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Phenol photonitration upon UV irradiation of nitrite in aqueous solution I: Effects of oxygen and 2-propanol

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Abstract

Nitrophenols are formed in aqueous solution upon UV irradiation of phenol and nitrite. The formation of nitrophenols is enhanced by dissolved oxygen and inhibited by the addition of 2-propanol. The mechanism of phenol photonitration involves both $\cdot NO_2$ (or N_2O_4), reacting with phenol, and 4-nitrosophenol, which is oxidised to 4-nitrophenol. A reaction scheme is proposed based on experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nitrite; Photochemical transformations; Photolysis; Nitroaromatic compounds

1. Introduction

Among nitrogen inorganic species, nitrite is less common than nitrate in the environmental compartments, as it is relatively unstable and can be involved in many chemical and biological processes. The most important one is the oxidation to nitrate, nitrite being an intermediate in the oxidation of nitrogen-containing organic matter. As a consequence, the presence of nitrite in water usually indicates recent microbial contamination. However, its higher reactivity and impact on human health balance its lower concentration. Both nitrate and nitrite are involved in human methaemoglobinaemia (oxidation of haemoglobin to methaemoglobin, which is unable to transport oxygen to the tissues), but the toxicity of nitrate is thought to be solely the consequence of its reduction to nitrite. The relative potency of nitrite and nitrate with respect to their health impact was assumed to be 10:1 on a molar basis. On this ground the concentration level prescribed by the WHO guidelines for drinking-water quality is lower for nitrite than for nitrate (Guidelines, 1996).

Nitrite can absorb in the UV region of solar radiation to a greater extent than nitrate and the resulting photodissociation leads to the formation of reactive species ($\cdot OH, \cdot O_2^-$, aquated $e^-, \cdot NO_2, \cdot NO$; Fischer and Warneck, 1996), which can then promote transformation of water-dissolved organic molecules. As a consequence, nitrite can act as an environmental factor as nitrate does (Hoigné, 1990), the lower concentration of the former in environmental compartments being partially counterbalanced by its higher reactivity.

Nitrite and nitrous acid are also an important source of radicals in the atmosphere. The radical $\cdot OH$ photoformation, resulting from UV irradiation of N(III), has been recently studied and its environmental significance assessed (Arakaki et al., 1999). N(III) plays a relevant role as an environmental factor in atmospheric acidic water droplets.

Nitrite is also a nitrating agent that can be used in the synthesis of nitroderivatives of aromatic compounds (Uemura et al., 1978). The process used for synthetic purposes is an electrophilic aromatic substitution involving NO_2^+, which takes place at strongly acidic pH, the nitrating reagent being for instance a trifluoroacetic

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acid solution of $NaNO_2$. Moreover, referring to nitrite photodissociation, one of its products is $^{\cdot}NO_2$, which is involved in the nitration of aromatic molecules, though the details of the mechanism of these reactions are often unclear (Boule et al., 1999). As an example, the relative role of $^{\cdot}OH$ and $^{\cdot}NO_2$ in phenol photonitration is controversial and has been the object of recent debate (Louw and Santoro, 1999; Dzengel et al., 1999a; Dzengel et al., 1999b). Phenol nitration upon nitrite irradiation was excluded by Machado and Boule (1995).

Such considerations account for the importance to assess the nitration of aromatic molecules in general and of phenol in particular, in the presence of nitrite under different conditions, such as UV irradiation in aqueous solution and in semiconductor suspension (Vione, 1998). Semiconductor oxides themselves are important environmental factors (Hoigné, 1990).

2. Experimental

2.1. Reagents and materials

$NaNO_2$ (purity grade > 97%) was purchased from Carlo Erba. Nitrite concentration in the cells was 0.10 M, achieved by addition of $NaNO_2$. Phenol concentration was 1.1×10^{-3} M.

2.2. Irradiation experiments

The UV source (irradiance maximum at 360 nm, total photon flux in the cells 3.6×10^{-7} Ein/s) has already been described (Vione et al., 2001a). The lamp irradiance spectrum together with the absorption spectra of nitrite and phenol are reproduced in Fig. 1.

Experimental details not included here are reported elsewhere (Vione et al., 2001a).

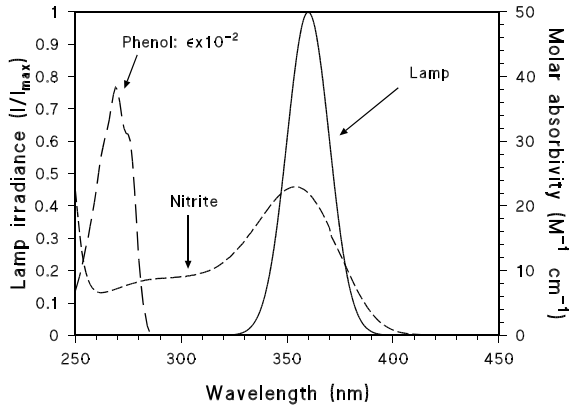


Fig. 1. Irradiance spectrum of the Philips TL K 05 lamp (irradiance maximum at 360 nm), phenol and nitrite spectra.

2.3. Kinetic simulations

Concentration of nitrogen-containing radicals in irradiated nitrite solutions were estimated with the CKS package (IBM, 2000), which runs simulation of complex kinetic systems by using Monte Carlo techniques.

3. Results and discussion

3.1. Kinetic analysis of photoinduced reactions in nitrite solutions

UV irradiation of nitrite solutions between 300 and 400 nm leads to nitrite photodissociation followed by a number of other processes. Data taken from published results (#: Grätzel et al., 1969; §: Fischer and Warneck, 1996) are summarised below:

§ $NO_2^- + h\nu \rightarrow {}^{\cdot}NO + {}^{\cdot}O^-$ $[\Phi_{360\ nm} \approx 0.025]$ (1a)

§ ${}^{\cdot}O^- + H^+ \leftrightarrow {}^{\cdot}OH$ $[pK_{a,1b} = 11.9]$ (1b)

§ ${}^{\cdot}OH + NO_2^- \rightarrow OH^- + {}^{\cdot}NO_2$
$[k_2 = 1.0 \times 10^{10}\ M^{-1}s^{-1}]$ (2)

§ $NO_2^- + h\nu \rightarrow {}^{\cdot}NO_2 + e_{aq}^-$
$[\Phi_3 \leqslant 0.076\Phi_{1a}]$ (3)

