. Dilute (0.05 M) buffer solutions were prepared by mixing the appropriate amounts of sodium carbonate and bicarbonate (Sigma-Aldrich; pH 9.5) or sodium acetate and acetic acid (Sigma-Aldrich; pH 4.5).

2.2. Photolysis Setup. The photolysis setup is shown in Figure 1 of Abida et al.[48] Briefly, the experiments were conducted using a custom-built Pyrex photoreactor (internal volume 275 cm^3). Samples of frozen solutions were prepared by placing 4 mL of precooled aqueous solution onto the bottom of the photoreactor tube, which was temperature-controlled using a circulating chiller/circulator. The ice temperature was 253 K in all experiments unless stated otherwise. The reactor was continuously (i.e., during sample freezing and irradiation) flushed with ultrapure ("zero") air (Praxair) at a flow rate of (1.4 ± 0.1) L min^{-1}. The zero air entered the reaction chamber near the top and exited via a side arm located 1 cm above the ice surface, minimizing the residence time of evolving gases in the chamber. Upon freezing, polycrystalline ice pellets with an average thickness of about 2 mm and an area of approximately 19.6 cm^2 were obtained.

The photolysis light source was a 150 W xenon arc lamp (ORIEL 96000) equipped with an IR filter (ORIEL 81096) and a digital exposure controller (ORIEL 68951). Its output was directed through a Pyrex window ($\lambda > 300$ nm) at the top of reactor. The incident light flux was measured offline by ferrioxalate actinometry[64] to be 1.5×10^{16} photon s^{-1} cm^{-2}.

2.3. Quantification of Photolysis Products. Concentrations of gas-phase nitrogen oxides were primarily monitored using a commercial NO/NO_y chemiluminescence (CL) analyzer (Thermo 42TL), calibrated against a blue diode laser cavity ring-down spectrometer (CRDS) as described earlier.[48] The CL instrument is equipped with a heated Mo catalyst; even though this instrument is marketed as a NO_x analyzer, the catalyst was found to reduce various components of NO_y ($= NO + NO_2 + \sum PN + \sum AN + HNO_3$ ...) to NO. In a separate experiment, we verified that the CL NO_x analyzer was sensitive to HONO and HNO_3. A thermal decomposition CRDS was used for selective measurement of either NO_2, NO_2 plus total peroxy nitrates ($\sum$PAN), or NO_2 + $\sum$PAN + total alkyl nitrates ($\sum$AN).[65,66] The TD-CRDS was connected to the photoreactor via PFA Teflon tubing and compression fittings; the exhaust of the TD-CRDS was then sampled by the CL analyzer. Potential interferences in the blue diode laser CRDS are discussed in the Supporting Information (SI). In some experiments, iodide ion chemical ionization mass spectrometry (CIMS) was used as described by Abida et al.[48] to confirm the evolution of HNO_2 and HNO_3. For selected experiments, organic photoproducts formed were monitored by HPLC (see the SI).

3. RESULTS

3.1. Photochemical Conversion of NO_3^- to NO_y in the Presence of Organic Modifiers. Figure 1 shows representative time series of NO_y released from irradiated frozen solutions containing 1.0 M $NaNO_3$. Irradiation was commenced at $t = 0$. In the absence of organic additives, approximately 2.1 parts-per-billion by volume (ppbv, 10^{-9}) of NO_y were observed. The addition of $HCOO^-$, phenol, toluene, or MSA^- lowered the amount of NO_y produced, with the lowest amount (400 parts per trillion by volume, or 400 pptv) observed in the presence of formate. When MSA ($pK_a \approx -0.6$;[67] the pH of a 10 mM solution prior to freezing was measured at 3.1) or 4-CP (10 mM) was added, more NO_y was evolved than was in their absence. In the case of MSA, the yield of NO_y approximately doubled to 4.0 ppb, whereas the addition of 4-CP increased the yield of NO_y by a factor of approximately six to about 12 ppbv.

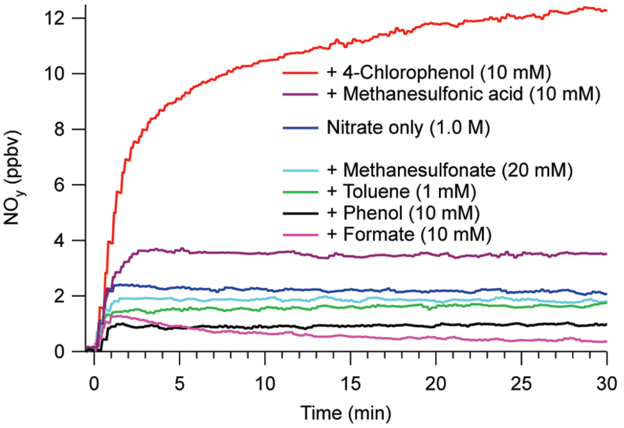

Figure 1. Production of gas-phase NO_y upon irradiation of frozen ($T = -20$ °C) solutions containing 1.0 M $NaNO_3$ and the organic additive at the concentration indicated. Irradiation was commenced at $t = 0$. While most organic compounds suppress, MSA and 4-CP enhance NO_y production.

