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Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by excitation of nitrite and nitrate ions

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Abstract

The excitation of nitrite and nitrate ions in the presence of phenolic compounds may induce oxidation, nitration and nitrosation. Oxidation occurs whatever the substituents and can be attributed to hydroxyl radicals formed in the photolysis of ions. Nitration and nitrosation are not observed in the presence of electron-withdrawing substituents. When nitrite ions are excited in the presence of phenol or resorcinol the observed *para* nitrosation can be attributed to nitrogen oxides formed in the photolysis of NO_2^-. It is enhanced by increasing nitrite concentration. From the influence of oxygen it is concluded that two mechanisms compete, one involving N_2O_3 and the other the radical adduct phenol...$NO_2^{\cdot}$. This reaction does not occur with pyrocatechol and hydroquinone. With these substrates nitration is observed but mainly in the presence of oxygen.

Reactions are more complex when nitrate ions are excited in the presence of phenol or resorcinol. The formation of nitro and nitroso derivatives is attributed to the nitrogen oxides $NO_2^{\cdot}$ and N_2O_4. With pyrocatechol and hydroquinone, nitrosation does not occur and nitration is favoured by deoxygenation. In environmental conditions nitration or nitrosation by excitation of NO_2^- are highly unlikely. Their occurence upon excitation of NO_3^- depends on the concentration of phenolic compounds and on the pH of the solution.

Keywords: Photonitration; Photonitrosation; Phenolic derivatives; Nitrite ions; Nitrate ions

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1. Introduction

Nitrate ions absorb sunlight in the UV range and their photolysis leads to the formation of nitrite ions and hydroxyl radicals which can oxidize most of organic compounds. Thus their excitation have a depolluting influence which has been already mentioned in literature [1–3]. But the formation of mutagens by photochemical reaction of aromatic compounds in nitrate aqueous solution has been also observed and attributed to a photochemical nitration [4,5]. This reaction can result from the direct excitation of aromatic compounds in the presence of nitrate ions [6] or from the excitation of nitrate ions [7,8].

Nitrate ions absorb at $\lambda < 350$ nm with a maximum at 302 nm ($\epsilon = 7.2\ M^{-1}\ cm^{-1}$). Their photolysis involves two pathways [9,10]:

$$NO_3^{-*} \longrightarrow NO_2^- + O(^3P) \qquad (1)$$

$$NO_3^{-*} \longrightarrow NO_2^{\cdot} + O^{\cdot -} \qquad (2)$$

$$O^{\cdot -} + H_2O \longrightarrow {}^{\cdot}OH + OH^- \qquad (3)$$

Oxidations are generally attributed to hydroxyl radicals which are more reactive than atomic oxygen. The quantum yield of $^{\cdot}OH$ formation in the range 305–313 nm was evaluated at $(0.9–1.7) \times 10^{-2}$ [3,10,11] i.e. much higher than the quantum yield of the other pathway (1.1×10^{-3}) according to Warneck and Wurzinger [10].

Most often nitrite ions are present in natural waters only at very low concentration, but they absorb a larger part of solar energy than nitrate ions, since their molar extinction coefficient at 352 nm is about three times as high as that of nitrate ions at 302 nm. Their photolysis leads to induced oxidations, but nitration or nitrosation may also occur [12–14] and carcinogens or mutagens may be formed [12,13,15].

Nitrite ions absorb at wavelengths shorter than 400 nm ($\epsilon_{352} = 22\ M^{-1}\ cm^{-1}$). Their photolysis yields nitrogen monoxide and hydroxyl radicals [16,17]:

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$$\begin{aligned} NO_2^{-*} &\longrightarrow NO^{\cdot} + O^{\cdot -} \\ O^{\cdot -} + H_2O &\longrightarrow {}^{\cdot}OH + OH^- \end{aligned} \qquad (4)$$

The quantum yield of formation of hydroxyl radicals increases with decreasing wavelength from 0.015 ± 0.005 at ca. 370 nm [18] to 0.11 ± 0.01 at 254 nm [19]. The same value 0.07 was obtained in the range 298–313 nm by different authors [11,18,19]. In acidic medium the quantum yield of nitrous acid dissociation is much higher and it is wavelength independent ($\phi = 0.45 \pm 0.10$) [19].