§ $O_2 + e_{aq}^- \rightarrow {}^{\cdot}O_2^-$
$[k_4 = 1.9 \times 10^{10}\ M^{-1}s^{-1}]$ (4)

§ ${}^{\cdot}NO + {}^{\cdot}O_2^- \rightarrow ONOO^-$
$[k_5 = 6.7 \times 10^9\ M^{-1}s^{-1}]$ (5)

§ $ONOO^- + H^+ \leftrightarrow ONOOH$ $[pK_{a,6} = 6.6]$ (6)

§ $ONOOH \rightarrow NO_3^- + H^+$ $[k_7 = 0.7\ s^{-1}]$ (7)

§ $ONOOH \rightarrow {}^{\cdot}NO_2 + {}^{\cdot}OH$ $[k_8 \leqslant 0.3\ s^{-1}]$ (8)

§ $2{}^{\cdot}NO + O_2 \rightarrow 2{}^{\cdot}NO_2$
$[2k_9 = 4.2 \times 10^6\ M^{-2}s^{-1}]$ (9)

§ ${}^{\cdot}NO + {}^{\cdot}NO_2(+H_2O) \rightarrow 2NO_2^- + 2H^+$
$[k_{10} = 1.6 \times 10^8\ M^{-1}s^{-1}]$ (10)

$2{}^{\cdot}NO_2 \leftrightarrow N_2O_4$
$[k_{11} = 4.5 \times 10^8\ M^{-1}s^{-1};$
$k_{-11} = 6.9 \times 10^3\ s^{-1}]$ (11)

$N_2O_4(+H_2O) \rightarrow NO_2^- + NO_3^- + 2H^+$
$[k_{12} = 1 \times 10^3\ s^{-1}]$ (12)

§ ${}^{\cdot}NO_2 + O_2^- \rightarrow NO_2^- + O_2$
$[k_{13} = 4.5 \times 10^9\ M^{-1}s^{-1}]$ (13)

§ $NO_3^- + {}^{\cdot}NO \rightarrow {}^{\cdot}NO_2 + NO_2^-$
$[k_{14} \leqslant 4 \times 10^4\ M^{-1}s^{-1}]$ (14)

§ ${}^{\cdot}O_2^- + NO_2^- \rightarrow$ products
$[k_{15} = 5 \times 10^6\ M^{-1}s^{-1}]$ (15a)

As to the "products" in reaction (15a), Fischer and Warneck (1996) made the hypothesis that this reaction yields $\cdot NO_2$, so a possible process might be:

$$\cdot O_2^- + NO_2^- + 2H^+ \rightarrow H_2O_2 + \cdot NO_2 \quad [k_{15} = 5 \times 10^6\ M^{-1}s^{-1}] \tag{15b}$$

The rate constant for reaction (14) is presumably much lower than the upper limit. As a matter of fact, the 360 nm irradiation of a mixture of nitrite 0.1 M and nitrate 0.1 M does not yield a significant increase in $[\cdot NO_2]$, as detected by the formation of phenol nitroderivatives.

Reaction (10) does not describe the complete mechanism of the hydrolysis of $\cdot NO$ and $\cdot NO_2$. Replacing Eq. (10) by the following couple of reactions (Grätzel et al., 1970) allows also the evaluation of N_2O_3 levels:

$$\cdot NO + \cdot NO_2 \rightarrow N_2O_3 \quad [k_{16} = 1.1 \times 10^9\ M^{-1}s^{-1}] \tag{16}$$

$$N_2O_3(+H_2O) \rightarrow 2NO_2^- + 2H^+ \quad [k_{17} = 5.3 \times 10^2\ s^{-1}] \tag{17}$$

However, the values of k_{16} and k_{17} are not exactly compatible with that of k_{10}. In particular, compared to reaction (10), reactions (16) and (17) are faster and have a more important relative role as a sink for $\cdot NO$. The implications of this will be discussed later.

Nitrite acts as an efficient $\cdot OH$ scavenger, as can be seen from reaction (2). The rate constant for the reaction between $\cdot OH$ and NO_2^- is very near that for the reaction between $\cdot OH$ and phenol ($k = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$; Buxton et al., 1988). In our system the concentration of nitrite is nearly 100 times that of phenol ($[NO_2^-] = 0.10$ M, $[\text{Phenol}] = 1.1 \times 10^{-3}$ M), thus, based on the kinetic constants reported, 98.5% of photoformed $\cdot OH$ reacts with nitrite and only the remaining 1.5% with phenol.

The high number of processes induced by nitrite photocleavage makes desirable any possible simplification when experimental results have to be interpreted. In order to state which reactions are relevant and which play a negligible role in the system, with particular attention to the processes controlling $[\cdot NO_2]$ and $[\cdot NO]$, an attempt to perform a kinetic analysis applying the steady-state approximation to the concentration of the intermediates was made. The reactions (1a), (1b), (2) and (10) constitute a null cycle to which the steady-state approximation can be easily applied. The calculations give $[\cdot OH] = 1.5 \times 10^{-15}$ M and $[\cdot NO_2] = [\cdot NO] = 9.7 \times 10^{-8}$ M. However, the addition to this system of reactions (11) and (12), which add to reaction (10) as a sink for nitrogen dioxide, leads to a process with the following equivalent stoichiometry:

$$3NO_2^- + H_2O \rightarrow 2\cdot NO + NO_3^- + 2OH^- \tag{18}$$

This means that $\cdot NO$ does not reach a steady-state concentration, conversely it accumulates. Since the steady-state approximation is no longer valid and in order to include a higher number of reactions in the kinetic analysis, further calculations have been carried out with the CKS package (IBM, 2000). Results from both the exact solution of the system composed by reactions (1a), (1b), (2) and (10) (Maple 6, Waterloo Software) and the steady-state approximation exactly match the output of CKS simulation.

In the simulations both oxygen-free and aerated systems were considered. For the former reactions (1a)–(3), (10)–(12) were taken into account. For the latter, all the reactions with the exception of reaction (14). Moreover, the effect of substituting reaction (10) with the couple (16) and (17) was assessed.