3.2. Photochemical Conversion of NO_3^- to NO_y in the Presence of *para*-Halogenated Phenols. Figure 2 shows a comparison of NO_y observed upon irradiation of ice samples containing 1.0 M $NaNO_3$ and 10 mM 4-HP, 4-FP, 4-BP, or 4-CP. The shaded areas show the amounts of NO_2 observed by

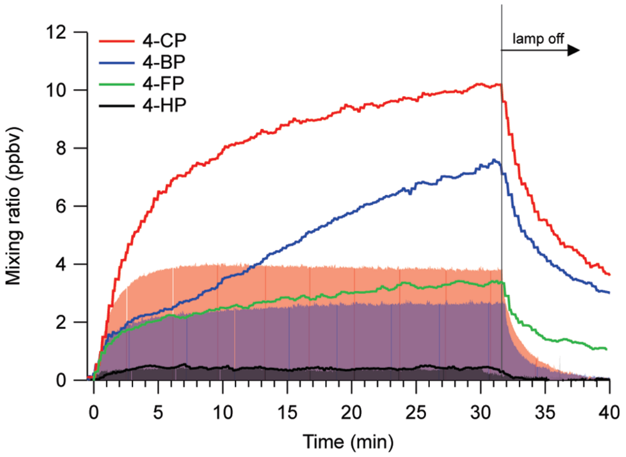

Figure 2. Comparison of photochemical production of NO_y from photolysis of 1.0 M $NaNO_3$ in the presence of 10 mM 4-CP, 4-BP, 4-FP, or 4-HP at −20 °C. The shaded areas indicate the fraction of NO_y due to NO_2 measured by CRDS. The lamp was switched off after 1/2 h.

CRDS at 405 nm (see the SI for a discussion of potential positive interferences). NO data and the NO_2 data for 4-FP are shown in Figure S-1 (SI). Considerable differences are seen in the yield of nitrogen oxides. The highest amounts of NO_y and NO_2 were observed in the presence of 4-CP, followed by 4-BP, 4-FP, and 4-HP. In the case of 4-HP (and likely also 4-FP; see the SI), most (∼85%) of the NO_y observed was in the form of NO_2. In the presence 4-BP and 4-CP, a high NO_2 content was observed in the early phase of the irradiation, which stabilized over the course of a few minutes. In both cases, mixing ratios of NO_z ($=NO_y - NO_x$) continued to increase during the irradiation experiment. Using CIMS, we identified (see Figure S-2 (SI) for an example) the NO_z species as HONO (95%) and HNO_3 (5%). When the lamp was switched off after 1/2 h of irradiation, the 405 nm CRDS absorption signal returned to the baseline relatively quickly (except for 4-FP; see the SI), whereas NO_z decayed more slowly. The latter behavior is identical to our previous observations of HONO in highly acidic samples.[48,49]

Figure 3 shows the TD-CRDS signal observed as a function of the TD-CRDS inlet temperature for a set of three experiments, in which the TD-CRDS sampled the effluent of the photoreactor after about 1/2 h of irradiation. When 4-CP or 4-BP were present in the ice, the TD-CRDS signal increased until a plateau was reached at an inlet temperature of about 400−420 °C. This temperature profile is consistent with the presence of alkyl nitrates (∑AN) in the effluent.[65,68] We verified the absence of nitryl chloride ($ClNO_2$), which dissociates at the same inlet temperature as ∑AN,[69] offline by measuring the effluent using chemical ionization mass spectrometry (Figure S-2, SI). In contrast to 4-BP and 4-CP, we found no evidence for alkyl nitrate formation in the presence of 4-FP (Figure 3) or in the absence of the other organic additives (data not shown). Table 1 summarizes the mixing ratios of the NO_y components for the data shown in Figures 2 and 3.

