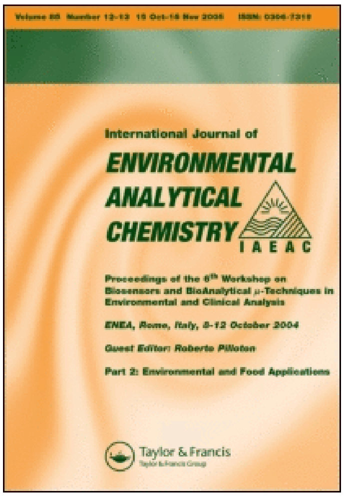

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PHENOL PHOTONITRATION AND PHOTONITROSATION UPON NITRITE PHOTOLYSIS IN BASIC SOLUTION

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Nitrophenols have been detected in some Antarctic lakes, the water of which is basic and rich in nitrate, nitrite and other nutrients. Nitrate or nitrite photolysis could be a possible reaction to explain the presence of these compounds. This work presents evidence for the formation of 2-nitrophenol (2NP), 4-nitrophenol (4NP) and 4-nitrosophenol (4NOP) upon UV irradiation of phenol and nitrite in aerated basic solutions.

The pH dependence of the 2NP initial formation rate is different from those of 4NP and 4NOP. The dependence of the first mainly reflects the phenol/phenolate equilibrium, with phenol yielding 2NP at a higher rate than phenolate. In the case of 4NOP, the initial formation rate *vs* pH has a maximum at pH 9.5. The pH dependence of 4NOP formation rate suggests that three pathways are likely to operate: nitrosation of undissociated phenol by N_2O_3, prevailing at pH < 8.7, nitrosation of phenolate by N_2O_3, prevailing in the pH interval 8.7–10.8, and reaction between phenoxyl radical and $^\bullet NO$, prevailing at pH > 10.8. Phenol nitrosation by N_2O_3 is favoured when phenol is negatively charged (phenolate), but it is also disfavoured at alkaline pH values, owing to the depletion of N_2O_3 (the nitrosating agent) by basic hydrolysis. Differently from 2NP, the initial formation rate *vs* pH of 4NP is very similar to that of 4NOP, suggesting that 4NP may originate from the oxidation of 4NOP. Moreover, while in neutral and acidic solutions the formation rate of 2NP is slightly higher than that of 4NP, in the pH interval 8–12 the formation of 4NP is much more rapid than that of 2NP. This indicates that the pH of natural waters influences the ratio of nitroisomers.

Keywords: Nitrophenol; Nitrite photolysis; Photonitration; Photonitrosation

INTRODUCTION

The formation of nitrophenols from phenol can take place following the UV photolysis of nitrate [1–4] and nitrite [5]. Both nitrate [6] and nitrite [7] yield $^\bullet NO_2$ and N_2O_4 on UV irradiation and subsequent photolysis. Nitrite photolysis also yields N_2O_3 [7–9]:

$$NO_3^- \xrightarrow{h\nu} {}^\bullet NO_2 + {}^\bullet OH \qquad [\Phi_1 = 0.010]\,[6] \tag{1}$$

$$2^\bullet NO_2 \rightleftharpoons N_2O_4 \qquad [K_{eq,2} = 1.53 \times 10^{-5}\,M]\,[8] \tag{2}$$

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$$NO_2^- \xrightarrow{h\nu} {}^{\bullet}NO + {}^{\bullet}OH \qquad [\Phi_{3,360\,nm} \approx 0.025]\,[7] \tag{3}$$

$$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^- \qquad [k_4 = 1 \times 10^{10}\,M^{-1}]\,[7] \tag{4}$$

$${}^{\bullet}NO + {}^{\bullet}NO_2 \rightarrow N_2O_3 \qquad [k_5 = 1.6 \times 10^{8}\,M^{-1}]\,[7] \tag{5}$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2 \qquad [k_6 = 2 \times 10^{3}\,s^{-1}]\,[9] \tag{6}$$

The reaction between phenol and ${}^{\bullet}NO_2$ (or N_2O_4) is one of the pathways in phenol photonitration. Another pathway involves phenol nitrosation by N_2O_3, followed by nitrosophenol oxidation to nitrophenol [5]. The ${}^{\bullet}NO_2/N_2O_4$ pathway is relevant in the presence of both nitrate and nitrite, while the N_2O_3 pathway is only relevant in the case of NO_2^-. The first pathway predominates at neutral pH.