Fig. 2 reports the results for the simulations in deoxygenated solution ((a): reaction (10); (b): reactions

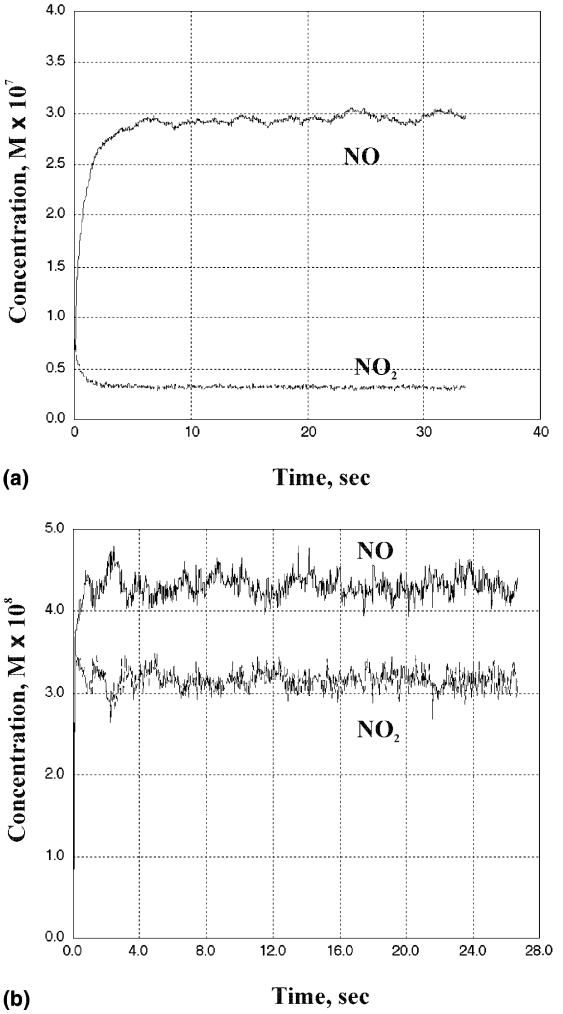


Fig. 2. Simulation of the 360 nm irradiation of $NaNO_2$ 0.1 M in the absence of oxygen. (a) Reaction (10); (b) reactions (16) and (17) (CKS package, IBM).

(16) and (17)), Fig. 3 the results in aerated systems ((a): reaction (10); (b): reactions (16) and (17)). The substitution of reaction (10) with reactions (16) and (17) has limited influence on [$^{\cdot}NO_2$], but a relevant one on [$^{\cdot}NO$]. Specifically, reactions (16) and (17) lead to a faster hydrolysis of $^{\cdot}NO$ than reaction (10). On the other hand, the hydrolysis of $^{\cdot}NO_2$ via reactions (11) and (12) compensates the differences in rates of reactions (10) and (16), (17), thus keeping [$^{\cdot}NO_2$] almost constant in both cases.

In the presence of oxygen, [$^{\cdot}NO$] and [$^{\cdot}NO_2$] are controlled by reactions (1a)–(4), (10)–(12) and (15b). Reactions (5), (8), (9) and (13) play a negligible role. Reaction (9) is a three-molecular reaction with relatively low rate constant, while reactions (5), (8) and (13) all involve O_2^-, which is efficiently scavenged by nitrite in reaction (15b).

When nitrite alone is present in the solution, reaction (15b) can play a role only if $\Phi_3 \neq 0$. If $\Phi_3 \approx 0$, the system would be described only by reactions (1a)–(2), (10)–(12). On the contrary, in the presence of organic compounds such as phenol in oxygenated solution, $^{\cdot}O_2^-$ and $HO_2^{\cdot}$ can also generate by reaction between molecular oxygen and organic radicals (see Scheme 1), thus reaction (15b) may be relevant also if $\Phi_3 \approx 0$.

The concentration of $^{\cdot}NO_2$ is enhanced by dissolved O_2 (compare Figs. 2 and 3). In the absence of oxygen, [$^{\cdot}NO_2$] $\approx 3 \times 10^{-8}$ M, while in oxygenated solution [$^{\cdot}NO_2$] $\approx 4.5 \times 10^{-8}$ M. The effect of oxygen is mainly due to the contribution by reaction (15b). On the other hand, the presence of oxygen depletes [$^{\cdot}NO$], although the actual value of its concentration varies according to the model in use. This depletion is mainly due to the enhancement of [$^{\cdot}NO_2$], influencing the mutual hydrolysis. The concentration of N_2O_3 is very little influenced by O_2. In both cases, [N_2O_3] $\approx 3 \times 10^{-9}$ M, unless depletion processes with oxidants such as superoxide and hydrogen peroxide, generated by other sources, take place.

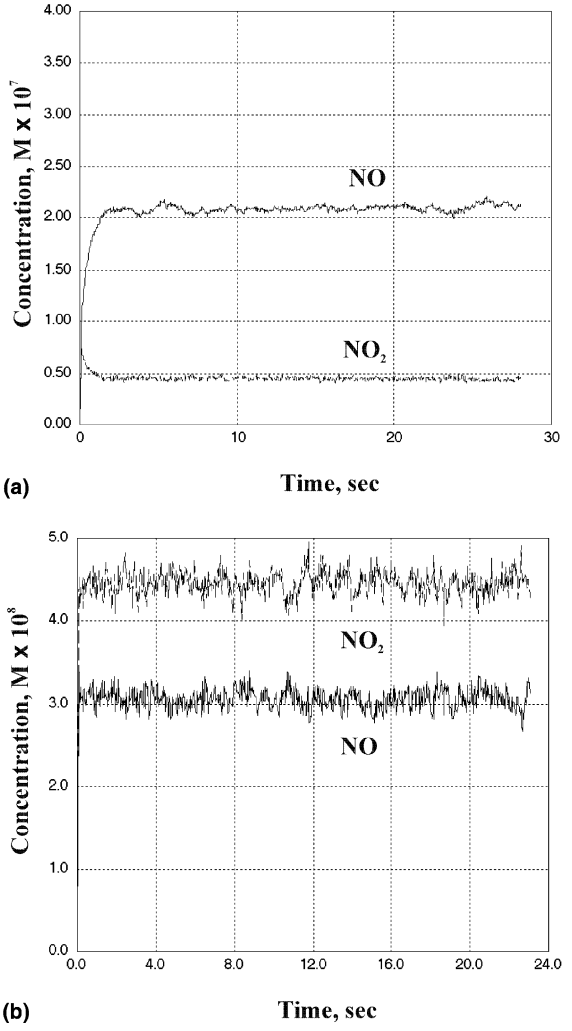
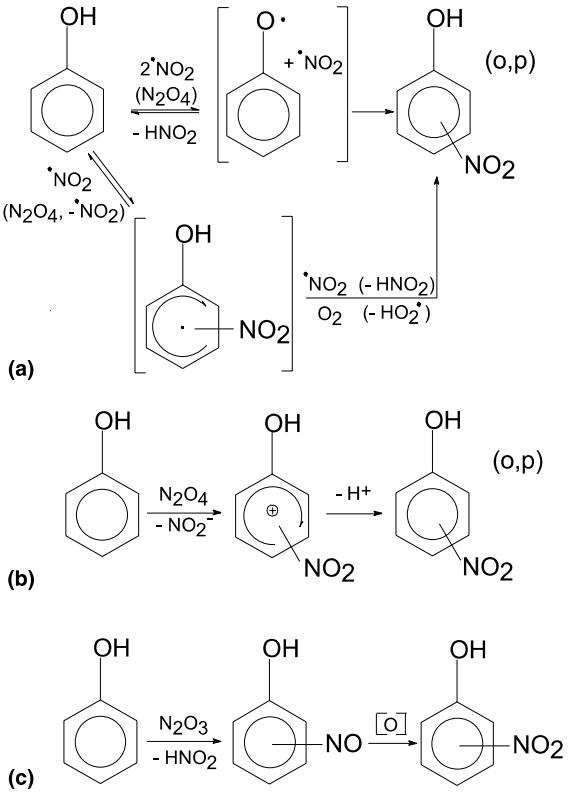