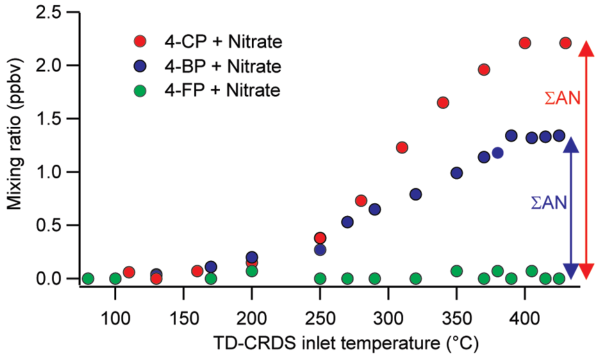

Figure 3. TD-CRDS inlet temperature scan to measure the total alkyl nitrate (∑AN) emitted from irradiated ice samples containing 1.0 M $NaNO_3$ and 10 mM 4-CP, 4-BP, or 4-FP. The increase in NO_2 signal between inlet temperatures of ∼250 and ∼400 °C is consistent with thermal dissociation of compounds of molecular formula $RONO_2$, where R is an alkyl group.

Table 1. Yields of NO_y species (in ppbv) Observed after 1/2 h of Irradiation for the Experiment Shown in Figure 2

species	4-HP	4-FP	4-BP	4-CP
NO (obs)	0.1	0.4	0.3	0.6
NO_2 (obs)	0.4	3.7[a]	2.6	3.8
∑AN (obs)	n/d	0.0	1.3	2.2
HONO (+ HNO_3)[b]			3.2	3.6
NO_y (obs)	0.7	3.7	7.4	10.2

[a] The upper limit of the absorption measurement at 405 nm is possibly affected by an interference; see SI. [b] Calculated by the difference ($=NO_y - NO - NO_2 -$ ∑AN).

Figure 4 shows the amount of NO_y observed after 1/2 h of irradiation as a function of the 4-XP concentration added to the ice samples. The amount of NO_y produced is dependent on the identity of the halogen atom, X, and the concentrations of 4-XP. The latter relationship is nonlinear.

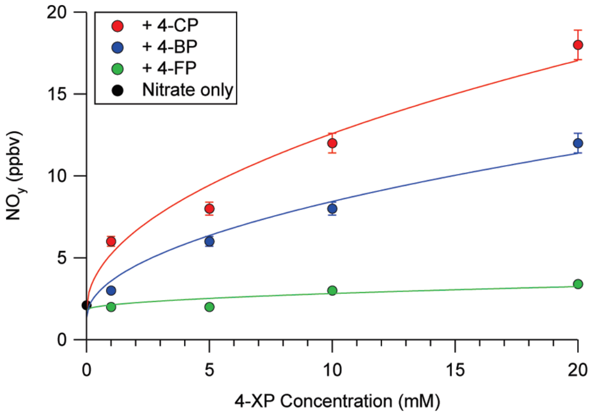

Figure 4. Production of gas-phase NO_y from an irradiated frozen solution containing 1.0 M $NaNO_3$ as a function of *para*-halogenated phenol concentration at −20 °C. The trend lines are fits of observed NO_y against the square root of concentration and are intended as visual guidelines only without physical meaning.

3.3. Roles of OH and H^+ in the Photoconversion of NO_3^- to NO_y in the Presence of 4-CP.

To probe the mechanism of the photochemistry of NO_3^- in the presence of 4-CP, isopropanol was added as a OH radical trap. Figure 5 shows the effect of adding 0.5% v/v isopropanol to an ice sample containing 1.0 M $NaNO_3$ and 10 mM 4-CP prior to freezing. The addition of isopropanol decreased the amount of

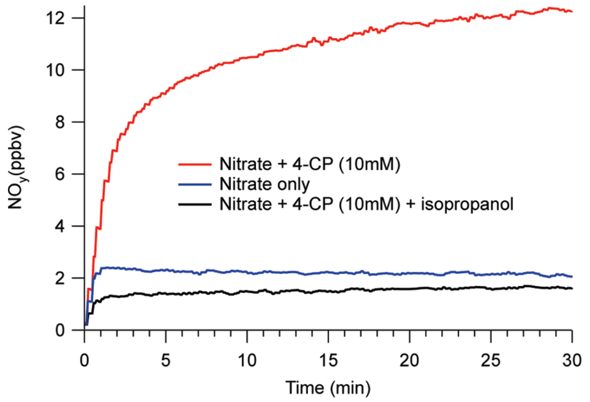

Figure 5. Effect of adding isopropanol (0.5% v/v) on the photochemical production of NO_y from 1.0 M $NaNO_3$ in ice in the presence of 10 mM 4-CP at −20 °C. The $NaNO_3$ only case (see Figure 1) is shown for comparison.

NO_y released from the irradiated ice surface to a level below that in the absence of organic additives.

The pH was measured for two samples containing 20 mM 4-CP and 1.0 M $NaNO_3$ before freezing and for thawed solutions after the irradiation; before freezing and irradiation, the sample pHs were 7.20 and 7.33, respectively. After 2 h of irradiation, the pH values of the thawed samples were 4.72 and 5.18, respectively. pH values observed in irradiated samples containing only $NaNO_3$ were above 5.5.