In acidic nitrite solutions phenol nitration mainly occurs via a dark process involving nitrous acid [10]. This process can also take place in acidic nitrate solutions under illumination [11], since nitrate UV photolysis yields nitrite [6]:

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O \qquad [\Phi_7 = 0.001] \tag{7}$$

Phenol is a weak acid with $pK_a = 9.7$ at ionic strength 0.1 [12]. The reactivity of phenolate (PhO^-) is different from that of phenol. For instance, phenolate is more activated than phenol to one-electron transfer reactions (including reaction with ${}^{\bullet}NO_2$) [13] and to electrophilic processes [14].

$$PhO^- + {}^{\bullet}NO_2 \rightarrow PhO^{\bullet} + NO_2^- \qquad [k_8 = 8.6 \times 10^{6}\,M^{-1}] \tag{8}$$

$PhO^{\bullet}$ is the phenoxyl radical. The reaction between ${}^{\bullet}NO_2$ and undissociated phenol is much slower than reaction (8) [13].

The purpose of this work is to assess phenol photonitration and photonitrosation following nitrite photolysis in basic solutions. To compare the reactivity of undissociated phenol and that of phenolate, the solution pH has been varied in a wide range around phenol pK_a.

The conditions explored in this work are relevant to some ecosystems, in particular at the lower end of the considered pH range. Nitrophenols have been detected in Antarctic lakes, the water of which is basic and contaminated by seabird droppings. Nitrate or nitrite photolysis is one of the hypotheses advanced to explain the presence of these compounds in water and sediments [15].

EXPERIMENTAL

Reagents and Materials

Phenol (purity grade > 99%), 2-nitrophenol (98%), 4-nitrophenol (> 99%), and 4-nitrosophenol (60%) were purchased from Aldrich, NaOH (> 99%), $NaH_2PO_4 \cdot H_2O$ (> 99%), NaCl (> 99.5%), CH_2Cl_2 (SupraSolv for organic trace analysis) and acetonitrile (LiChrosolv gradient grade) from Merck, $NaNO_2$ (> 97%) from Carlo Erba, Na_2SO_4 (Pestinorm, > 99.5%) from Prolabo.

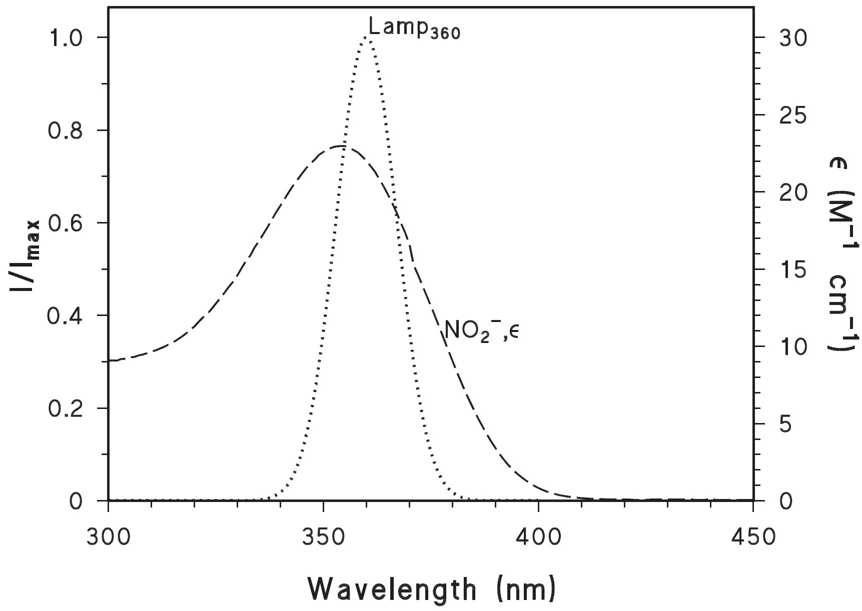

FIGURE 1 Lamp irradiance spectrum and nitrite absorption spectrum.

Procedures

The pH of the solutions was measured with a combined pH electrode and a Metrohm 713 pH meter. Irradiation was carried out in Pyrex glass cells (solution volume 5 mL) under an array of three 40 Watt Philips TL K05 lamps, emitting a photon flux of 3.6×10^{-7} Ein s^{-1} in the cells, actinometrically determined [16]. The lamp irradiance spectrum, together with the nitrite absorption spectrum, is reported in Fig. 1.

Solutions were analysed by HPLC using isocratic elution of the samples with a 30/70 mixture of acetonitrile/aqueous NaH_2PO_4 (50 mM, pH 4.5). The retention times were: phenol 3.65 min, 2-nitrophenol (2NP) 9.10 min, 4-nitrophenol (4NP) 5.30 min, 4-nitrosophenol (4NOP) 2.05 min. The column dead time was 0.90 min and the detection wavelengths 210 nm (phenol and 2NP) and 315 nm (4NP and 4NOP).