Fig. 3. Simulation of the 360 nm irradiation of $NaNO_2$ 0.1 M in the presence of oxygen. (a) Reaction (10); (b) reactions (16) and (17) (CKS package, IBM).



Scheme 1. Reaction mechanisms proposed for phenol photonitration.

To summarise, we propose that [$^{\cdot}NO_2$] and [$^{\cdot}NO$] be controlled by the following reactions:

$$NO_2^- + h\nu \rightarrow {}^{\cdot}NO + {}^{\cdot}O^- \quad (1a)$$

$${}^{\cdot}O^- + H^+ \leftrightarrow {}^{\cdot}OH \quad (1b)$$

$${}^{\cdot}OH + NO_2^- \rightarrow OH^- + {}^{\cdot}NO_2 \quad (2)$$

$$NO_2^- + h\nu \rightarrow {}^{\cdot}NO_2 + e_{aq}^- \quad (3)$$

$${}^{\cdot}NO + {}^{\cdot}NO_2 + H_2O \rightarrow 2NO_2^- + 2H^+ \quad (10)$$

$$2{}^{\cdot}NO_2 \leftrightarrow N_2O_4 \quad (11)$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (12)$$

$$O_2 + e_{aq}^- \rightarrow {}^{\cdot}O_2^- \quad (4)$$

$${}^{\cdot}O_2^- + NO_2^- + 2H^+ \rightarrow H_2O_2 + {}^{\cdot}NO_2 \quad (15b)$$

The first seven reactions describe the system in deoxygenated solution; the last two take place in the presence of oxygen.

3.2. Mechanisms of phenol photonitration

The concentration trend with time has been followed for phenol, 2- and 4-nitrophenol and 4-nitrosophenol. 3-nitrophenol and dihydroxybenzenes, if present, are under the detection limits of the analytical method (about 5×10^{-7} M).

Different paths have been proposed for phenol nitration upon nitrate photoexcitation. They can serve as a starting point for the interpretation of phenol transformation in the presence of nitrite and are summarised in Scheme 1.

A first proposal concerns a radical mechanism involving reaction between phenol and two $^{\cdot}NO_2$ (or N_2O_4). The radical intermediate might be hydroxynitrocyclohexadienyl (Dzengel et al., 1999a; Vione et al., 2001a) or phenoxyl (Coombes et al., 1994). The two proposed pathways are reported in Scheme 1 (mechanism (a)).

According to mechanism (a), $^{\cdot}NO_2$ or N_2O_4 reacts with phenol via hydrogen atom abstraction or via addition to the ring. Direct electron transfer between phenol and nitrogen dioxide, yielding phenol radical cation and nitrite, is thermodynamically allowed ($E^0(^{\cdot}NO_2/NO_2^-) = 1.03$ V, $E^0(PhOH^{\cdot+}/PhOH) = 0.97$ V; Alfassi et al., 1990):

$$PhOH + {}^{\cdot}NO_2 \rightarrow PhOH^{\cdot+} + NO_2^- \quad (19)$$

However, phenol radical cation is a very strong acid ($pK_a = -1.9$; Dixon and Murphy, 1976) and, in aqueous solution, it almost instantaneously dissociates to phenoxyl:

$$PhOH^{\cdot+} \rightarrow PhO^{\cdot} + H^+ \quad (20)$$

As a consequence, both hydrogen atom abstraction and direct electron transfer yield phenoxyl as reaction product, and the two pathways for phenol oxidation are equivalent with respect to nitration processes.

Another proposal (b) concerns a molecular nitration involving electrophilic attack by N_2O_4 on phenol (Machado and Boule, 1995). Up to now, it has been difficult to decide whether phenol nitration follows a radical or an electrophilic path and whether it involves $^{\cdot}NO_2$ or N_2O_4 (Machado and Boule, 1995; Vione et al., 2001a). As the purpose of the present work is to demonstrate the possibility of phenol photonitration in the presence of nitrite and to study the effects of oxygen and 2-propanol on the process, detailed kinetic analysis and discussion on the mechanism will be given in a forthcoming paper (Vione et al., 2001c).

Another path (c) involves first phenol nitrosation, followed by a fast oxidation of the nitrosoderivative to the nitroderivative. This process is quite common in aromatic nitration (Ridd, 1998). In this work we have found convincing evidence of a relevant role played by mechanism (c).

Finally, an $^{\cdot}OH$-mediated reaction has been proposed (Niessen et al., 1988; Louw and Santoro, 1999). It implies a first reaction between phenol and $^{\cdot}OH$ yielding phenoxyl radical. This radical can then react either with $^{\cdot}NO_2$ to give nitrophenols or with $^{\cdot}OH$ to give dihydroxybenzenes. Some studies in which nitrate was irradiated concluded that $^{\cdot}OH$-induced phenol nitration does not occur in the presence of dissolved oxygen (Machado and Boule, 1995; Vione et al., 2001a). Such a mechanism may however have some importance in the absence of oxygen (Dzengel et al., 1999b; Vione et al., 2001a).

