UNIVERSITÀ DEGLI STUDI DI TORINO

INHIBITION VS. ENHANCEMENT OF THE NITRATE-INDUCED PHOTOTRANSFORMATION OF ORGANIC SUBSTRATES BY THE •OH SCAVENGERS BICARBONATE AND CARBONATE

Davide Vione,[a]∗ Swapan Khanra,[a,b] Simona Cucu Man,[c] Pratap Reddy Maddigapu,[a] Radharani Das,[a,d] Cecilia Arsene,[c] Romeo-Iulian Olariu,[c] Valter Maurino,[a] Claudio Minero [a]

a Dipartimento di Chimica Analitica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy. http://www.chimicadellambiente.unito.it

b Department of Chemical Engineering, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata 700009, India.

c Department of Chemistry, "Al. I. Cuza" University of Iasi, Carol I Bd. 11, 700506 Iasi, Romania.

d Department of Chemical Engineering, Haldia Institute of Technology, ICARE complex, Haldia-721657, India.

∗ Corresp. author. Ph. +39-011-6707874; Fax +39-011-6707615; E-mail: *davide.vione@unito.it*
URL: *http://naturali.campusnet.unito.it/cgi.bin/docenti.pl/Show?_id=vione*

Abstract

Contrary to common expectations, the hydroxyl scavengers carbonate and bicarbonate are able to enhance the phototransformation by nitrate of a number of substituted phenols. Carbonate and bicarbonate, in addition to modifying the solution pH, are also able to induce a considerable formation of the carbonate radicals upon nitrate photolysis. The higher availability of less reactive species than the hydroxyl radical would contribute to substantially enhance the photodegradation of the phenols/phenolates that are sufficiently reactive toward the carbonate radical. This phenomenon has a potentially important impact on the fate of the relevant compounds in surface waters. In contrast, the degradation of compounds that are not sufficiently reactive toward $CO_3^{-\bullet}$ is inhibited by carbonate and bicarbonate because of the scavenging of •OH.

Keywords. Photodegradation; photochemistry; pollutant fate; peroxynitrite; inorganic carbon.

Introduction

Photochemical processes are important pathways for the transformation of organic pollutants in surface waters. Direct and indirect photolysis reactions, the latter photosensitised by dissolved organic matter (DOM), nitrate, nitrite, and Fe(III) contribute to the removal of many xenobiotics

from the aquatic systems (Lam et al., 2003; Canonica et al., 2006; Canonica, 2007). Photochemistry can determine the impact of an organic pollutant to surface waters, partly because it can induce the degradation of the primary species, and partly because it produces transformation intermediates. Pollutant degradation might potentially lead to depollution, and in this respect the photochemical processes could be seen as a self-decontamination pathway for aquatic systems. However, the transformation intermediates have an impact of their own, which is sometimes higher compared to the parent compound (Brigante et al., 2005; Chiron et al., 2006 & 2007; Virag et al., 2007).

The assessment of the impact of organic xenobiotics to surface waters will become an increasingly stringent requirement, in so far as the new European law on chemicals (REACH: Registration, Evaluation, and Authorisation of CHemicals) will require producers to provide evidence that their substances are safe to use and pose no risk (or limited risk) to human health and the environment (Lahl and Hawxwell, 2006). The oxidation of organic pollutants by the radical $^{\bullet}$OH is one of the most straightforward ways to achieve photochemical decontamination. The hydroxyl radical in freshwater is photochemically produced by the irradiation of nitrate, nitrite and DOM, but it is also scavenged by a number of solutes, among which are the DOM itself and inorganic carbon (carbonates and bicarbonates). The scavenging of the hydroxyl radicals significantly decreases their ability to induce pollutant degradation (Brezonik and Fulkerson-Brekken, 1998). The reaction between $^{\bullet}$OH and carbonate (second-order rate constant 3.9×10^8 M^{-1} s^{-1}; Buxton et al., 1988) or bicarbonate (8.5×10^6 M^{-1} s^{-1}) yields the carbonate radical, CO$_3^{-\bullet}$, which is reactive toward easily oxidised substrates (Huang and Mabury, 2000a/b; Canonica et al., 2005) but, in general, less reactive than $^{\bullet}$OH (Buxton et al., 1988; Neta et al., 1988; Mazellier et al., 2007). In natural waters the radical CO$_3^{-\bullet}$ can reach a higher steady-state concentration than $^{\bullet}$OH because of its lower reactivity, considering that it undergoes lesser scavenging by DOM. In some cases the result is an enhancement of the photodegradation reactions, but more often the higher availability of CO$_3^{-\bullet}$ could not compensate for its lower reactivity compared to $^{\bullet}$OH (Lam and Mabury, 2005).

The carbonate radical usually reacts via one-electron oxidation toward organic molecules (Neta et al., 1988), which in many cases would lead to decontamination. Because of $^{\bullet}$OH scavenging, it is expected that carbonate and bicarbonate would inhibit the transformation of many organic substrates in the presence of nitrate under irradiation (Lam and Mabury, 2005), in particular in the absence of DOM.

However, a recent study has shown that the situation is not necessarily that straightforward. NaHCO$_3$ below 5 mM concentration is able to inhibit the degradation of phenol upon nitrate irradiation, in keeping with the scavenging of $^{\bullet}$OH, but the degradation rate of phenol starts increasing above 5 mM NaHCO$_3$ (Chiron et al., 2009). Considering that the variation of pH cannot account for such a result, two possible explanations can be advanced. The first is that bicarbonate enhances the photolysis of nitrate through a solvent-cage effect, reacting with photolysis-derived $^{\bullet}$OH before it leaves the surrounding cage of the water molecules. The photolysis of nitrate yields $^{\bullet}$OH + $^{\bullet}$NO$_2$, surrounded by water; the recombination of the radicals inside the solvent cage to yield back NO$_3^-$ + H$^+$ decreases the quantum yield of $^{\bullet}$OH photoproduction (Bouillon and Miller, 2005).

The scavenging of in-cage $^\bullet$OH by bicarbonate and carbonate would be able to prevent recombination and, as a consequence, the generation rate of $CO_3^{-\bullet}$ + $^\bullet$OH with $NaHCO_3$ would be higher than for $^\bullet$OH alone without bicarbonate. An alternative explanation concerns the generation of peroxynitrite, $ONOO^-$, upon nitrate photoisomerisation (Mack and Bolton, 1999). In the presence of bicarbonate, the species $ONOO^-$ can be transformed into $CO_3^{-\bullet}$ + $^\bullet$NO$_2$ (Goldstein et al., 2001; Squadrito and Pryor, 2002).

The two processes could well be operational at the same time, and both of them would increase the photogeneration rate of $CO_3^{-\bullet}$ and $^\bullet$NO$_2$. Interestingly, the nitration of phenol is enhanced upon addition of $NaHCO_3$ above 5 mM (Chiron et al., 2009), in keeping with a higher production of $^\bullet$NO$_2$. The generation of toxic nitrophenols as secondary pollutants would partially compensate for the increased degradation of phenol in the presence of nitrate and $NaHCO_3$. Note that bicarbonate has been shown to enhance the degradation of dimethyl sulphide (Bouillon and Miller, 2005) and bisphenol A (Espinoza et al., 2007) upon nitrate photolysis.

The effect of bicarbonate on the photodegradation of organic compounds induced by nitrate irradiation would be a balance between the increased photogeneration of reactive transients on the one hand, and the replacement of $^\bullet$OH with a less reactive species ($CO_3^{-\bullet}$, albeit in higher amount) on the other. The balance could be different for compounds with different reactivity toward the carbonate radical. In this work the effect of bicarbonate was studied in the presence of various substrates of environmental concern, showing different reactivity toward $CO_3^{-\bullet}$. The results allow for a first generalisation of the bicarbonate effect on the nitrate-induced photodegradation of organic compounds. It will be seen that in many cases the $^\bullet$OH scavengers carbonate and bicarbonate are able to considerably enhance the photodegradation of substituted phenols.

Experimental

Reagents and materials

Nitrobenzene (purity grade >99%), 4-fluorophenol (99%), 4-chlorophenol (>99%), 4-bromophenol (99%), 4-iodophenol (99%), 4-nitrophenol (98%), catechol (>99%), and 1,4-benzoquinone (98%) were purchased from Aldrich, H_3PO_4 (85%), $NaH_2PO_4 \cdot H_2O$ (>98%), $Na_2HPO_4 \cdot 2H_2O$ (>98%), and $NaNO_3$ (>99.5%) from VWR Int., acetonitrile (Supergradient HPLC grade) from Scharlau. All reagents were used as received, without further purification. Water used was of Milli-Q quality.

Irradiation experiments

Irradiation was carried out in cylindrical Pyrex glass cells (4.0 cm diameter, 2.3 cm height), containing 5 mL aqueous solution. To achieve selective excitation of nitrate, the radiation source was a 100 W Philips TL 01 UVB lamp, with emission maximum at 313 nm. The lamp emission spectrum is reported elsewhere (Vione et al., 2008). The total photon flux in the cells was 2.7 W

m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter, corresponding to 1.8×10^{-6} einstein L^{-1} s^{-1} in solution.

