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Photochemically induced nitration and hydroxylation of organic aromatic compounds in the presence of nitrate or nitrite in ice

Nina Matykiewiczová [a], Romana Kurková [a], Jana Klánová [a], Petr Klán [b,*]

[a] RECETOX, Masaryk University, Kamenice 126/3, 625 00 Brno, Czech Republic
[b] Department of Organic Chemistry, Faculty of Science, Masaryk University, Kotlarska 2, 611 37 Brno, Czech Republic

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Abstract

The photochemistry of three model aromatic compounds (phenol, anisole, and 4-methoxyphenol; $c = 10^{-3}$ mol L^{-1}) in frozen aqueous solutions containing sodium nitrite or nitrate ($c = 10^{-2}$ to 10^{-1} mol L^{-1}) at −15 °C was investigated. Nitration, hydroxylation, and coupling reactions were found to be the principal chemical processes, presumably taking place in a layer covering the ice crystal surfaces where both hydrophobic organic and water-soluble inorganic compounds were accumulated prior to and during irradiation. While the primary photoproducts were identified at low reaction conversions, exhaustive (quartz- or Pyrex-filtered) UV-irradiation produced a very complex mixture of compounds. The photoreactions proceeded predominantly by the nitrite or nitrate photoexcitation but chemistry of the excited organic chromophores was also observed. Phenol and 4-methoxyphenol photolysis afforded the corresponding nitro- and hydroxycompounds, in addition to biphenyl and diphenylether derivatives. Qualitatively the same photoproducts were produced in the presence of nitrite as well as nitrate; therefore both anions were the source of the NO_x or HO radicals. In contrast, irradiation of anisole under the same reaction conditions afforded phenol nearly exclusively. It is demonstrated that the OH group of phenols played an important role in the course of hydroxylation and nitration reactions. The results from this study may support assumptions according to which photolysis of nitrate in the snowpack is responsible for oxidation of organic precursors to their hydroxy or carbonyl derivatives.
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1. Introduction

The absorption spectra of both the nitrite (NO_2^-) and nitrate (NO_3^-) ions in aqueous solutions contain weak $n \rightarrow \pi^*$ bands (λ_{max} (NO_2^-) ~355 nm; λ_{max} (NO_3^-) ~305 nm) [1]. The photochemistry of nitrite irradiated at 250–400 nm is known to be very complex and it essentially results in the formation of $NO^\bullet$ and $O^{\bullet-}$ (Eq. (1)), where the latter species can be protonated to form $HO^\bullet$ (Eq. (2)). NO_2^- and $NO^\bullet$ can be oxidized by $HO^\bullet$ or by dissolved oxygen, respectively, to form $NO_2^\bullet$ (Eqs. (3) and (4)) [1–3].

$$NO_2^- + h\nu \rightarrow NO^\bullet + O^{\bullet-} \qquad (1)$$

$$O^{\bullet-} + (H^+) \rightarrow HO^\bullet + HO^- \qquad (2)$$

$$NO_2^- + HO^\bullet \rightarrow NO_2^\bullet + HO^- \qquad (3)$$

$$2NO^\bullet + O_2 \rightarrow 2NO_2^\bullet \qquad (4)$$

In contrast, the nitrate photochemistry in aerated aqueous solutions results in two main processes, shown in Eqs. (5) and (6), from which the former, producing reactive hydroxyl radical and nitrogen dioxide, requires a source of the proton [1].

$$NO_3^- + h\nu \rightarrow NO_2^\bullet + O^\bullet \xrightarrow{H_2O} NO_2^\bullet + HO^\bullet + HO^- \qquad (5)$$

$$NO_3^- + h\nu \rightarrow NO_2^- + O^\bullet \qquad (6)$$

It is now well established that nitrite/nitrate photolysis in natural waters can trigger hydroxylation, nitration, and nitrosation reactions of many organic pollutants [3–5]. Possible formation of highly mutagenic/carcinogenic nitrocompounds [6] is unquestionably of great environmental interest.

Distribution of inorganic nitrate in Antarctic ice is relatively constant comparing to other ions; mean levels in ice cores and

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* Corresponding author. Tel.: +420 549494856; fax: +420 549492688.
E-mail address: klan@sci.muni.cz (P. Klán).

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surface snow usually vary from 20 to 80 $\mu g\,L^{-1}$ [7], but the concentration may occasionally reach higher values in the surface snow [8]. There is increasing evidence for post-depositional photochemical alterations of nitrate in natural ice and snow. NO_3^- photolysis in ice or snowpack causes that the $NO_x^\bullet$, HONO, and hydroxyl radicals are produced [8–15]. Dubowski et al. determined the quantum yield of nitrate photodegradation in ice samples by measuring the $NO_2^\bullet$ release (Eq. (5)) and the NO_2^- production (Eq. (6)) [16,17]. Photochemical production and release of gaseous $NO_2^\bullet$ and desorption of $NO_x^\bullet$ from nitrate-doped ice was recently studied by Boxe and collaborators [18,19]. In addition, the quantum yield of the $HO^\bullet$ formation (Eq. (5)) in ice was found by Chu and Anastasio to be pH (the value prior to freezing) and temperature dependent [20]. The same authors have later demonstrated that the largest portion of $HO^\bullet$ produced on polar snow originates from the H_2O_2 photolysis [21]. Jacobi et al. have also recently evaluated the importance of the photolysis of both H_2O_2 and nitrate as the sources of $HO^\bullet$ in artificial snow [22].