Reaction between phenol and $^{\cdot}OH$ can also yield dihydroxycyclohexadienyl. A nitration path was postulated, requiring addition of $^{\cdot}NO_2$ to this radical and formation of nitrophenols due to the elimination of a water molecule. This reaction mechanism has been proposed in analogy with nitration of benzene upon radiolysis of aqueous nitrate (Eberhardt, 1975) and with nitration of atmospheric PAHs (Pitts et al., 1985). However, this path should lead to 3-nitrophenol as a major intermediate, which is not the case.

In the system under study nitrite can efficiently scavenge $^{\cdot}OH$ (reaction (2)). In these conditions an $^{\cdot}OH$-mediated nitration process is very probably efficiently inhibited, even in the absence of dissolved oxygen. Furthermore, Fig. 4 reports the initial rates for the formation of 2- and 4-nitrophenol in the presence of phenol 1.1×10^{-3} M as a function of nitrite concentration. If the main pathway for phenol nitration was initiated by $^{\cdot}OH$, the initial rate should have a maximum for $[NO_2^-] \approx 0.01$ M, where the steady-state concentration of $^{\cdot}OH$ under such conditions is maximum (Vione et al., 2001b, Fig. 9). As the

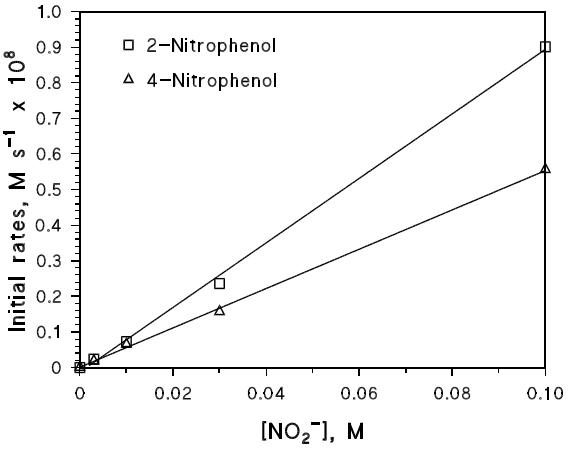


Fig. 4. Effect of nitrite concentration on the initial rates of nitrophenol formation in the presence of phenol 1.1×10^{-3} M (aerated solution). Irradiation at 360 nm.

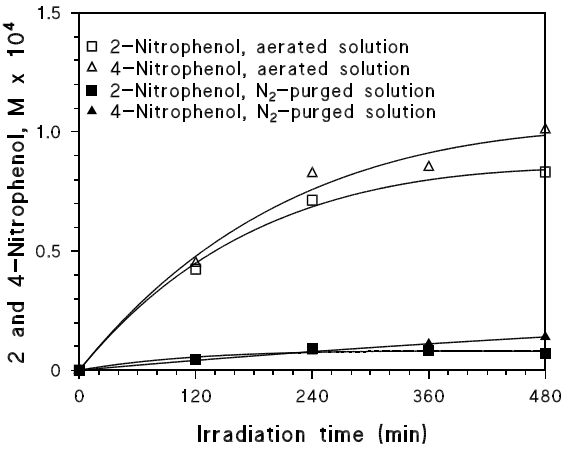


Fig. 5. Effect of dissolved oxygen on the formation of 2- and 4-nitrophenol. Initial conditions: phenol, 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5. Irradiation at 360 nm.

nitrophenol formation rate constantly increases with increasing $[NO_2^-]$ in the range 0.003–0.100 M, ·OH-mediated phenol nitration can be excluded as a major pathway.

A previous study by Machado and Boule (1995) indicated that no nitrophenols form upon 365 nm irradiation of nitrite and phenol. On the contrary, we have found relevant amount of nitrophenols under irradiation with UV light around 360 nm. However, the reactant concentrations they used were different from those utilised in the present work, and the different results can be easily accounted for. Machado and Boule (1995) studied the photoinduced reactions in systems containing phenol 5×10^{-4} M and nitrite 1×10^{-3} M, while we have used quite higher concentrations of both (phenol 1.1×10^{-3} M, nitrite 0.1 M). In addition, the ratio $[NO_2^-]$/[Phenol] was 2 in their case, 90.9 in ours. When that ratio is low, phenol can efficiently compete with nitrite for reaction with ·OH, thus lowering the yield in $\cdot NO_2$.

Furthermore, when we illuminated phenol 1.1×10^{-3} M in the presence of nitrite 1×10^{-3} M (Vione et al., 2001b), nitrophenols were below detection limit, thus confirming the results obtained by Machado and Boule (1995).

3.3. Effect of dissolved oxygen

To perform experiments in the absence of oxygen, solutions in the cells (pH = 6.5) were degassed by bubbling with a stream of high-purity nitrogen before irradiation. Results are shown in Fig. 5. It appears that dissolved oxygen favours the formation of nitrophenols: the ratio of the initial rates of formation is around 8.6 in the conditions employed.

A possible explanation can be given considering the processes following nitrite photolysis. In the absence of dissolved oxygen, $[\cdot NO_2] \approx 3 \times 10^{-8}$ M. In aerated solutions, $[\cdot NO_2] \approx 4.5 \times 10^{-8}$M. From Fig. 4 and from the processes initiated by nitrite photolysis (reactions (1a),(1b),(2),(3), (10),(11),(12), and (4), (15b)) it can be inferred that the rate of nitrophenol formation has a second-order dependence with respect to $[\cdot NO_2]$ (or a first-order dependence with respect to $[N_2O_4]$, since $[N_2O_4] \propto [\cdot NO_2]^2$). Thus, a 50% increase in $[\cdot NO_2]$ should result in a 125% increase in nitrophenol formation rate, only partially explaining the effect of oxygen.