Experiments were conducted in which the proton concentration of samples containing 10 mM 4-CP and 1.0 M $NaNO_3$ were buffered using acetic acid/acetate at pH 3.6 and sodium bicarbonate and carbonate at pH 9.6 (measured prior to freezing). Figure 6 shows the effect on the photoconversion of NO_3^-. When the proton concentration is buffered, less NO_y is evolved from the ice than that under unbuffered conditions. Under basic conditions, evolution of NO_y is lower than that under unbuffered conditions, consistent with the results that we reported earlier.[49]

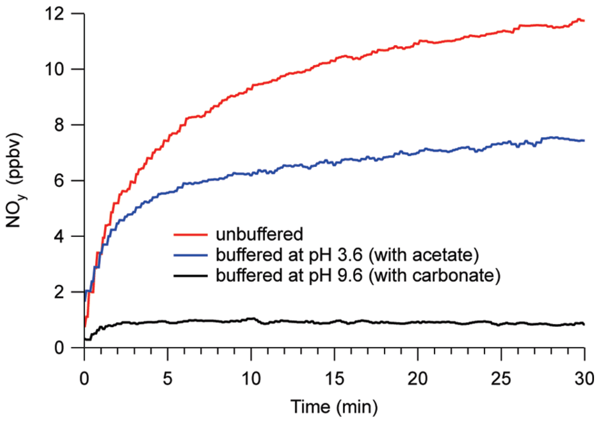

Figure 6. Effect of buffering on the photochemical production of NO_y from 1.0 M $NaNO_3$ in the presence of 10 mM 4-CP at −20 °C.

4. DISCUSSION

4.1. Suppression of Gas-Phase NO_y Production from NO_3^- Photolysis by OH Radical Quenchers. This study has shown that the rate of photochemical recycling of ice-phase NO_3^- to gas-phase nitrogen oxides is strongly affected by the presence of organic molecules. The majority of the compounds tested in this work lowered the amount of gas-phase NO_y generated photochemically (Figure 1), which at neutral to basic pH is mainly in the form of NO_2.[49]

The lowest NO_y (and NO_2) mixing ratios were observed in the presence of 10 mM formate (Figure 1). Dubowski et al.[36] investigated the yields of condensed-phase NO_2^- from NO_3^- photolysis and rationalized higher NO_2^- yields in the presence of formate by scavenging of OH radicals by organic compounds to reduce the rate of NO_2^- to NO_2 conversion and by reaction of NO_2 with the superoxide anion (O_2^-):

$$NO_2^- + OH \rightarrow NO_2 + OH^- \tag{4}$$

$$O_2^- + NO_2 \rightarrow O_2 + NO_2^- \tag{5}$$

The superoxide anion is generated by the following reaction sequence:

$$HCO_2^- + OH \rightarrow H_2O + CO_2^- \tag{6}$$

$$CO_2^- + O_2 \rightarrow O_2^- + CO_2 \tag{7}$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad pK_a = 4.8 \tag{8}$$

The pK_a is from Buxton et al.[70] Reaction 5 converts the volatile NO_2 to nonvolatile NO_2^- and is thus predicted to suppress NO_2 formation. The low rate of NO_2 production from NO_3^- photolysis in the presence of formate observed in this work is consistent with the above mechanism. Interestingly, the photochemical production of NO_y in the presence of formate does not appear to achieve a steady state, which is in contrast to what is observed in the presence of other species, for which the NO_2 production stabilizes within a few minutes after the lamp has been switched on (Figure 1). This result implies that a secondary product, whose concentration builds up relatively slowly during the photolysis experiments, suppresses NO_2 formation by reducing NO_2 to NO_2^- via the CO_2^-/O_2^- pathway (reactions 5−8).

Dubowski et al.[36] also suggested that removal of OH by the organic molecule reduces the rate of reaction 4, that is, the conversion of NO_2^- to NO_2, and could explain the higher yield of NO_2^- in their experiments. In a follow-up study, Minero et al.[47] pointed out that if reaction 4 was dominant, the NO_2^- yield should scale with the product of the OH loss-rate coefficient of the organic additive (Table 2) and its concentration. Studying the yield of NO_2^- from NO_3^- photolysis in aqueous solution, Minero et al.[47] observed a lower rate of NO_2^- production in the presence of MSA^- than that in the presence of formate, even when MSA^- was present at concentrations several-fold that of formate. From this observation, the authors concluded that reaction 4 is a minor pathway.