In the case of GC-MS analyses, the NaCl was added to the aqueous samples followed by extraction with CH_2Cl_2. After separation, the CH_2Cl_2 extract was dried over anhydrous Na_2SO_4 and concentrated under a gentle stream of high-purity nitrogen. The extracts were analysed by GC (Hewlett Packard 6890 equipped with a mass selective detector model HP 5973) using a phenyl-methylsilicone capillary column (HP 5MS, 30-m length, 0.25-mm i.d., 0.25-μm film thickness). The conditions employed were: carrier flow 1 mL/min (He), injector temperature 300°C, oven temperature 70°C (3 min), then to 300°C at 10°C/min, manual splitless injection (1 μL).

RESULTS AND DISCUSSION

Several experiments were performed at different pH values. An example of the time evolution of phenol, 2NP, 4NP, and 4NOP upon irradiation of nitrite in aerated solution is reported in Fig. 2 (pH 9.1).

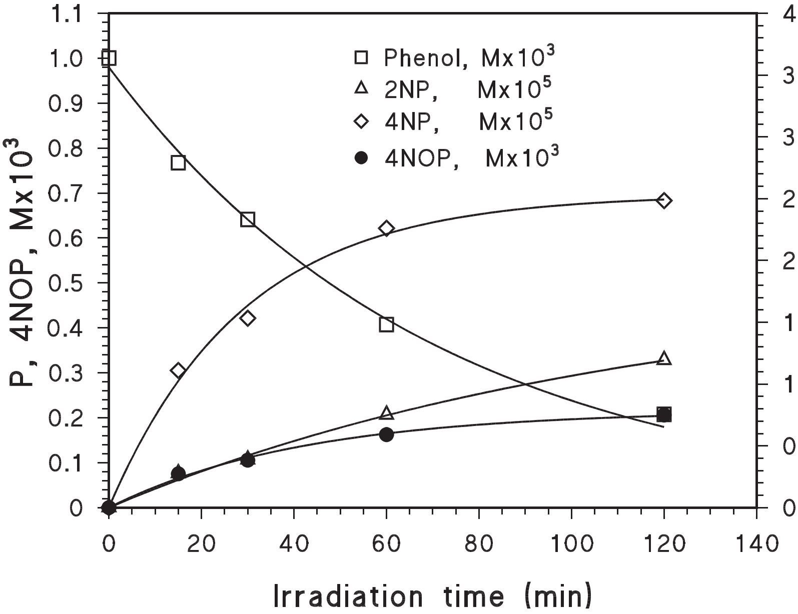

FIGURE 2 Time evolution of phenol, 2NP, 4NP and 4NOP upon 360 nm irradiation of $NaNO_2$ (0.10 M) and phenol (1.1×10^{-3} M), pH 9.1, aerated solution.

Figure 3 reports the initial formation rate of 2NP, calculated as the slope of concentration *vs* time curves for $t \rightarrow 0$. The corresponding pH trends for 4NP and 4NOP are reported in Figs. 4 and 5, respectively.

The pH trend of the initial formation rate of 2NP, 4NP, and 4NOP indicates that an acid–base equilibrium is most likely involved in the mechanism. The $pH_{1/2}$ of the curve of Fig. 3 is compatible with the pK_a of phenol (the $pH_{1/2}$ is the pH value corresponding to the curve flexus). The curve also shows that a higher formation rate of 2NP occurs in the presence of phenol than of phenolate. The formation rate of 2NP is about constant as a function of pH for $pH > 11$, which can be ascribed to the constant concentration with pH of phenolate (PhO^-). On the contrary, phenol concentration decreases with increasing pH ($[PhOH] \propto [H^+]/K_a$).

The 2NP initial formation rate in the presence of undissociated phenol is due to the $^\bullet NO_2/N_2O_4$ pathway [5]. A similar mechanism as that proposed for phenol can be hypothesised for phenolate, too. Under this hypothesis, $^\bullet NO_2$ (or N_2O_4) would react with phenolate via addition to the aromatic ring [reaction (9)], followed by hydrogen atom abstraction by oxygen to yield 2NP [or 4NP, reaction (10)]:

$$PhO^- + {}^\bullet NO_2 \rightarrow O_2N\text{–}PhO^{-\bullet} \tag{9}$$

$$O_2N\text{–}PhO^{-\bullet} + O_2 \rightarrow (2NP \text{ or } 4NP) + O_2^{-\bullet} + H^+ \tag{10}$$

Both 2NP and 4NP are dissociated to the corresponding nitrophenolates at $pH > 7$ [12]. Nitration via reactions (9) and (10) would be favoured in the presence of dissolved oxygen. Figure 6 shows the time evolution of 2NP at pH 12.2, in aerated solution and in the absence of dissolved oxygen (cells purged for 20 min with high-purity nitro-

