Phototransformation of resorcinol induced by excitation of nitrite and nitrate ions. II: Nitrate ions

F. Machado [a] & P. Boule [a]

[a] Laboratoire de Photochimie Moléculaire et Macromoléculaire , URA CNRS , 433 Université Blaise Pascal (Clermont-Ferrand), Aubière Cedex, 63177, France
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PHOTOTRANSFORMATION OF RESORCINOL INDUCED BY EXCITATION OF NITRITE AND NITRATE IONS. II: NITRATE IONS

F. MACHADO and P. BOULE

Laboratoire de Photochimie Moléculaire et Macromoléculaire URA CNRS
433 Université Blaise Pascal (Clermont-Ferrand) 63177 Aubière Cedex, France

The excitation of nitrate ions in an aqueous solution of resorcinol (I) at pH = 5.5–6.5, leads to a mixture of 1,2,3-trihydroxybenzene (II), 1,2,4-trihydroxybenzene (III), 4-nitrosoresorcinol (V) and 4-nitroresorcinol (VII). A secondary formation of 2,4-dinitrosoresorcinol (VI) was also detected.

Products II and III result from hydroxylation of I by hydroxyl radicals formed in the photolysis of NO_3^-. . Product III does not accumulate in the solution.

The formations of products V and VII do not involve hydroxyl radicals but result from dark reactions of I with nitrogen oxides (NO_2^- or N_2O_4) formed in the solution. Their formation is favoured in acidic medium. At pH = 3.1 they correspond to more than 50% of resorcinol transformed. In unbuffered solution the initial formation of V is lower than the formations of II and III but its formation rate increases with irradiation time.

KEY WORDS: Photoreactions, phenolic compounds, resorcinol, nitrate ions

1 INTRODUCTION

Nitrate ions are often present in natural waters; their concentration was evaluated to be c.a. 10 μM^1 in sea water. The maximum of the UV absorption band is located at 302 nm (molar extinction coefficient = 7.2 M^{-1} cm^{-1}). The excitation of nitrate ions leads either to atomic oxygen or to hydroxyl radicals according to the two following pathways[2–5]:

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

$$NO_3^-{}^* \longrightarrow NO_2^- + O^{\cdot-} \quad 2$$

$$O^{\cdot-} + H^+ \longrightarrow {}^{\cdot}OH \quad 3$$
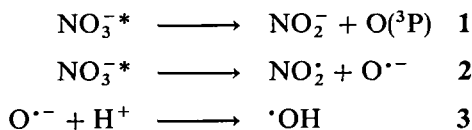
$$\text{pKa of } {}^{\cdot}OH = 11.9^6$$

The quantum yields of both photodissociations were evaluated by Warneck and Wurzinger[5].

$$\Phi_{OH} = (9.2 \pm 0.4) \times 10^{-3} \qquad \Phi_O = (1.1 \pm 0.4) \times 10^{-3}$$

More recently Zepp et al.[7] obtained values somewhat higher for the formation rate of hydroxyl radicals in pH range 6.2–8.2:

$$\Phi_{OH}(20°C) = (13 \pm 2) \times 10^{-3} \qquad \Phi_{OH}(30°C) = (17 \pm 3) \times 10^{-3}$$

which are in very good agreement with the results of Zellner et al.[8]. Hydroxyl radicals are more reactive than $O(^3P)$ both in the gas phase[9] and in aqueous solution[10] and the observed reactions are generally attributed to hydroxyl radicals. Nitrate ions are often considered as one of the main sources of hydroxyl radicals in natural waters and they have some useful influence in the photodegradation of organic pollutants. But nitrate ions can also induce the formation of nitro [11–13] or nitroso[13] derivatives with phenolic compounds. So it is important to determine what are the parameters which influence the orientation of the reaction. Resorcinol was chosen as the substrate to study the mechanisms of the reactions because this compound is largely used in the industrial field, and its induced phototransformation involves several pathways. The reactions induced by excitation of nitrite ions has been described in the first part of this work; they are involved as secondary reactions when the phototransformation is induced by excitation of nitrate ions. In the presence of nitrite ions most of the hydroxyl radicals formed react with NO_2^-, whereas when ˙OH are produced from NO_3^- they mainly react with the substrate.

The aim of the present work is to analyse the products of the phototransformation induced by excitation of nitrate ions, to compare the ratios of the various pathways and to study the mechanism of the observed reactions.