The aim of the present work is to study the influence of substituents of the aromatic ring on the orientation of the reaction, and the mechanisms of photonitration and photonitrosation, in order to forecast the occurence of these reactions in environmental conditions. The reactions induced by nitrite ions are first considered because they are less complex than the reaction induced by nitrate ions in which they are involved as secondary reactions. Their knowledge is thus useful to understand reactions induced by nitrate ions. A special attention is focussed on the reactions of nitration and nitrosation.

2. Experimental details

2.1. Reactants

Most of reactants were 'pro-analysi' i.e. >99% and used as received.

- Benzoquinone was sublimed under vacuum before use, to eliminate traces of hydroquinone. It was obtained as yellow crystals.
- Hydroxybenzoquinone, which is an unstable compound, was obtained from a solution of 1,2,4-trihydroxybenzene oxidized by O_2 at pH 8–9. The solution was acidified after few minutes to prevent further oxidation.

Some nitro and nitroso derivatives were synthetized:

- Nitrohydroquinone from the oxidation of 2-nitrophenol by sodium peroxodisulfate [20]. The structure was checked by NMR: δppm ($CDCl_3$) 7.1 d; 7.2 dd; 7.5 d.
- 4-nitroresorcinol from resorcinol and nitric acid [21].
- 4-nitrosoresorcinol from resorcinol and isopentyl nitrite in the presence of KOH [22].
- 2,4-dinitrosoresorcinol from resorcinol and sodium nitrite (mole ratio 1:2) in acidic solution [23]. Its structure was checked by M.S. (m/e = 168) and NMR: δppm (CD_3OD) 6.6 q; 8.1 d.

2.2. Irradiations and analyses

For analytical and preparative purposes solutions containing nitrate ions were irradiated in polychromatic light in the range 290–340 nm using Duke UVB low pressure lamps GL 20 W. Solutions with nitrite ions were irradiated at 365nm in a water-cooled reactor in borosilicated glass using black light MAW 125 (Mazda) or HPW 125 (Philips) lamps (about 85% of the light emitted on the 365 nm mercury line).

For determination of quantum yields, solutions were irradiated in monochromatic parallel beam at 313 or 365 nm using a Bausch and Lomb monochromator equipped with a high pressure mercury lamp. Phenol and dihydroxybenzenes do not absorb at these wavelengths, excepted hydroquinone at 313 nm. The photon flux was evaluated with ferrioxalate as actinometer.

Irradiated solutions were analysed in HPLC with a classical C_{18} column (250 mm × 4 mm). Three chromatographs were used: Beckman with UV detection, Waters with photodiode array detector and Merck with UV and fluorescence detections (mainly for titration of trihydroxybenzenes formed).

3. Results and discussion

3.1. Reactions induced by nitrite ions

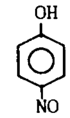
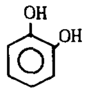
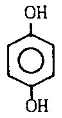
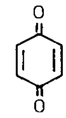
3.1.1. Phenol

Air-saturated or deoxygenated solutions of phenol 5×10^{-4} M and sodium nitrite 10^{-3} M were irradiated at 365 nm. Solutions were buffered at pH 7.0–7.5 to prevent dark reaction of nitrous acid ($pKa = 3.37$) and the increase of pH due to the photolysis of nitrite ions. No reaction was observed, after several hours, in solutions kept in the dark. Borate was prefered to phosphate to buffer the solutions because it was observed that the latter (7×10^{-3} M) reduces the transformation rate and inhibits the formation of nitrosophenol. In all cases the concentration of borate was limited to 7×10^{-3} M.

The main photoproducts in aerated solutions were 4-nitrosophenol, hydroquinone, pyrocatechol and benzoquinone, whereas in deoxygenated solutions only 4-nitrosophenol was detected. The absence of oxygen enhances nitrosation. The mass balances are given in Table 1. In these conditions the quantum yield of the photoinduced transformation was evaluated at 4.0×10^{-3}.