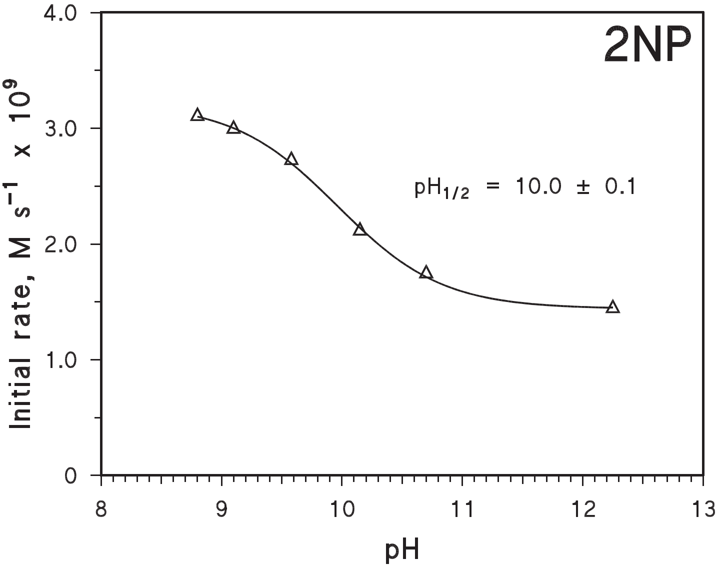

FIGURE 3 Initial formation rate of 2NP as a function of pH upon 360 nm irradiation of $NaNO_2$ (0.10 M) and phenol (1.1×10^{-3} M), aerated solution.

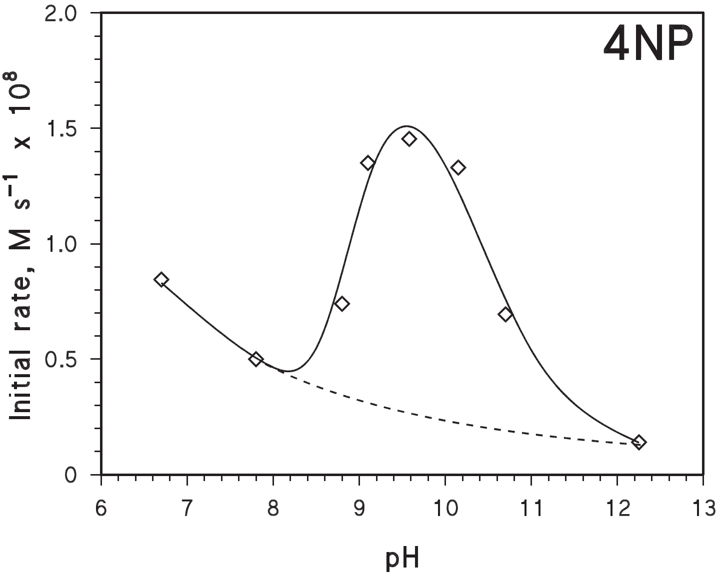

FIGURE 4 Initial formation rate of 4NP as a function of pH upon 360 nm irradiation of $NaNO_2$ (0.10 M) and phenol (1.1×10^{-3} M), aerated solution.

gen). Oxygen enhances the formation of 2NP, consistent with reactions (9) and (10). In the absence of oxygen the initial formation rate of 2NP is about one tenth of the rate in aerated solution. The production of 2NP in deoxygenated solution might be due either to the abstraction of hydrogen by $^{\bullet}OH$, $^{\bullet}NO_2$ and $PhO^{\bullet}$, performing like oxygen in reaction (10), or to a nitration pathway involving the phenoxyl radical.

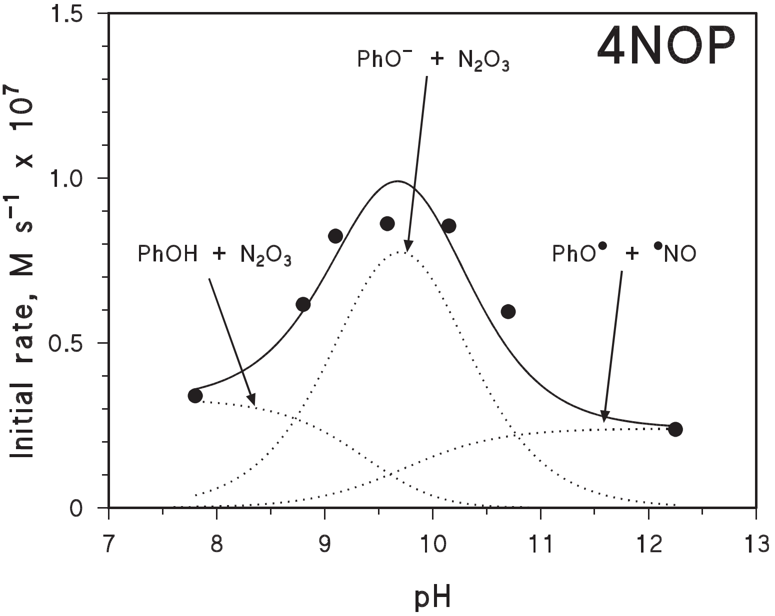

FIGURE 5 Initial formation rate of 4NOP as a function of pH upon 360 nm irradiation of $NaNO_2$ (0.10 M) and phenol (1.1×10^{-3} M), aerated solution. Fitting according to Eq. (20) (solid curve) is superimposed on the data. The dotted curves represent the contributions to 4NOP by $PhOH + N_2O_3$, $PhO^- + N_2O_3$, and $PhO^\bullet + {}^\bullet NO$, respectively.