In deoxygenated solution the pseudo-first-order degradation constant for phenol is higher than in the presence of oxygen (see Table 1). At the same time, the formation rate of 4-nitrosophenol is higher in the absence of dissolved oxygen than in its presence (see Fig. 6). Phenol nitrosation was proposed to be due to electrophilic substitution by N_2O_3 (Pires et al., 1994). N_2O_3 forms via reaction between ·NO and $\cdot NO_2$, but its concentration does not depend on the presence of O_2

Table 1
Pseudo-first-order degradation constants for phenol 1.1×10^{-3} M

$[NO_2^-]$ (M)	pH	Notes	k_D (s^{-1})
0.003	6.5		2.0×10^{-5}
0.010	6.5		2.5×10^{-5}
0.030	6.5		4.2×10^{-5}
0.100	6.5		7.0×10^{-5}
0.100	6.5	N_2 purged	2.0×10^{-4}
0.100	6.5	2-propanol 2.00 M	2.2×10^{-5}

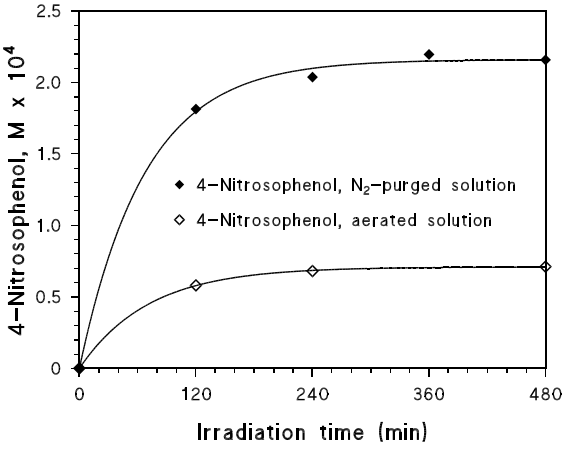


Fig. 6. Effect of dissolved oxygen on the formation of 4-nitrosophenol. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5. Irradiation at 360 nm.

when reactions (1a),(1b),(2),(3), (10),(11),(12) and (4), (15b) are taken into account. The lower formation rate of 4-nitrosophenol in aerated solution is probably due to depletion of $\cdot NO$ or N_2O_3, reacting with H_2O_2. Hydrogen peroxide can originate from nitrite photolysis (reactions (3), (4) and (15b)) and from the interaction of organic radical intermediates and O_2 (see Scheme 1 for the formation of superoxide, together with reaction (15b); for reaction (21), see Pietsch and Meyer, 1936):

$$2\cdot NO + H_2O_2 \rightarrow 2HNO_2 \quad (21)$$

The depletion of $\cdot NO$ and/or N_2O_3 can explain the lower formation of 4-nitrosophenol and the lower reactivity of phenol in the presence of oxygen.

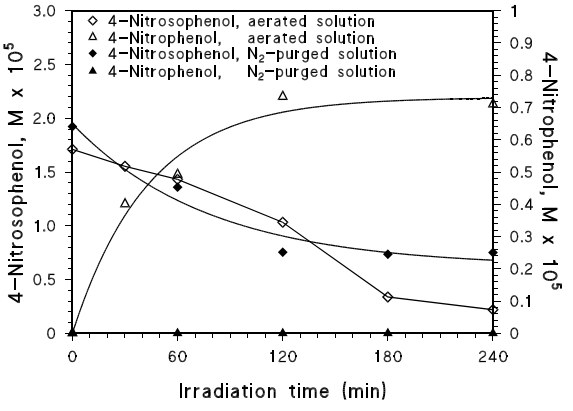


Fig. 7. Degradation of 4-nitrosophenol in aerated and N_2-purged solutions. Initial conditions: 4-nitrosophenol 1.7×10^{-5} M, $NaNO_2$ 0.10 M, pH = 6.5. Irradiation at 360 nm.

In the presence of dissolved oxygen, 4-nitrosophenol can be oxidised to 4-nitrophenol (see Fig. 7; a similar contribution by 2-nitrosophenol is reasonable). As 4-nitrosophenol and 4-nitrophenol form in comparable amounts upon phenol and nitrite irradiation (compare Figs. 5 and 6), the oxidation of 4-nitrosophenol gives a relevant contribution to the formation of 4-nitrophenol.

In the absence of oxygen, 4-nitrosophenol transforms, but does not yield 4-nitrophenol (Fig. 7). The fact that 4-nitrophenol forms upon phenol and nitrite irradiation also in the absence of oxygen indicates that the oxidation of 4-nitrosophenol is not the only path yielding the nitroderivative, the other path being the reaction between phenol and $\cdot NO_2$ (or N_2O_4). The latter reaction path is favoured by oxygen as well, although to a lesser extent ($[\cdot NO_2]$ is higher in oxygenated solution, as already discussed).

In summary, in oxygenated solution there are two paths leading to nitrophenols: one is phenol nitration by $\cdot NO_2$ (mechanism (a) in Scheme 1), the other is the oxidation of the nitrosoderivatives (mechanism (c) in Scheme 1). In the absence of oxygen, mechanism (a) is inhibited to a certain extent due to the lower $[\cdot NO_2]$, while mechanism (c) does not occur. These two effects account for the lower formation of nitrophenols in the absence of oxygen.

3.4. Effect of 2-propanol

2-propanol 2.00 M was added to the aerated system. This molecule is an $\cdot OH$ scavenger through the following process, finally yielding acetone (Warneck and Wurzinger, 1988):

$$(CH_3)_2CHOH + \cdot OH \rightarrow (CH_3)_2COH\cdot + H_2O \quad (22)$$
$$(CH_3)_2COH\cdot + O_2 \rightarrow HO_2^{\cdot} + (CH_3)_2CO \quad (23)$$

In the absence of 2-propanol, 98.5% of photoformed $\cdot OH$ reacts with nitrite and 1.5% with phenol. The rate constant for reaction between 2-propanol and $\cdot OH$ is 3.0×10^9 M^{-1} s^{-1} (Buxton et al., 1988). In the presence of 2-propanol 2.00 M, 85.5% of $\cdot OH$ reacts with 2-propanol, 14.3% with NO_2^- and a residual 0.2% with phenol. As a consequence, 2-propanol interferes with reaction (2) and lowers the production of $\cdot NO_2$ through this reaction. The initial formation rate of nitrophenols is about halved in the presence of 2-propanol 2.00 M (see Fig. 8). However, if reaction (2) is the main source of $\cdot NO_2$ its inhibition should lower nitrophenol formation to a far larger extent, namely the ratio between initial formation rates should be about 7. Thus, in this system reaction (2) should have a minor influence on $[\cdot NO_2]$. This may happen because the sequence of reactions (22), (23) and (15b) is operating (pK_a of superoxide

