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Phenol photonitration upon UV irradiation of nitrite in aqueous solution II: effects of pH and TiO_2

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Abstract

Phenol photonitration and photonitrosation were studied both in homogeneous and in heterogeneous phase in the presence of TiO_2 particles. The effect of pH as well as of the semiconductor particles on the kinetics and products of the reaction was observed. Formation of nitrophenols is enhanced at acidic pH, due to thermal processes initiated by nitrous acid, as well as in the presence of TiO_2, due to the photocatalytic oxidation of nitrite.

Keywords: Nitrite; Nitrous acid; Photochemical transformations; Photolysis; Nitroaromatic compounds; Photocatalysis; Titanium dioxide

1. Introduction

Phenol photonitration upon nitrite UV photolysis follows two paths (Vione et al., 2001b). One is started by the reaction between phenol and $^{\cdot}NO_2$ (or N_2O_4), the other is due to the oxidation of the nitrosoderivatives.

This paper describes the effects of pH and of the presence of TiO_2 on phenol photonitration and photonitrosation. The influence of pH on nitrophenol formation has been studied for the irradiation of nitrate (Machado and Boule, 1995; Dzengel et al., 1999; Vione et al., 2001a), and all the authors concluded that nitrophenols form in larger amount at acidic pH. It is interesting to control if this effect is linked only to the presence of nitrate or if it is specific of the organic substrate.

The effect of TiO_2 aqueous suspensions has been assessed for nitrate (Vione, 1998; Dzengel et al., 1999; Vione et al., 2001a), but never for nitrite. TiO_2 inhibits phenol photonitration in the presence of nitrate, very probably because it inhibits nitrate photolysis, and it is interesting to control if this effect is maintained also in the case of nitrite.

2. Experimental

Extensive accounts of the experimental details have been reported elsewhere (Vione et al., 2001a; Vione et al., 2001b). The pH values of the solutions (and suspensions) were adjusted by adding NaOH (purity grade 99%, Merck) or $HClO_4$ (70%, Merck) as needed. They were used as received, without further purification. Use of HNO_3 was avoided to prevent interference, as nitrate itself shows certain photoactivity (Niessen et al., 1988; Guillaume et al., 1989; Machado and Boule, 1995; Vione, 1998; Dzengel et al., 1999; Vione et al., 2001a).

In addition to the already described 360 nm lamp, we also used a 312 nm UV source (100 W Philips TL 01 lamp), producing a photon flux of 1.3×10^7 Ein/s in the cells. The optical path b and the volume V of sample in

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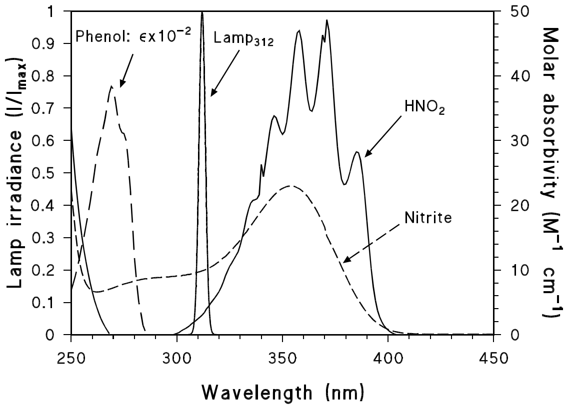


Fig. 1. Irradiance spectrum of the Philips TL 01 lamp (irradiance maximum at 312 nm), spectra of phenol, nitrite and nitrous acid.

the irradiation cells were 0.4 cm and 5 ml, respectively. The lamp irradiance spectrum, together with the absorption spectra of nitrite, nitrous acid and phenol, are reproduced in Fig. 1.

3. Results and discussion

Various reaction mechanisms have been proposed for phenol photonitration (Niessen et al., 1988; Machado and Boule, 1995; Dzengel et al., 1999; Louw and Santoro, 1999; Vione et al., 2001a). An extensive review of the literature concerning these mechanisms is reported in Vione et al. (2001a). However, the results of a work on phenol nitration by $^{\cdot}NO_2$ in the dark (Coombes et al., 1994), and the demonstration of the contribution by 4-nitrosophenol, brought us to propose also other reaction pathways (Vione et al., 2001b). The latter are the basis for the discussion in this work.

While the relevant contribution of 4-nitrosophenol is probably specific of nitrite photolysis, the mechanism involving $^{\cdot}NO_2$ (or N_2O_4) is probably the same for the irradiation of both nitrite and nitrate.

3.1. Effect of pH

Phenol solutions (1.1×10^3 M) were irradiated in the presence of 0.10 M sodium nitrite at pH 3.0, 4.5, 6.5 and 10.5 in homogeneous phase. Concentration vs. time curves for nitrophenols at different pHs are shown in Fig. 2 ((a) 2-nitrophenol; (b) 4-nitrophenol). Phenol degradation curves are not shown: pseudo-first order degradation constants for phenol in all performed experiments are reported in Table 1.