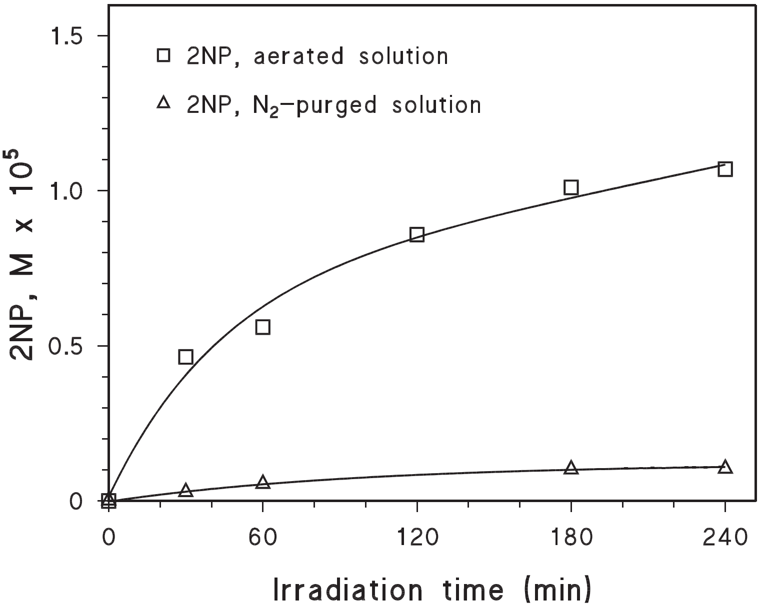

FIGURE 6 Time evolution of 2NP in aerated solution and in the absence of oxygen. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH 12.2, irradiation at 360 nm.

Phenoxyl could be formed by a fast reaction of phenolate with $^{\bullet}NO_2$ [reaction (8)], and then react with $^{\bullet}NO_2$ to yield 2NP and 4NP [reaction (11)] [17]:

$$PhO^{\bullet} + {}^{\bullet}NO_2 \rightarrow 2NP \text{ or } 4NP \tag{11}$$

Other possible sources of phenoxyl are the reactions of phenol and phenolate with $^{\bullet}OH$, with almost the same reaction constant [18] independent of pH:

$$PhOH + {}^{\bullet}OH \rightarrow PhO^{\bullet} + H_2O \tag{12}$$

$$PhO^{-} + {}^{\bullet}OH \rightarrow PhO^{\bullet} + OH^{-} \tag{13}$$

The importance of reactions (12) and (13) is limited by the low steady-state concentration reached by $^{\bullet}OH$ in the presence of 0.10 M NO_2^- (around 10^{-15} M) [5] and by the fact that $^{\bullet}OH$ reacts with aromatic substrates mainly via addition to the ring [19].

The initial formation rate of 4NP as a function of pH is shown in Fig. 4. It is different from that of 2NP (Fig. 3). This is worthy of note since 2NP and 4NP have always shown parallel behaviour in neutral and acidic solutions, in the presence of both nitrate and nitrite under UV irradiation [4,5,10,11]. Furthermore, under the conditions studied previously, the initial formation rate of 2NP has always been a little higher than that of 4NP. On the contrary, the comparison between Figs. 3 and 4 indicates that the initial formation rate of 4NP around pH 10 is almost an order of magnitude higher than that of 2NP. However, the dotted line superimposed in Fig. 4 indicates that a background process of formation of 4NP is still operating, yielding 4NP at a rate comparable with that of 2NP (see Fig. 3). Such a background process is most likely due to the $^{\bullet}NO_2/N_2O_4$ pathway [reactions (9) and (10)], yielding both 2NP and 4NP.

The pH dependence of the 4NP formation rate differs from that of 2NP in the interval $8 < pH < 12$, where the initial formation rate of 4NP has a peak. The peak of 4NP is very similar to that of 4NOP (Fig. 5). A possible explanation is that 4NP in the pH interval 8–12 mainly originates from the oxidation of 4NOP. In previous work we have demonstrated that the oxidation of 4NOP to 4NP can actually take place in the presence of irradiated nitrite and dissolved oxygen [5].