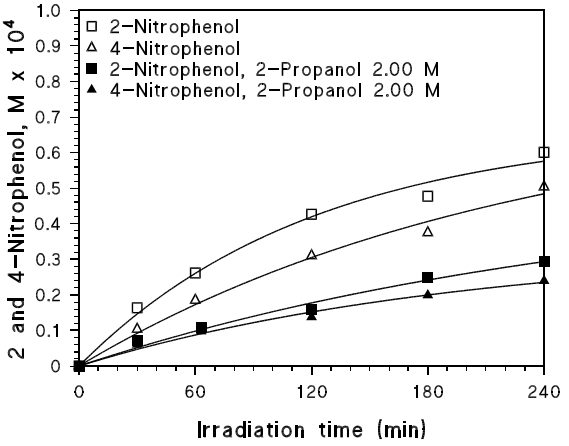


Fig. 8. Effect of 2-propanol 2.00 M on nitrophenol formation (aerated solution). Initial conditions: phenol, 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5. Irradiation at 360 nm.

is 4.8), regenerating $\cdot NO_2$ and compensating for the inhibition of reaction (2).

At the same time, the formation of 4-nitrosophenol is inhibited by 2-propanol to a far larger extent than the formation of nitrophenols (see Fig. 9 and compare with Fig. 8). This difference is difficult to explain in the hypothesis of the depletion of $\cdot NO_2$, which contributes both to phenol nitration and to its nitrosation via N_2O_3. Our hypothesis is that the addition of 2-propanol depletes $\cdot NO$ rather than $\cdot NO_2$. This probably happens since hydrogen peroxide and/or superoxide oxidise $\cdot NO$ (reactions (5), (21)) and/or N_2O_3. The formation of H_2O_2 in the presence of 2-propanol is higher than in aerated solutions without the alcohol, because of an

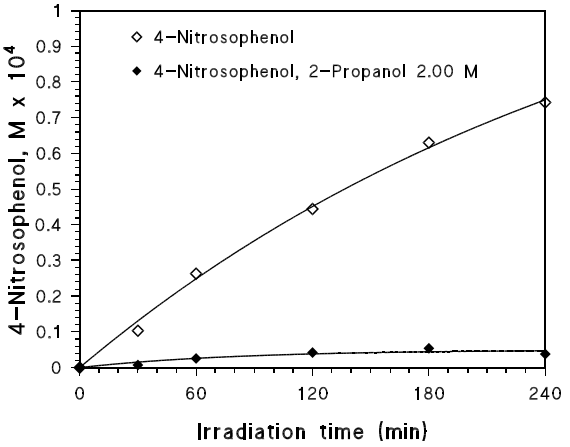


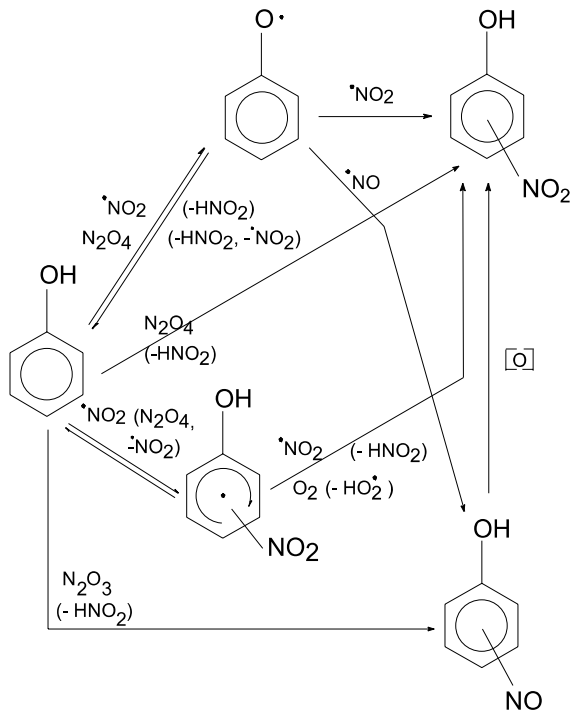
Fig. 9. Effect of 2-propanol 2.00 M on the formation of 4-nitrosophenol (aerated solution). Initial conditions: phenol, 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5. Irradiation at 360 nm.

enhanced formation of $HO_2^{\cdot}/\cdot O_2^-$ through reactions (22),(23). In the absence of 2-propanol, the formation of $\cdot O_2^-$ depends on reactions (3) and (4), in the presence of 2-propanol it depends on reactions (1a/b) and (22),(23), with $\Phi_{1a} \geqslant 13\Phi_3$.

The depletion of 4-nitrosophenol inhibits the formation of 4-nitrophenol through mechanism (c). A similar effect probably takes place with the ortho derivative, thus explaining why nitrophenols formation is inhibited by 2-propanol. If this scenario is correct, Fig. 8 indicates that mechanism (a) and mechanism (c) for nitrophenol formation (see Scheme 1) have a comparable weight in the absence of 2-propanol, since the inhibition of mechanism (c) halves the formation rate of 2- and 4-nitrophenol.

4. Conclusions

Irradiation of nitrite 0.1 M in aqueous solution leads to the formation of $\cdot NO_2$ in relevant concentration, mainly via reactions (2), (3) and, in aerated systems, (15b). The radical $\cdot NO_2$ (or the dimer N_2O_4) can be involved in the photoinduced nitration of organic matter, as demonstrated by phenol nitration. Nitrite photolysis also yields $\cdot NO$, which reacts with $\cdot NO_2$ to give N_2O_3,



Scheme 2. Early steps in reaction pathways proposed for the transformation of phenol in the presence of nitrite.

probably responsible for the formation of 4-nitrosophenol.

The formation of nitrophenols can also occur via the oxidation of the nitrosoderivatives, which takes place in the presence of nitrite, light and oxygen. This process probably has a role comparable with that of the nitration via $\cdot NO_2$.

2-Propanol acts as a scavenger of $\cdot OH$, but very probably it does not deplete $\cdot NO_2$. On the contrary, it can lower $\cdot NO$ and N_2O_3 concentration levels through generation of active oxygen species. The consequence is an almost complete inhibition of the formation of 4-nitrosophenol, together with a partial depletion of nitrophenol formation.