When the concentration of nitrite ions was increased up to 5×10^{-2} M the only photoproduct detected in aerated solution was 4-nitrosophenol. The specificity of the reaction can be attributed to the quenching of ${}^{\cdot}OH$ by nitrite ions. It can be deduced that the formation

Table 1
nfluence of oxygen on the formation of photoproducts in a solution of phenol (5×10^{-4} M) and nitrite ions (10^{-3} M) buffered at pH 7.4 nd irradiated during 1 h at 365 nm. Concentrations are given in μM. (N.D. = not detected)

	Conversion extent (%)				
erated	10.5	18	3.1	1.1	3.7
eoxygenated	11.4	37	N.D.	N.D.	N.D.

f 4-nitrosophenol involves a reaction of nitrogen dioxide.

$$\text{OH}+\text{phenol}\longrightarrow\ldots \qquad (5)$$

$$k_5=1.8\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$$

$$\text{OH}+\text{NO}_2^-\longrightarrow\text{NO}_2^{\cdot}+\text{OH}^- \qquad (6)$$

$$k_6=10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$$

Solutions of phenol 5×10^{-4} M and nitrite ions 10^{-3} M were also irradiated in the presence of formate ions used as ·OH quencher.

$$\text{OH}+\text{HCO}_2^-\longrightarrow\text{CO}_2^{\cdot-}+\text{H}_2\text{O} \qquad (7)$$

$$k_7=3.2\times10^{9}\ \text{M}^{-1}\ \text{s}^{-1}$$

From the rate constants k_5, k_6 and k_7 given in literature [24] the percentage of hydroxyl radicals reacting with each species can be calculated. In the presence of formate ions 5×10^{-2} M, 90% of hydroxyl radicals react with formate ions, 5% with NO_2^- and 5% with phenol. In aerated solution the photo-oxidation was drastically inhibited, but the formation of 4-nitrosophenol was only 75% reduced. It can be deduced that the photo-oxidation is initiated by ·OH, but 4-nitrosophenol can be formed without the involvement of these radicals. In the absence of oxygen the transformation of phenol is much slower, only traces of 4-nitrosophenol were detected.

3.1.2. *Resorcinol*

Air-saturated or deoxygenated solutions of resorcinol (5×10^{-4} M) and nitrite ions (10^{-3} M) were irradiated at 365 nm. Phosphates were used to buffer the solutions at pH 7.2 since no significant influence of phosphate concentration on the reaction was noted, when its concentration was in the range 6.7×10^{-3} M–2.7×10^{-2} M. No reaction was observed after several hours in the dark. The only products of phototransformation identified in the presence or in the absence of oxygen were 4-nitrosoresorcinol and 2,4-dinitrosoresorcinol. The latter results from the nitrosation of the former in a second stage of the reaction, since it was only detected after several hours of irradiation. The quantum yield of the induced transformation was estimated at 1.2×10^{-2}. The absence of expected trihydroxybenzenes, in aerated solution, can be explained by their oxidability.

As it appears in Table 2, in the absence of formate ions the formation of 4-nitrosoresorcinol is not much influenced by oxygen. The quenching effect of formate ions 5×10^{-2} M on hydroxyl radicals can be estimated at 91%. Nevertheless in aerated solution the formation of 4-nitrosoresorcinol is only 62% inhibited. It can be deduced that the reaction involves other reacting species than ·OH. As it was suggested for phenol, nitrosation seems to be attributed to a dark reaction of nitrogen dioxide formed in the solution. It was observed indeed that, in the absence of light excitation, nitrogen dioxide (gas) reacts with resorcinol in a solution buffered at pH 7.2 with formation of 4-nitroso- and 2,4-dinitrosoresorcinol, whereas the limited nitrosation observed in a degassed solution stirred in the presence of nitrogen monoxide can be attributed to a contamination of NO by traces of NO_2 or O_2 [14].

3.1.3. *Pyrocatechol, hydroquinone, nitrophenols*

Air-saturated solutions of pyrocatechol 5×10^{-4} M and nitrite ions 10^{-3} M, buffered at pH 6.0 with phosphates are stable during several hours in the dark. These solutions were irradiated at 365 nm as in both cases of phenol and resorcinol. The main photoproducts were hydroxybenzoquinone and 4-nitropyrocatechol formed with about the same rate. The quantum yield

Table 2
Influence of oxygen and formate ions on the formation of 4-nitrosoresorcinol in a solution of resorcinol 5×10^{-4} M and nitrite ions 10^{-3} M buffered at pH 7.2 and irradiated during 2 h at 365 nm

	Resorcinol transformed (10^{-5} M)	4-Nitrosoresorcinol formed (10^{-5} M)
air-saturated	8.1	6.1
deoxygenated	8.2	7.0
air-saturated + HCO_2^- (5×10^{-2} M)	4.6	2.3
deoxygenated + HCO_2^- (5×10^{-2} M)	≤1.0	0.3

of the transformation of pyrocatechol was evaluated at 5.6×10^{-3}.