The conceivable oxidation of 2NOP is unlikely to play a relevant role in the formation of 2NP. 2NOP was not detected in GC-MS runs. As far as HPLC measures are concerned, no commercial standard is available. However, 2NOP can be expected to elute later than 4NOP, similar to the way in which 2NP elutes later than 4NP. No peak of relevant intensity that can be attributed to 2NOP could be observed in the time interval 2.10–4.00 min, either at 210 or at 315 nm.

As 4NP in basic solution would derive from 4NOP oxidation, the formation of the latter would be the key factor explaining the pH trend for both. Phenol nitrosation in the dark, in the presence of $^{\bullet}NO + {}^{\bullet}NO_2$, has been described as favoured in basic solution. The reactive species was proposed to be N_2O_3, involved in an electrophilic mechanism (A-S_E2) [8]. Electrophilic attack by N_2O_3 on the organic substrate is favoured if the latter carries a negative charge, as in the case of phenolate. Thus, nitrosation of phenolate by N_2O_3 is expected to occur at a higher rate than the corresponding nitrosation of undissociated phenol ($k_{15} \gg k_{14}$).

$$\mathrm{PhOH} + \mathrm{N_2O_3} \xrightarrow{k_{14}} \mathrm{4NOP} + \mathrm{NO_2^-} + \mathrm{H^+} \tag{14}$$

$$\mathrm{PhO^-} + \mathrm{N_2O_3} \xrightarrow{k_{15}} \mathrm{4NOP} + \mathrm{NO_2^-} \tag{15}$$

The formation of 4NOP can also take place upon the reaction between $\mathrm{PhO^{\bullet}}$ and $\mathrm{^{\bullet}NO}$ [reaction (16)]. Reaction (16) is analogous to reaction (11) and has been described as occurring at a relevant rate in the gas phase [20]:

$$\mathrm{PhO^{\bullet}} + \mathrm{^{\bullet}NO} \xrightarrow{k_{16}} \mathrm{4NOP} \tag{16}$$

Thus, the initial formation rate of 4NOP as a function of the pH (> 7) can be expressed as:

$$\frac{d[\mathrm{4NOP}]}{dt} = k_{14}\,[\mathrm{PhOH}]\,[\mathrm{N_2O_3}] + k_{15}[\mathrm{PhO^-}]\,[\mathrm{N_2O_3}] + k_{16}[\mathrm{PhO^{\bullet}}]\,[\mathrm{^{\bullet}NO}].$$

Since $\mathrm{PhO^{\bullet}}$ mainly originates from phenolate [reaction (8)] and $[\mathrm{^{\bullet}NO}]$ can be considered constant (under stationary conditions), $k_{16}\,[\mathrm{PhO^{\bullet}}]\,[\mathrm{^{\bullet}NO}] \propto [\mathrm{PhO^-}]$. As a consequence, the following relationship can be derived:

$$k_{16}[\mathrm{PhO^{\bullet}}][\mathrm{^{\bullet}NO}] = k' C_{\mathrm{Ph}} \frac{K_a}{[\mathrm{H^+}] + K_a}, \tag{17}$$

where C_{Ph} is the total phenol concentration ($[\mathrm{PhOH}] + [\mathrm{PhO^-}]$, 1.1×10^{-3} M in this study), and K_a the acid dissociation constant of phenol.

The nitrosating agent $\mathrm{N_2O_3}$ is not stable in aqueous solution, as it reacts with $\mathrm{H_2O}$ [reaction (6)], but also with $\mathrm{OH^-}$ [reaction (18)] [9]. Reaction (18) predominates over reaction (6) at pH > 10:

$$\mathrm{N_2O_3} + \mathrm{OH^-} \rightarrow \mathrm{2NO_2^-} + \mathrm{H^+} \quad [k_{18} = 2.5 \times 10^7\ \mathrm{M^{-1}}] \tag{18}$$

Based on reactions (6) and (18), the following relationship holds for $\mathrm{N_2O_3}$:

$$[\mathrm{N_2O_3}] = \frac{k''}{k_6 + k_{18}[\mathrm{OH^-}]} = \frac{k''[\mathrm{H^+}]}{\left(k_6[\mathrm{H^+}] + k_{18}K_{\mathrm{W}}\right)}, \tag{19}$$

where K_{W} is the ionic product of water (at ionic strength 0.1).