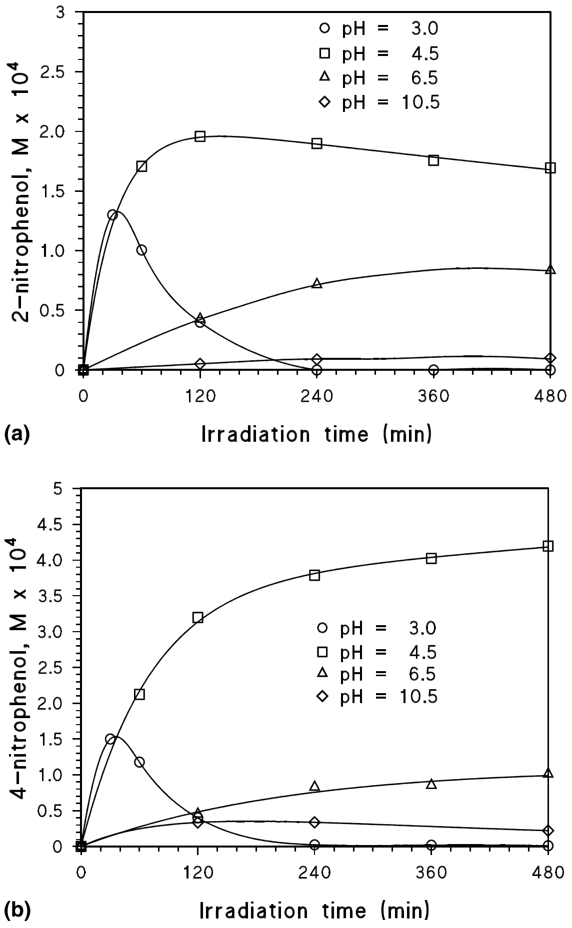


Fig. 2. pH dependence for nitrophenol formation in homogeneous phase. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH adjusted with the addition of $HClO_4$, irradiation at 360 nm. (a) 2-nitrophenol; (b) 4-nitrophenol.

The shapes of the curves in Fig. 2 indicate that the rates of both nitrophenol formation and transformation increase with decreasing pH. Nitrophenol yields in the presence of nitrite are quite high when compared to those obtained with nitrate in the same irradiation conditions (Vione et al., 2001b), mostly due to the higher absorption of nitrite at the irradiation wavelength (360 nm).

Production of $^{\cdot}NO_2$ upon nitrite photoexcitation is pH-dependent in reaction 2 (Fischer and Warneck, 1996):

$$NO_2^- + h\nu \rightarrow {}^{\cdot}NO + {}^{\cdot}O^- \quad [\Phi_1(360\ \text{nm}) \approx 0.025] \tag{1}$$

$${}^{\cdot}O^- + H^+ \leftrightarrow {}^{\cdot}OH \quad [pK_{a,2} = 11.9] \tag{2}$$

$${}^{\cdot}OH + NO_2^- \rightarrow OH^- + {}^{\cdot}NO_2 \quad [k_3 = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}] \tag{3}$$

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

pH	Irradiation wavelength (nm)	$[\mathrm{NO_2^-}]$ (M)	$\mathrm{TiO_2}$ (g/l)	k_D ($\mathrm{s^{-1}}$)
3.0	360	0.100	–	3.3×10^{-4}
4.5	360	0.100	–	3.0×10^{-4}
6.5	360	0.100	–	7.0×10^{-5}
10.5	360	0.100	–	1.6×10^{-4}
2.0	dark	0.001	–	2.7×10^{-5}
2.0	312	0.001	–	2.8×10^{-5}
6.5	360	0.100	0.10	1.3×10^{-4}
6.5	360	0.100	0.50	1.1×10^{-4}
6.5	360	0.100	2.00	5.3×10^{-5}
3.0	360	0.100	0.50	5.5×10^{-4}
4.5	360	0.100	0.50	1.5×10^{-4}
10.5	360	0.100	0.50	6.3×10^{-5}

[a] Conditions are reported in the table.

However, protonation of ${}^{\bullet}\mathrm{O^-}$ should be very fast in aqueous solution. If so, on a mere thermodynamic basis, it cannot explain the pH effect in the range 3.0–10.5. A significant variation in nitrophenol formation should occur only around pH = 12.