The photochemical behaviour was also observed with higher concentrations of nitrite or in the presence of formate ions. When $NO_2^- = 5 \times 10^{-3}$ M the formation of 4-nitropyrocatechol is increased about 3.5 fold and that of hydroxybenzoquinone is reduced approximately in the same proportion. It was noted that the formation of hydroxybenzoquinone is completely inhibited by formate ions 5×10^{-2} M and it can be deduced that hydroxyl radicals are involved in this reaction. The formation of 4-nitropyrocatechol is partly inhibited.

Oxygen also has a large influence on the induced phototransformation of pyrocatechol. In deoxygenated solution the quantum yield is initially 3.0×10^{-3} i.e. about halved compared with air-saturated solution, the formation of hydroxybenzoquinone is completely inhibited and that of 4-nitropyrocatechol is reduced by about ten times. The absence of nitrosation in air-saturated solution cannot be attributed to the oxidation of an oxidable nitrosopyrocatechol since no nitrosoderivative was detected in deoxygenated solution. The absence of nitrosation is the main difference between the behaviours of pyrocatechol and resorcinol, with the fact that oxygen favours the nitration.

The absence of nitrosation was also noted with hydroquinone. When an aerated solution of hydroquinone and nitrite ions, in the same conditions of concentration and pH than for pyrocatechol, was irradiated at 365 nm the only photoproducts initially observed were benzoquinone and hydroxybenzoquinone with the same initial rates. Some nitrohydroquinone was also detected, but only after several hours of irradiation. The formation of benzoquinone and hydroxybenzoquinone is decreased by more than 5-fold in the absence of oxygen and completely inhibited by formate ions.

With hydroquinone, a special behaviour was noted in unbuffered deoxygenated solutions irradiated at 365 nm in the presence of nitrite ions, as it appears on Fig. 1. The UV bands located at 430, 403, 315 and 308 nm are characteristic of semiquinone anion. The formation of this intermediate is initially self-accelerated and then decreased. When the irradiation is stopped, the semiquinone anion may be observed for more than one hour. This result is explained by the following sequence: induced oxidation of hydroquinone into benzoquinone, increase of pH due to reactions (3) and (6) (this increase can reach several units in unbuffered solution), deprotonation of hydroquinone and reversible electron transfer between benzoquinone and the dianionic form of hydroquinone [25]

$$Q^{2-} + Q \rightleftharpoons 2Q^{\bullet -}$$

$$Q^{\bullet -} + H^+ \rightleftharpoons QH^{\bullet} \quad pKa = 4.0 \text{ [26]}$$