Table 2. Reaction Rates of Selected Organic Species with OH in Aqueous Solution at Room Temperature[70]

species	rate constant ($M^{-1} s^{-1}$)
phenol	$(0.65–1.8) \times 10^{10}$
4-CP	7.6×10^9
formate	3.2×10^9
toluene	3.0×10^9
isopropanol	1.9×10^9
MSA^-	1.3×10^9

Figure 7 gives a graphical overview of extent of change in NO_y, ΔNO_y, observed in this work plotted against the rate constants of the organic modifiers with respect to reaction with OH in aqueous solution. In the interpretation of this plot, the following four simplifying assumptions are made: (1) that the organic additive concentrations are equal as the freezing ice concentrates them near the surface, (2) that the organic additives do not themselves absorb light and initiate photochemistry, (3) that rate coefficients for reaction of OH with organics in the ice's surface layer correlate with those observed in aqueous solution at room temperature, and (4) that reactions with secondary species do not dominate the chemistry. Some of these assumptions are questionable, as recent studies by the Donaldson group[71−73] and the greater suppression of NO_2 by formate after prolonged irradiation (see above) have shown. However, relevant data, for example, on OH rate coefficients in the liquid-like ice surface layer, are sparse or do not exist, and Figure 7 at least allows for a qualitative analysis.

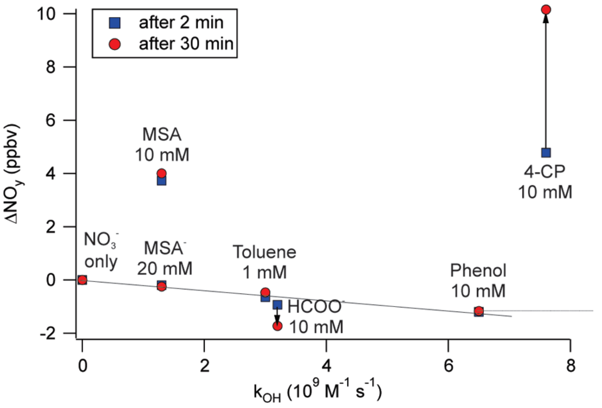

Figure 7. Plot of suppression of NO_y production relative to "pure" 1.0 M $NaNO_3$, ΔNOy, as a function of the OH rate constant of the organic molecule added.

If reaction 4 were dominant, one would predict a larger yield of NO_2 with a more efficient OH scavenger. Figure 7 generally shows the opposite trend. Neglecting the *para*-halogenated phenols and MSA (both are discussed below), the slope observed is consistent with reaction 5 as a dominant factor because reaction of OH with organic compounds in the presence of O_2 produces HO_2/O_2^-. Thus, the trends in gas-phase NO_2 production observed in this work are consistent with the conclusions by Minero et al.[47] based on observations of NO_2^- in the condensed phase.

4.2. Promotion of NO_y Production from NO_3^- Photolysis by Acidic Conditions.

It is well established that the acidity plays a key role in the photochemical volatilization of nitrogen oxides from ice. Under acidic conditions, NO_2^-, peroxynitrite ($ONOO^-$), and peroxynitrate ($O_2NO_2^-$) are protonated to form HONO, HO_2NO_2, and HOONO, which partition to the gas phase.[16,48] Furthermore, acidic conditions promote the formation of NO_2, which has been rationalized by formation of HOONO as a volatile intermediate.[49] The observations in the presence of 10 mM MSA^- at either neutral or acidic conditions (Figure 1) clearly demonstrate that acidification of the ice promotes the photochemical evolution of NO_y from NO_3^- photolysis. In the acidified sample, the yield of NO_y increases by a factor of approximately 2, whereas the yield in the presence of MSA^- is slightly lower than for pure $NaNO_3$ in ice. The amount of NO_y observed under acidic condition is consistent with the trend of NO_y observed as a function of acidity that we reported earlier using oxalic acid/oxalate, phosphate, or acetic acid/acetate buffers (see Figure 2 in ref 49).

This observation suggests that the nature of the organic modifier and differences in the rates of O_2^-/HO_2 formation play minor roles in acidified samples. Under acidic conditions, O_2^-, generated from oxidation of the organic compound, is protonated to HO_2, which does not convert NO_2 to NO_2^-. Thus, suppression of NO_2 and NO_y formation via reaction 5 is not expected in acidified samples.

4.3. Promotion of NO_y Production from NO_3^- Photolysis by *para*-Halogenated Phenols.

The efficient production of NO_y in the presence of 4-CP and 4-BP (Figure 2) is surprising, in particular because the presence of 4-HP suppresses NO_y formation. It is clear that this effect is accompanied by acidification of the ice sample as the pH of the thawed solution dropped considerably during photolysis and buffering of the ice reduced the amount of NO_y produced (Figure 6). It is also clear from the isopropanol experiment (Figure 5) that radical species are key intermediates. The questions arise why the ice samples become acidic upon irradiation and why the 4-CP promoted production of NO_y is suppressed by isopropanol.