Photolysis of $\mathrm{HNO_2}$ is more efficient than nitrite photolysis (Fischer and Warneck, 1996):

$$\mathrm{HNO_2} + h\nu \rightarrow {}^{\bullet}\mathrm{NO} + {}^{\bullet}\mathrm{OH} \quad [\Phi_4(360\ \mathrm{nm}) \approx 0.317] \tag{4}$$

$${}^{\bullet}\mathrm{OH} + \mathrm{HNO_2} \rightarrow {}^{\bullet}\mathrm{NO_2} + \mathrm{H_2O} \quad [k_5 \approx 2.6 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}] \tag{5}$$

and the decadic absorption coefficient for $\mathrm{HNO_2}$ at 360 nm is 1.7 times that of $\mathrm{NO_2^-}$ (Fischer and Warneck, 1996). At ionic strength 0.1 ($\mathrm{NaNO_2}$ 0.1 M), $\mathrm{p}K_{\mathrm{a(HNO_2)}} = 2.9$ (Martell and Smith, 1974; however, different authors report slightly different values), so at pH = 4.5 the ratio $[\mathrm{NO_2^-}]/[\mathrm{HNO_2}]$ is 38.9. This means that the photolysis of nitrous acid should increase the rate of ${}^{\bullet}\mathrm{NO_2}$ production by 55% at pH = 4.5, when compared with pH = 6.5. Kinetic calculations, performed according to Vione et al. (2001b), show that nitrophenol formation should be consequently increased by at most 140%. As a consequence, it is not possible to explain only on this ground the at least four-fold increase in nitrophenol formation between pH 6.5 and pH 4.5 (see Fig. 2).

Another explanation for the pH effect has been given in the case of nitrate irradiation (Vione et al., 2001a). After photoformation, ${}^{\bullet}\mathrm{NO_2}$ can undergo dimerisation to yield $\mathrm{N_2O_4}$, which disproportionates into nitrite and nitrate (Grätzel et al., 1969):

$$2{}^{\bullet}\mathrm{NO_2} \leftrightarrow \mathrm{N_2O_4} \quad [k_6 = 4.5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}} \quad k_{-6} = 6.9 \times 10^3\ \mathrm{s^{-1}}] \tag{6}$$

$$\mathrm{N_2O_4} + \mathrm{H_2O} \rightarrow \mathrm{NO_2^-} + \mathrm{NO_3^-} + 2\mathrm{H^+} \quad [k_7 = 1 \times 10^3\ \mathrm{s^{-1}}] \tag{7}$$

In addition, $\mathrm{N_2O_4}$ is well known to react with alkali (Durrant, 1964):

$$\mathrm{N_2O_4} + 2\mathrm{OH^-} \rightarrow \mathrm{NO_2^-} + \mathrm{NO_3^-} + \mathrm{H_2O} \tag{8}$$

For instance, alkaline traps are used for its adsorption. The hypothesis is that $\mathrm{N_2O_4}$ is more stable in acidic solution than in neutral to basic ones.

Fig. 3 reports the initial rates for the formation of 2-nitrophenol, 4-nitrophenol and 4-nitrosophenol as a function of pH. In this case the irradiation was performed at 312 nm instead of 360 nm, but the processes following nitrite photolysis are the same at the two wavelengths (Fischer and Warneck, 1996). The only differences are Φ_1, $\Phi_4(312\ \mathrm{nm}) > \Phi_1, \Phi_4(360\ \mathrm{nm})$ and $\varepsilon_{312}(\mathrm{HNO_2}, \mathrm{NO_2^-}) < \varepsilon_{360}(\mathrm{HNO_2}, \mathrm{NO_2^-})$, partially compensating each other. Nitrite concentration was 10^{-3} M.

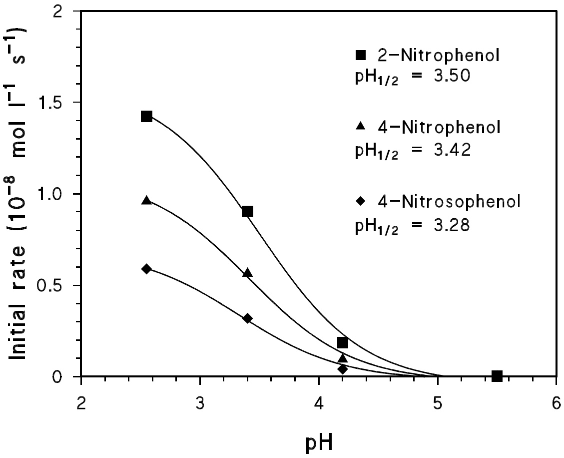


Fig. 3. Effect of pH on the formation of 2- and 4-nitrophenol and of 4-nitrosophenol. Initial conditions: phenol 1.1×10^{-3} M, $\mathrm{NaNO_2}$ 0.001 M, pH adjusted with the addition of $\mathrm{HClO_4}$, irradiation at 312 nm.