From Eqs. (17) and (19) and the acid–base equilibrium $\mathrm{PhOH/PhO^-}$, the initial formation rate of 4NOP can be expressed as follows:

$$\frac{d[\mathrm{4NOP}]}{dt} = C_{\mathrm{Ph}} \left\{ \frac{k''[\mathrm{H^+}]}{\left(k_6[\mathrm{H^+}] + k_{18}K_{\mathrm{W}}\right) \cdot \left(K_a + [\mathrm{H^+}]\right)} \left(k_{14}[\mathrm{H^+}] + k_{15}K_a\right) + \frac{k'K_a}{K_a + [\mathrm{H^+}]} \right\}, \tag{20}$$

where k', $k''k_{14}$ and $k''k_{15}$ are the fitting parameters. The values of parameters are: $k' = 2.6 \times 10^{-5}\ \mathrm{s^{-1}}$, $k''k_{14} = 6.2 \times 10^{-2}\ \mathrm{s^{-2}}$, $k''k_{15} = 6.0 \times 10^{-1}\ \mathrm{s^{-2}}$. The fitting gives

$k_{15} \approx 10\,k_{14}$, consistently with the hypothesis $k_{15} \gg k_{14}$. The curve fitting according to Eq. (20) is superimposed on the experimental data in Fig. 5, with excellent agreement.

Examination of Eq. (20) reveals that three domains are possible: (i) if the last RHS term is negligible with respect to the first, and $k_{14}[H^+] \gg k_{15}K_a$, reaction (14) prevails; (ii) if the last RHS term is negligible with respect to the first, and $k_{15}K_a \gg k_{14}[H^+]$, reaction (15) prevails; (iii) if the first RHS term is negligible with respect to the last, reaction (16) prevails. Figure 5 reports the contributions to 4NOP from $PhOH + N_2O_3$ [reaction (14)], $PhO^- + N_2O_3$ [reaction (15)] and $PhO^\bullet + {}^\bullet NO$ [reaction (16)]. Reaction (14) ($PhOH + N_2O_3$) prevails at $pH < 8.7$, reaction (15) ($PhO^- + N_2O_3$) at $8.7 < pH < 10.8$, and reaction (16) ($PhO^\bullet + {}^\bullet NO$) at $pH > 10.8$. The maximum in the 4NOP initial formation rate is due to the contribution of reaction (15), and in particular to the opposite effects of increasing phenolate concentration and decreasing N_2O_3 concentration with increasing pH.

The formation of 4NOP via reaction (16) is likely to be a major sink of phenoxyl radical, so that only a small fraction of this radical is available for the nitration pathway [reaction (11)] at pH 12.2. We thus propose that reaction (16) is a significant nitrosation pathway for aqueous solutions of phenol, which substitutes for the well-established pathway based on N_2O_3 under conditions where N_2O_3 is depleted by basic hydrolysis.

ENVIRONMENTAL IMPLICATIONS

Nitrophenols have been detected in the water of some Antarctic lakes (Carezza Lake, Edmonson Point and Tarn Flat) during the Italian Expeditions in the Antarctic in the years 1994–1999. Lake sediments and snow samples (collected in locations near the lakes) were also analysed for nitrophenol content [15]. The field data are reported in Ref. [15], Table V. The concentrations of 2NP and 4NP are often comparable in lake water, while 4NP prevails in sediments and in snow. The nitrophenol content of the snow gives information on the possibility of nitrophenol formation in the atmosphere, followed by deposition in the lakes. The concentration of 4NP in snow is lower than in lake water, and 2NP is below the detection limit. As the nitrophenol concentration in lake water is almost constant in the time period considered, an accumulation process is ruled out. As a consequence, atmospheric deposition can be expected to make a secondary contribution to the concentration of nitrophenols in lake water.

The presence of 4NP alone in snow is, however, interesting in itself. In fact, phenol nitration in the gas phase in the presence of ${}^\bullet OH + {}^\bullet NO_2$ or ${}^\bullet NO_3 + {}^\bullet NO_2$ only yields 2NP [22]. The two isomers 2NP and 4NP have been separately detected in rainwater in urban areas, their separate presence suggesting the existence of two different formation pathways [23,24]. Phenol nitration in solution always yields 2NP and 4NP in similar amounts, usually with a slight excess of 2NP [1–5,10,11,21,25,26]. The photolysis of nitrite at pH $\approx$ 10, which yields 4NP at a higher rate than 2NP as shown in this article, is very unlikely to be operational at the pH of atmospheric hydrometeors. However, the concentration of 2NP observed in rainwater samples may be lower than that of 4NP even in the presence of similar formation rates, owing to the higher vapour pressure of 2NP [25]. As a consequence, the prevalence of 2NP in precipitation would indicate that a gas-phase nitration is operating, while the prevalence of 4NP is compatible with a liquid-phase nitration. In the case of the Antarctic snow, the prevalence of 4NP might indicate either transport from the continents or the presence