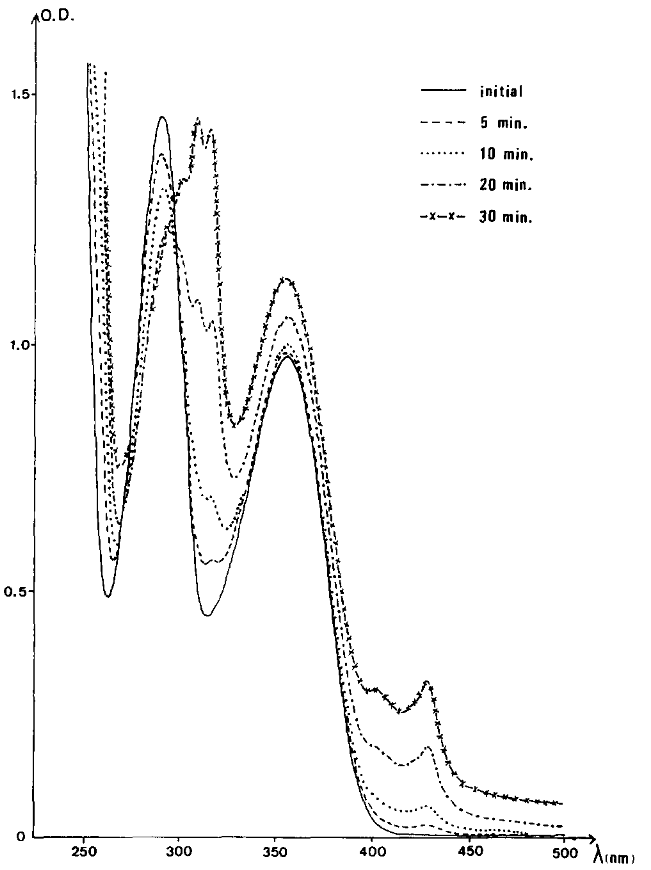


Fig. 1. Evolution of the UV spectrum of an unbuffered deoxygenated solution of hydroquinone 4×10^{-4} M and nitrite ions 10^{-2} M irradiated at 365 nm.

With nitrophenols it was previously shown that the excitation of nitrite ions does not induced any nitration or nitrosation [19]. The main reactions are *ortho* and *para* hydroxylations.

3.2. Reactions induced by nitrate ions

3.2.1. Phenol and resorcinol

The phototransformation of phenol induced by excitation of nitrate ions was related by Niessen et al. [7]. Photoproducts can be listed into three classes:

- oxidation: hydroquinone, pyrocatechol, resorcinol, benzoquinone, hydroxybenzoquinone
- nitration: 2-nitrophenol, 4-nitrophenol, 4-nitropyrocatechol
- nitrosation: 4-nitrosophenol

The oxidation was attributed to hydroxyl radicals, but nitration and nitrosation were also explained by radicals recombinations. Reactions of the same type were observed with resorcinol, but the mechanism proposed for nitration and nitrosation of phenol did not fit with the influence of oxygen and formate ions and it was suggested that these reactions involve nitrogen oxides $NO_2^{\bullet}$ and N_2O_4 [8]. The study of the induced transformation of phenol is presently completed for a better understanding of the reactions of nitration and nitrosation.

Air-saturated or degassed solutions of phenol 5×10^{-4} M or 10^{-4} M, were irradiated in monochromatic parallel beam at 313 nm in the presence of nitrate ions (4×10^{-3}–10^{-1} M), in order to selectively excite nitrate. The quantum yield of phenol transformation was 4.4×10^{-3} when phenol concentration was 5×10^{-4} M, and 3.5×10^{-3} with phenol 10^{-4} M whatever NO_3^- concentration. The concentration of nitrate does not affect the quantum yield. The influence of phenol concentration can be explained by its reaction with the short life intermediates generated in the photolysis of NO_3^-.

The kinetics of the main photoproducts formed in air-saturated solution irradiated in the range 300–340 nm are given in Fig. 2. Solutions were buffered at pH 5.5 (phosphates) in order to prevent the variation of pH during long irradiations.

Pyrocatechol accumulates better than hydroquinone. This can be related to the photo-oxidation of the latter which absorbs at longer wavelength than pyrocatechol. Formations of benzoquinone and hydroxybenzoquinone were not reported in Fig. 2 because they initially appear as minor photoproducts. 4-nitropyrocatechol, in contrast to 2-nitro- and 4-nitrophenol, has a typical kinetics of a secondary photoproduct. It is attributed to the nitration of pyrocatechol. The hydroxylation of 4-nitrophenol is most probably a minor pathway since the formation of nitrophenols is much slower than that of pyrocatechol and the hydroxylation of 2-nitrophenol was not observed. Moreover the initial formation of 4-nitropyrocatechol is more important than that of 4-nitrophenol. The influence of oxygen and formate ions appears in Table 3. The presence of oxygen does not significantly influence the oxidation, but inhibits nitration and nitrosation. It was observed that this inhibition is almost the same in oxygen saturated solution. Oxygen has thus a limited influence. Formate ions favour nitration in aerated solution but inhibit it in deoxygenated medium. Thus nitration cannot be attributed to a mechanism involving hydroxyl radicals, but can be explained by reactions of nitrogen dioxide, as it will be presented in Section 4.