The curves show a trend similar to an acid–base equilibrium for both nitration and nitrosation, with very similar $pH_{1/2}$s. This similarity is partially obvious, since about 50% of nitrophenol formation is due to the oxidation of the nitrosoderivatives (Vione et al., 2001b). However, also the concurrent mechanism for nitrophenol formation needs having the same pH dependence, otherwise the curves would not approach zero around neutrality. This means that phenol nitration and nitrosation have a common pH-dependent step.

The combination of reaction (7) with reaction (8), with reaction (8) much faster than reaction (7), can give a pH dependence similar to that shown in Fig. 3. However, the presence of an inflection point at $pH \approx 3.4$ requires $k_8 \approx 3 \times 10^{14}\ M^{-1}\ s^{-1}$, which is not reasonable in aqueous solution.

Dark experiments have been performed to assess the weight of the dark processes at acidic pH, and the results compared with those obtained under irradiation. Fig. 4 shows the results of the reaction between phenol 1.1×10^{-3} M and HNO_2 1.0×10^{-3} M, at pH = 2 for the addition of $HClO_4$, in the dark and upon 312 nm irradiation. In the case of dark reactions, cells were wrapped in double aluminium foil and were kept under the same lamp and magnetic stirrer used for illumination experiments, in order to obtain the same temperature and stirring conditions.

The figure indicates that nitrophenols and 4-nitrosophenol form in practically the same amount both in the dark and under illumination, in particular when focusing on the initial rates, meaning that dark processes prevail over photolytic ones at acidic pH.

Phenol nitration and nitrosation in the dark may be due to nitrous acid thermal dismutation, which yields $^{\cdot}NO_2$ among the products (Park and Lee, 1988):

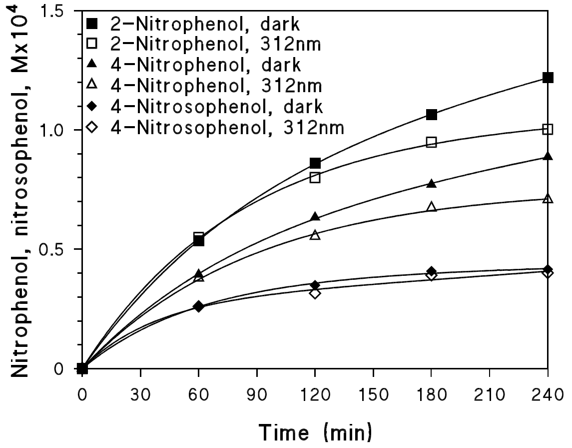


Fig. 4. Formation of nitrophenols and of 4-nitrosophenol in the dark and under 312 nm irradiation. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.001 M, pH = 2.0 ($HClO_4$).

$$2HNO_2 \rightarrow {}^{\cdot}NO_2 + {}^{\cdot}NO + H_2O \quad [k_9 = 28.6\ M^{-1}\ s^{-1}\ \text{at 303 K}] \tag{9}$$

The value of $pH_{1/2}$ given in Fig. 3 for 2- and 4-nitrophenol and for 4-nitrosophenol is compatible with the pK_a of nitrous acid, within experimental error. This means that the acid/base equilibrium HNO_2/NO_2^- can explain the effect of pH on phenol nitration and nitrosation.

Formation of $^{\cdot}NO_2$ upon photolysis of HNO_2 1.0×10^{-3} M (reactions (4) and (5)), combined with the hydrolysis of nitrogen dioxide (reactions (6), (7) and (10); Fischer and Warneck, 1996):

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

with the additional approximation $[^{\cdot}NO_2] = [^{\cdot}NO]$ (introduced to perform steady-state calculations), gives a steady-state concentration $[^{\cdot}NO_2] = 5.2 \times 10^{-8}$ M. The thermal decomposition of nitrous acid (reaction (9)), together with reactions (6), (7) and (10), with the same approximation, gives $[^{\cdot}NO_2] = 3.0 \times 10^{-7}$ M. The numerical values are probably not very accurate, but their ratio is and demonstrates that the thermal dismutation of nitrous acid gives a much more important contribution to $[^{\cdot}NO_2]$ than its photolysis. This is further confirmed by the similarity of phenol pseudo-first order degradation constants in the dark and under illumination (Table 1): irradiation of the solutions has little or no effect on the system.

The formation of $^{\cdot}NO_2$ in reaction (9) can explain the effect of pH on phenol nitration. Furthermore, reaction (9) leads to enhanced formation of N_2O_3, which probably is the reactive species for phenol nitrosation (Pires et al., 1994). For the rate constant see Grätzel et al. (1969):

$$^{\cdot}NO + {}^{\cdot}NO_2 \rightarrow N_2O_3 \quad [k_{11} = 1.1 \times 10^9\ M^{-1}\ s^{-1}] \tag{11}$$

The pH dependence for the formation of N_2O_3 (reactions (9) and (11)) thus explains the pH dependence for the formation of 4-nitrosophenol.