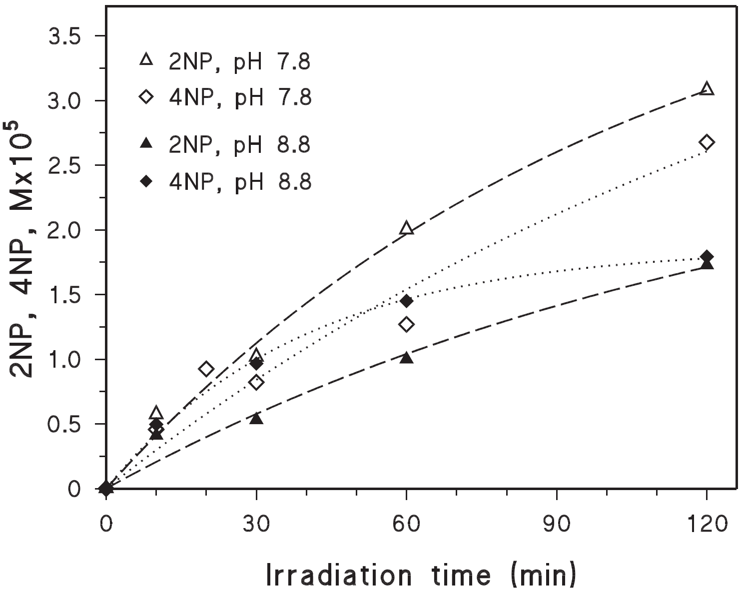

FIGURE 7 Time evolution of 2NP and 4NP in aerated solution at pH 7.8 and 8.8. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, irradiation at 360 nm.

of a condensed-phase nitration mechanism operating in the Antarctic troposphere, as already hypothesised for the nitro-polyaromatic hydrocarbons detected on Antarctic particulate [27].

In the case of lake water, both 2NP and 4NP have been detected. Their concentrations are often comparable and, as atmospheric deposition can account only for a minor fraction of water-dissolved nitrophenols, an *in situ* formation pathway is very likely to be operating. Nitrite photolysis is a possible candidate, in particular at the pH values of the water of the studied lakes (around 8), where negligible phenol photonitration occurs on nitrate photolysis [4]. The relative concentrations of 2NP and 4NP can partially depend on the partitioning equilibrium between water and sediments. The interpretation of such an equilibrium is, however, not straightforward, since the more hydrophobic 2NP should be preferentially partitioned on the sediments, although its concentration could be lowered by its higher volatility. A possible explanation for the difference in the concentration ratios of 2NP and 4NP is fluctuation in the pH values. In fact, the formation rate of 2NP is higher than that of 4NP at $pH < 8$, while the formation rate of 4NP is higher at $pH > 8$, owing to the contribution by the oxidation of 4NOP (see Fig. 7).

CONCLUSIONS

The formation of 2NP, 4NP and 4NOP from phenol in basic nitrite solutions under UV irradiation has some peculiar features. The most interesting one is the difference in the initial formation rates of 2NP and 4NP in the pH interval 8–12, while the two compounds show very similar behaviour in neutral and acidic solutions of nitrite and nitrate [4,5,10,11].

The 2NP initial formation rate indicates that the nitration of phenol is more efficient than the nitration of phenolate under the studied conditions. Nitration of undissociated phenol occurs via reaction with $^{\bullet}NO_2/N_2O_4$ [5]. The effect of oxygen at pH 12.2 suggests that a similar pathway may also occur in the presence of phenolate [reactions (9) and (10)]. The phenoxyl pathway to nitrophenol formation [reactions (8) and (11)] occurs at a lower rate than reactions (9) and (10), possibly because of phenoxyl consumption in reaction (16).

The 4NP initial formation rate has a different pH dependence from that of 2NP, with a maximum around pH 9.5. Moreover, the initial formation rate of 4NP is considerably higher than that of 2NP at $8 < pH < 12$. However, Fig. 4 shows that a minor pathway of 4NP formation is operating even at $8 < pH < 12$, yielding 4NP in a comparable amount to 2NP. This suggests that the formation of 2NP and 4NP partially follow a common pathway, but that another pathway is operating in the case of 4NP, prevailing in the pH interval 8–12. The maximum in the pH trend of 4NP is very similar to that observed for 4NOP, suggesting that 4NP in basic nitrite solution may originate from the oxidation of 4NOP. This result confirms the possibility of the oxidation of 4NOP to 4NP upon nitrite photolysis in aerated solution, as already hypothesised in a previous work [5,21].

The formation of 4NOP from phenol is likely to follow three pathways: reaction between undissociated phenol and N_2O_3, prevailing at $pH < 8.7$; reaction between phenolate and N_2O_3, prevailing at $8.7 < pH < 10.8$; and reaction between phenoxyl and $^{\bullet}NO$, prevailing at $pH > 10.8$. The basic hydrolysis of N_2O_3 limits the role of the otherwise very fast reaction (15), and accounts for the maximum around pH 9.5 of the 4NOP initial formation rate. This mechanism opens new perspectives for the understanding of environmental nitration processes.

Acknowledgements

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