Analytical determinations

After the scheduled irradiation time, the solutions were HPLC analysed with a VWR-Hitachi LaChrom Elite chromatograph, equipped with a model L-2200 autosampler, L-2130 pump for low-pressure gradients, L-2300 column oven, Merck HIBAR 250-4 column (25.0×0.4 cm, packed with LiChrospher 100 CH-18/2, particle diameter 10 μm), and L-2455 photodiode array detector. Eluent flow rate was 1.00 mL min^{-1} in the isocratic mode, with a mixture of acetonitrile and aqueous H$_3$PO$_4$ (pH 2.8). Table 1 reports the eluent composition for the different analytes under study, together with the detection wavelength λ and the retention time t_R (the column dead time was 1.50 min). The solution pH was measured with a combined glass electrode, connected to a Metrohm 713 pH meter.

Initial rates and relative uncertainty

The time evolution data of the substrates were fitted with the equation *[P]$_t$ = [P]$_0$ exp($-k^d_P$ t)*, where [P]$_t$ is the substrate concentration at the time t, [P]$_0$ the initial concentration, and k^d_P the pseudo-first order rate constant for substrate degradation. The initial degradation rate is given by k^d_P [P]$_0$. The rate data are reported together with the associated standard errors (intra-series variability, $\pm \sigma$, derived from the goodness of the fit of the equation to the experimental data). Inter-series variability (repeated runs) was around 15%.

Table 1. Liquid chromatography (HPLC) conditions adopted for the analysis of the different compounds under study.

Compound	% CH$_3$CN	λ, nm	t_R, min
Nitrobenzene	55	264	5.40
4-Fluorophenol	40	280	4.28
4-Chlorophenol	50	220	4.83
4-Bromophenol	60	226	3.64
4-Iodophenol	70	233	3.16
4-Nitrophenol	35	210	6.29
Catechol	25	210	4.46
1,4-Benzoquinone	15	227	6.43

Results and Discussion

The transformation of different organic compounds at 25 μM initial concentration was studied in the presence of 10 mM $NaNO_3$, and of $NaHCO_3$ at concentrations up to around 10-15 mM. The addition of $NaHCO_3$ significantly increased the solution pH, in a similar way for the different compounds under study. The main problems connected with the pH change are the modification of the photochemistry of nitrate, the potentially different quantum yields for the direct photolysis of the compounds that undergo acid-base equilibria, and the possible change of the reaction rate constants of the same compounds with the photogenerated reactive radical species (mainly $^\bullet OH$; Mack and Bolton, 1999).

The photolysis of nitrate yields $^\bullet OH$ both directly (reaction (1)), and indirectly via its photoisomerisation to peroxynitrite/peroxynitrous acid (reactions (2-4)) (Mack and Bolton, 1999). The problem is that peroxynitrous acid (HOONO, with pKa ≈ 7; Mark et al., 1996) can produce $^\bullet OH$ upon decomposition but peroxynitrite does not, and an increase of pH would therefore reduce the yield of $^\bullet OH$ photoproduction (Mack and Bolton, 1999).

$$NO_3^- + h\nu + H^+ \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad\qquad (1)$$
$$NO_3^- + h\nu \rightarrow ONOO^- \qquad\qquad (2)$$
$$ONOO^- + H^+ \rightleftarrows HOONO \qquad\qquad (3)$$
$$HOONO \rightarrow {}^\bullet OH + {}^\bullet NO_2 \qquad\qquad (4)$$
$$HOONO \rightarrow NO_3^- + H^+ \qquad\qquad (5)$$
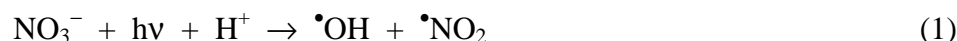
Note that reaction (1) appears to be dependent on pH because the primary photolysis event yields $^\bullet O^-$ instead of $^\bullet OH$, and a subsequent protonation of $^\bullet O^-$ is required to produce the hydroxyl radical. However, the acid-base equilibrium $^\bullet OH$ / $^\bullet O^-$ has $pK_a ≈ 12$ and is therefore not significant under the adopted pH conditions (Mack and Bolton, 1999).

Note that also $^\bullet NO_2$ would be formed in the presence of $NaNO_3 + NaHCO_3$ under irradiation. Its reactivity is limited by the efficient hydrolysis into nitrite and nitrate, but nitrogen dioxide has the ability to nitrate aromatic compounds (Dzengel et al., 1999; Vione et al., 2004 & 2005). However, as a difference with phenol (Chiron et al., 2009), no nitroderivatives were detected in the present study under the adopted irradiation conditions.

As far as the direct photolysis is concerned, the conjugate bases of the acidic aromatic substrates often show a shift of the absorption toward the visible, and in some cases have higher photolysis quantum yields than the undissociated compounds (with some exceptions; Vione et al., 2009a). For the reasons cited above it is important to take into account the effects of pH on nitrate photochemistry, on the direct photolysis of the aromatic substrates, and on their reactivity toward the photogenerated transients. These effects are not necessarily connected with the presence of carbonate or bicarbonate. Accordingly, the irradiation experiments were also carried out in the presence of 10 mM $NaNO_3$ and of a phosphate buffer ($NaH_2PO_4 + Na_2HPO_4$), at the same total

concentration adopted in the corresponding runs with NaHCO$_3$ and the same pH (within 0.1 pH units). The phosphate results are compared to those of the corresponding runs with NaHCO$_3$. Note that at the adopted concentration values, the phosphate species would not be able to scavenge $^{\bullet}$OH to a significant extent (Buxton et al., 1988). Accordingly, the added phosphate is only expected to modify the solution pH. It was also studied the direct photolysis as a function of pH, in the absence of nitrate, upon addition of the same concentrations of NaHCO$_3$ as for the nitrate runs. The results concerning nitrobenzene and catechol will be presented first because of their significance.

Photodegradation of nitrobenzene

Nitrobenzene is an interesting substrate to start with because it is a reasonably selective probe for the $^{\bullet}$OH radicals in aqueous solution (Watts and Linden, 2007), although some interfering reactions cannot be excluded (Vione et al., in press). Figure 1 reports the initial degradation rate of nitrobenzene upon irradiation of nitrate, as a function of the concentration of NaHCO$_3$ or the phosphate buffer. The direct photolysis rates of nitrobenzene are also reported. Note the pH of the solutions on the upper X-axis. The reported pH values are those measured in the presence of NaNO$_3$ + NaHCO$_3$; in the other cases they were the same within 0.1 pH units.

Nitrobenzene undergoes little to negligible direct photolysis. In the presence of nitrate + phosphate, the degradation rate of nitrobenzene decreases with increasing phosphate (and pH). The stabilisation of the rate above 5 mM phosphate is most likely connected to the pH trend, which reaches a plateau under the same conditions. In the system under study it is expected that the degradation rate of nitrobenzene is proportional to the photogeneration rate of the $^{\bullet}$OH radicals (Watts and Linden, 2007), which shows a significant decrease with pH in the basic range (reactions (1-5)) (Mark et al., 1996; Mack and Bolton, 1999). Note that the pH trend of nitrobenzene degradation, the rate of which decreases by a factor of about 2 between pH 6.6 and 8.5, is similar to that observed with phenol under comparable conditions (Chiron et al., 2009).

It is possible to deduce the pH effect on the photoproduction of $^{\bullet}$OH, from the data of nitrobenzene photodegradation rate with the phosphate buffer (R$_{NBz}$). The phosphate data of Figure 1 were fitted numerically with a simple function that foresees a plateau at elevated phosphate concentration (fit variables were R$^{\circ}_{NBz}$, a and b):

$$R_{NBz} = R^{\circ}_{NBz} \cdot \left(\frac{C_{Phosphate} + a}{b \cdot C_{Phosphate} + a} \right) \qquad (6)$$

R$^{\circ}_{NBz}$ is the photodegradation rate of nitrobenzene upon nitrate irradiation in the absence of bicarbonate or phosphate, and C$_{Phosphate}$ (in molarity) is the total concentration of the phosphate buffer. The numerical coefficients a and b obtained from the data fitting were 0.0075 and 2.25, respectively. Figure 1 shows the good agreement between the fitting equation and the experimental data.

The Figure also shows that $NaHCO_3$ inhibits the degradation of nitrobenzene more than phosphate, therefore suggesting that the effect of bicarbonate is not only connected to pH. In the presence of $NaHCO_3$, both the carbonate and the bicarbonate ions are able to scavenge $^\bullet OH$. Obviously the merely pH-dependent effect would still be operational, and it could be assessed by replacing $C_{Phosphate}$ with C_{NaHCO3} in equation (6). The degradation rate of nitrobenzene in the presence of $NaNO_3 + NaHCO_3$ was fitted with equation (7), which was derived from (6) by taking into account the competition for $^\bullet OH$ between the aromatic substrate and the inorganic carbon species.

$$\left(R_{NBz}\right)_{pH} = R^{\circ}_{NBz} \cdot \left(\frac{C_{NaHCO3} + a}{b \cdot C_{NaHCO3} + a}\right) \cdot \left(\frac{k_{NBz} \cdot [NBz]}{k_{NBz} \cdot [NBz] + k_{HCO3-} \cdot [HCO_3^-] + k_{CO32-} \cdot [CO_3^{2-}]}\right) \quad (7)$$

[NBz] is the initial concentration of nitrobenzene (25 µM), and k_{NBz}, k_{HCO3-} and k_{CO32-} are the reaction rate constants of $^\bullet OH$ with nitrobenzene, bicarbonate and carbonate (3.9×10^9, 8.5×10^6 and 3.9×10^8 M^{-1} s^{-1}, respectively; Buxton et al., 1988). For a and b they were adopted the values obtained by fitting of the phosphate data (0.0075 and 2.25). Such a procedure is based upon the hypothesis that the merely pH-dependent effect of bicarbonate is the same or comparable to that of the phosphate buffer. The values of $[HCO_3^-]$ and $[CO_3^{2-}]$ as a function of C_{NaHCO3} were determined by simple calculations of solution equilibria, considering that

$$[H^+] = \sqrt{\frac{Ka_1 \cdot Ka_2 \cdot C_{NaHCO3} + Ka_1 \cdot K_W}{C_{NaHCO3} + Ka_1}} \quad (8)$$

where Ka_1 and Ka_2 are the acidic dissociation constants of carbonic acid, and K_W is the auto-protolysis constant of water (Martell et al., 1997). The very good fit of equation (7) to the experimental data is reported in Figure 1 (note that the only fit variable was R°_{NBz}). The nitrobenzene trend can thus be accounted for by the reaction with $^\bullet OH$, in agreement with the literature reports that nitrobenzene does not react with $CO_3^{-\bullet}$ to a significant extent (Neta et al., 1988). Very understandably, bicarbonate could not be able to enhance the degradation of a substrate that does not undergo acid-base equilibria, and reacts negligibly with $CO_3^{-\bullet}$.