In neutral solution, however, the thermal decomposition of HNO_2 plays a negligible role and no nitrophenols form in the dark. The formation of 2- and 4-nitrophenol at pH = 6.5, in the presence of $NaNO_2$ under illumination (see Fig. 2), is thus due to reactions (1)–(3) and not to reaction (9).

3.2. Effect of TiO_2

TiO_2 is a semiconductor oxide showing relevant photochemical activity (Bahnemann et al., 1994), as it can efficiently catalyse both oxidation and reduction processes involving organic and inorganic molecules in aqueous solution. Among the possible applications, titanium dioxide heterogeneous photocatalysis is a very promising advanced oxidation process for water detoxification.

In this work, we were interested in studying the interaction between titanium dioxide and nitrite. A first set of irradiation experiments was performed in the presence of TiO_2 at pH = 6.5, TiO_2 concentration being varied in the range 0–2.00 g/l. Formation curves for nitrophenols are shown in Fig. 5 ((a) 2-nitrophenol; (b) 4-nitrophenol). When focusing on the initial rates, it can be seen that the formation of nitrophenols increases when increasing the concentration of the photocatalyst. In the presence of titanium dioxide and nitrite 0.1 M, 4-nitrosophenol is quickly transformed, but only a very small fraction yields 4-nitrophenol (see Fig. 6). On the contrary, in the presence of nitrite 0.1 M only, a relevant fraction of 4-nitrosophenol transforms into 4-nitrophenol (Vione et al., 2001b): we conclude that phenol nitration under photocatalytic conditions only involves $^{\cdot}NO_2$ or N_2O_4. A very limited formation of 4-nitrophenol from 4-nitrosophenol in the presence of titanium dioxide, but without nitrite, has already been observed by Piccinini et al. (1997).

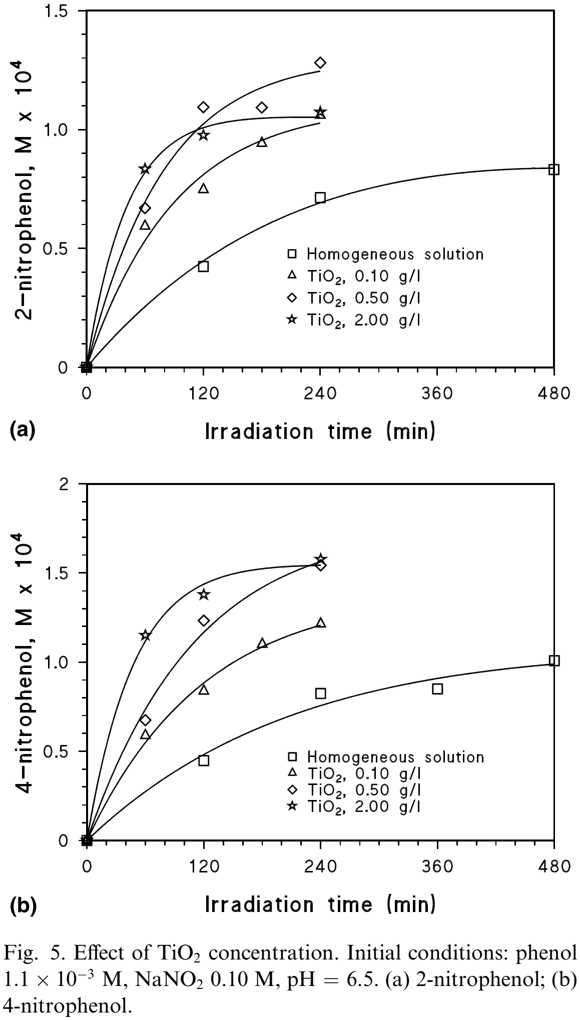


Fig. 5. Effect of TiO_2 concentration. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5. (a) 2-nitrophenol; (b) 4-nitrophenol.

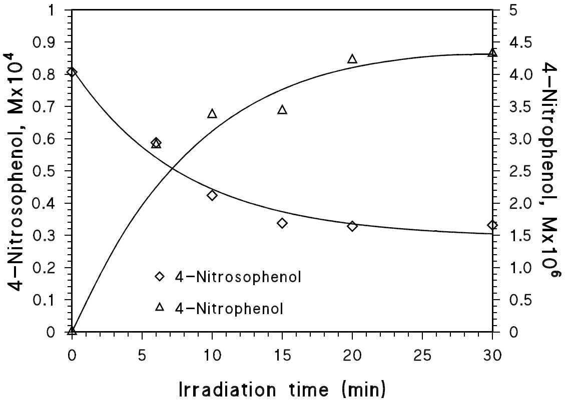


Fig. 6. Degradation of 4-nitrosophenol in the presence of titanium dioxide. Initial conditions: 4-nitrosophenol 8.1×10^5 M, $NaNO_2$ 0.10 M, TiO_2 0.50 g/l.