Recent research results have provided sufficient evidence that some organic compounds may undergo light-induced chemical transformations in ice or snow [23–27] with possible toxicological consequences [28]. In addition, it was suggested that $HO^\bullet$ could oxidize organic precursors to produce carbonyl compounds, such as formaldehyde, in the snowpack [29–31]. The laboratory experiments have shown that the photolysis of frozen aqueous solutions of organic aromatic photosensitive compounds, such as chlorophenols, in the presence of H_2O_2 produces a complex mixture of products [32].

The aim of the present laboratory model study was to evaluate qualitatively and quantitatively light-induced chemical transformations that occur in frozen aqueous solutions of the three aromatic compounds (phenol, anisole, and 4-methoxyphenol) in the presence of inorganic nitrite and nitrate. Specific photochemical reactivity, mechanistic considerations, and possible implications for the environment are discussed in this paper.

2. Experimental

2.1. Instrumentation

The spectra of liquid aqueous solutions were measured on a Unicam UV4 (Cambridge, UK) against a pure water sample in quartz cells with a 1-cm optical path length. The solidified samples in Plastibrand cuvettes (transparent at >280 nm) containing the aqueous solutions were prepared by freezing at −20 °C. The spectra of frozen solutions and the reference spectra of pure ice were measured on a Lambda 19 UV/vis/NIR spectrophotometer (Perkin-Elmer) using a 60-mm integrating sphere immediately after removing the cuvettes from the cold environment as described earlier [33]. Although the sample temperature was not controlled during the absorption measurements, no changes of the spectra were observed within the time period necessary for duplicate consecutive experiments. The averaged spectral background of pure ice was subtracted from each spectrum and the spectra shown are averaged from two independent measurements.

A gas chromatograph HP 6890 equipped with a mass selective detector HP 5972 and a J&W Scientific fused silica column DB-5MS was used. The mass spectra were collected in the scan *m/z* range of 50–550 for identification purposes. HPLC analyses were performed on a HP 1100 liquid chromatographic system, equipped with a diode array photometric detector and Polaris C18-A or Ace 5 C18 columns. A Dionex ICS-1000 ion chromatographic system, consisting of Ionpac AG9-HC and AS9-HC columns, a suppressor Dionex AMMS III, and a conductivity detector, were used for determination of the NO_2^- and NO_3^- concentrations. Low-temperature experiments were accomplished in a cryostat box MLW MK70. The pH of the solutions was measured by a pH meter Multical 526 (WTW).

2.2. Chemicals

Benzene, phenol, anisole, 4-methoxyphenol, sodium nitrite, sodium nitrate (99+; Sigma–Aldrich), dichloromethane, methanol (HPLC grade; Labscan), and acetic acid (p.a.; Lachema) were used as received. The following compounds were used as the analytical standards in GC–MS measurements: nitrobenzene, pyrocatechol, hydroquinone, 2-nitrophenol, 4-nitrophenol, 4-methoxy-2-nitrophenol, and nitrosobenzene (Sigma–Aldrich). Water was purified on an Osmonics 2 and a Millipore Simplicity 185.

2-Hydroxy-5,4′-dimethoxydiphenylether (**10**). This compound, used as an analytical standard, was prepared by a quartz-filtered photolysis of neat 4-methoxyphenol. The product was separated by column chromatography. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.80 (s, 6H, 2× OCH_3), 5.71 (s, 1H, OH), 6.70–7.00 (m, 7H, aromatics). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 56.1, 115.8, 116.2, 116.3, 116.4, 118.0, 125.3, 130.6, 146.9, 154.4 (broad). MS (30 eV) (EI) *m/z*: 246 (M^+), 216, 201, 124, 109, 86, 84; $C_{14}H_{14}O_4$.

2.3. Sample irradiation, extraction, and analysis

All aqueous solutions, containing phenol, anisole, or 4-methoxyphenol ($c = 10^{-3}$ mol L^{-1}), with or without an excess of nitrite or nitrate ($c = 10^{-2}$ or 10^{-1} mol L^{-1}), were bubbled with either nitrogen or oxygen for 30 min prior to freezing. Samples in 13 mm × 100 mm quartz (transparent at >254 nm) or Pyrex (an additional Pyrex sleeve eliminated wavelengths below 300 nm) tubes, sealed with septa, were solidified in a cryostat box filled with ethanol as a cooling medium at −15 °C, and irradiated using a 125-W medium-pressure mercury lamp (Teslamp). After irradiation, thawed sample solutions were extracted with dichloromethane (for GC–MS) or analyzed directly on HPLC. Identification and quantification of the photoproducts was carried out by comparison of their retention times and/or MS spectra with those of the authentic compounds or the mass spectral library. The nitrite or nitrate concentrations were analyzed using an ion chromatograph. The analytical data reported are the average results obtained from at least triplicate measurements and the relative standard deviation was found below 10% in all analyses. The chemical yields of nitrophenol photoproduction from phenol in the presence of nitrite were corrected because nitrophenols were also found to be formed in a small amount (<10% of the total conversion) in dark. No other experimental systems underwent dark reactions within the time necessary for the corresponding photochemical experiment. When specific NO_3^- excitation was needed, the photochemical irradiation was carried out on an optical bench consisting of a high-pressure 350 W Hg lamp, an Oriel CornerStone 130 1/8 m monochromator with grating 200–1600 nm set to 313 ± 5 nm, and a 1-cm quartz cell in a Peltier sample holder (−25 °C). The light intensity was monitored by a Si photodiode detector (UV enhanced) with an Oriel OPM multifunction optical power meter controlled by TRACQ32 software.