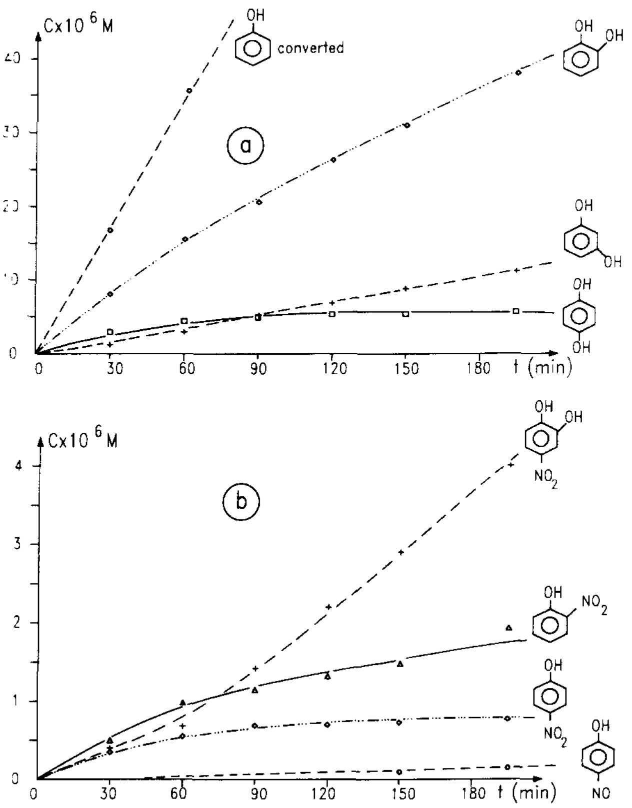


Fig. 2. Kinetics of formation of the main photoproducts formed in an air-saturated solution of phenol (5×10^{-4} M) and nitrate ions (5×10^{-2} M) buffered at pH 5.5 and irradiated in the range 300–340 nm. Photon flow absorbed in 10 ml $\simeq 43 \times 10^{15}$ photons s^{-1}. (a) Photoproducts of oxidaton; (b) Photoproducts of nitration and nitrosation.

It was also observed that nitration and nitrosation are favoured by decreasing pH. This influence cannot be attributed to nitrous acid formed in the photolysis of nitrate ions, since dark reaction of nitrous acid only leads to the formation of 4-nitrosophenol.

Resorcinol and phenol have similar behaviours, but the formation of 4-nitrosoresorcinol is, in all cases, higher than the formation of 4-nitroresorcinol and *ortho* nitration does not occur [8]. The quantum yield of the induced transformation is 2.8×10^{-3} with resorcinol 5×10^{-4} M and 1.0×10^{-3} with resorcinol 10^{-4} M. As it appears in Table 4 the ratio nitro/nitroso is not influenced by the presence of formate ions or oxygen. Deoxygenation and formate ions enhance both reactions, but formate ions have only a little influence in deoxygenated solution. No difference was observed between air-saturated and oxygen-saturated solutions.

As observed with phenol nitration and nitrosation are enhanced by decreasing pH.

3.2.2. *Pyrocatechol, hydroquinone*

The main photoproducts of transformation of pyrocatechol induced by excitation of nitrate ions are hydroxybenzoquinone and 4-nitropyrocatechol. No nitroso derivative was detected. The quantum yield was evaluated at 2.9×10^{-3} in unbuffered solution irradiated at 313 nm. Nitration is enhanced by deoxygenation and by formate ions in aerated solution, but reduced by formate in the absence of oxygen.

It is not possible to selectively excite nitrate ions in the presence of hydroquinone, because both absorb in the same range. The induced transformation can be pointed out by comparing the transformation rates for various concentrations of hydroquinone, but it was concluded that the direct transformation is much more efficient than the induced one.

Table 3
Influence of oxygen and formate ions (5×10^{-2} M) on the phototransformation of phenol (5×10^{-4} M) induced by excitation of nitrate ions (5×10^{-2} M) in the range 300–340 nm. Solution buffered at pH 5.5. Irradiation time 1 h. Values are given in μM. (N.D. = not detected)

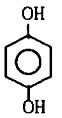
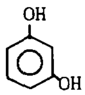
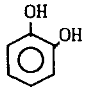
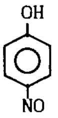
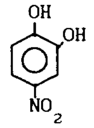
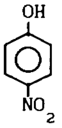
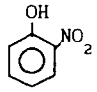
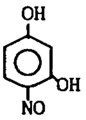
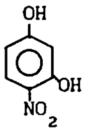
	Phenol transf.							
air-saturated	30	4.4	2.9	15.5	N.D.	0.68	0.55	0.98
air-sat. + HCO_2^-	≤5.0	0.60	N.D.	0.84	N.D.	N.D.	0.57	1.46
deoxygenated	34	3.2	3.2	15.6	0.14	1.6	2.05	4.5
deoxyg. + HCO_2^-	≤5.0	0.53	N.D.	0.62	N.D.	N.D.	0.60	1.36