Photodegradation of catechol

Figure 2 reports the degradation rate of catechol (pK$_a$ ≈ 9.5) (Martell et al., 1997) in the presence of $NaNO_3$ + phosphate and of $NaNO_3$ + $NaHCO_3$ under irradiation, and upon irradiation in the presence of $NaHCO_3$, without nitrate. The degradation rates in the absence of nitrate are accounted for by thermal transformation rather than the direct photolysis. Indeed, the electron abstraction from cathecol to yield the semiquinone radical or 1,2-benzoquinone is favoured with increasing pH (Schweigert et al., 2001). To check for thermal degradation, the irradiation cells were wrapped in

aluminium foil and put under the lamp in the same conditions adopted for the irradiation runs. In the case of catechol, about the same degradation rates were obtained in the two series of experiments. Among the studied substrates, evidence of thermal degradation was only found for catechol and 1,4-benzoquinone.

In the presence of nitrate + phosphate, the degradation rate of catechol is affected to a very limited extent. This suggests that the decrease of the $^\bullet$OH photogeneration rate by nitrate under basic conditions is roughly compensated for by the increased thermal degradation of catechol.

Compared to the phosphate buffer, catechol degradation is significantly enhanced in the presence of $NaHCO_3$. The approximately constant trend with phosphate (and pH as a consequence) is interesting because it provides a constant baseline. Over that baseline, the catechol / $NaHCO_3$ data would measure the increase of the photogeneration rate of reactive species carried out by bicarbonate (mainly $CO_3^{-\bullet}$; Chiron et al., 2009). Interestingly, it has been shown that the carbonate radical and similar species can replace $^\bullet$OH as effective oxidants under definite conditions (Bahnemann et al., 1981 & 1983; Forni et al., 1982).

Let R°_{NO3-} be the formation rate of the reactive species upon nitrate irradiation, in the absence of bicarbonate. It would vary with pH, but in the case of catechol the thermal degradation would introduce a rough compensation: it is reasonable to hypothesise that the mere variation of pH upon addition of $NaHCO_3$ would have the same, almost negligible effect on the degradation rate of catechol that was observed with the phosphate buffer. The additional photoformation rate of the reactive species induced by bicarbonate (R_{NO3-}) could be obtained upon numerical fitting of the $NaHCO_3$ data of Figure 2. The degradation rate of catechol at a given C_{NaHCO3} ($R_{Catechol}$) would be the sum of the baseline (and approximately constant) $R^\circ_{Catechol}$, plus the effect of bicarbonate unaccounted for by pH (R_{NO3-}). The experimental data could be fitted with the phenomenological equation (9), which allows for the quantification of R_{NO3-} vs. C_{NaHCO3} (with $R^\circ_{Catechol}$ and α as fit variables).

$$R_{Catechol} = R^o_{Catechol} + R_{NO3-} = R^o_{Catechol} \cdot \left(1 + \frac{\alpha \cdot C_{NaHCO3}}{C_{NaHCO3} + 0.061}\right) \qquad (9)$$

It was obtained $\alpha = 11.3$ upon numerical fitting of the experimental data. The value of α would be roughly proportional to the reactivity of catechol with the species produced by nitrate in the presence of bicarbonate. Figure 2 shows the very good quality of the fit. $R^\circ_{Catechol}$ would measure the formation rate of the reactive species in the presence of nitrate alone, without bicarbonate or phosphate (mainly $^\bullet$OH; Mack and Bolton, 1999). The application of eq. (6) to the nitrobenzene data of Figure 1, and of eq. (9) to the catechol data of Figure 2, yielded in fact $R^\circ_{Catechol} \approx R^\circ_{NBz} \approx 2 \times 10^{-9}$ M s^{-1}. This result is expected because catechol and nitrobenzene are the only scavengers of $^\bullet$OH in each respective system.

Photodegradation of 1,4-benzoquinone

Figure 3 reports the degradation rate of 1,4-benzoquinone (BQ) in the presence of $NaNO_3$, with $NaHCO_3$ or phosphate, and in the presence of $NaHCO_3$, without nitrate. The decrease of BQ initial degradation rate with increasing phosphate, analogous to that already observed for nitrobenzene, can be ascribed to a lower generation rate of $^\bullet OH$ by nitrate under basic conditions. In the case of BQ this effect cannot obviously be compensated for by acid-base equilibria. The further decrease of the degradation rate with increasing $NaHCO_3$, again in analogy with the nitrobenzene findings, suggests that the scavenging of $^\bullet OH$ by bicarbonate and carbonate is more important than the presumably low reactivity between benzoquinone and $CO_3^{-\bullet}$.

The degradation of BQ without nitrate is mainly accounted for by the direct photolysis, and only to a lesser extent by the thermal decomposition. The importance of the direct photolysis could explain why the degradation of BQ is considerably faster than for the other substrates. However, the degradation rate of BQ with nitrate alone is about 1×10^{-8} M s^{-1} higher than the rate of the direct photolysis under comparable conditions. By comparison, the nitrobenzene and catechol data suggest that the photoformation rate of $^\bullet OH$ from nitrate is $R^\circ_{\bullet OH,NO3-} \approx 2\times10^{-9}$ M s^{-1}. The reason of the difference might be the involvement of the photoexcited states of benzoquinone (Puranik and Umapathy, 2002) in the transformation reactions.

The rate data of BQ in the presence of phosphate were fitted with equation (10), which is a modified version of eq. (6) to take the direct photolysis into account (R°_{BQ}, a, b, and c as fit variables). The data fitting yielded $a = 0.0134$, $b = 9.87$, and $c = 1.2\times10^{-8}$ M s^{-1}. The values of a and b are different compared to nitrobenzene, possibly because of the involvement of BQ excited states in the reactions. The value of c obtained from the fitting is slightly lower than the rate of BQ direct photolysis. The photolysis would be slower in the presence of nitrate, and the likely reason is the competition between BQ and nitrate for the absorption of UVB radiation.

$$R_{BQ} = R^\circ_{BQ} \cdot \left(\frac{C_{Phosphate} + a}{b \cdot C_{Phosphate} + a} \right) + c \tag{10}$$

The bicarbonate data were fitted with equation (11), which is a modification of (7), adopting $a = 0.0134$, $b = 9.87$, $c = 1.2\times10^{-8}$ M s^{-1}, $k_{BQ} = 1.2\times10^9$ M^{-1} s^{-1}, and R°_{BQ} as the only fit variable. The good fit between eq. (11) and the experimental data indicates that the bicarbonate effect on BQ degradation is mainly due to the scavenging of $^\bullet OH$.

$$\left(R_{BQ} \right)_{pH} = R^\circ_{BQ} \cdot \left(\frac{C_{NaHCO3} + a}{b \cdot C_{NaHCO3} + a} \right) \cdot \left(\frac{k_{BQ} \cdot [BQ]}{k_{BQ} \cdot [BQ] + k_{HCO3-} \cdot [HCO_3^-] + k_{CO32-} \cdot [CO_3^{2-}]} \right) + c \tag{11}$$

Photodegradation of 4-nitrophenol

Figure 4 reports the degradation rate of 25 μM 4-nitrophenol (4NP) upon irradiation of 10 mM NaNO$_3$, as a function of the concentration of NaHCO$_3$ or phosphate, and without nitrate upon addition of bicarbonate. Note that 4NP undergoes direct photolysis to a negligible extent.

Interestingly, the degradation rate of 4NP is almost unaffected by phosphate. The decrease of the formation rate of $^\bullet$OH upon basification is likely compensated for by the higher reactivity of the 4-nitrophenolate under irradiation (the pK$_a$ of 4NP is around 7.1) (Martell et al., 1997). Indeed, the reaction rate constant of the undissociated 4NP with $^\bullet$OH is approximately one half than that of the nitrophenolate (Buxton et al., 1988). By analogy with the $^\bullet$OH reactivity, the nitrophenolate could also undergo faster degradation upon reaction with other photogenerated transients (e.g. peroxynitrite and nitrogen dioxide).