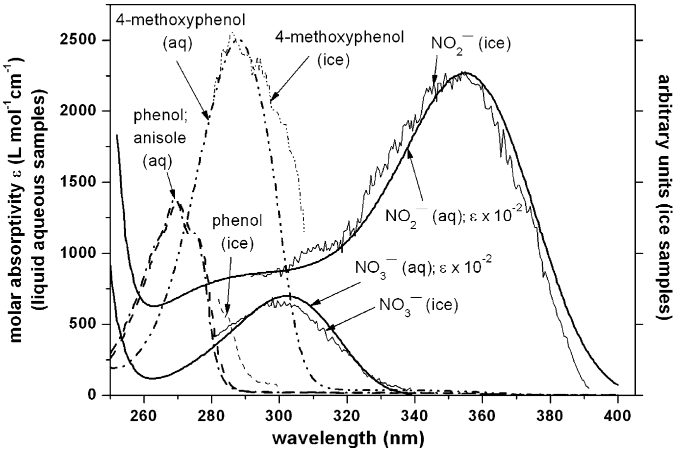


Fig. 1. Absorption spectra of sodium nitrite (–), sodium nitrate (–), phenol (- -), anisole (- · · -), and 4-methoxyphenol (- · · · -) in aqueous (aq; 20 °C; 250–400 nm) and frozen solutions (ice; frozen at −20 °C; measured above 280 nm; normalized).

3. Results

The absorption spectra of nitrite, nitrate, and three organic aromatic compounds (phenol, anisole, and 4-methoxyphenol) measured in liquid (20 °C) and frozen (−20 °C) aqueous solutions are compared in Fig. 1. Phenol and anisole absorb strongly below 300 nm, while 4-methoxyphenol, nitrate, and nitrite have stronger absorption also above this wavelength (Fig. 1). The measurements of ice samples in the Plastibrand cuvettes were limited to a wavelength range above 280 nm. The absorption maxima values obtained for the NO_2^-, NO_3^-, and 4-methoxyphenol ice samples were found essentially the same or only slightly shifted compared to those measured for the corresponding solutions. Since λ_{max} of monochlorophenols in liquid and frozen solutions were also found to be comparable [23], it is reasonable to believe that the absorption characteristics of phenol ice samples correspond to those obtained in liquid solutions (Fig. 1). Such results suggest that phenol and 4-methoxyphenol are not largely dissociated in frozen aqueous solutions; λ_{max} of phenolate ions are substantially bathochromically shifted. Heterogeneity and lower transparency of the ice samples decreased the signal-to-noise ratio and a noticeable band broadening can be attributed to light scattering and reflection.

The ice samples were UV-irradiated in a cryostat box in quartz (>250 nm) or Pyrex (>300 nm) tubes. The Pyrex-filtered light was used to simulate natural solar radiation, while quartz-filtered light was used to study photochemical behavior of compounds, which are excited only by a shorter wavelength radiation. The total irradiation time (1–4 h) was adjusted to keep the conversions below 10% in order to avoid secondary photoreactions. The analyses of the photoproducts became, however, very difficult at conversions below 2%. The complete mass balance was never achieved in any of the analyses and always declined with increasing conversions of the starting material.

In order to evaluate the acidity changes in the samples, pH of the aqueous solutions of $NaNO_2$ or $NaNO_3$ or their mixtures with aromatic compounds (phenol, anisole, and 4-methoxyphenol) prior to and after freezing (and subsequent

