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Nitrate Induced Photooxidation of Phenol and *o*-Substituted Phenolic Compounds in Aqueous Solution

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The excitation of nitrate ions at 313 nm in the presence of phenol, 2-chlorophenol or 2-methylphenol in aqueous solution produced a complex mixture of compounds. The photoproducts were identified by LC-MS. Nitration, hydroxylation and coupling reactions were found to be the principal chemical processes. Cl/OH, CH_3/OH substituted and hydroxylated phenolic derivatives are formed in very small amount. In contrast with phenol, no nitroso derivative was detected by 2-chlorophenol and 2-methylphenol under the same reaction conditions. Both nitrosation and nitration are attributed to reactions of nitrogen oxides $NO_2^{\bullet}$ and N_2O_4. Nitration and nitrosation are favoured in acidic medium. Kinetic studies were compared by varying environmental parameters including substrate and NO_3^- concentrations, oxygen content, pH and ethanol. The influence of substituted phenols is investigated by comparing their initial rates of degradation. Degradation pathways involving $^{\bullet}OH$ and $NO_2^{\bullet}$ radicals as reactive species are proposed.

Key Words: Hydroxylation, Nitration, Nitrosation, Phenol, 2-Chlorophenol, 2-Methylphenol.

INTRODUCTION

Aromatic compounds such as phenol, chlorophenol and methylated phenols represent an important class of common water pollutants. They are used for making a variety of specific chemicals, such as fungicides, herbicides, antioxidants, phenols developer, adhesives and wood preservatives[1]. It has been recognized that $^{\bullet}OH$ plays an important role in the degradation of organic compounds in natural water[2,3]. There are many sources of $^{\bullet}OH$ photoformation in natural waters, such as the photolysis of nitrate ions (NO_3^-), nitrite (HNO_2 and NO_3^-)[4,5], hydrogen peroxide (H_2O_2)[6] and dissolved organic matter[7,8] and the photo-Fenton reaction[9,10].

Nitrate ions are usually present in natural waters at concentration depending on geographic location and agricultural activities (classically 10^{-5}-10^{-3} M range)[11]. These ions absorb light at λ_{max} 302 nm ($\varepsilon = 7.2$ M^{-1} cm^{-1}). Irradiation of nitrate ions in aquatic environment follows two major pathways (eqns. 1 and 2) Zepp *et al.* [4] and Warneck and Wurzinger[12].

$$NO_3^- + h\nu \longrightarrow NO_2^\bullet + O^{\bullet-} \tag{1}$$

$$NO_3^- + h\nu \longrightarrow NO_2^- + O\,(^3p) \tag{2}$$

$$O^{\bullet-} + H^+ \rightleftharpoons {}^\bullet OH \qquad pK_{\cdot OH} = 11.9 \tag{3}$$

$$NO_2^\bullet + NO_2^\bullet \longrightarrow N_2O_4 \qquad k = 4.5 \times 10^8\ M^{-1}\ s^{-1} \tag{4}$$

$${}^\bullet OH + NO_2^- \longrightarrow NO_2^\bullet + OH^- \qquad k = 1.0 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5}$$

$${}^\bullet OH + NO_2^\bullet \longrightarrow HOONO \qquad k = 1.3 \times 10^9\ M^{-1}\ s^{-1} \tag{6}$$

$$O\,(^3p) + NO_3^- \longrightarrow NO_2^- + O_2 \tag{7}$$

$$NO_2^- + h\nu \longrightarrow NO^\bullet + O^{\bullet-} \tag{8}$$

$$NO_2^\bullet + NO^\bullet \longrightarrow N_2O_3 \qquad k = 1.1 \times 10^9\ M^{-1}\ s^{-1} \tag{9}$$

$$N_2O_3 + H_2O \longrightarrow 2NO_2^- + 2H^+ \qquad k = 5.3 \times 10^2\ s^{-1} \tag{10}$$

$O^{\bullet-}$ is rapidly protonated to its conjugate acid, the hydroxyl radical (eqn. 3) a potent oxidant that reacts much more rapidly with most organic chemicals than atomic oxygen O (^{3}p)[4]. The reactive $^\bullet$OH can perform oxidation of dissolved organic molecules or undergo self quenching with NO_2^- (eqn. 5). $NO_2^\bullet$ can achieve (i) nitration of dissolved organics due to $NO_2^\bullet$ or N_2O_4 form issuing from (eqn. 4) or (ii) quenching of $^\bullet$OH (eqn. 5) especially in the absence of dissolved organics[12].