The addition of NaHCO$_3$ inhibits the degradation of 4NP, probably because of the $^\bullet$OH scavenging by carbonate and bicarbonate. The trend expected for the $^\bullet$OH scavenging is described by eq. (7), replacing NBz with 4NP, with $a = 0.0075$ and $b = 2.25$, and k$_{4NP}$ as for the nitrophenolate. Eq. (7) is shown as a solid line on Figure 4. Clearly, bicarbonate inhibits the transformation of 4NP less than expected from the scavenging of $^\bullet$OH. To account for such a disagreement, it is possible to hypothesise a reaction between 4NP and the reactive species formed from nitrate and bicarbonate (mostly CO$_3^{-\bullet}$; Chiron et al., 2009). Literature data show that the second-order rate constant for the reaction between the 4-nitrophenolate and CO$_3^{-\bullet}$ is 4.8×10^7 M^{-1} s^{-1} (Neta et al., 1988), significant albeit much lower than the 7.6×10^9 M^{-1} s^{-1} for the reaction with $^\bullet$OH (Buxton et al., 1988).

A suitable equation to describe the trend of 4NP vs. bicarbonate should consider altogether the pH trend of nitrate photolysis (eq. 6), the competition of 4NP with carbonate and bicarbonate for the reaction with $^\bullet$OH (eq. 7), and the production of reactive species by nitrate as enhanced by bicarbonate (eq. 9). One would therefore obtain equation (12) to describe the trend of 4NP:

$$\left(R_{4NP}\right)_{pH} = R^{\circ}_{4NP} \cdot \left(\frac{C_{NaHCO3} + a}{b \cdot C_{NaHCO3} + a} \right) \cdot \left(\frac{k_{4NP} \cdot [4NP]}{k_{4NP} \cdot [4NP] + k_{HCO3-} \cdot [HCO_3^-] + k_{CO32-} \cdot [CO_3^{2-}]} \right) \cdot \left(1 + \frac{\alpha \cdot C_{NaHCO3}}{C_{NaHCO3} + 0.061} \right)$$

(12)

With $a = 0.0075$, $b = 2.25$, k$_{4NP}$ as for the nitrophenolate, and R$^{\circ}_{4NP}$ and α as fit variables, one gets a reasonable fit to the experimental data as shown in Figure 4. It is α = 1.96 for 4NP, much lower than for catechol. This finding is in agreement with the fact that, unlike catechol, the degradation of 4NP is inhibited and not enhanced by bicarbonate.

Photodegradation of 4-halogenophenols

Figure 5 reports the initial degradation rates of 4-fluoro-, 4-chloro-, 4-bromo- and 4-iodophenol (4FP, 4CP, 4BP, 4IP) upon irradiation in the presence of $NaNO_3$ + $NaHCO_3$ or the phosphate buffer, and upon direct photolysis without nitrate in the presence of bicarbonate.

All the four compounds undergo acid-base equilibria, with pK_a values in the 9 to 10 range (4FP: 9.9; 4CP: 9.4; 4BP: 10; 4IP: 9.2) (Martell et al., 1997). The behaviour of 4CP is remarkable because this compound undergoes direct photolysis to a very significant extent under basic conditions, since the chlorophenolate is photochemically unstable (Grabner and Richard, 2005; Czaplicka, 2006). Interestingly, the comparison of the direct photolysis and phosphate data suggests that a possible reaction might take place between bicarbonate or carbonate and the excited states of 4CP. It could explain the peculiarly elevated degradation rate of 4CP in the presence of $NaHCO_3$, with or without nitrate. The direct photolysis is significant but less important for the remaining compounds, and the trend with phosphate would include the contributions of the undissociated phenols and of the phenolates toward the direct photolysis and the reaction with $^\bullet OH$. The phosphate trends of 4FP and 4IP could be considered as roughly constant (very roughly in the case of 4FP), while in the case of 4BP there is a slight increase of the kind $R_{4BP} \approx R^\circ_{4BP} + (4.4 \pm 1.1) \times 10^{-7} C_{Phosphate}$.

Given the nature of the phosphate baseline, the bicarbonate data of 4FP and 4IP were fitted with eq. (9), obviously by replacing catechol with the relevant compound, while for 4BP the term $(4.4 \pm 1.1) \times 10^{-7} C_{NaHCO3}$ was added at the RHS of the equation. The data concerning 4CP were not fitted because of the high importance of the direct photolysis. The fit yielded $\alpha \approx 5$ for 4FP, 17 for 4BP, and 15 for 4IP. Figure 5 shows the good quality of the fit to the experimental data. Interestingly, fluorine as the most electronegative substituent gave the lowest value of α, which is expected because 4FP should have lower electron density on the aromatic ring compared to 4BP or 4IP. The low electron density of 4FP would result into lower reactivity compared to 4BP or 4IP.

Environmental significance

Under the hypothesis that the degradation of catechol is mainly accounted for by the reactions with $^\bullet OH$ and $CO_3^{-\bullet}$, and that catechol is the major sink of these species in solution, the increase of the generation rate of $^\bullet OH$ + $CO_3^{-\bullet}$ carried out by bicarbonate in the presence of nitrate under irradiation would be expressed by R_{NO3-} in eq. (9). Furthermore, the good fit of eqs. (6) and (7) to the experimental nitrobenzene data of Figure 1 suggests that the degradation rate of nitrobenzene is similar or at least proportional to the photogeneration rate of $^\bullet OH$. Accordingly, a suitable phenomenological equation to describe the trend of the $^\bullet OH$ photogeneration rate by nitrate under basic conditions is eq. (6), provided that R_{NBz} and R°_{NBz} are replaced by $R_{\bullet OH,NO3-}$ and $R^\circ_{\bullet OH,NO3-}$. The two latter quantities represent the photoformation rate of $^\bullet OH$ by nitrate, respectively in the presence and in the absence of the phosphate buffer. Considering that bicarbonate would have about the same effect on pH under the adopted laboratory conditions and in natural systems (Chiron et al.,

2009), equation (6) would be relevant for the environmental cases provided that $C_{Phosphate}$ is replaced by the total amount of inorganic carbon, expressed in moles of C per litre, hereafter [IC]. In summary, one gets eq. (13):

$$R_{\bullet OH,NO3-} = R^{\circ}_{\bullet OH,NO3-} \cdot \left(\frac{[IC]+a}{b \cdot [IC]+a} \right) \tag{13}$$

By combination of eqs. (9) and (13), one gets that the total formation rate of the reactive transients in the presence of nitrate and bicarbonate under irradiation ($R_{tot}^{NO3-/HCO3-}$) would be given by $R_{\bullet OH,NO3-} + R_{NO3-}$, as follows:

$$R_{tot}^{NO3-/HCO3-} = R^{\circ}_{\bullet OH,NO3-} \cdot \left(\frac{[IC]+a}{b \cdot [IC]+a} + \frac{\alpha \cdot [IC]}{[IC]+0.061} \right) \tag{14}$$

with $a = 0.0075$, $b = 2.25$, and $\alpha = 11.3$. Figure 6 reports eq. (14) ($R_{tot}^{NO3-/HCO3-}$ / $R^{\circ}_{\bullet OH/NO3-}$ vs. [IC]), which shows an interesting monotonic increase. This means that the α term, which increases with [IC], prevails over the term containing a and b that decreases with [IC].

An important issue is that the formation of reactive species, described by equation (14), would take place upon reaction between $^{\bullet}OH$ and carbonate/bicarbonate when the former is still inside the solvent cage after nitrate photolysis, or via peroxynitrite + bicarbonate (Chiron et al., 2009), rather than upon scavenging of $^{\bullet}OH$ by carbonate/bicarbonate in the solution bulk. Accordingly, while the bulk process is expected to undergo inhibition by DOM, the same is not necessarily true of the reactions described phenomenologically by equation (14). Additional research will be conducted to understand if and to what extent DOM can scavenge solvent-cage $^{\bullet}OH$ or peroxynitrite.

In the first metre of the Lake Greifensee (Switzerland) under summertime irradiation conditions, it is $R^{\circ}_{\bullet OH,NO3-} \approx 1.3 \times 10^{-11}$ M s^{-1}, and the formation rate of $CO_3^{-\bullet}$ through scavenging of $^{\bullet}OH$ by carbonate and bicarbonate ([IC] $\approx$ 2 mM) would be $R_{CO3-\bullet} = 2 \times 10^{-12}$ M s^{-1} (Canonica et al., 2005). Despite $R_{CO3-\bullet} = 0.15 \, R^{\circ}_{\bullet OH,NO3-}$, because of the lower scavenging by DOM the carbonate radical could still account for the degradation of easily oxidised substrates (e.g. aniline, 4-hydroxybenzoate), to a comparable or even higher extent than $^{\bullet}OH$ (Vione et al., 2009b). Very interestingly, from eq. (14) one gets that the total formation rate of the reactive species in the first metre of the Lake Greifensee would be $R_{tot}^{NO3-/HCO3-} = 1.5 \times 10^{-11}$ M s^{-1}. The direct generation rate of $CO_3^{-\bullet}$ from nitrate + bicarbonate would be at least 2×10^{-12} M s^{-1}, roughly equal to the formation rate of the carbonate radical upon scavenging of $^{\bullet}OH$ by HCO_3^- and CO_3^{2-}. The total formation rate of $CO_3^{-\bullet}$ (around 4×10^{-12} M s^{-1}) would therefore be double compared to the contribution of the scavenging alone. The effect would be even more marked for carbonate-richer environments, and the consequence is that the role of $CO_3^{-\bullet}$ in surface-water photochemistry could be considerably higher than is usually assumed. DOM could scavenge the radicals after their formation, as it already does with $^{\bullet}OH$ and $CO_3^{-\bullet}$ from the "traditional" processes, but it is less likely to prevent their

formation (Chiron et al., 2009). Accordingly, carbonate and bicarbonate could significantly enhance the photodegradation by nitrate of electron-rich compounds in surface waters. Such an effect would take place instead of the expected inhibition of photodegradation, with potentially very important consequences on the fate of many electron-rich phenolic pollutants in surface waters.