Table 1
The photolysis of phenol in frozen aqueous solutions at −15 °C

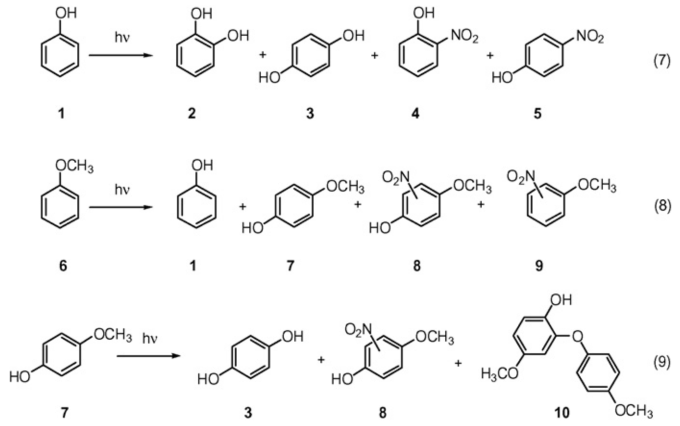
Composition[a]	Filter	Conversion (%)	Chemical yields (%)			
			2	**3**	**4**	**5**
N_2	Quartz	n.d.	n.d.	n.d.	n.a.	n.a.
O_2		2	0.1	0.2	n.a.	n.a.
N_2; NO_2^-		4	Traces	Traces	0.2[b]	0.3[b]
O_2; NO_2^-		5	0.1	0.2	0.3[b]	0.3[b]
N_2; NO_3^-		4	0.2	0.6	1.1	0.4
O_2; NO_3^-		6	0.3	1.3	0.5	0.2
N_2; NO_3^-[c]		2	Traces	Traces	0.7	0.2
O_2; NO_3^-[c]		4	0.2	0.1	0.3	0.1
N_2; NO_2^-	Pyrex	7	0.1	0.1	0.1	0.4
O_2; NO_2^-		4	0.1	0.1	0.2	0.6
N_2; NO_3^-		3	Traces	Traces	0.1	0.4
O_2; NO_3^-		2	Traces	Traces	0.1	0.4

Irradiated for 4 h (quartz) or 1 h (Pyrex); n.d. = not detected; n.a. = not applied.

[a] [PhOH] = 10^{-3} mol L^{-1}; [$NaNO_2$] or [$NaNO_3$] = 10^{-1} mol L^{-1}.

[b] The yields of nitrophenol photoproduction are corrected because nitrophenols were formed in a small amount (<10% of the total conversion) in dark.

[c] [PhOH] = 10^{-3} mol L^{-1}; [$NaNO_2$] or [$NaNO_3$] = 10^{-2} mol L^{-1}.



Scheme 1.

melting), as well as after quartz-filtered UV-irradiation, were measured. Acidity was also evaluated in unfrozen layers of partially frozen mixtures (when >80% of the volume was frozen). The corresponding pH values (weakly basic for NO_2^- and neutral for NO_3^- solutions) essentially remained constant within 10% of the initial value in all cases.

Table 1 lists the photoproducts obtained by irradiation of degassed or oxygenated frozen solutions of phenol (**1**) under different experimental conditions. While the starting compound in deoxygenated samples was found to be photostable in the absence of nitrate or nitrite, it produced two major oxidation products, catechol (**2**) and hydroquinone (**3**), in the samples, which were purged with oxygen prior to freezing (Scheme 1; Eq. (7)). When sodium nitrite or nitrate was added, dihydroxybenzenes (**2** and **3**), 2-nitrophenol (**4**), and 4-nitrophenol (**5**) were the major photoproducts identified. The photonitration process displayed an apparent regioselectivity – only the *ortho* and *para* isomers were produced. Relative phenol consumption was found somewhat higher upon irradiation through a Pyrex filter (1-h irradiation; Table 1), where nitrite or nitrate absorbed predominantly, compared to that observed in quartz vessels (4-h irradiation). When the samples containing phenol and nitrate were irradiated on an optical bench at 313 nm, where NO_3^- absorbs exclusively, **4** and **5** were identified as the major products (not shown). In addition, a GC–MS analysis of dichloromethane extracts was carried out to identify other photoproducts to explain why the complete mass balance was never achieved. Thus, besides the primary photoproducts, which served to evaluate the principal photochemical processes, many unidentified compounds, having larger masses corresponding to coupling products, were observed (Table 2). Exhaustive irradiation produced unidentified high-mass products only.

The major product from the photolysis of anisole (**6**) in frozen aqueous solutions in the presence of NO_2^- or NO_3^- was phenol (**1**) (Table 3; Eq. (8)). The anisole degradation efficiency was generally lower compared to that of phenol under the same irradiation conditions, including the experiments in quartz vessels, despite the fact that phenol and anisole have almost identical absorption characteristics (Fig. 1). Practically no nitrated or hydroxylated photoproducts, such as 4-methoxyphenol (**7**) or methoxynitrophenols (**8**), were identified. Only addition of acetic acid (AcOH) triggered the photoinduced formation of methoxynitrophenols. For comparison, irradiated ice samples containing anisole and hydrogen peroxide ($c = 10^{-2}$ mol L^{-1}), as a source of the hydroxyl radicals [32], provided exclusively 4-methoxyphenol (**7**). A number of higher-mass products were identified in most experiments.

The major products obtained from photolysis of 4-methoxyphenol (**7**) in the presence of NO_2^- or NO_3^- in ice were methoxynitrophenols (**8**) and 2-hydroxy-5,4′-dimethoxydiphenylether (**10**) (Table 4; Eq. (9)). A methoxy group “substitution” product, hydroquinone (**3**), was detected in traces only. This compound degraded apparently more efficiently (a lower irradiation time was needed for the 4-methoxyphenol degradation) compared to **1** or **6**. Coupling reactions accounted for the poor mass balance again.