2 NOTATIONS
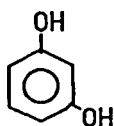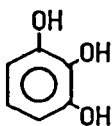
I   II   III   IV

V   VI   VII

3 EXPERIMENTAL DETAILS

3.1 Chemicals

Resorcinol (I) was provided by Merck ($>99\%$) and used without further purification.

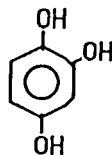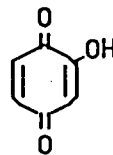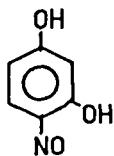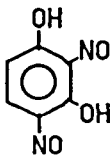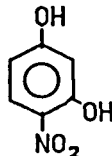1,2,3-trihydroxybenzene (II) and 1,2,4-trihydroxybenzene (1,2,4-benzenetriol) (III) were provided by Aldrich and Touzart et Matignon respectively.

A solution of hydroxybenzoquinone (IV), which is an unstable compound, was obtained by oxidizing an aqueous solution of III in the pH range 7–9. The solution was acidified after a few minutes to prevent further oxidation.

4-nitrosoresorcinol (V) was prepared from resorcinol and isopentyl nitrite in the presence of an alcoholic solution of potassium hydroxide[14].

2,4-dinitrosoresorcinol (VI) was obtained by nitrosation of resorcinol by sodium nitrite (mole ratio 1:2) in acidic solution[15]. Its structure was controlled by MS and NMR (δ ppm 6.58 [q] and 8.08 [d]).

4-nitroresorcinol (VII) was prepared by nitration of resorcinol according to Ref.[16].

3.2 Irradiations, analyses and stabilities of solutions

For preparative purposes solutions were irradiated in polychromatic light in the range 300–340 nm. For determination of quantum yields monochromatic parallel beam (313 nm) was used.

Techniques of irradiation and analysis are described in the first part of this work.

Solutions were irradiated in unbuffered medium (pH = 5.5) or at pH 6.5 (with phosphates) to prevent oxidations by HNO_2 formed in the photolysis of NO_3^- and oxidations of trihydroxybenzenes that occur in basic solutions.

An unbuffered solution of resorcinol 5×10^{-4} M with potassium nitrate 5×10^{-2} M is stable during several weeks. In the presence of nitrite ions 10^{-3} M a low transformation is observed (few % in 3 hours). At pH = 6.5, no reaction was observed after 3 hours.

The trihydroxybenzenes were detected with Merck chromatograph equipped with a fluorescence detector.

Anticipating analytical results, we have studied the stabilities of 1,2,3-trihydroxybenzene (II) and 1,2,4-trihydroxybenzene (III) in the range pH = 5.5–7.5. In air-saturated unbuffered solutions of II and III kept in the dark, a low evolution was observed ($<10\%$ in 3 hours). In the same conditions but in the presence of $NaNO_2 \cdot 10^{-3}$ M the oxidation of III and II were c.a. 40% and $\leq 5\%$ respectively after 3 hours. This transformation can be attributed to traces of HNO_2. At pH = 7.5 (phosphate buffer) this reaction is negligible, but the oxidation of anionic forms of trihydroxybenzenes occurs. In these conditions a solution of II (10^{-3} M) is about 32% oxidized after 150 minutes and the oxidation of a solution of III (10^{-3} M) was evaluated to be 48% after 45 minutes.

Thus to minimize oxidation by oxygen and by nitrite ions formed in the photolysis of nitrate ions, the solutions were irradiated in the range pH = 5.5–6.5.

4 RESULTS

4.1 Dark reactions with nitrogen oxides

It was indicated in the first part of this work (reactions induced by excitation of nitrite ions) that in a deoxygenated solution of resorcinol and nitrogen monoxide, a limited formation of V with traces of VII was observed. This reaction was attributed to traces of NO_2^- contained in $NO^{\cdot}$.

The reaction of resorcinol with nitrogen dioxide in a solution buffered at pH $\simeq 7.2$ to limit the formation of HNO_2, leaded to the formation of V (major product), VI and VII.

4.2 Analytical and kinetic study of the induced phototransformation

The quantum yield of the phototransformation of an air-saturated or degassed unbuffered solution of resorcinol (5×10^{-4} M) induced by excitation of nitrate ions (5×10^{-2} M) was evaluated to be $(2.8 \pm 0.2) \times 10^{-3}$. No influence of oxygen on the quantum yield was observed. This value is normally lower than the quantum yield given in literature for the formation of hydroxyl radicals, because the concentration of substrate is too low to prevent in-cage recombination.