4.3.1. Direct Photolysis of para-Halogenated Phenols.

One conceivable explanation for the observed acidification of the ice samples is direct photoexcitation of the *para*-halogenated phenols. Phenols are known to be fairly acidic in their excited singlet states. The pK_a^* of 4-CP, for example, is approximately 3.2, whereas its ground-state pK_a is 9.42.[74] However, the pK_a^*'s of 4-HP, 4-FP, and 4-BP, respectively, equal 4.0, 4.4, and 3.1.[74] Thus, the pK_a^* values of excited-state phenols are inconsistent with the trend shown in Figure 2. On the other hand, direct photolysis of 4-CP (at 266 nm) is known to yield *para*-benzoquinone (BQ) and the strong acid HCl ($pK_a \approx -8$)[67] as an elimination product.[54,75] In this work, BQ was observed as a photoproduct by HPLC (see Figure S-3 in the SI). Production of HCl in the surface would produce very acidic conditions, in particular in a thin aqueous surface layer, and promote the production of NO_y. Similarly, photolysis of 4-BP yields the strong acid HBr[55] ($pK_a \approx -9$)[67] and promotes NO_y formation, as observed. Because the acidity of strong acids in aqueous media is limited to that of the hydronium cation, H_3O^+, one might expect the photolysis of 4-CP to have the same effect on pH as the photolysis of 4-BP. However, Durand et al.[55] have evaluated the relative photoreactivities of halogenated phenols and reported that 4-CP is more reactive (judged by the amount of halogenated phenol remaining at the end of the photolysis experiment) than 4-FP, which in turn is more reactive than 4-BP. Even though 4-FP is more reactive than 4-BP, photolysis of 4-FP "only" produces the weak acid HF ($pK_a \approx +3.2$),[67] and the NO_y yield is consequently lower. Phenol does not eliminate an acid and thus has the lowest NO_y yield. Thus, the order observed (4-CP > 4-BP > 4-FP > 4-HP) is consistent with what one might expect based on the existing literature.

One could argue that it is unfeasible that direct photoexcitation of *para*-halogenated phenols takes place in our experiments because the absorption spectra of *para*-halogenated phenols in aqueous solution do not overlap with the lamp's emission spectrum (Figure S-5, SI). However, the Donaldson group recently showed that the absorption spectra of simple aromatic compounds in the ice surface layer can be significantly red shifted to wavelengths above 300 nm, rationalized by self-association of the aromatic rings.[73] Furthermore, Klánova et al. reported that the absorption spectrum of 4-CP in ice overlaps slightly with the actinic spectrum.[76] To investigate if direct photolysis of 4-CP was a significant factor in our experiments, photolysis experiments on ice containing only 4-CP were conducted. After >60 min of irradiation in the absence of NO_3^-, no 4-CP degradation products were observed by HPLC (see SI). Furthermore, a direct photolysis mechanism would not explain the results of the radical quenching experiment (Figure 5). Thus, we conclude that it is unlikely that direct photolysis of *para*-halogenated phenols is mainly responsible for the observed promotion of NO_y formation.

4.3.2. Reaction of para-Halogenated Phenols with OH. An alternative explanation for the observed acidification of the irradiated ice sample and promotion of NO_y formation is that the *para*-halogenated phenols react with OH produced from NO_3^- photolysis and eliminate halogen acids, promoting the formation of volatile nitrogen oxides. The reaction of 4-CP with OH in aqueous solution has been studied both experimentally[23,77−84] and theoretically[85,86] and has been reviewed by Burrows et al.[87] The products of this reaction in aerated aqueous solution are 4-chlorocatechol (4-chloro-1,2-dihydroxybenzene; CC) and hydroquinone (1,4-dihydroxybenzene, HQ); usually, only trace amounts of BQ have been observed.[77,78] In ice at −20 °C with H_2O_2 as the OH source, Klánova et al. observed CC as the major product and trace levels of HQ and coupling products.[61] Schedel et al. used NO_3^- photolysis to generate OH in aqueous solution and reported formation of (among others) CC, BQ, 2-nitrohydroquinone (2NHQ), and 2-hydroxybenzoquinone (2HBQ) with relative yields that depend on the NO_3^- concentration; at a NO_3^- concentration of 0.05 M, a greater amount of BQ was observed than that in the presence of 0.01 M.[23] In this work, BQ and CC were observed as the major organic products, and 2NHQ was observed as the minor organic product by HPLC (Figure S-3, SI). HQ was not observed; however, we cannot rule out that HQ was present and coeluted with another (more abundant) species. The relatively high yield of BQ is consistent with the results by Schedel et al.[23] because the NO_3^- concentration in the ice's liquid-like surface layer was likely higher than the 1.0 M solution prior to freezing.