Conclusions

It was studied the effect of the $^\bullet$OH scavengers bicarbonate and carbonate on the rate of photodegradation upon nitrate irradiation of different compounds (substituted phenols, nitrobenzene, benzoquinone). The following conclusions could be obtained:

(i) The mere basification of the solution decreases the generation rate of $^\bullet$OH by irradiated nitrate, most likely because of the acid-base equilibrium between HOONO and ONOO$^-$. Peroxynitrite is in fact unable to yield $^\bullet$OH (Mack and Bolton, 1999). The decrease with pH of the rate of $^\bullet$OH photogeneration by nitrate would be the only operational effect for the compounds that do not undergo acid-base equilibria, such as nitrobenzene and benzoquinone. They show, therefore, a decreasing degradation rate with increasing pH.

(ii) The presence of bicarbonate and carbonate would further decrease the availability of $^\bullet$OH through scavenging. However, because of different effects (Chiron et al., 2009), the generation rate of $^\bullet$OH + $CO_3^{-\bullet}$ in the presence of $NaHCO_3$ would be higher than that of $^\bullet$OH alone in its absence. The budget could still lead to a decrease of the transformation rate of the substrates that are poorly reactive toward $CO_3^{-\bullet}$, such as nitrobenzene, 1,4-benzoquinone, and 4-nitrophenol. They are electron-poor systems that require $^\bullet$OH to be effectively degraded. For more electron-rich systems such as the 4-halogenophenols and catechol the addition of $NaHCO_3$ significantly enhances the phototransformation kinetics. The rate constant with $CO_3^{-\bullet}$ is 4.8×10^7 M^{-1} s^{-1} for 4NP that undergoes a slight inhibition of degradation in the presence of $NaHCO_3$ ($\alpha \approx 2$), and 1.8×10^8 M^{-1} s^{-1} for 4BP, the degradation of which is enhanced by bicarbonate ($\alpha \approx 17$). It could therefore be inferred that the value of the carbonate rate constant for which there is a transition between enhancement and inhibition should be somewhere around 10^8 M^{-1} s^{-1}. An overview of the data (where available) of $k_{\bullet OH}$, $k_{CO3-\bullet}$, pK_a and α for the different compounds under study is reported in Table 2.

(iii) The degradation rates of the substrates under study could be fitted well by eqs. (6,7,9-12). The abundance of possible fitting equations is just apparent because eq. (12) is a generalised case for (6) and (7). Accordingly, eq. (12) is reduced to (7) for $\alpha = 0$, and to (6) for both $\alpha = 0$ and $[HCO_3^-] = [CO_3^{2-}] = 0$. Additionally, (10) and (11) differ from (6) and (7) only by the presence of a constant *c*. As a consequence, the main choice is between eqs. (9) and (12), with (9) being more suitable in the presence of a constant pH (phosphate) baseline. In some cases eqs. (9) or (12) have to be modified to take the direct photolysis into account.

The significance of the reported findings should be stressed because a substantial degradation enhancement was observed with a number of substrates, upon addition of the $^\bullet$OH scavengers carbonate and bicarbonate. It should also be pointed out that the described phenomenon is independent of the fact that $CO_3^{-\bullet}$ can reach a higher steady-state concentration in surface waters compared to $^\bullet$OH. In other words, the effect described in this work would solely be connected to a higher generation rate of the reactive species, induced by bicarbonate in the presence of nitrate under irradiation. The well-known ability of $CO_3^{-\bullet}$ to undergo scavenging by DOM to a lesser extent than $^\bullet$OH in natural systems (Huang and Mabury, 2000a; Canonica et al., 2005) is a different phenomenon, but it could further amplify the impact of an increased photogeneration rate of $CO_3^{-\bullet}$ in surface waters.

Acknowledgements

Table 2. Data concerning the studied substrates, relevant to the results of the present study. The values of $k_{\bullet OH}$ are taken from Buxton et al. (1988), those of $k_{CO3-\bullet}$ from Neta et al. (1988), those of pK_a from Martell et al. (1997). The values of α were obtained in the present study.

Compound	pK_a	$k_{\bullet OH}$, M^{-1} s^{-1}	$k_{CO3-\bullet}$, M^{-1} s^{-1}	α
Nitrobenzene	N/a	3.9×10^9	N/a	0
4-Fluorophenol	9.9	N/a	N/a	5
4-Chlorophenol	9.4	7.6×10^9	1.9×10^8 (*)	N/a
4-Bromophenol	10	N/a	1.8×10^8 (*)	17
4-Iodophenol	9.2	N/a	N/a	15
4-Nitrophenol	7.1	3.8×10^9	4.8×10^7 (*)	1.96
		7.6×10^9 (*)		
Catechol	9.5	1.1×10^{10}	N/a	11.3
1,4-Benzoquinone	N/a	1.2×10^9	N/a	0

N/a: Not applicable or not available

(*): the datum is referred to the phenolate

References

Bahnemann, D., Asmus, K.-D. and Willson, R. L. (1981) Free radical reactions of the phenothiazine, metiazinic acid. Journal of the Chemical Society, Perkin Transactions 2, 890-895.

Bahnemann, D., Asmus, K.-D. and Willson, R. L. (1983) Free radical induced one-electron oxidation of the phenothiazines chlorpromazine and promethazine. Journal of the Chemical Society, Perkin Transactions 2, 1661-1668.

Bouillon, R. C. and Miller, W. L. (2005) Photodegradation of dimethyl sulfide (DMS) in natural waters: Laboratory assessment of the nitrate-photolysis-induced DMS oxidation. Environmental Science & Technology 39, 9471-9477.

Brezonik, P. L. and Fulkerson-Brekken, J. (1998) Nitrate-induced photolysis in natural waters: Controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents. Environmental Science & Technology 32, 3004-3010.

Brigante, M., DellaGreca, M., Previtera, L., Rubino, M. and Temussi, F. (2005) Degradation of hydrochlorothiazide in water. Environmental Chemistry Letters 2, 195-198.

Buxton, G. V., Greenstock, C. L., Helman, W. P. and Ross, A. B. (1988) Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/^{\bullet}O^{-}$) in aqueous solution. Journal of Physical and Chemical Reference Data 17, 513-886.

Canonica, S., Kohn, T., Mac, M., Real, F. J., Wirz, J. and Von Gunten, U. (2005) Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. Environmental Science & Technology 39, 9182-9188.

Canonica, S., Hellrung, B., Müller, P. and Wirz, J. (2006) Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones. Environmental Science & Technology 40, 6636-6641.

Canonica, S. (2007) Oxidation of aquatic organic contaminants induced by excited triplet states. Chimia 61, 641-644.

Chiron, S., Minero, C. and Vione, D. (2006) Photodegradation processes of the Antiepileptic drug carbamazepine, relevant to estuarine waters. Environmental Science & Technology 40, 5977-5983.

Chiron, S., Minero, C. and Vione, D. (2007) Occurrence of 2,4-dichlorophenol and of 2,4-dichloro-6-nitrophenol in the Rhone River Delta (Southern France). Environmental Science & Technology 41, 3127-3133.

Chiron, S., Barbati, S., Khanra, S., Dutta, B. K., Minero, C., Maurino, V., Pelizzetti, E. and Vione, D. (2009) Bicarbonate-enhanced transformation of phenol upon irradiation of hematite, nitrate, and nitrite. Photochemical and Photobiological Sciences 8, 91-100.

Czaplicka, M. (2006) Photo-degradation of chlorophenols in the aqueous solution. Journal of Hazardous Materials 134, 45-59.

Dzengel, J., Theurich, J. and Bahnemann, D. (1999) Formation of nitroaromatic compounds in advanced oxidation processes: Photolysis versus photocatalysis. Environmental Science & Technology 33, 294-300.

Espinoza, L. A. T., Neamtu, M. and Frimmel, F. H. (2007) The effect of nitrate, Fe(III) and bicarbonate on the degradation of bisphenol A by simulated solar-UV irradiation. Water Research 41, 4479-4487.

Forni, L., Bahnemann, D. and Hart, E. J. (1982) Mechanism of the hydroxide ion initiated decomposition of ozone in aqueous solution. Journal of Physical Chemistry 86, 255-259.

Goldstein, S., Czapski, G., Lind, J. and Merenyi, G. (2001) Carbonate radical ion is the only observable intermediate in the reaction of peroxynitrite with CO_2. Chemical Research in Toxicology 14, 1273-1276.

Grabner, G. and Richard, C. (2005) Mechanisms of direct photolysis of biocides based on halogenated phenols and anilines. In: The Handbook of Environmental Chemistry, Vol. 2, Part M (Environmental Photochemistry Part II), Boule, P., Bahnemann, D. W. and Robertson, P. K. J. (eds.), Springer, Berlin, pp. 161-192.

Huang, J. P. and Mabury, S. A. (2000a) Steady-state concentrations of carbonate radicals in field waters. Environmental Toxicology and Chemistry 19, 2181-2188.

Huang, J. P. and Mabury, S. A. (2000b) A new method for measuring carbonate radical reactivity toward pesticides. Environmental Toxicology and Chemistry 19, 1501-1507.