Nitrate ion is a source of hydroxyl radical. The quantum yields of the formation rate of hydroxyl radicals in pH range 6.2-8.2 were evaluated by Zepp *et al.*[4]; $\phi(OH^\bullet) = (13 \pm 2) \times 10^{-3}$ and $\phi(OH^\bullet) = (17 \pm 3) \times 10^{-3}$ at 20 °C and 30 °C, respectively and the results obtained by Zellner *et al.*[6] are in good agreement with those of Zepp *et al.*[4]. The quantum yield of formation of hydroxyl radicals increases with decreasing wavelength from 0.015 ± 0.005 at *ca.* 370 nm[13] to 0.11 ± 0.01 at 254 nm[14]. In acidic medium the quantum yield of nitrous acid dissociation is much higher and it is wavelength independent ($\phi = 0.45 \pm 0.1$)[14].

It is now well established that the excitation of nitrate ions in the presence of phenolic derivatives leads to several types of reactions *viz.*, oxidation, nitration and nitrosation. There ratio depending on the pH[15], but nitration or nitrosation may also occur[16]. Possible formation of highly mutagenic/carcinogenic nitrocompounds[17] is unquestionably of great environmental interest. Furthermore, the obtained photoproducts were found sometimes even more toxic than the parent compound[18,19]. On the other hand, it has been reported that bicarbonate (HCO_3^-) and chloride (Cl^-) ions, are common ionic species in water and have high reaction rate constants with $^\bullet$OH, act as $^\bullet$OH scavengers[20,21]. It is expected that natural waters contain many other $^\bullet$OH scavengers in addition to these.

The objective of the present study was to identify the photoproducts resulting from the excitation of nitrate ions in the presence of phenol, 2-chlorophenol and 2-methylphenol. The influence of substituted phenols is investigated by comparing their initial rates of degradation. Kinetic studies were carried out in detail to explore its reactivity and the effects of environmental parameters including substrate and oxygen content, pH, ethanol and NO_3^- concentrations. The mechanisms of this reaction are proposed.

EXPERIMENTAL

Phenol, 2-chlorophenol and 2-methylphenol of high grade were purchased from Fluka (> 98 %). Reference compounds used for HPLC analysis were provided by Merck except chlorobenzoquinone was synthesized in our laboratory according to the method of Bruce and Chaudry[22] and 3-chlorocatechol was obtained by chlorination of catechol by sulphuryl chloride[23]. Their structures were controlled by 400 MHz NMR.

Photochemical reactor: Several devices were used to study the photochemical transformations. Solutions containing nitrate ions were irradiated at 313 nm (Duke Sun Lamp GL 20 W). The lamp being located along one focal axis and the reactor in Pyrex along the other. A device in which the reactor was surrounded by 3 fluorescent lamps in a cylindrical mirror was used to study the transformation of substrates. For determination of quantum yields, solutions were irradiated in monochromatic parallel beam at 313 nm. The photon flow was evaluated using potassium ferrioxalate as actinometer as 0.32 1015 photon cm^{-2} s^{-1}.

Analyses: UV spectra were recorded on Secomam 1000 PC. High performance liquid chromatography (HPLC) analyses were carried out on a waters chromatograph equipped with a detector model LC Spectrometer Lambda-Max 481 and a reverse phase m BONDAPAC C_{18} (250 mm × 4.6 mm) column. A mixture $MeOH/H_2O$ 30/70 (v/v) was used as the eluent. For GC-MS analyses the solutions were extracted with ether and injected in a capillary column FS SE 30 length 25 m, internal diameter 0.25 mm. The spectrometer was Nermag service 32 equipped with FID detection.