Table 4
Influence of oxygen and formate ions on the formation of 4-nitro- and 4-nitrosoresorcinol in a solution of resorcinol (5×10^{-4} M) and nitrate ions (5×10^{-2} M) buffered at pH 6.5 and irradiated in the range 300–340 nm during 3.5 h. Values are given in μM

		
air or oxygen-saturated	7.8	2.8
air sat. + HCO_2^- (5×10^{-2} M)	24	10
deoxygenated	17	8.6
deoxygenated + HCO_2^- (5×10^{-2} M)	16	7.6

3.2.3. *Chlorophenols and nitrophenols*

It was previously observed that the excitation of nitrate ions in the presence of chlorophenols [27] or nitrophenols [19] induces *ortho* and *para* hydroxylations with respect to phenol function. No product of nitration or nitrosation was detected and it can be concluded that these reactions are unfavoured by electron-withdrawing substituents.

4. Mechanisms and general discussion

Most often the first step in the oxidation can be attributed to the reaction of hydroxyl radical. According to the conditions (oxygen concentration, oxidability of radicals formed) the second step may be dimerisation, disproportionation or oxidation by oxygen. The aim of the present work is mainly to explain nitration and nitrosation. They result from electrophilic reactions unfavoured by electron-withdrawing substituents. The formation of nitro- and nitrosophenols cannot be attributed to a reaction of $NO^{\bullet}$ or $NO_2^{\bullet}$ with phenoxyl radical resulting from the oxidation of phenolic compounds by hydroxyl radicals, since nitration and nitrosation occur when hydroxyl radicals are quenched by NO_2^- or HCO_2^-. Both nitration and nitrosation are enhanced by increasing concentration of NO_2^- and, with NO_3^- in aerated solution, by the presence of HCO_2^-. Nitrous acid is involved only in acidic solutions and does not induce the nitration of phenol and resorcinol. Nitration and nitrosation can be related to the presence of nitrogen dioxide in the solution. Nitrosation of phenol and resorcinol by exciting NO_2^- does not occur when $NO_2^{\bullet}$ is not formed (deoxygenated solution with $^{\bullet}OH$ quencher). It can be a result of N_2O_3 according to the following scheme:

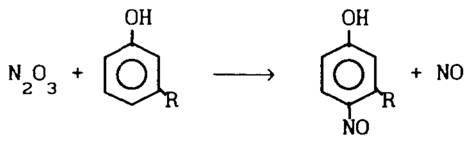
$$NO_2^{-*} \longrightarrow NO^{\bullet} + O^{\bullet -} \qquad (4)$$

$$O^{\bullet -} + H_2O \longrightarrow {}^{\bullet}OH + OH^- \qquad (3)$$

$${}^{\bullet}OH + NO_2^- \longrightarrow NO_2^{\bullet} + OH^- \qquad (6)$$

$$NO_2^{\bullet} + NO^{\bullet} \longrightarrow N_2O_3 \qquad (8)$$

$k_8 = 1.1\times10^9$ M^{-1} s^{-1} [28]



(9)

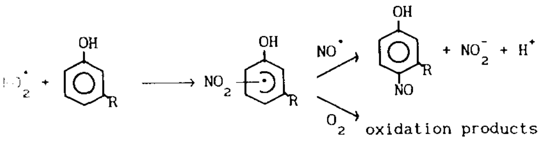
R = H or OH

$$N_2O_3 + H_2O \longrightarrow 2NO_2^- + 2H^+ \qquad (10)$$

$k_{10} = 530$ s^{-1} [28] or 68 s^{-1} [29]

The ratio nitrosation/oxidation increases with increasing concentration of nitrite because of reaction (6). The inhibiting effect of formate ions is attributed to the quenching of hydroxyl radicals which competes with reaction (6). In aerated solution $NO_2^{\bullet}$ can nevertheless be formed by oxidation of $NO^{\bullet}$. Nitrosation was not observed with pyrocatechol and hydroquinone, and nitration of pyrocatechol is favoured by oxygen. It may be assumed that N_2O_3 does not react with these substrates in the absence of oxygen.