4. Discussion

When aqueous solutions of inorganic or organic compounds are frozen, the solutes became spontaneously segregated at the grain boundaries of polycrystalline ice [33–36]. They are not incorporated into the solid ice crystals but they accumulate in a layer [20,37] surrounding the crystal walls, eventually solidify as temperature decreases. As a result, the solute concentrations dramatically increase. The local concentration values of the solutes were not directly available in this work, however, based on analogies with other frozen aqueous solutions [33,37], we can assume that they are more than six orders of magnitude higher at −15 °C compared to those of the initial liquid solutions. This relatively high temperature also guarantees partial diffusion of the molecules at the grain boundaries of ice [38].

4.1. Phenol

Direct photoexcitation of phenol in aqueous solutions to both the S_2 ($\lambda_{ex} = 193$ nm) and S_1 ($\lambda_{ex} = 266$ nm) absorption bands is known to lead to phenoxyl radical, hydrated electron, and hydrogen atom formation (Scheme 2, Eq. (10)) [39,40], the quantum

Table 2
Higher-mass photoproducts identified in the phenol photolysis in either degassed or oxygenated frozen aqueous solutions containing NO_2^-/NO_3^- at −15 °C

Conditions[a]	Photoproducts[b]
−15 °C; NO_2^-	A large number of nitro- and/or hydroxycompounds in the *m/z* range of 200–400
−15 °C; NO_3^-	Dihydroxybiphenyls (*m/z* = 186); hydroxydiphenylethers (*m/z* = 186); trihydroxybiphenyls (*m/z* = 202); dihydroxydiphenylethers (*m/z* = 202)

[a] [PhOH] = 10^{-3} mol L^{-1}; [$NaNO_2$] or [$NaNO_3$] = 10^{-1} mol L^{-1}; irradiation in quartz vessels for 4 h.

[b] A GC–MS analysis of the dichloromethane extracts.

Table 3
Anisole (**6**) photolysis in frozen aqueous solutions (−15 °C)[a]

Composition[b]	Filter	Conversion (%)	Chemical yields (%)		
			1	**7**	**8**
N_2	Quartz	n.d.	n.d.	n.d.	n.a.
O_2		<1	n.d.	n.d.	n.a.
N_2; NO_2^-		<2[c]	1.2	n.d.	n.d.
O_2; NO_2^-		<2[c]	0.9	n.d.	n.d.
N_2; NO_2^-; AcOH[d]		5[c]	0.6	n.d.	0.4
O_2; NO_2^-; AcOH		10[c]	0.5	n.d.	0.3
N_2; NO_3^-		n.d.	n.d.	n.d.	n.d.
O_2; NO_3^-		<1	Traces	Traces	n.d.
N_2; NO_3^-; AcOH		1[c]	n.d.	n.d.	n.d.
O_2; NO_3^-; AcOH		6[c]	0.3	Traces	Traces
O_2; H_2O_2		<2[c]	n.d.	0.1	n.d.
N_2 or O_2; NO_2^-	Pyrex	<1	n.d.	n.d.	n.d.
N_2 or O_2; NO_3^-		<1	n.d.	n.d.	Traces

[a] n.d. = not detected; n.a. = not applied.
[b] [PhOMe] or [AcOH] = 10^{-3} mol L^{-1}; [NaNO$_2$], [NaNO$_3$], or [H$_2$O$_2$] = 10^{-2} mol L^{-1}; irradiated in quartz and Pyrex vessels for 4 h.
[c] Production of higher-mass photoproducts was observed.
[d] Traces of **9** were detected.

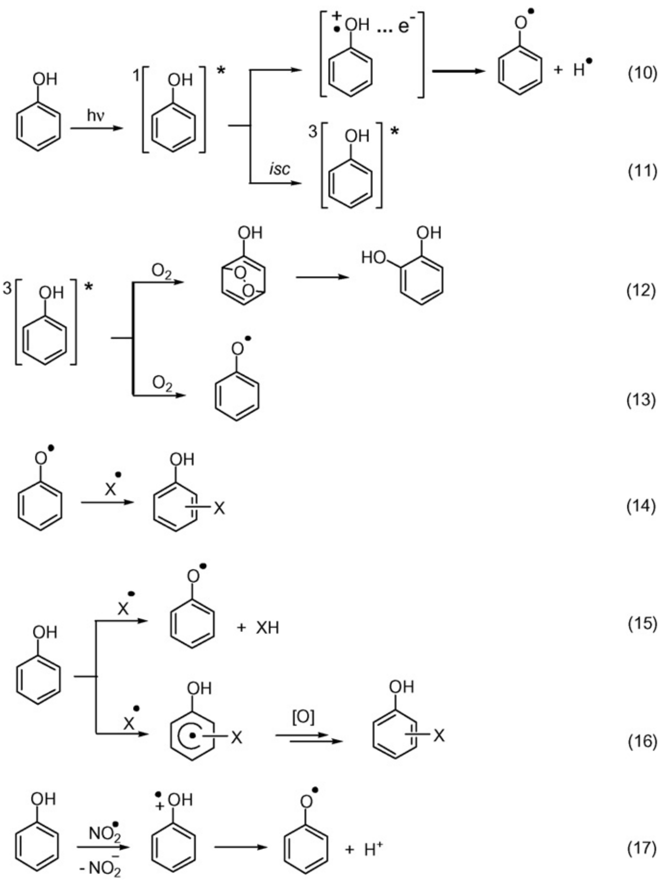
yield of which depends on solvent, pH, excitation wavelength, and temperature [41]. The excited singlet of phenol, furthermore, intersystem crosses to the triplet (k_{isc} ∼10^8 s^{-1}) [42] (Eq. (11)), and both states can understandably channel into various physical and chemical processes. Table 1 reveals that phenol (in the absence of nitrate or nitrite) in frozen solutions, irradiated at >250 nm, degraded only in the presence of oxygen to form catechol (**2**) and hydroquinone (**3**), possibly *via* an endoperoxide intermediate [43] (Eq. (12)). Oxygen can, however, also abstract hydrogen from the OH group of the triplet phenol [43] to form phenoxyl radical (Eq. (13)), which can undergo various reactions, such as coupling with oxygen or the second phenoxyl radical to form peroxy radicals or dihydroxybiphenyls (Eq. (14)), respectively. Indeed, most of the starting material was consumed by producing high-mass coupling products. Since the solutes could not escape from the sealed frozen samples by evaporation, oligomerization was evidently the major sink of the starting organic material.