Titanium dioxide can interfere with various processes linked with nitrite photolysis because of light absorption and scattering, and so also with light-induced $^{\cdot}NO_2$ formation. This interference is of the same kind as that on nitrate photolysis (Dzengel et al., 1999; Vione et al., 2001a). Another effect to be expected in the presence of the photocatalyst is enhanced nitrophenol degradation with respect to homogeneous solution (Maurino et al., 1997). This should result in further depletion of nitrophenol concentration. In particular, nitrophenol degradation can become relevant at high irradiation times and high photocatalyst concentration (see Fig. 5). These observations indicate that TiO_2 must also have a relevant positive effect on the formation of nitrophenols, as its overall effect is positive. Such an effect can be a TiO_2-induced formation of $^{\cdot}NO_2$, via the valence-band holes or the surface-adsorbed hydroxyl radicals:

$$NO_2^- + h^+ \rightarrow {}^{\cdot}NO_2 \qquad (12)$$

$$NO_2^- + {}^{\cdot}OH_{ads} \rightarrow {}^{\cdot}NO_2 + OH^- \qquad (13)$$

This is confirmed by the results obtained by Minero et al. (1996), who found nitrate as the oxidation product of nitrite under photocatalytic conditions. Nitrate forms in these systems via hydrolysis of nitrogen dioxide (reactions (6) and (7)).

Reaction (13) is similar to the process taking place in homogeneous solution, involving homogeneous $^{\cdot}OH$ (Fischer and Warneck, 1996; Vione et al., 2001b), and it is thermodynamically allowed below pH = 8.5. In fact, the redox couple $^{\cdot}NO_2/NO_2^-$ has $E^0 = 1.03$ (Bard et al., 1985), while the couple $^{\cdot}OH_{ads}/H_2O$ has $E^0 \approx 1.5$ V

(Lawless et al., 1991), this reduction potential decreasing with increasing pH.

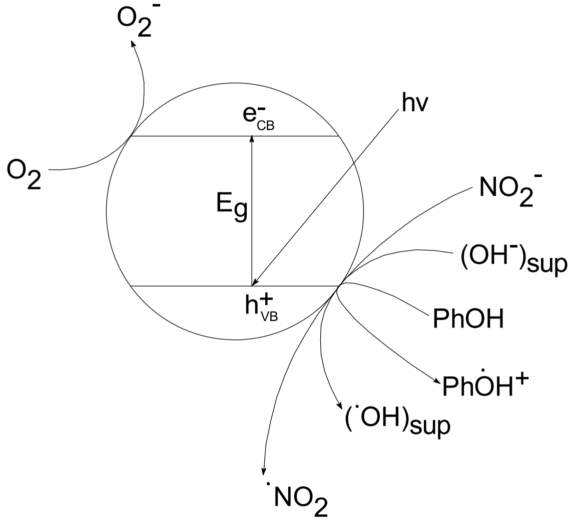
Reaction (12) is possible at any pH. In fact, $E^0(h^+) = 3.05$ V (Pelizzetti and Serpone, 1986) and, although decreasing with increasing pH, it is always higher than $E^0(\cdot NO_2/NO_2^-)$.

The different processes, which can take place in the presence of TiO_2, are summarised in Scheme 1 (Bahnemann et al., 1994).

The pH effect already seen in homogeneous phase is maintained in the presence of TiO_2 suspensions. Formation curves for nitrophenols at pH = 3.0, 4.5, 6.5 and 10.5 in the presence of 0.50 g/l TiO_2 are shown in Fig. 7 ((a) 2-nitrophenol; (b) 4-nitrophenol).

Phenol pseudo-first order degradation rate constant is very little modified by the addition of the photocatalyst (Table 1): this probably means that titanium dioxide inhibits phenol transformation via nitrite photolysis, but at the same time induces photocatalytic phenol transformation, the two effects compensating each other.

Fig. 8 shows the formation curves for 4-nitrosophenol at pH = 6.5, both in homogeneous phase and in the presence of 0.50 g/l TiO_2. The main effect of the photocatalyst seems to be the degradation of 4-nitrosophenol, as its formation rate seems very similar in both homogeneous phase and TiO_2 suspension. Indeed, the pseudo-first order degradation rate constant for 4-nitrosophenol is 1.1×10^{-4} s^{-1} in homogeneous phase (pH = 6.5, $NaNO_2$ 0.1 M) and 3.75×10^{-3} s^{-1} when 0.50 g/l TiO_2 is added to the system. A similar enhancement in 4-nitrosophenol degradation by TiO_2 has already been observed by Piccinini et al. (1997), that work being carried out in the absence of nitrite.



Scheme 1. Reactions taking place on TiO_2 surface.