Figure 8 gives an overview of the reactions that are likely taking place in our experiments. The first step is production of OH by photolysis of NO_3^- (there is also secondary production from NO_2^- photolysis, which is neglected here). Then, one of several reactions may happen. The hydroxyl radical can add at the 2 position of the aromatic ring to form the 4-chloro-1,2-dihydroxycyclohexadienyl radical (4C1,2D$^{\bullet}$), which converts to CC and HQ. Formation of HQ has been rationalized by dismutation reactions between 4-CP$^{\bullet}$ and 4-chlorodihydroxycyclohexadienyl radicals (4CD$^{\bullet}$).[78] Alternatively, reaction of 4CD$^{\bullet}$ with O_2 can lead to ring opening, loss of aromaticity, and HO_2 production (not shown).[80,82] An alternative (minor) reaction is abstraction of the phenolic hydrogen by OH to form the 4-chlorophenoxy radical (4-CP$^{\bullet}$), which is believed to react further to generate HCl and nonaromatic products.[87] A third possibility is that OH adds to the aromatic ring at the 4 position, forming the 4-chloro-1,4-dihydroxycyclohexadienyl radical (4C1,4D$^{\bullet}$), which eliminates HCl to form the benzosemiquinone radical (BSQ$^{\bullet}$).[78,80] In studies that did not use NO_3^- as the source of OH, BSQ$^{\bullet}$ was reduced to HQ. To account for the formation of BQ in the presence of NO_3^- in this study and the work by Schedel et al.,[23] we propose that BQ is formed by oxidation of HQ and/or BSQ$^{\bullet}$ and speculate that this oxidation is accompanied by reduction of NO_3^- or O_2.

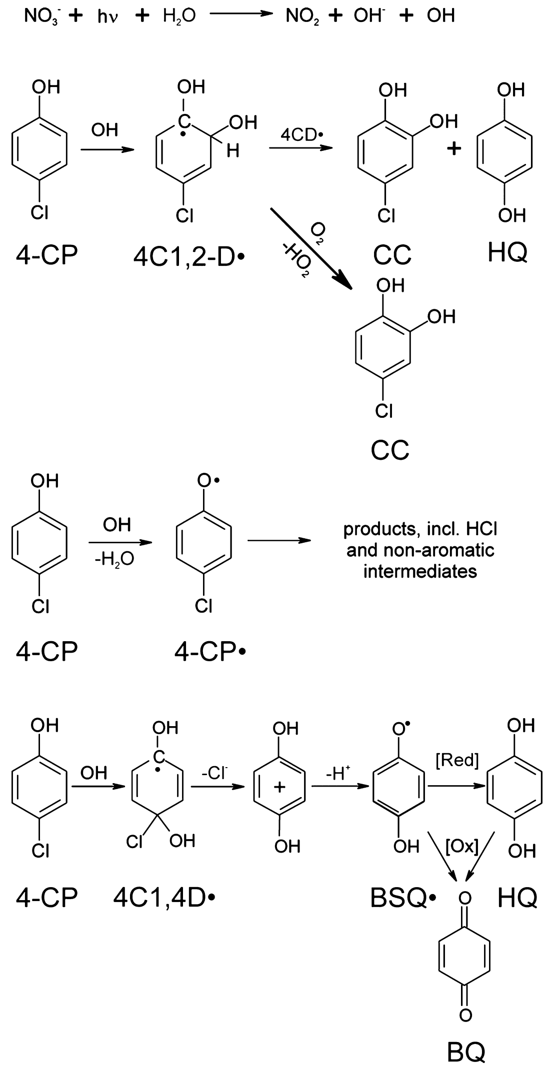

Figure 8. Proposed chemical transformation pathways during nitrate-induced photo-oxidation of 4-CP.

In the above mechanism, HCl is eliminated from 4-CP and acidifies the ice's surface. This acidification is primarily responsible for the observed high yield of gas-phase nitrogen oxides in the presence of 4-CP, as is evident from the suppression of NO_y production in the presence of a mildly basic buffer (Figure 5). However, additional volatile nitrogen oxides may be produced by reduction of NO_3^- by HQ or BSQ$^{\bullet}$ or other intermediate species such as 4CD$^{\bullet}$ or BSQ$^{\bullet}$. It is also possible that the species being reduced is NO_3^{-*}, as suggested by Minero et al.[47] For example, one could envision that NO_3^{-*} undergoes an electron transfer to 4-CP; halogenated phenols are generally good electron acceptors. Clearly, more studies will be needed to determine if any of these pathways are significant.