Phenol, nitrate, and nitrite absorb the quartz-filtered radiation (Fig. 1). The addition of sodium nitrite or nitrate to the irradiated frozen samples triggered the expected nitration and hydroxylation reactions (Eq. (7) in Scheme 1), also known to occur in aqueous solutions [3,4,44,45], in both degassed and oxygenated samples (Table 1). The ground state phenol, as an

Table 4
4-Methoxyphenol (**7**) photolysis in frozen aqueous solutions at −15 °C[a]

Composition[b]	Conversion (%)	Chemical yields (%)		
		3	**8**	**10**
N_2	12[c]	n.d.	n.a.	0.6
O_2	8[c]	Traces	n.a.	0.1
N_2; NO_2^-	10[c]	n.d.	1.3	1.0
O_2; NO_2^-	13[c]	Traces	1.7	0.9
N_2; NO_3^-	4[c]	n.d.	1.8	0.5
O_2; NO_3^-	7[c]	n.d.	1.3	0.4

[a] n.d. = not detected; n.a. = not applied.
[b] [4-Methoxyphenol] = 10^{-3} mol L^{-1}; [NaNO$_2$] or [NaNO$_3$] = 10^{-2} mol L^{-1}; irradiation in quartz vessels for 1 h.
[c] Production of higher-mass photoproducts was observed.



Scheme 2. X$^\bullet$ = NO$^\bullet$; NO$_2^\bullet$; HO$^\bullet$; PhO$^\bullet$.

activated aromatic system, readily undergoes the hydrogen atom abstraction (Eq. (15)) or radical addition reactions (Eq. (16)) by species initially formed by photolysis of phenol itself (such as $PhO^•$) [43] or of nitrite or nitrate (such as $NO^•$, $NO_2^•$, $HO^•$) [44,46,47]. As a result, the hydroxylated and nitrated products in frozen solutions could be produced by the radical addition according to Eqs. (14) and (16). It is interesting that the product distribution was not very different when the phenol photolysis took place in the presence of either nitrite or nitrate; therefore, $HO^•$ and $NO_x^•$ had to be produced in sufficient quantities in both systems (Eqs. (1)–(5)). Since production of high mass hydroxylated and nitrated products in the presence of nitrite or nitrate was the major sink of phenol (Table 2), the phenoxyl radical or its derivatives were evidently formed.

The microscopic acidity of ice should be a key parameter for the evaluation of any chemical transformation in ice [48]. The nitrite ion and nitrous acid (HONO) represent a conjugate pair in acidic aqueous solutions [44,49], but above pH 5, the solutions contain mostly the former ion [50]. Nevertheless, pH of the unfrozen solution is known to decrease during the freezing aqueous salt solutions [36,51]. If pH containing NO_2^- drops below 5 by assistance of the electrostatic force generated by the freezing potential [52], HONO must become one of the absorbing species. Despite the fact that pH in the liquid samples prior to and after freezing as well as in unfrozen layers of partially frozen solutions was found to be unchanged, we cannot exclude the possibility that highly concentrated layers were more acidic than the corresponding bulk liquid solutions and that the photoreaction mechanisms are more complex.