RESULTS AND DISCUSSION

Photodegradation kinetics of phenol 2-chlorophenol and 2-methylphenol induced by nitrate ions: The absorption spectra of nitrate (NO_3^-) ions in aqueous solutions contain weak $n \rightarrow \pi^*$ bands λ_{max} (NO_3^-) 302 nm). Phenol, 2-chlorophenol and 2-methylphenol confirmed to be reasonably photostable in aqueous solution under irradiation in the 300-400 nm wavelength range. The absorption spectra of nitrate and three organic aromatic compounds (phenol, 2-chlorophenol and 2-methylphenol) measured in aqueous solutions are compared in Fig. 1. Phenol, 2-chlorophenol and 2-methylphenol absorb strongly below 300 nm, while nitrate have stronger absorption also above this wavelength. Under irradiation at 313 nm, direct photolysis of phenol, 2-chlorophenol and 2-methylphenol is negligible.

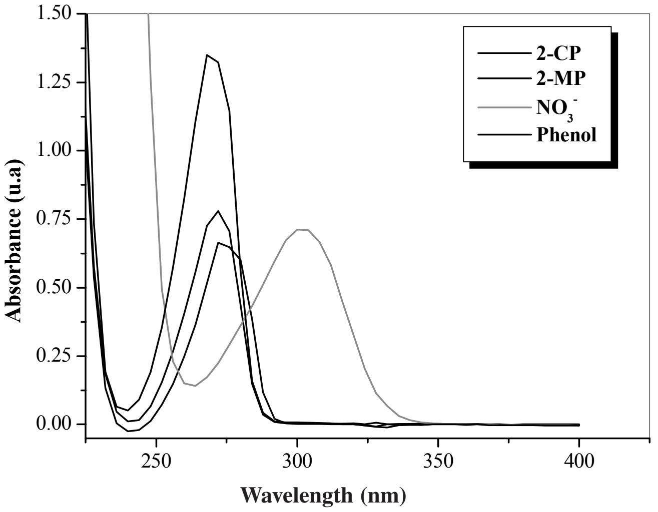
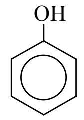
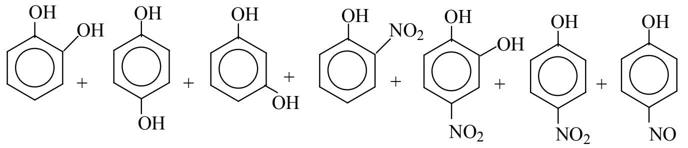


Fig. 1. Absorption spectra of potassium nitrate, phenol, 2-chlorophenol and 2-methylphenol in aqueous solution

Phenol: The phototransformation of phenol induced by excitation of nitrate ions was related by Niessen *et al.*[15] and was completed for better understanding of the mechanism involved by Machado *et al.*[24] and Matykiewiczová *et al.*[25].

When an aerated solution of phenol (5×10^{-4} M) and potassium nitrate (2×10^{-2} M) was irradiated at 313 nm, a mixture of products was formed. Pyrocatechol was the main aromatic intermediate, hydroquinone and resorcinol appeared as minor primary products. 2-Nitrophenol, 4-nitrophenol, 4-nitrosophenol and 3-nitropyrocatechol were also detected. 3-nitropyrocatechol results from the nitration of pyrocatechol initially formed. These results are in good agreement with analytical results given in the literature[15,24,26]. The photonitration process displayed an apparent regioselectivity, only the *ortho* and *para* isomers were produced. The nature and results of intermediates are summarized in Table-1.

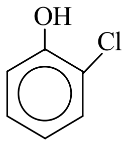
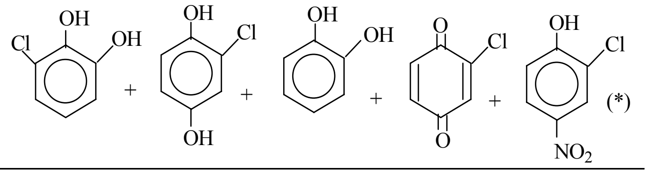
TABLE-1
PHOTOPRODUCTS OBTAINED BY IRRADIATION 12 h AT 313 nm AN AIR-SATURED SOLUTION OF PHENOL (5×10^{-4} M) AND POTASSIUM NITRATE (2×10^{-2} M) pH = 6.5

Reactant	Intermediate products
	

2-Chlorophenol: Table-2 lists the photoproducts obtained by irradiation of aerated aqueous solutions of 2-chlorophenol (5×10^{-4} M) and nitrate ions (2×10^{-2} M). The main products are 3-chloropyrocatechol and chlorohydroquinone. Only trace of pyrocatechol was detected. Chlorobenzoquinone was also identified as a secondary intermediate species.