But this mechanism of nitrosation is not consistent with the inhibiting effect of oxygen on the formation of 4-nitrosophenol and 4-nitrosoresorcinol. So an alternative pathway is suggested:



Similar mechanisms are suggested to explain reactions induced by exciting nitrate ions. It is a little more complex since both nitration and nitrosation occur with phenol and resorcinol. Two competitive pathways are also necessary to explain the oxygen effect.

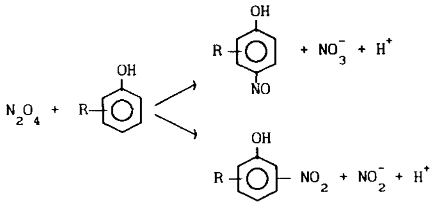
$$NO_3^{-}{}^* \longrightarrow NO_2^\bullet + O^{\bullet-} \quad (1)$$

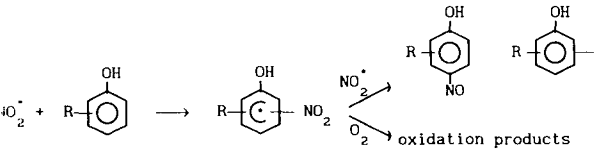
$$2NO_2^\bullet \longrightarrow N_2O_4 \quad (11)$$

$k_{11} = 4.5 \times 10^8$ M^{-1} s^{-1} [30]

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

$k_{12} = 10^3$ s^{-1} [30]





The latter sequence does not explain the limited influence of oxygen when the concentration is increased from 2.6×10^{-4} M (air-saturated solutions) to 1.2×10^{-3} M (oxygen saturation). It can be concluded that both molecular and radical mechanisms are involved.

With pyrocatechol and hydroquinone the formation of nitroso does not occur.

The enhancing effect of H^+ on nitration and nitrosation cannot be explained only by the formation of nitrous acid. It seems likely that the protonation of N_2O_4 favours its electrophilic reaction with the phenolic ring.

Formate ions enhance nitration and nitrosation induced by nitrate ions in the presence of oxygen because they inhibit the recombination $NO_2^\bullet + {}^\bullet OH \rightarrow NO_2^- + H^+$. In deoxygenated solution the inhibition of nitration and nitrosation is tentatively explained by the oxidation of the intermediate radical anion $CO_2^{\bullet-}$ by $NO_2^\bullet$ whereas in aerated solution this species is oxidized by oxygen:

$$HCO_2^- + {}^\bullet OH \longrightarrow CO_2^{\bullet-} + H_2O \quad (7)$$

$$CO_2^{\bullet-} + NO_2^\bullet \longrightarrow CO_2 + NO_2^-$$

$$CO_2^{\bullet-} + O_2 \longrightarrow CO_2 + O_2^{\bullet-}$$

5. Conclusions

The excitation of nitrite or nitrate ions may induce oxidation, nitration or nitrosation on phenolic derivatives. Oxidation occurs in all cases whereas nitration and nitrosation are inhibited by electron-withdrawing substituents.

Nitrosation is not observed with pyrocatechol and hydroquinone. With phenol and resorcinol, nitrosation is the main reaction induced by exciting nitrite ions when the concentration of the latter is rather high ($\approx 5 \times 10^{-2}$ M), but it decreases with decreasing concentration. This reaction is due to nitrogen oxides $NO_2^\bullet$ or N_2O_3 formed in the photolysis of nitrite ions. In the presence of oxygen, the excitation of nitrite ions induces nitration of pyrocatechol. This reaction is reduced ten-fold in the absence of oxygen.

The excitation of nitrate ions induces nitrosation and nitration of phenol and resorcinol. The quantum yield of the induced transformation of substrate does not depend on nitrate concentration; its order of magnitude is 10^{-3} for [phenol] = 10^{-4} M. These reactions result from $NO_2^\bullet$ and N_2O_4. They compete with the hydrolysis of the latter. Nitration and nitrosation are favoured by decreasing pH.

In environmental conditions the concentration of nitrite is generally too low to induce nitrosation. The main reaction induced by nitrite excitation is oxidation. With nitrate ions the orientation depends on the concentration of phenolic substrate. Nitration and nitrosation might be involved if the concentration is high enough to compete the hydrolysis of N_2O_4.

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