The HPLC chromatogram of an irradiated solution is given in Figure 1. The kinetics of formation of the main products appears on Figure 2. It can be noted that products II, III and VII have kinetics of primary photoproducts whereas VI (dinitrosoresorcinol) is clearly a secondary product. The case of mononitrosoresorcinol (V) seems to be more complex.
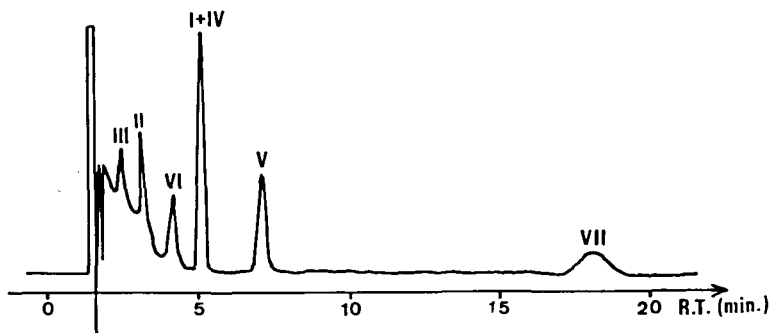
Figure 1 HPLC chromatogram of an unbuffered air-saturated solution of resorcinol (5×10^{-4} M) and potassium nitrate (5×10^{-2} M) irradiated during 1 hour (conversion extent 12–14%). HPLC conditions column C_{18} (250 × 4 mm)—Eluent MeOH/H_2O 40:60.
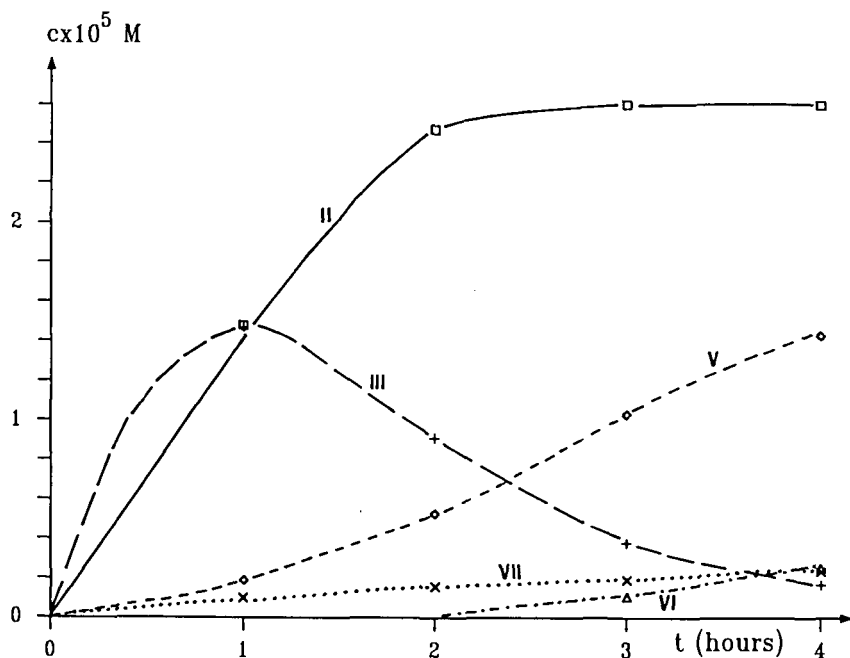
Figure 2   Kinetics of phototransformation of an air-saturated solution of resorcinol (5×10^{-4} M) and KNO$_3$ (5×10^{-2} M) irradiated in the range 300–340 nm in unbuffered solution (pH $\simeq 5.7$).

4.3   Influence of pH

An acidic air-saturated solution (pH $= 3.1$) of resorcinol (5×10^{-4} M) and potassium nitrate (5×10^{-2} M) was irradiated in the range $\lambda = 300$–340 nm. The quantum yield of phototransformation was about 30% higher than at pH $= 5.7$. In a solution irradiated during 2 hours, 4-nitrosoresorcinol (V) accounted for about 45% of the transformation. The formation of 4-nitroresorcinol (VII) was also observed, but no trihydroxybenzene was detected. This absence of trihydroxybenzenes can be attributed to their oxidation by nitrous acid resulting from photolysis of nitrate ions. The influence of pH on the mass balance appears in Table 1.