Lahl, U. and Hawxwell, K. A. (2006) Reach - The European chemicals law. Environmental Science & Technology 40, 7115-7121.

Lam, M. W., Tantuco, K. and Mabury, S. A. (2003) PhotoFate: A new approach in accounting for the contribution of indirect photolysis of pesticides and pharmaceuticals in surface waters. Environmental Science & Technology 37, 899-907.

Lam, M. W. and Mabury, S. A. (2005) Photodegradation of the pharmaceuticals atorvastatin, carbamazepine, levofloxacin, and sulfamethoxazole in natural waters. Aquatic Sciences 67, 177-188.

Mack, J. and Bolton, J. R. (1999) Photochemistry of nitrite and nitrate in aqueous solution: A review. Journal of Photochemistry and Photobiology A: Chemistry 128, 1-13.

Mark, G., Korth, H.-G., Schuchmann, H.-P. and von Sonntag, C. (1996) The photochemistry of aqueous nitrate ion revisited. Journal of Photochemistry and Photobiology A: Chemistry 101, 89-103.

Martell, A. E., Smith, R. M. and Motekaitis, R. J. (1997) Critically selected stability constants of metal complexes database, version 4.0.

Mazellier, P., Busset, C., Delmont, A., and De Laat, J. (2007) A comparison of fenuron degradation by hydroxyl and carbonate radicals in aqueous solution. Water Research 41, 4585-4594.

Neta, P., Huie, R. E. and Ross, A. B. (1988) Rate constants for reactions of inorganic radicals in aqueous solution. Journal of Physical and Chemical Reference Data 17, 1027-1234.

Puranik, M. and Umapathy, S. (2002) Excited state structure and dynamics of p-benzoquinone and bromanil from time-resolved resonance Raman spectra and simulation. Bulletin of the Chemical Society of Japan 75, 1057-1064.

Schweigert, N., Zehnder, A. B. J. and Eggen, R. I. L. (2001) Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals. Environmental Microbiology 3, 81-91.

Squadrito, G. L. and Pryor, W. A. (2002) Mapping the reaction of peroxynitrite with CO_2: Energetics, reactive species, and biological implications. Chemical Research in Toxicology 15, 885-895.

Vione, D., Maurino, V., Minero, C. and Pelizzetti, E. (2004) Phenol nitration upon oxidation of nitrite by Mn(III,IV) (hydr)oxides. Chemosphere 55, 941-949.

Vione, D., Maurino, V., Minero, C. and Pelizzetti, E. (2005) Aqueous atmospheric chemistry: Formation of 2,4-dinitrophenol upon nitration of 2-nitrophenol and 4-nitrophenol in solution. Environmental Science & Technology 39, 7921-7931.

Vione, D., Maurino, V., Cucu Man, S., Khanra, S., Arsene, C., Olariu, R. I. and Minero, C. (2008) Formation of organobrominated compounds in the presence of bromide under simulated atmospheric aerosol conditions. ChemSusChem 1, 197-204.

Vione, D., Maurino, V., Minero, C., Duncianu, M., Olariu, R. I., Arsene, C., Sarakha, M. and Mailhot, G. (2009a) Assessing the transformation kinetics of 2- and 4-nitrophenol in the atmospheric aqueous phase. Implications for the distribution of both nitroisomers in the atmosphere. Atmospheric Environment 43, 2321-2327.

Vione, D., Maurino, V., Minero, C., Carlotti, M. E., Chiron, S. and Barbati, S. (2009b) Modelling the occurrence and reactivity of the carbonate radical in surface freshwater. Comptes Rendus Chimie 12, 865-871.

Vione, D., Ponzo, M., Bagnus, D., Maurino, V., Minero, C. and Carlotti, M. E. (in press). Comparison of different probe molecules for the quantification of hydroxyl radicals in aqueous solution. Environmental Chemistry Letters, DOI: 10.1007/s10311-008-0197-3.

Virag, D., Naar, Z. and Kiss, A. (2007) Microbial toxicity of pesticide derivatives produced with UV-photodegradation. Bulletin of Environmental Contamination and Toxicology 79, 356-359.

Wardman, P. (1989) Reduction potentials of one-electron couples involving free radicals in aqueous solution. Journal of Physical and Chemical Reference Data 18, 1637-1717.