Practically no nitrated or nitrosated photoproducts were identified. Only addition of acetic acid triggered the photoinduced formation of 4-nitro-2-chlorophenol was detected in traces.

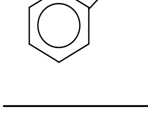
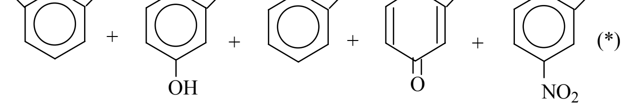
TABLE-2
PHOTOPRODUCTS OBTAINED BY IRRADIATION 12 h AT 313 nm AN AIR-SATURED SOLUTION OF 2-CHLOROPHENOL (5×10^{-4} M) AND POTASSIUM NITRATE (2×10^{-2} M) pH = 5.5

Reactant	Intermediate products
	

(*) Acidic medium pH = 4

2-Methylphenol: When nitrate ions are excited in the presence of 2-methyl phenol, it can be noted that products of hydroxylation are observed. In this condition the main photoproduct is 3-methylpyrocatechol, only traces of pyrocatechol and methylhydroquinone were detected. Methylbenzoquinone appears as a secondary product. Most often *ortho* and *para* hydroxylation with respect to phenolic group are observed. The primary products observed may be explained by a radical mechanism involving hydroxyl radicals. In contrast with phenol, no nitrated and nitrosoted derivatives were detected. 4-Nitro-2-methylphenol appear in acidic medium. The same phenomenon was observed with 2-chlorophenol. The nature and results of intermediates are summarized in Table-3.

TABLE-3
PHOTOPRODUCTS OBTAINED BY IRRADIATION 12 h AT 313 nm AN AIR-SATURED SOLUTION OF 2-METHYLPHENOL (5×10^{-4} M) AND POTASSIUM NITRATE (2×10^{-2} M) pH = 6.8

Reactant	Intermediate products
	

(*) Acidic medium pH = 4

Influence of oxygen, pH, concentration of nitrate ions, of the substituents and ethanol

Effect of oxygen concentration: The influence of the concentration of molecular O_2 on the transformation of phenol was studied by comparing the kinetics of transformation in different conditions. Experiments were conducted at phenol (5×10^{-4} M) and nitrate (2×10^{-2} M) by varying oxygen content in the solution using nitrogen, air or oxygen as purging gas. The transformation of phenol is about faster in the air saturated than in solution degassed. The decrease of the degradation rate in the presence of N_2 only might indicate that O_2 is involved in some extent in the induced phototransformation process. On the other side, the stabilization of k' when replacing air by oxygen might be due to a non necessary excess of O_2. As for NO_3^- induced photodegradation, the observed pseudo-kinetic constants do not differ between air and oxygen conditions. Oxygen has no influence on this process. Similar result was obtained with 2-chlorophenol and 2-methyl phenol. The kinetics pseudo-constants (k') are summarised in Table-4.

TABLE-4
KINETIC PSEUDO-CONSTANTS (k′) OF PHENOL, 2-CHLOROPHENOL AND 2-METHYLPHENOL (5×10^{-4} M) DEGRADATION PHOTO-INDUCED BY NO_3^- IONS (2×10^{-2} M)

Compound	Kinetic pseudo-constants (k′) (10^{-4} min^{-1})		
	Nitrogen	Air	Oxygen
Phenol	4.8	6.2	6.4
2-Chlorophenol	7.2	8.7	8.8
2-Methylphenol	8.2	9.8	10.2

pH: The influence of pH on nitrate induced photodegradation was studied in the pH range 4-8 using 2×10^{-2} M NO_3^- solutions. The pseudo-kinetic constants increased when the solution of phenol, 2-chlorophenol or 2-methylphenol was acidified at pH 4.0, Table-5.