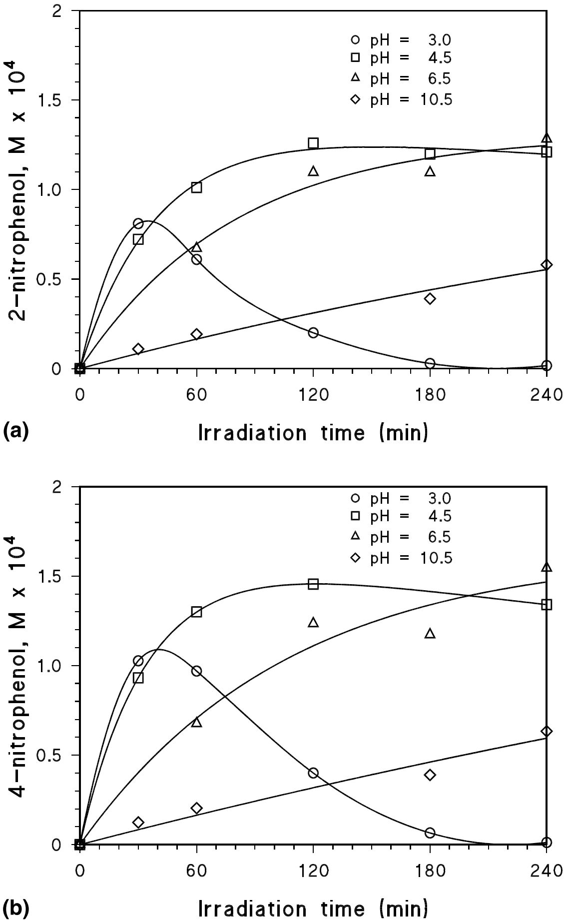


Fig. 7. pH dependence for nitrophenol formation in the presence of TiO_2. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, TiO_2 0.50 g/l. (a) 2-nitrophenol; (b) 4-nitrophenol.

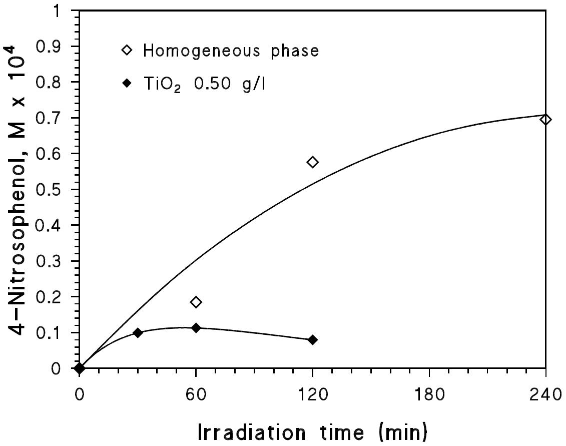


Fig. 8. Formation of 4-nitrosophenol. Initial conditions: phenol 1.1×10^{-3} M, $NaNO_2$ 0.10 M, pH = 6.5.

N_2O_3, the reactive species for phenol nitrosation, forms via reaction between $^{\cdot}NO$ and $^{\cdot}NO_2$ (Fischer and Warneck, 1996). Another conceivable nitrosation path, namely, the reaction between phenoxyl radical and $^{\cdot}NO$ (Machado and Boule, 1995), is inhibited in our system as phenoxyl forms via reaction between phenol and $^{\cdot}OH$. Here $^{\cdot}OH$ is efficiently scavenged by nitrite.

TiO_2 interferes with nitrite photolysis, depleting $^{\cdot}NO$, but at the same time favours the formation of $^{\cdot}NO_2$. The two effects probably compensate each other, so that the formation rate of 4-nitrosophenol is very similar in homogeneous solution and in semiconductor suspension. In addition, the photocatalyst degrades 4-nitrosophenol, and this seems to be its main effect.

3.3. Nitrite as $^{\cdot}OH$ source

As already cited, nitrite photolysis generates nitric oxide and hydroxyl radical. The photolysis and the subsequent reaction between nitrite and $^{\cdot}OH$ control the hydroxyl steady-state concentration (reactions (1)–(3)).

When only nitrite is present in the solution, $[^{\cdot}OH]$ is given by:

$$[^{\cdot}\mathrm{OH}]_{ss} = \frac{\Phi_1 I_0 (1 - 10^{-\varepsilon b[\mathrm{NO}_2^-]})}{k_3 V[\mathrm{NO}_2^-]}, \qquad (14)$$

where I_0 is the irradiation intensity, ε the molar absorbivity of nitrite, b the optical path of the solution and V its volume. In the presence of $^{\cdot}OH$ scavengers other than nitrite, such as phenol, other reactions are to be considered (Buxton et al., 1988):

$$\mathrm{Phenol} + {}^{\cdot}\mathrm{OH} \rightarrow \mathrm{products}$$
$$[k_{15} = 1.4 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}] \qquad (15)$$

Catechol and hydroquinone are two of the products of reaction (15).