Table 1   Mass balances in a solution of resorcinol (5×10^{-4} M) and KNO$_3$ (5×10^{-2} M) irradiated at two different pH

Concentration of photoproducts after 2 hours (10^{-5} M)	I reacted	II	III	V	VI	VII
pH $= 5.7$	10	2.5	0.9	0.5	Tr	0.15
pH $= 3.1$	13	—	—	6.1	Tr	2.8

Table 2 Influence of oxygen and formate ions on the formation of 4-nitrosoresorcinol (V) and 4-nitroresorcinol (VII) in a solution of resorcinol (5×10^{-4} M) and KNO_3 (5×10^{-2} M) irradiated in the range 300–340 nm

Concentration of photoproducts after 3.5 hours (10^{-5} M)	Without formate		Formate ions 5×10^{-2} M	
	Air-saturated	Deoxygenated	Air-saturated	Deoxygenated
V	0.78	1.68	2.40	1.61
VII	0.28	0.86	1.00	0.76

4.4 Influence of oxygen and formate ions on the formation of nitro and nitrosoresorcinol

Formate ions (5×10^{-2} M) were used as $\cdot OH$ quenchers, to determine if these radicals are involved in the formation of nitro and nitroso derivatives. Air-saturated and deoxygenated solutions of resorcinol (5×10^{-4} M) and KNO_3 (5×10^{-2} M) were irradiated during the same time (3.5 hours) with and without formate ions. The solutions were buffered at pH = 6.5 to prevent reactions of nitrous acid (pKa = 3.37). In these conditions the percentage of $\cdot OH$ radical quenched by formate ions can be evaluated to be 96% from the rate constants given by Buxton et al.[17]

$$\cdot OH + I \longrightarrow \cdots \qquad 4 \quad k_4 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

$$\cdot OH + HCO_2^- \longrightarrow CO_2^{\cdot-} + H_2O \quad 5 \quad k_5 = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$\cdot OH + HPO_4^{2-} \longrightarrow \cdots \qquad 6 \quad k_6 = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$
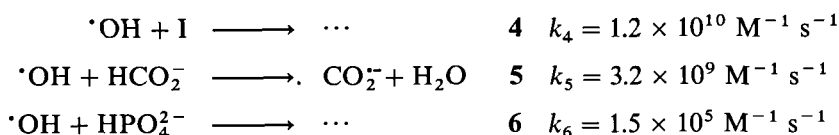
The reaction with phosphate ions used as buffer (0.013 M) can be neglected. The presence of formate ions completely inhibits the formation of II and III.

The influence of oxygen and formate ions on the rates of formation of nitro and nitrosoresorcinol appears in Table 2. It was observed that the formations of products V and VII are significantly modified when an aerated solution is deoxygenated and that formate ions do not significantly influence the ratio [V]/[VII].

5 DISCUSSION AND MECHANISMS

The formation of trihydroxybenzenes II and III, which is inhibited by formate ions, is attributed to the reaction of hydroxyl radicals on resorcinol. The hydroxylation occurs in ortho and para positions with respect to phenol functions with similar efficiencies. This orientation corresponds to the electrophilic behaviour of hydroxyl radicals. Product II accumulates better in the solution than product III. This phenomenon can be correlated to their different reactivities with nitrite ions: The low accumulation and the disappearance of II is attributed to its oxidation by nitrite ions formed in the photolysis of nitrate ions.