Preliminary experiments show that 4-CP is able to promote the photoreduction of NO_2^- to NO (Figure S-7, SI). However, an even greater effect was seen in the presence of phenol. The reversed order is rationalized in part by the lack of a reaction corresponding to reaction 5, as O_2^- does not react with NO as it does with NO_2, and the resulting lack of suppression of volatile nitrogen oxides formation from NO_2^- photolysis. More studies are needed to elucidate the details of the photochemical transformation of NO_2^- in the presence of para-substituted phenols in ice.

Finally, there may be secondary photochemistry to consider. For example, many of the secondary products formed from 4-CP have absorption spectra (e.g., Figure S-4, SI) that at least partially overlap with the lamp's excitation spectrum, making them prone to photoexcitation. However, given the short irradiation times and corresponding low conversion rates in this study, we believe such secondary photochemistry did not impact the results.

4.4. Photonitration. The photoconversion of nitrate in the presence of aromatic compounds can, in principle, lead to formation of nitroaromatic compounds, which are generally carcinogenic. Several groups[23,29] have studied the phototransformation of NO_3^- in the presence of 2-, 3-, and 4-CP and found minor nitration products; there is also evidence for proton-concentration-dependent photonitration.[28] In this study, we observed trace amounts of 2NHQ. The mechanism for 2NHQ formation is not obvious. We speculate that 2NHQ is formed from reaction of $BSQ^•$ with NO_2.

We also observed evidence for significant formation of volatile alkyl nitrates (Figure 3). We are certain that the observed organic nitrates are alkyl nitrates as nitroaromatic compounds are more thermally stable.[88] It is well documented that 4-CP readily ring opens upon photo-oxidation to form nonaromatic adducts.[82] Many of the intermediate products formed are unsaturated and are prone to addition reactions (e.g., of the NO_3 radical). Furthermore, many of the intermediates include alkoxy and organic peroxy radicals, which can form adducts with NO_2.[89] Photochemical formation of alkyl nitrates in natural snow and ice has been observed in field measurements.[90] The formation of alkyl nitrates from 4-CP observed in this work is likely one of many pathways for their generation.

5. CONCLUSIONS

It is well established that the photochemical recycling of NO_3^- to volatile nitrogen oxides has consequences on the composition of the overlying atmosphere. Here, the rate of photochemical conversion of NO_3^- from snow and ice to nitrogen oxides that partition to the gas phase was found to be strongly affected by the presence of organic compounds and the ice's acidity. While most of the organic compounds tested lowered the yield of NO_y, OH-induced photodegradation of 4-CP and 4-BP increased the yield of NO_y, rationalized by acidification due to elimination of HCl and HBr. In addition, we demonstrated that NO_3^--induced photochemistry could result in photonitration of aromatic compounds, which is of health concerns. For example, *p*-nitrobenzoquinone was identified during the irradiation of nitrate in the presence of 4-CP. Finally, we showed that volatile alkyl nitrates can be generated from NO_3^- photolysis in snow and ice.

One of the implications of this study is that in quantitative studies (e.g., measurements of quantum yields), both liquid- and gas-phase products need to be taken into account. Further, the compounds used in this study, while common in ice, are just a small subset of the many compounds that have been found in ambient snow and ice samples (e.g., see refs 5, 13, and 91). Key experimental improvements will be the use of lower, more realistic, concentrations of NO_3^- than were used in this study and improved ice preparation techniques, such as the shock-freezing technique to produce artificial snow grains.[43,92−94] Future experiments also need to take control of the acidity of the ice, if possible. Potential effects of repeated freeze/thaw cycles (which concentrate species near the surface)[50,51] should be considered. Finally, the effects of adding mixtures of organic compounds, including organic photodegradation products, on the photochemical conversion of NO_3^- to NO_y in snow and ice should be investigated. These mixtures of the organic compounds should not only resemble those occurring in pristine environments but also those found in polluted environments in cold climates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Discussion of potential interferences with CRDS NO_2 measurements and description of photoproduct analysis by HPLC. Six figures: Time series of NO_y, NO_2, and NO mixing ratios. Sample chemical ionization mass spectrum and HPLC chromatogram with PDA spectra. Lamp emission and absorption spectra of nitrate and 4-CP. Photochemical production of NO_y as a function of temperature. Photochemical production of NO and NO_y from frozen solutions containing nitrite. This material is available free of charge via the Internet at http://pubs.acs.org.

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