TABLE-5
KINETIC PSEUDO-CONSTANTS (k′) OF PHENOL, 2-CHLOROPHENOL AND 2- METHYLPHENOL ($C_0 = 5 \times 10^{-4}$ M) DEGRADATION PHOTO-INDUCED BY NO_3^- IONS (2×10^{-2}M) AT VARIOUS pH VALUES

Compound	Kinetic pseudo-constants (k′) (10^{-4} min^{-1})			
	pH unbuffered	pH = 4	pH = 6	pH = 8
Phenol	6.2	10.4	6.0	4.3
2-Chlorophenol	8.7	12.2	7.6	6.2
2-Methylphenol	9.8	14.0	10.6	7.2

pH = 4 buffered with phthalate; pH = 6 buffered with phosphate; pH = 8 buffered with borate.

The rate of nitration is higher in acidic solution than neutral medium. This phenomenon can be attributed to a nitration by HNO_2 (pKa = 3.4).

$$HNO_2 + h\nu \longrightarrow {}^{\bullet}OH + NO^{\bullet}\ [\phi = 0.35\text{-}0.45]^{6,26,27}$$

In acidic solution, the formation of 4-nitrosophenol may be attributed to a reaction between HNO_2 and phenol. HNO_2 can also nitrate phenol in the dark[26] in the presence of which oxidation and nitration processes of aromatic compounds can take place[27]. The UV irradiation of nitrous acid causes photolysis, generating ${}^{\bullet}OH$ and $NO^{\bullet}$ with average quantum yield near 0.4 in the wavelength range 280-385 nm[6,9,28,29].

It was observed that nitration and nitrosation are favoured by decreasing pH. This influence can be attributed to nitrous acid formed in the photolysis of nitrate ions. A very interesting aspect of phenol nitration upon nitrate photolysis is the pH trend in the acidic range. Many authors agree that the formation of 2- and - 4-nitrophenol is favoured by decreasing pH[24,26,30].

Effect of nitrate ion concentration: To evaluate the influence of the nitrate ion concentration on the kinetics, experiments were conducted at $[NO_3^-]$ varying from 5×10^{-4} M to 2×10^{-2} M (Table-6). At the lower concentration values *e.g.*, 0.5×10^{-3} M, over 10 % degradation was reached within 12 h irradiation even for 5×10^{-4} M of phenol. In these conditions, the degradation rate still increased but with less intensity. However, proportionality was not noticed in the 0.5×10^{-3} M to 20×10^{-3} M $[NO_3^-]$ range for the 5×10^{-4} M concentration of phenol, 2-chlorophenol and 2-methylphenol. Considering the effect of $[NO_3^-]$ in all these experiments, the OH radicals constitute the main active species generated after irradiation. When NO_3^- concentration was increased from 5×10^{-3} M to 2×10^{-2} M, the relative yields of dihydroxybenzenes increased to some extent, which is in accord with the observation that phenol efficiently competes with nitrite eqn. 2 for reaction with ${}^{\bullet}OH$ eqn. 5, lowering thus the yield[31] of $NO_2^{\bullet}$. The production of

TABLE-6
KINETIC PSEUDO-CONSTANTS (k′) AND DEGRADATION RATES ($k'C_0$) OF PHENOLIC COMPOUNDS [5×10^{-4} M] DEGRADATION PHOTO-INDUCED BY NO_3^- IONS

NO_3^- (10^{-3} M)	Kinetic pseudo-constants (k′) (10^{-4} min^{-1})			Degradation rates ($k'C_0$) (10^{-7} M min^{-1})		
	Phenol	2-Chloro phenol	2-Methyl phenol	Phenol	2-Chloro phenol	2-Methyl phenol
0.5	0.86	1.2	1.6	0.43	0.6	0.8
1.0	4.2	5.2	5.8	2.1	2.6	2.9
5.0	4.6	5.8	6.4	2.3	2.9	3.2
10	5.8	8.2	8.9	2.9	4.1	4.4
20	6.6	8.6	9.3	3.3	4.3	4.7