It was previously shown that the phototransformation of resorcinol induced by excitation of nitrite ions yields 4-nitrosoresorcinol (V) as the major product. In the present study, V cannot be only attributed to a secondary reaction involving the excitation of nitrite ions formed by photolysis of nitrate ions for the following reason: After irradiating during one hour the formation of V is higher than the formation of VII whereas the conversion 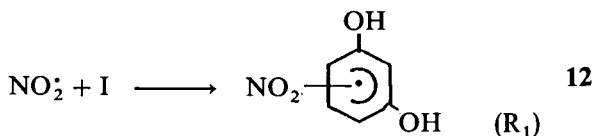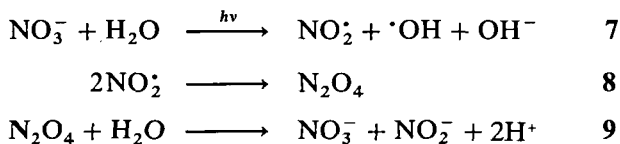of NO_3^- into NO_2^- can be evaluated to be $\leq 0.2\%$. At higher conversion extent both photolyses of NO_2^- and NO_3^- are involved in the formation of V. Dinitrosoresorcinol (VI) is formed from V in a further stage of the reaction.
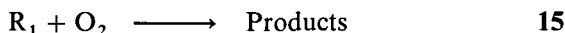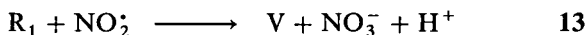
From results given in Table 2 it appears that formate ions, which quench about 96% of hydroxyl radicals, have no influence on the formation of V in deoxygenated solution, and do not inhibit the formation of VII both in air-saturated and in deoxygenated medium. Thus it can be deduced that hydroxyl radicals are not involved in these reactions, they only contribute to the formation of trihydroxy-benzenes (II and III). The first step of the reaction is most likely the formation of an adduct [I...$\cdot$OH] as it was established by Land and Ebert with phenol[18]. This adduct can disproportionate or can be oxidized into trihydroxybenzene by oxygen or by nitrogen dioxide. Knispel *et al.* have estimated the rate constants of the reactions of [benzene...$\cdot$OH] adduct and [toluene ...$\cdot$OH] adduct with $NO_2^\cdot$ gas phase to be about 1.5×10^5 times higher than the rate constants with O_2,[19]. If the same order of magnitude is applied to [resorcinol...$\cdot$OH] in aqueous solution the reaction with $NO_2^\cdot$ would be faster than the oxidation by O_2. The formation of hydroxybenzoquinone (IV) results from the oxidation of III. The formations of products V, VI and VII are attributed to nitrogen oxides N_2O_4, $NO_2^\cdot$ or N_2O_3. The following schemes are suggested for the formations of V and VII.

Scheme I:

$$NO_3^- + H_2O \xrightarrow{h\nu} NO_2^\cdot + {}^\cdot OH + OH^- \qquad 7$$

$$2NO_2^\cdot \longrightarrow N_2O_4 \qquad 8 \quad k_8 = 4.5 \times 10^8 \ M^{-1} \ s^{-1}{}^{20}$$

$$N_2O_4 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \qquad 9 \quad k_9 = 10^3 \ s^{-1}{}^{20}$$

$$N_2O_4 + I \longrightarrow V + NO_3^- + H^+ \qquad 10$$

$$N_2O_4 + I \longrightarrow VII + NO_2^- + H^+ \qquad 11$$

Scheme II:

$$NO_3^- + H_2O \xrightarrow{h\nu} NO_2^\cdot + {}^\cdot OH + OH^- \qquad 7$$

$$2NO_2^\cdot \longrightarrow N_2O_4 \qquad 8$$

$$N_2O_4 + H_2O \longrightarrow NO_3^- + NO_2^- + 2H^+ \qquad 9$$

$$NO_2^\cdot + I \longrightarrow NO_2 \underset{OH}{\overset{OH}{\text{—}}}\!\!\left\langle\text{—}\cdot\right\rangle \qquad 12 \qquad (R_1)$$

$$R_1 + NO_2^{\cdot} \longrightarrow V + NO_3^- + H^+ \qquad \textbf{13}$$

$$R_1 + NO_2^{\cdot} \longrightarrow VII + NO_2^- + H^+ \qquad \textbf{14}$$

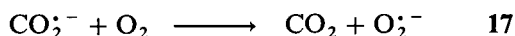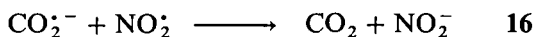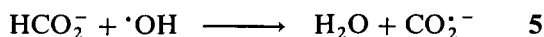$$R_1 + O_2 \longrightarrow Products \qquad \textbf{15}$$
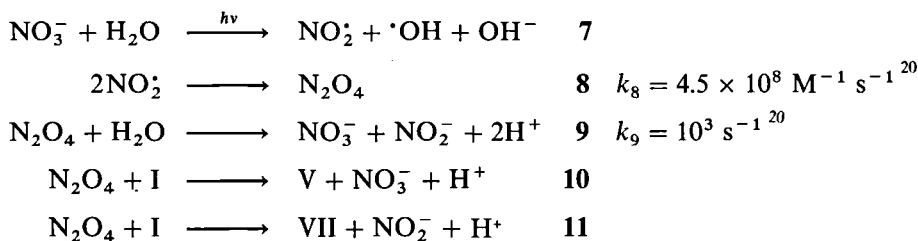
In Figure 2 the initial ratio hydroxylation/nitration + nitrosation is ≥ 10. The fact that hydroxylation is the main pathway can be explained either by the oxidation of [resorcinol ...'OH] adduct by $NO_2^{\cdot}$ or by the involvement of reaction 9.