The early steps in reaction pathways proposed for the transformation of phenol in the presence of nitrite are reported in Scheme 2. Studies on the detailed kinetic aspects of the system (dependence on the type of substrate and its concentration as well as on O_2 and NO_2^- concentration) are under way in order to gain more insight about the finer details of the overall photonitration and nitrosation process (Vione et al., 2001c).

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References

Alfassi, Z.B., Huie, R.E., Neta, P., Shoute, C.T., 1990. Temperature dependence of the rate constants for reaction of inorganic radicals with organic reductants. J. Phys. Chem. 94, 8800–8805.

Arakaki, T., Miyake, T., Hirakawa, T., Sakugawa, H., 1999. pH dependent photoformation of hydroxyl radical and absorbance of aqueous-phase N(III) (HNO_2 and NO_2^-). Environ. Sci. Technol. 33, 2561–2565.

Boule, P., Bolte, M., Richard, C., 1999. Phototransformations induced in aquatic media by $NO_3^-NO_2^-$, Fe^{III} and humic substances. In: Boule, P., (Ed.), The Handbook of Environmental Chemistry, vol. 2.L (Environmental Photochemistry), Springer, Berlin, pp. 181–215.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot OH/\cdot O^-$) in aqueous solution. J. Phys. Chem. Ref. Data 17, 1027–1284.

Coombes, R.G., Diggle, A.W., Kempsell, S.P., 1994. The mechanism of nitration of phenol and 4-methylphenol by nitrogen dioxide in solution. Tetrahedron Lett. 35, 6373–6376.

Dixon, W.T., Murphy, D., 1976. Determination of the acidity constants of some phenol radical cations by means of electron spin resonance. J. Chem. Soc., Faraday Trans. II, 1221–1230.

Dzengel, J., Theurich, J., Bahnemann, D., 1999a. Formation of nitroaromatic compounds in advanced oxidation processes: photolysis versus photocatalysis. Environ. Sci. Technol. 33, 294–300.

Dzengel, J., Theurich, J., Bahnemann, D., 1999b. Response to comment on formation of nitroaromatic compounds in advanced oxidation processes: photolysis versus photocatalysis. Environ. Sci. Technol. 33, 3282.

Eberhardt, M.K., 1975. Radiation-induced homolytic aromatic substitution. III. Hydroxylation and nitration of benzene. J. Phys. Chem. 79, 1067–1069.

Fischer, M., Warneck, P., 1996. Photodecomposition of nitrite and undissociated nitrous acid in aqueous solution. J. Phys. Chem. 100, 18749–18756.

Grätzel, M., Henglein, A., Lilie, J., Beck, G., 1969. Pulsradiolytische Untersuchung einiger Elementarprozesse der Oxydation und Reduktion des Nitritions. Ber. Bunsenges. Phys. Chem. 73, 646–653.

Grätzel, M., Taniguchi, S., Henglein, A., 1970. Pulsradiolytische Untersuchung der NO-Oxydation und des Gleichgewichts $N_2O_3 \leftrightarrow NO + NO_2$ in wäßriger Lösung. Ber. Bunsenges. Phys. Chem. 74, 488.

Guidelines for Drinking-Water Quality, 1996. second ed. World Health Organisation, Geneva, pp. 313–323.

Hoigné, J., 1990. Formulation and calibration of environmental reaction kinetics: oxidations by aqueous photooxidants as an example. In: Stumm, W., (Ed.), Aquatic Chemical Kinetics, Wiley (Chapter 2) pp. 43–70.

IBM, 2000 www.almaden.ibm.com/st/msim/ckspage.html, last accessed July 2000.

Louw, R., Santoro, D., 1999. Comment on formation of nitroaromatic compounds in advanced oxidation processes: photolysis versus photocatalysis. Environ. Sci. Technol. 33, 3281.

Machado, F., Boule, P., 1995. Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by excitation of nitrite and nitrate ions. J. Photochem. Photobiol. A: Chem. 86, 73–80.

Niessen, R., Lenoir, D., Boule, P., 1988. Phototransformations of phenol induced by excitation of nitrate ions. Chemosphere 17, 1977–1984.

Pietsch, E., Meyer, R.J., 1936. Gmelins Handbuch der Anorganischen Chemie, vol. 4 (Stickstoff), Verlag Chemie, Berlin, p. 725.

Pires, M., Rossi, M.J., Ross, S.R., 1994. Kinetic and mechanistic aspects of the NO oxidation by O_2 in aqueous phase. Int. J. Chem. Kinetics 26, 1207–1227.

Pitts, J.N., Arey, J.S., Zielinska, B., Winer, A.M., Atkinson, R., 1985. Determination of 2-nitrofluoranthene and 2-nitropyrene in ambient particulate organic matter: evidence for atmospheric reactions. Atmos. Environ. 19, 1601–1608.

Ridd, J.H., 1998. Some unconventional pathways in aromatic nitration. Acta Chem. Scand. 52, 11–22.

Uemura, S., Toshimitsu, A., Okano, M., 1978. Nitration of aromatic hydrocarbons and ipso-nitrosodemetallation of arylmetal compounds in sodium nitrite-trifluoroacetic acid. J. Chem. Soc. Perkin Trans. I, 1076–1079.

Vione, D., 1998. Trasformazioni del fenolo indotte dalla fotolisi UV di ioni nitrato e nitrito in soluzione acquosa. Thesis, University of Torino.

Vione, D., Maurino, V., Minero, C., Vincenti, M., Pelizzetti, E., 2001a. Formation of nitrophenols upon UV irradiation of phenol and nitrate in aqueous solutions and in TiO_2 aqueous suspensions. Chemosphere 44 (2), 237–248.

Vione, D., Maurino, V., Minero, C., Vincenti, M., Pelizzetti, E., 2001b. Phenol Photonitration upon UV irradiation of nitrite in aqueous solution. II: Effects of pH and TiO_2. Chemosphere 45 (5), 907–914.

Vione, D., Maurino, V., Minero, C., Pelizzetti, E., 2001c. Phenol photonitration: a mechanistic study, in preparation.

Warneck, P., Wurzinger, C., 1988. Product quantum yields for the 305-nm photodecomposition of NO_3^- in aqueous solution. J. Phys. Chem. 92, 6278–6283.