Watts, M. J. and Linden, K. G. (2007) Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. Water Research 41, 2871-2878.
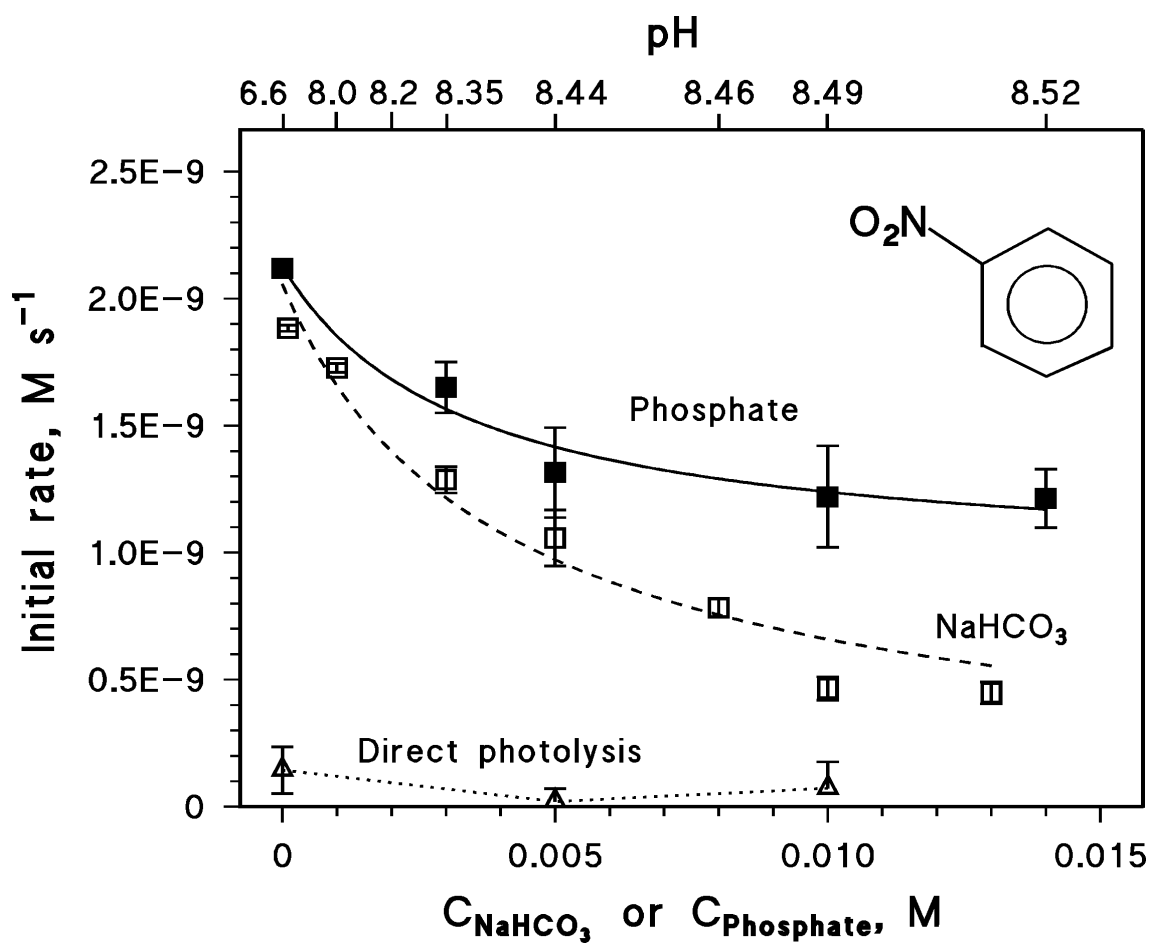
Figure 1. Initial degradation rate of 25 μM nitrobenzene upon UVB irradiation of 10 mM NaNO₃, as a function of the concentration of NaHCO₃ or the phosphate buffer, and upon direct photolysis under UVB irradiation (addition of NaHCO₃). The pH values are reported on the second X-axis, in correspondence to the adopted C_{NaHCO3}. In the case of the phosphate buffer, the pH is the same within 0.1 units. The phosphate data are fitted with eq. (6), the bicarbonate ones with eq. (7).
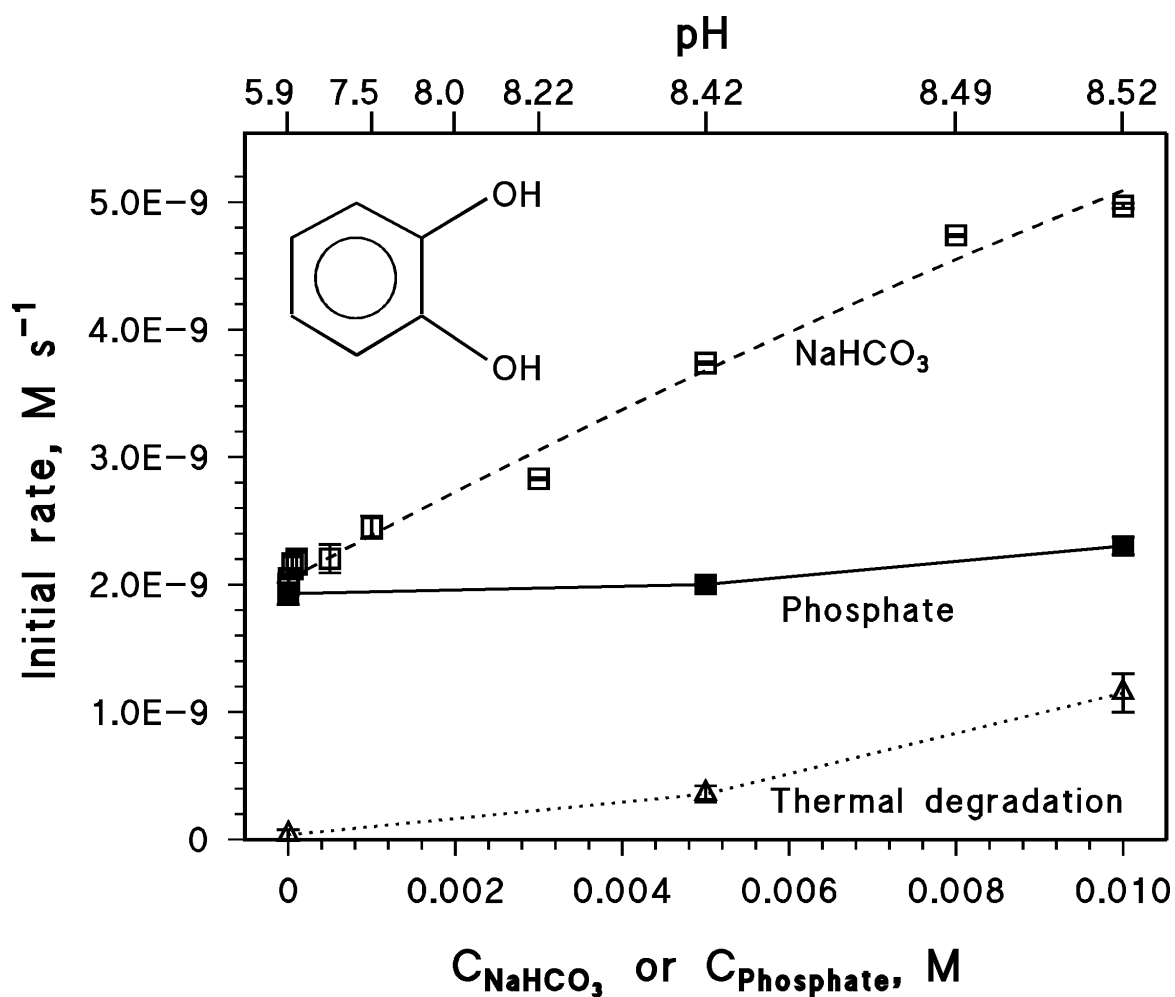
Figure 2. Initial degradation rate of 25 μM catechol upon UVB irradiation of 10 mM NaNO₃, as a function of the concentration of NaHCO₃ or the phosphate buffer, and upon direct photolysis under UVB irradiation (addition of NaHCO₃). Note the pH values on the second X-axis. The bicarbonate data were fitted with eq. (9).
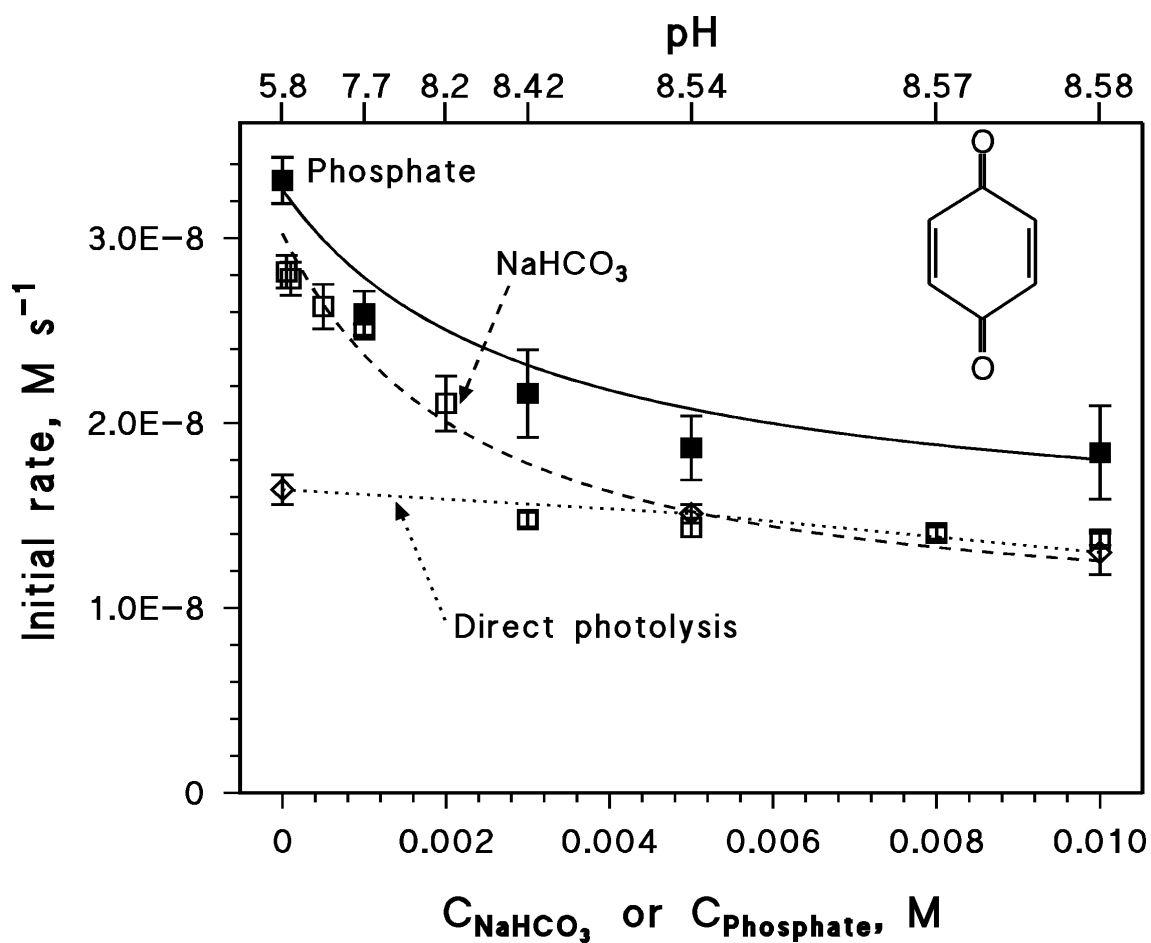
Figure 3. Initial degradation rate of 25 μM 1,4-benzoquinone upon UVB irradiation of 10 mM NaNO₃, as a function of the concentration of NaHCO₃ or the phosphate buffer, and upon direct photolysis under UVB irradiation (addition of NaHCO₃). Note the pH values on the second X-axis. The phosphate data were fitted with eq. (10), the bicarbonate ones with eq. (11).
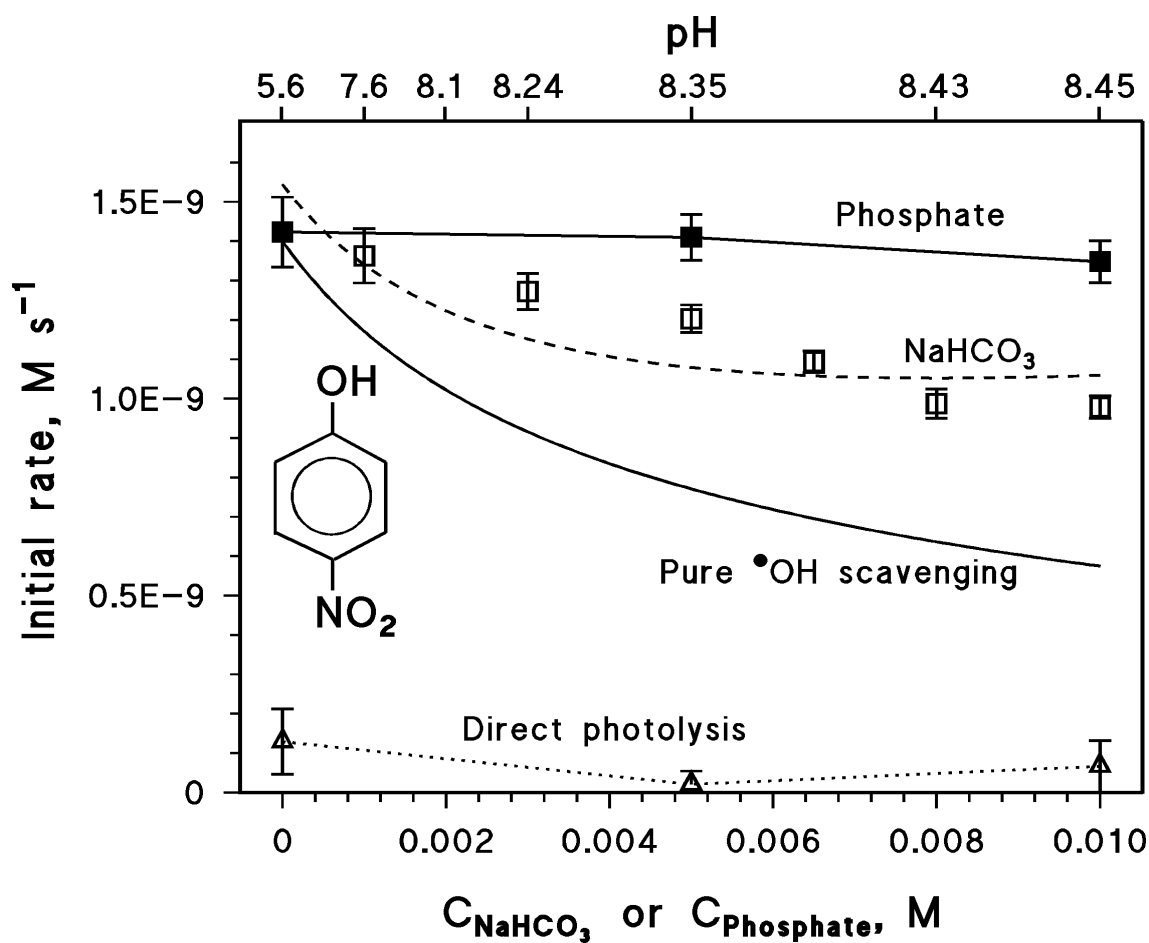
Figure 4. Initial degradation rate of 25 μM 4-nitrophenol upon UVB irradiation of 10 mM NaNO$_3$, as a function of the concentration of NaHCO$_3$ or the phosphate buffer, and upon direct photolysis under UVB irradiation (addition of NaHCO$_3$). Note the pH values on the second X-axis. The bicarbonate data were fitted with eq. (12). The trend expected by application of eq. (7) is also reported (pure •OH scavenging). In eq. (7) NBz should be replaced by 4NP, and k$_{4NP}$ is referred to the nitrophenolate.
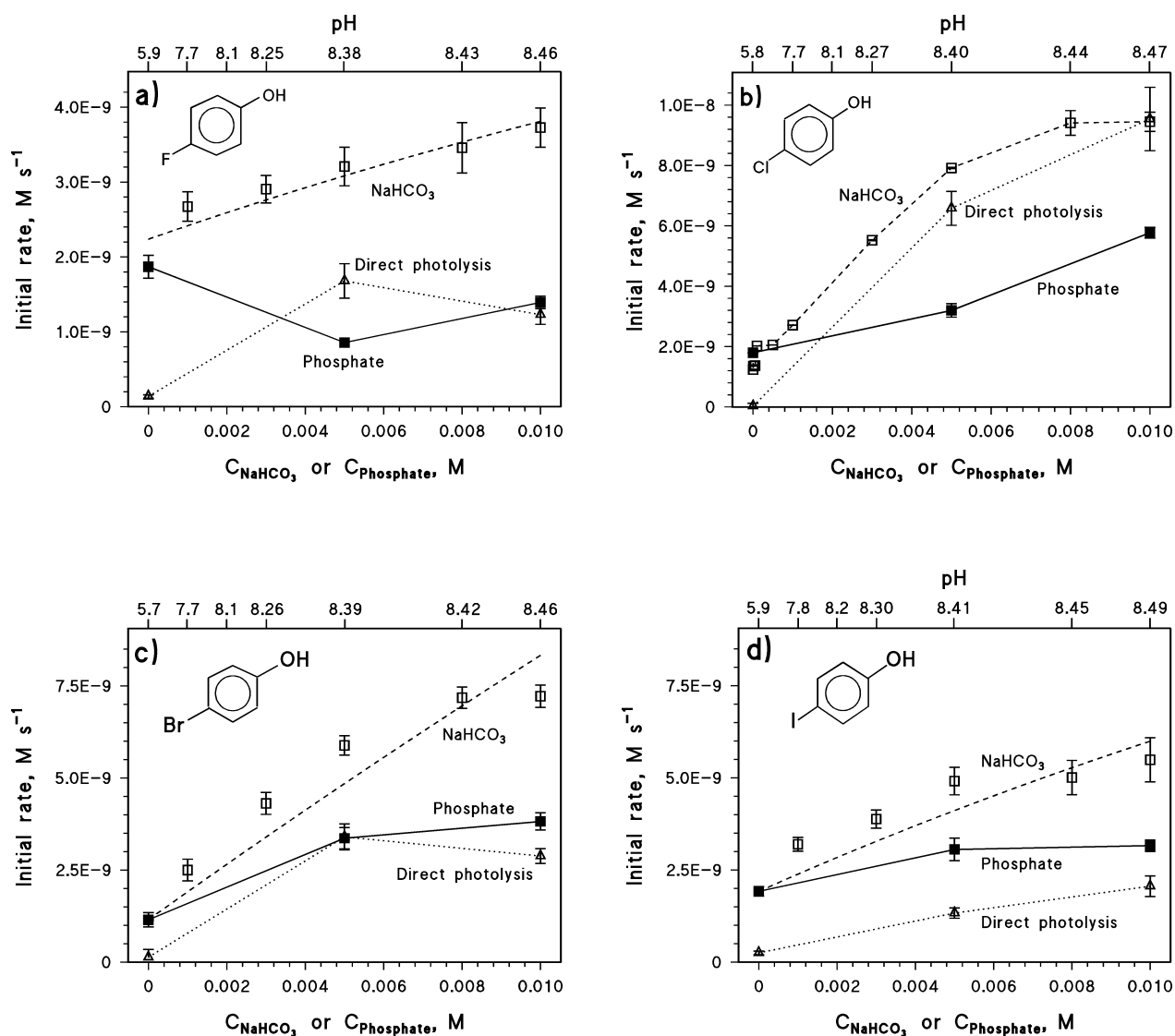
Figure 5. Initial degradation rate of 25 μM 4-fluorophenol (4FP, (a)), 4-chlorophenol (4CP, (b)), 4-bromophenol (4BP, (c)), and 4-iodophenol (4IP, (d)), upon UVB irradiation of 10 mM NaNO₃, as a function of the concentration of NaHCO₃ or the phosphate buffer, and upon direct photolysis under UVB irradiation (addition of NaHCO₃). Note the pH values on the second X-axis.