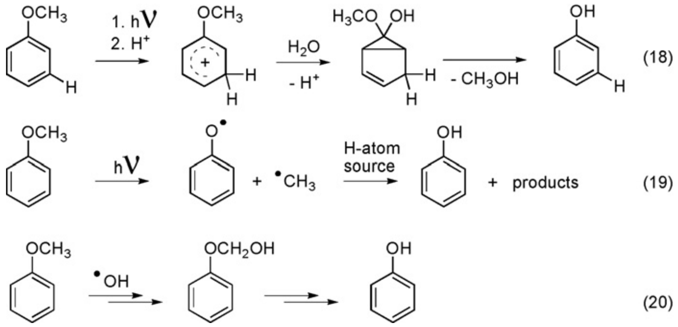
The partitioning between hydroxylation and nitration changed in oxygenated samples to some extent compared to degassed samples (Table 1). Oxygen was previously found to favor the formation of nitrophenols in liquid solutions containing phenol and nitrite ion [44], which is, however, not apparent from our results. We do not know the local oxygen concentration in the grain boundaries but it should not be very high because gases are efficiently removed by freezing the solutions. If we disregard any significant involvement of oxygen in the photonitration process (except oxidation of nitrosophenol or $NO^•$), radical substitution as well as the termination reactions (Eqs. (13)–(16)) must be generally responsible for the formation of **2**–**5**. The partitioning between those reactions will be strongly dependent on a steady-state concentration of the phenoxyl radicals; furthermore, the availability of an oxidation agent following the formation of a hydroxynitrocyclohexadienyl radical [53] prevents a reverse reaction. Photonitration of phenol was found to be strongly regioselective in frozen solutions; the $NO_x^•$ radicals preferentially added to the electron-rich *ortho* and *para* sites of phenol, as was also observed in liquid aqueous solutions [3,4], suggesting that the radical addition mechanism prevails (Eqs. (14) and (16)). In addition, a direct electron transfer between phenol and nitrogen dioxide, yielding phenol radical and nitrite, which is known to be thermodynamically favorable [54,55], could also participate. The phenol radical cation then readily loses the proton to form the phenoxyl radical (Eq. (17)). Hydrated electrons could subsequently be scavenged by nitrates, forming NO_3^{2-} radicals [42]. It is also understandable that the primary photoproducts **2**–**5** could undergo side-photoreactions. 4-Nitrophenol can, for example, photochemically produce hydroquinone or benzoquinone in ice as reported earlier [56]. Despite the fact that nitrosocompounds were not detected by our analytical methods, we cannot exclude that their subsequent oxidation [57] or other chemical alterations took place.

When the NO_3^- concentration was diminished from 10^{-1} to 10^{-2} mol L^{-1} (Table 1), the relative yields of dihydroxybenzenes decreased to some extent, which is in accord with the observation that phenol efficiently competes with nitrite (Eq. (6)) for reaction with $HO^•$ (Eq. (3)), lowering thus the yield of $NO_2^•$ [44]. For comparison, the change of the sodium nitrite or nitrate concentrations during the photolysis was followed in order to estimate the extent of the anion photodegradation (not shown). Quartz-filtered photolysis of pure nitrite or nitrate frozen solutions under the same experimental conditions shown in Table 1 revealed a very modest consumption (1–3%). The production of a small amount of nitrite from nitrate (and *vice versa*) was observed at the same time, which is in accord with the previous findings [17,19,20,22].

The irradiation of the samples by the Pyrex-filtered (>300 nm) light (phenol does not absorb; Fig. 1) offered an opportunity to study reactions triggered by a selective excitation of nitrite or nitrate. Interestingly, despite the fact that the total photon flux decreased due to a Pyrex filter, the relative consumption of the starting material was higher in the presence of both nitrite and nitrate than that observed in quartz vessels (notice the different irradiation times in Table 1). It is possible that the photolysis of phenol below 300 nm produces higher concentrations of quenchers, other than the parent molecules, and, at the same time, causes that the phenol concentration (availability) declines. Furthermore, since the same photoproducts were detected independently on the wavelength applied, we believe that the production of hydroxy- and nitrocompounds is due mostly to a direct photolysis of nitrite/nitrate even in the case that the sample is irradiated by quartz-filtered light.

4.2. *Anisole*

In order to find how important is the photonitration process *via* the $NO_2^•$ addition to the ground state aromatic compound having no free OH group, anisole (**6**) was photolyzed under the same reaction conditions as phenol. Practically no anisole consumption occurred in degassed or oxygenated samples in the absence of NO_2^-/NO_3^- and only traces of the products, 4-methoxyphenol and methoxynitrophenol, were found in the nitrite/nitrate presence (Table 3). The reactions afforded phenol as a major to exclusive photoproduct (Table 3; Eq. (8) in Scheme 1), which could be explained by the two known mechanisms (Scheme 3, Eqs. (18) and (19)). Excited methoxybenzenes in acidic aqueous solutions can be protonated on the ring and undergo the subsequent *ipso* substitution by a nucleophile (Eq. (18)) [58]. This reaction could be ruled out because water molecules are known to be largely excluded from nucleophilic reactions in ice below −10 °C [23]. However, the presence of acetic acid evidently enhanced the degradation



Scheme 3.

process, especially in oxygenated samples, which may partially but not fully advocate this mechanism. Methoxynitrophenol (**8**), observed in the presence of acetic acid, must be the product formed by nitration of the initially formed methoxyphenol (**7**). It implies that nitration of phenol is connected to the presence of the acidic hydroxy group. It is known that anisole is photolyzed into the corresponding methyl and phenoxyl radical [59] (Eq. (19)), which is a suitable intermediate for nitration or hydroxylation reactions (Eq. (14)). Since no nitrophenols or dihydroxybenzenes were identified, the steady-state concentration of phenoxyl radical was either very low or a hydrogen atom source was available by diffusion. The production of a relatively large amount of higher-mass products was observed again, suggesting that another anisole molecule or some of the organic radicals produced photochemically coupled with the phenoxyl radicals (Eq. (14)). A selective excitation of nitrate/nitrite (Pyrex filter) did not cause any degradation rate enhancement.