The corresponding steady-state concentration for $^{\cdot}OH$ in the presence of phenol thus becomes:

$$[^{\cdot}\mathrm{OH}]_{ss} = \frac{\Phi_1 \mathrm{I}_0 (1 - 10^{-\varepsilon b[\mathrm{NO}_2^-]})}{V(k_3[\mathrm{NO}_2^-] + k_{15}[\mathrm{Phenol}])}. \qquad (16)$$

As $\lim_{[\mathrm{NO}_2^-]\to 0}([^{\cdot}\mathrm{OH}]_{ss}) = \lim_{[\mathrm{NO}_2^-]\to\infty}([^{\cdot}\mathrm{OH}]_{ss}) = 0$, this function has a maximum for a value of $[NO_2^-]$, depending on the irradiation wavelength and on phenol concentration. For low values of $[NO_2^-]$, nitrite photolysis is negligible, while for very high values the reaction between nitrite and hydroxyl keeps $[^{\cdot}OH]_{ss}$ low.

Fig. 9 shows the trend of $[^{\cdot}OH]_{ss}$ with nitrite concentration, under the 360 nm light source (photon flux of 3.6×10^{-7} Ein/s in the cells), in the presence of phenol 1.1×10^{-3} M. The curve has a maximum for $[NO_2^-] = 0.012$ M in the present experimental conditions.

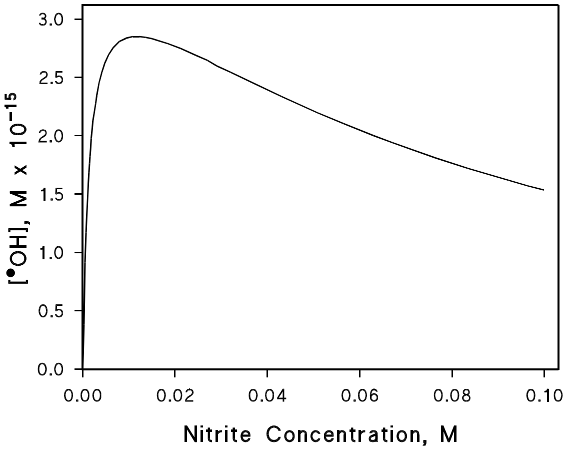


Fig. 9. $[^{\cdot}OH]_{ss}$ vs. $[NO_2^-]$, irradiation at 360 nm, phenol 1.1×10^{-3} M.

An important consequence of these considerations is that nitrite can control the concentration of hydroxyl in many environmental compartments. In this respect, the behaviour of nitrite is very different from that of nitrate, which can generate $^{\cdot}OH$ upon photolysis but is not a sink for it, so that $[^{\cdot}OH]_{ss}$ increases with increasing nitrate concentration (Zepp et al., 1987).

In acid solution, photoformation of $^{\cdot}OH$ occurs via photolysis of nitrous acid. In this case, reactions (4) and (5) substitute reactions (1)–(3), and similar considerations can be made. Nitrous acid can also undergo thermal decomposition (reaction (9)), yielding $^{\cdot}NO + {}^{\cdot}NO_2$. This work demonstrates that HNO_2 is a relevant source of nitric oxide and nitrogen dioxide via dark processes, which under certain conditions can have higher importance than UV photolysis.

4. Conclusions

UV irradiation of nitrite in aqueous solution leads to the formation of $^{\cdot}NO_2$, which is involved in phenol nitration. Nitrite photolysis also yields $^{\cdot}NO$, which reacts with $^{\cdot}NO_2$ to give N_2O_3, responsible for the formation of 4-nitrosophenol. The oxidation of 4-nitrosophenol (and possibly 2-nitrosophenol) in the presence of oxygen gives a further contribution to nitrophenol formation (Vione et al., 2001b).

Phenol photonitration and photonitrosation are pH-dependent and are higher at low pH. This effect of pH is due to thermal processes involving HNO_2, possibly to its thermal dismutation. Under the studied conditions, this thermal reaction largely prevails over nitrous acid photolysis.

Titanium dioxide in suspension partially interferes with nitrite photolysis through light absorption and scattering. At the same time, the holes and the adsorbed hydroxyls on the surface of the catalyst can react with nitrite to yield $^{\cdot}NO_2$. The net effect on nitrophenol formation is positive.

The effect of TiO_2 on the formation of 4-nitrosophenol indicates a good level of compensation between $^{\cdot}NO$ depletion, via inhibition of nitrite photolysis, and photocatalytic formation of $^{\cdot}NO_2$. The two radicals react to give the nitrosating agent, N_2O_3. In addition, TiO_2 degrades the organic compound. In the presence of TiO_2, the light induced transformation of 4-nitrosophenol gives 4-nitrophenol in negligible amount.

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