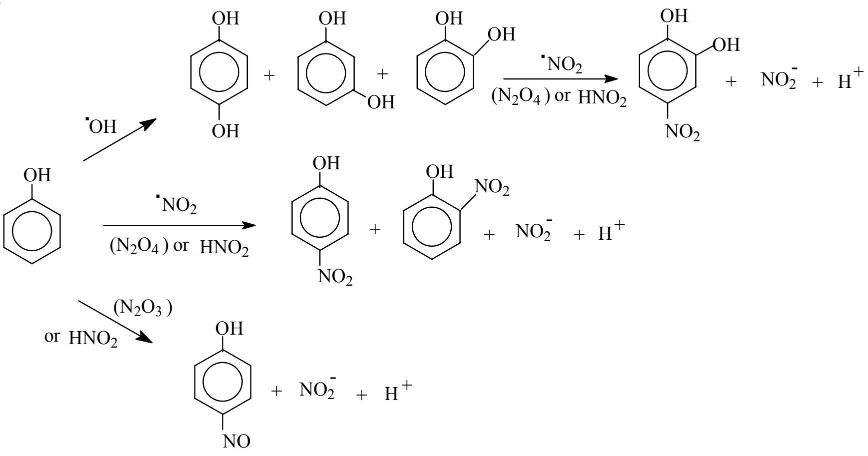
a small amount of nitrite from nitrate was observed at the same time, which is in accord with the previous findings[32-35]. At higher NO_3^- concentrations 2×10^{-2} M, the nitrated derivatives of phenol was found to be increased. We observed a progressive but low accumulation of nitrated derivatives (2-nitrophenol and 4-nitrophenol) when operating with phenol 5×10^{-4} M and $[NO_3^-]$ 2×10^{-2} M as starting conditions. After 12 h irradiation yielding 28 % phenol degradation.

Influence of the substituents on degradability: The influence of the substituent nature on the photodegradation of substituted phenols is investigated by comparing their initial rates of degradation (k'C$_0$), which is the decay of the phenolic compound concentration after 12 h of the photoreaction. In the various experiments carried out, the initial concentration in phenolic compound $[C_0] = 5 \times 10^{-4}$ M and the concentration of $[NO_3^-] = 2 \times 10^{-2}$ M, the Table-7 presents the initial degradation rates for these substituted phenols. These values are calculated and compared to the phenol, which is regarded as a reference compound. The photo-induced degradation of substituted phenols in the presence of NO_3^- follows a kinetics, showing rate constants that decrease in the order: 2-methylphenol > 2-chlorophenol > phenol.

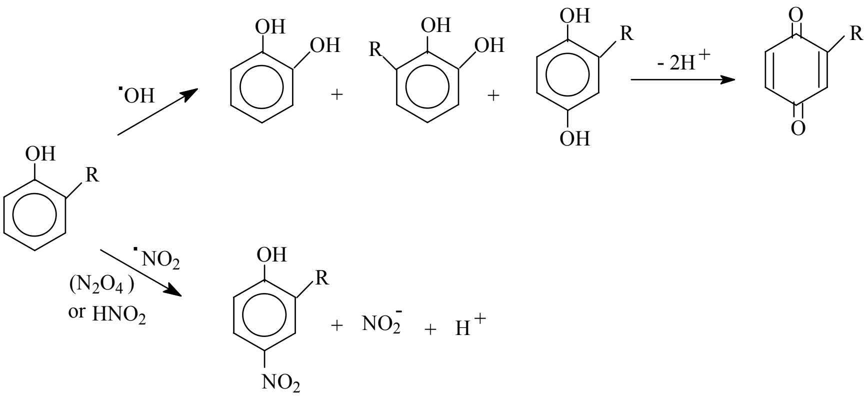
TABLE-7
KINETIC PSEUDO-CONSTANTS (k′) AND DEGRADATION RATES (k′C$_0$) OF PHENOLIC COMPOUNDS [5×10^{-4} M] DEGRADATION PHOTO-INDUCED BY NO_3^- IONS (2×10^{-2} M)

Kinetic pseudo-constants (k′) (10^{-4} min^{-1})			Degradation rates (k′C$_0$) (10^{-7} M min^{-1})		
Phenol	2-Chloro phenol	2-Methyl phenol	Phenol	2-Chloro phenol	2-Methyl phenol
6.6	8.6	9.3	3.3	4.3	4.7