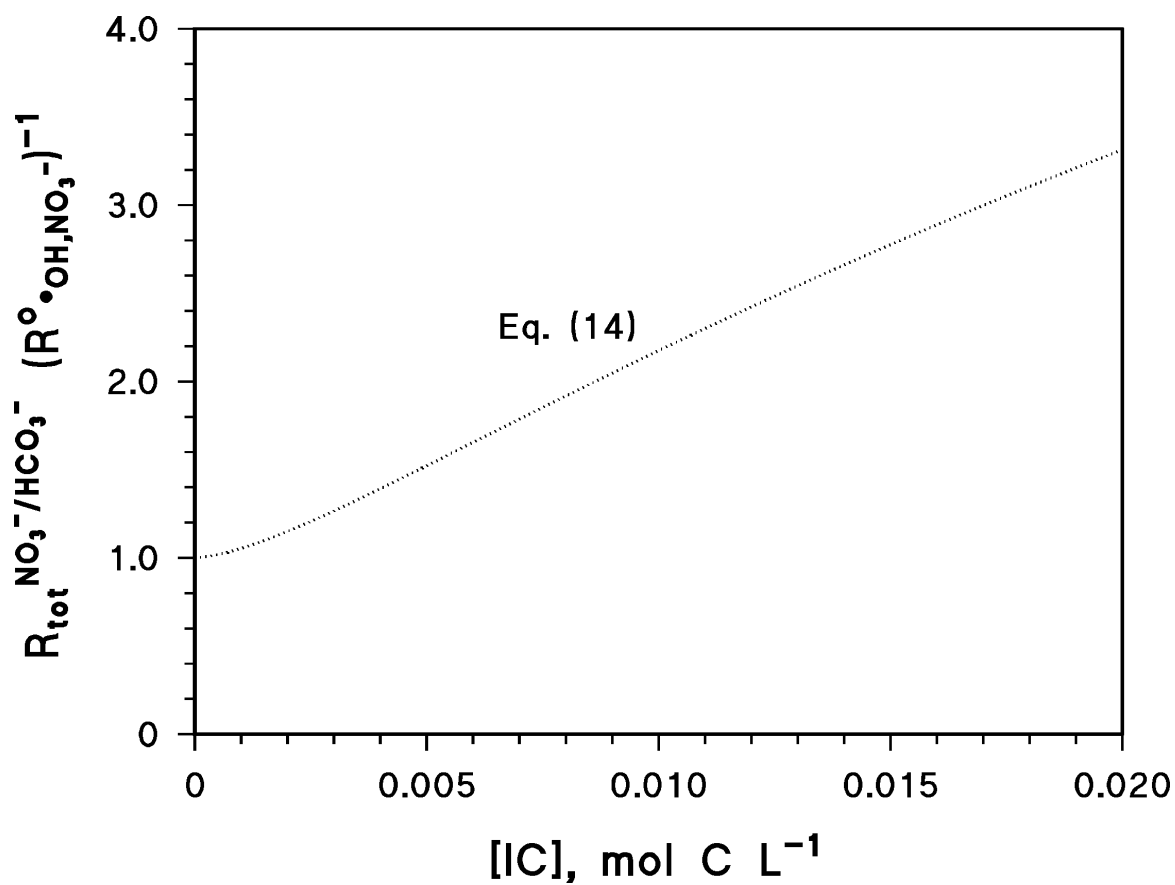**Figure 6.** Formation rate of reactive species ($R_{tot}^{NO3-/HCO3-}$ / $R^{\circ}_{\bullet OH/NO3-}$) as a function of the inorganic carbon, [IC] (eq. (14)). Note the monotonic increase of ($R_{tot}^{NO3-/HCO3-}$ / $R^{\circ}_{\bullet OH/NO3-}$) vs. [IC].