Oxidation of an alkoxy group by the hydroxyl radical (Eq. (20)) has been suggested to play a possible role in photodegradation of snow-phase lignin [31]. Photolysis of anisole in the presence of H_2O_2 did not, however, produce any significant amount of phenol (Table 3). A hydroxylated product, 4-methoxyphenol (**7**), was found only in traces, and we do not believe that this mechanism contributed significantly in our experiments.

4.3. *4-Methoxyphenol*

Photolysis of 4-methoxyphenol (**7**) was carried out to confirm our presumption according to which the acidic hydroxy group played an important role in the photonitration of phenol. While no primary nitrated products were found upon photolysis of anisole (**6**) in ice containing NO_2^- or NO_3^-, methoxynitrophenols (**8**) were the major products identified in both the degassed or oxygenated samples of **7**, in addition to 2-hydroxy-5,4′-dimethoxydiphenylether (**10**) (Table 4; Eq. (9) in Scheme 1). The latter compound was also found by irradiation of neat 4-methoxyphenol in the absence of NO_2^-/NO_3^- (see the Experimental section). The degradation efficiency of **7** was higher (Table 4) than those of phenol and anisole (Tables 1 and 3), partly because the starting material absorbs more significantly above 300 nm (Fig. 1). We hypothesize that the presence of the OH group can be important for two reasons: (i) excited phenol forms the phenoxyl radical, which readily couples with a species in the vicinity. The formation of dimeric products, also observed in photolysis of 2-methoxyphenol aqueous solutions [60], is satisfactory evidence of the phenoxyl radical intermediate formation; (ii) a weakly acidic hydroxy group on the aromatic ring or a presence of a weak acid can participate in primary nitrate or nitrite photochemistry, stimulating the production of $NO_x^•$ or $HO^•$ radicals (Eqs. (2) and (5)). However, recent results suggested that $NO_x^•$ [61,62] or $HO^•$ [20] production may increase under alkaline (or less acidic) conditions, thus the explanation (i) seems to be more reasonable. An alternative mechanism is offered in Eq. (18). While the phenoxyl radical production from phenol is uncomplicated (Eqs. (10), (13), (15) and (17)), anisole must be primarily converted to phenol, which was enhanced in the presence of an acid. In such a case, phenol is the starting material for subsequent reactions again. Finally, we cannot exclude that a possible increase in acidity can have an important effect on the HONO production from nitrite.

In conclusion, it was found that the photolysis of the frozen aqueous solutions of aromatic compounds in the presence of nitrate or nitrite produced essentially the same nitro- and hydroxyderivatives, which means that both anions were the source of $NO_x^•$ or $HO^•$ species. The phototransformations were found to occur primarily because of the NO_2^-/NO_3^- excitation and it was evident that hydrophobic organic compounds and hydrophilic (water-soluble) inorganic salts were located within the diffusion layer at the grain boundaries during the irradiation. The presence of the OH group on the aromatic system was found to be essential for efficient nitration and hydroxylation processes, possibly via the phenoxyl radical formation, but the exact mechanism remains unclear. In contrast to liquid aqueous solution photochemistry [3,44], the production of a large number of higher-mass products accompanied all photolyses in ice, because the local starting material concentrations increased in the grain boundaries during the freezing process.

4.4. *Environmental implications*

Hydroxybenzenes are known to be formed as intermediates in the photooxidation of aromatic compounds in nature. Trace levels of phenols, methoxyphenols, and nitrophenols have even been detected in snow samples from the polar regions or high mountains [31,63,64]. Various hypotheses suggest that t+he occurrence of these compounds in remote environments might reflect local atmospheric or snow (photo)chemistry. Recent reports indicate that nitrate, commonly found in the polar regions [7], is photochemically active in the snowpack [8–15] and it has been hypothesized about its account to post-depositional processes [65]. The flux of formaldehyde and acetaldehyde from sunlit snow containing a snow-phase organic matter was shown to be enhanced with the addition of nitrate, being a precursor to $HO^•$ [31]. Many field studies at different locations in polar and mid-latitude regions have established that nitrates [8,9,14] are sources of the hydroxyl or hydroperoxyl radicals emission to the atmosphere. However, it was demonstrated that the majority of $HO^•$ produced on polar snow originates from peroxide photolysis, while nitrate photolysis is only a minor contributor as a result of their different molar absorptivities and local concentrations [20,21].

Our experiments showed that photoinduced hydroxylation of aromatic compounds is one of the possible processes in ice in the presence of nitrite or nitrate; however, nitration can also be an alternative sink for the organic ice impurities. Choosing very simple organic molecules did not ease our experimental work and only higher, environmentally not very relevant, starting concentrations allowed us to identify the primary photoproducts. Larger reaction conversions produced a very complex mixture of compounds and we believe that exhaustive irradiation would eventually lead to the production of simple, perhaps gaseous compounds and, at the same time, of persistent organic oligomers/polymers, depending on the local concentration of the reactive species. In case that the starting concentrations of impurities in snow are very low (natural), the latter processes must, however, be largely diminished. Relatively higher NO_2^-/NO_3^- concentration in the snowpack could also filter off the incident solar radiation [66], preventing thus other photochemical processes within the photic layer [67,68].

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