Influence of ethanol: In order to determine if hydroxyl radicals are involved in the formation of hydroxyphenols, solution of phenol was irradiated in the presence of ethanol 2 % vol used as an $^{\bullet}$OH quencher. It can be noted that the formation of hydroxylated photoproducts was completely inhibited whereas the formation of nitration photoproducts was none affected. When a solution of phenol (5×10^{-4} M), potassium nitrate (2×10^{-2} M) and ethanol 2 % vol was irradiated at 313 nm in the pH 6.5, the formation of pyrocatechol, hydroquinone and resorcinol, are completely inhibited by ethanol as can be expected from an $^{\bullet}$OH-initiated pathway. On the contrary, a limited effect of ethanol on phenol nitration can be observed. This result indicates that, in the presence of alcohol, the formation of 2-nitrophenol, 4-nitrophenol, 4-nitrosophenol and 3-nitropyrocatechol are not mediated by $^{\bullet}$OH. The involvement of $^{\bullet}$OH is proved by the substantial inhibition of phenol degradation on addition of 2 % vol of ethanol as $^{\bullet}$OH scavenger.



R = Cl = CH$_3$



When nitrate ions are excited in the presence of phenolic derivatives, oxidation is the main pathway whatever the substitute on the ring. Most often *ortho* and *para* hydroxylation with respect to phenolic group are observed. The primary products observed may be explained by a radical mechanism involving hydroxyl radicals. Most likely the first step of the reaction is the formation of an intermediate adducts $^{\bullet}$OH...phenol as it has been observed with phenol[36-38], nitrophenols[14] and chlorophenols[39]. This adduct is transformed into substituted phenoxyl radical by eliminate ion of water[15]. The formation of pyrocatechol is higher with phenol which appear a minor primary photoproduct by 2-chlorophenol and 2-methylphenol. Substitution of chlorine by OH and methyl by OH are formed minorily. The formation of nitroso and nitro derivatives are observed with phenol. Nitration is located in *ortho* or *para* positions but nitrosation is only observed in *para* of OH with phenol. The formation of 4-nitro-2-methyl phenol from 2-methylphenol and of 4-nitro-2-chlorophenol from 2-chlorophenol is a consequence of the reaction of substrate in acidic pH with nitrogen dioxide ($NO_2^{\bullet}/N_2O_4$).

The formation of 4-nitrosophenol most likely takes place upon reaction between phenol and N_2O_3[15,24,26,40,41]. The influence of pH on the rate of nitration can be attributed to nitration by nitrous acid, but another explanation can be suggested with phenol both nitration and nitrosation are favoured by an acidic medium, whereas HNO_2 yields nitrosophenol as the main product[15]. Thus it can be assumed that H^+ enhances the reaction of $NO_2^{\bullet}$ or N_2O_4 with the phenolic ring.

Conclusion

In conclusion, it was found that the photolysis of the aqueous solutions of aromatic compounds in presence of nitrate produced a complex mixture of compounds. Nitration, hydroxylation and coupling reactions were found to be the principal chemical processes. The primary photoproducts were identified at low reaction conversions.

The formation of hydroxylated photoproducts was completely inhibited by ethanol 2 % vol used as an $^{\bullet}OH$ quencher. The presence of the OH group of phenols played an important role in the course of hydroxylation and nitration reactions. From the point of view of mechanisms, a comparison between the nitration processes of phenol and 2-chlorophenol and 2-methyl phenol under similar conditions is now possible. 2-Chlorophenol and 2-methylphenol behaves differently from phenol as they are nitrated in acidic solution and they are nitration are not inhibited by ethanol and by absence of oxygen. A very interesting aspect of 2-chlorophenol and 2-methylphenol nitration upon nitrate photolysis are the pH trend in the acidic range, the formation of 4-nitro-2-methylphenol from 2-methylphenol and of 4-nitro-2-chlorophenol from 2-chlorophenol is favoured by decreasing pH. The photo-induced degradation of the different organics in the presence of NO_3^- follows a kinetics, showing rate constants that decrease in the order: 2-methylphenol > 2-chlorophenol > phenol.

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