It can be deduced from Table 2 that in the absence of formate ions the formation of V and VII is inhibited by oxygen, but the presence of oxygen does not modify much the ratio [V]/[VII]. It was also noted that an increase of oxygen concentration does not increase the inhibition. Scheme II is consistent with the oxygen effect but cannot explain the limitation of the inhibition. The conclusion is that, most likely, both mechanisms are involved and that both of them lead to the same ratio [V]/[VII]. It was experimentally proven that the addition of $NO_2^{\cdot}$ (or most probably a mixture $NO_2^{\cdot}/N_2O_4$) to an aqueous solution of resorcinol leads to a mixture V + VII.

It could be expected that the presence of formate ions which inhibit the in-cage recombination

$$\cdot OH + NO_2^{\cdot} \longrightarrow NO_2^- + H^+$$
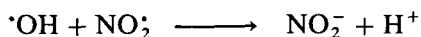
and the reaction of [resorcinol...'OH] adduct with $NO_2^{\cdot}$ should increase the formation rates of V and VII. This effect was observed indeed in air-saturated solution, but in degassed solution the formation of V and VII is not significantly affected by the presence of formate ions. This absence of effect of formate ions in the absence of oxygen is tentatively explained by the oxidation by nitrogen dioxide of the intermediate radicals formed from formate ions, whereas in air-saturated solution these radicals are oxidized by oxygen.

$$HCO_2^- + \cdot OH \longrightarrow H_2O + CO_2^{\cdot -} \qquad \textbf{5}$$

$$CO_2^{\cdot -} + NO_2^{\cdot} \longrightarrow CO_2 + NO_2^- \qquad \textbf{16}$$

$$CO_2^{\cdot -} + O_2 \longrightarrow CO_2 + O_2^{\cdot -} \qquad \textbf{17}$$

Several reactions (9, 11, 14, 16) lead to the formation of nitrite ions. It can also be assumed that $NO_2^{\cdot}$ can be reduced by trihydroxybenzenes and [resorcinol...'OH] adduct. This formation let understand the evolution of the concentration of product III which have a maximum value after about one hour, and the secondary formation of products V and VI, resulting from the excitation of nitrite ions in the solution. The molar absorption coefficient of NO_2^- is about two times that of NO_3^- in the irradiation range, and the quantum yield of 'OH formation is about 10 times higher with NO_2^- than with NO_3^-. Thus the photolysis of NO_2^- is not negligible after about one hour in our conditions, and the formation of V can be attributed to both photolyses of nitrate and nitrite ions.

It was observed that the yield of V and VII increases with decreasing pH. The protonation of nitrite ions might be suggested in the formation of V, but cannot explain the effect on the formation of VII. Another explanation can be suggested:

Most probably reactions 10 and 11 involve the intermediate formation of a complex $N_2O_4 \ldots I$. It can be assumed that the protonation of this intermediate favours the electrophilic substitution on the ring.

6 CONCLUSIONS

The photolysis of NO_3^- in the presence of resorcinol in the pH range 5.5–6.5 yields a mixture of trihydroxybenzenes (II and III), 4-nitrosoresorcinol (V), 4-nitroresorcinol (VII) and 2,4-dinitrosoresorcinol (VI).

Products II and III result from ortho and para hydroxylation of I. Product III is more oxidable than II and its disappearance is attributed to its oxidation by nitrite ions (or nitrous acid) formed in the solution.

The formations of V and VII do not involve hydroxyl radicals since they are not inhibited by formate ions. They are favoured by decreasing pH. They result from dark reactions of nitrogen oxides on resorcinol. Both reactions of NO_2^- and N_2O_4 are suggested to explain the influence of oxygen which partly inhibits the formation of V and VII in the absence of formate ions. The rate of nitrosation increases with irradiation time because of the excitation of nitrite ions resulting from the photolysis of nitrate ions.

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