Suppression of inhibition of substrate photodegradation by scavengers of hydroxyl radicals: the solvent-cage effect of bromide on nitrate photolysis

SUPPRESSION OF INHIBITION OF SUBSTRATE PHOTODEGRADATION BY SCAVENGERS OF HYDROXYL RADICALS: THE SOLVENT-CAGE EFFECT OF BROMIDE ON NITRATE PHOTOLYSIS.

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Abstract

In this paper we show that bromide scavenges the $^{\bullet}OH$ radicals formed upon photolysis of nitrate, before they leave the solvent cage. Bromide can thus inhibit the in-cage recombination between $^{\bullet}OH$ and $^{\bullet}NO_2$. The consequence is an increased generation of $^{\bullet}NO_2$ and nitrite and of $Br_2^{-\bullet}$ + $^{\bullet}OH$, compared to $^{\bullet}OH$ alone in the absence of bromide. We show that this effect compensates for the lower reactivity of $Br_2^{-\bullet}$ compared to $^{\bullet}OH$ toward certain organic substrates, e.g. phenol and tryptophan. Our findings could lead to a deep revision of the present views of the role of bromide in saltwater photochemistry.

Keywords: dibromine radical; nitrobenzene; bromophenol; solvent-cage effect; nitrogen dioxide; photolysis; sea-salt particles.

1. Introduction

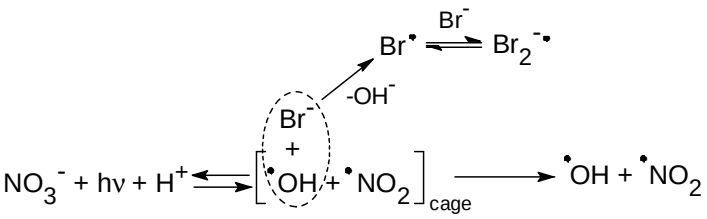
The nitrate ion is an important source of $^{\bullet}OH$ radicals in surface and atmospheric waters. It absorbs UVB radiation with a maximum around 305 nm, but the absorption of sunlight by nitrate is most efficient at around 315-320 nm (Zepp et al., 1987). The UV photolysis of nitrate yields $^{\bullet}OH$ and $^{\bullet}NO_2$. The former is a powerful oxidant, while the latter can be involved into nitration reactions (Nélieu et al., 2004).

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}OH + {}^{\bullet}NO_2 \qquad (1)$$

Nitrate at the observed environmental concentrations is able to induce significant photodegradation of organic substrates, including important pollutants, under laboratory conditions (Chiron et al., 2006). However, in real water bodies the photochemistry of nitrate is considerably inhibited by the scavenging of hydroxyl radicals that is carried out by dissolved organic matter and inorganic carbon (Brezonik and Fulkerson-Brekken, 1998). The bromide ion is the main scavenger of $^{\bullet}OH$ in saltwater. It is present at around 0.8 mM concentration in seawater and can reach 8 mM in aqueous sea-salt particles (Bouillon and Miller, 2005; George and Anastasio, 2007). Under these circumstances it is able to scavenge around 97% of the photogenerated $^{\bullet}OH$ radicals. The reaction between bromide and $^{\bullet}OH$ yields the radical anion $Br_2^{-\bullet}$, which is reactive but less than hydroxyl toward organic and inorganic compounds (Neta et al., 1988).

$$2\,Br^- + {}^{\bullet}OH \rightarrow Br_2^{-\bullet} + OH^- \qquad (2)$$

Based on these assumptions it could be hypothesised that bromide inhibits the degradation processes initiated by $^{\bullet}OH$, among which are those involved in the photochemistry of nitrate. However, it has been reported that the photodegradation of dimethylsulphide (DMS) upon nitrate photolysis is significantly enhanced by bromide (Bouillon and Miller, 2005). An important feature of DMS is its elevated reaction rate constant with $Br_2^{-\bullet}$ (2.2×10^9 M^{-1} s^{-1}, Neta et al., 1998), but still one could expect to observe no effect on degradation and not an enhancement. Bouillon and Miller have proposed some tentative hypotheses to account for the experimental data. The test of the hypotheses was out of the scope of their paper, but among the other possible explanations they have inferred that bromide could enhance the degradation of DMS through a solvent-cage effect on the photolysis of nitrate. Indeed, $^{\bullet}OH$ and $^{\bullet}NO_2$ that are formed in reaction (1) are at the beginning very near to one another and surrounded by the solvent molecules. Under these circumstances it is very likely that they react to yield back nitrate; only the non-recombined radical species are able to diffuse out of the solvent cage into the solution bulk. Bromide at sufficiently elevated concentration could be able to reach the surface of the water cage and therefore react with $^{\bullet}OH$ when it is still inside the cage (reaction 3). In this way the in-cage recombination between $^{\bullet}OH$ and $^{\bullet}NO_2$ would be inhibited by bromide, and the generation rate of $Br_2^{-\bullet}$ + $^{\bullet}OH$ with bromide could be higher than that of $^{\bullet}OH$ alone without Br^-. Such an effect allows for the possible enhancement of photodegradation by bromide as hydroxyl scavenger. Note that $^{\bullet}OH$ and $^{\bullet}NO_2$ are extremely unlikely to undergo significant recombination in the solution bulk, after they leave the solvent cage, because the hydroxyl radical in the bulk is much more likely to react with other $^{\bullet}OH$ scavengers than with $^{\bullet}NO_2$ (Minero et al., 2007).



(3)

The described solvent-cage effect, which was just a tentative hypothesis might have substantial implications for the environmental chemistry of the radical scavengers. It could completely reverse the current views concerning the role of the scavengers themselves in photochemistry. Furthermore, the solvent-cage inhibition of the photolysis reactions through radical-radical recombination is of considerable interest for the

photochemistry of the air-water interface of atmospheric droplets, where the solvent cage is incomplete (Nissenson et al., 2006; Khanra et al., 2008).

Given these premises, the main purpose of the present paper was that of testing the solvent-cage hypothesis for bromide on nitrate photolysis. Here we provide evidence for bromide to react with $^{\bullet}OH$ inside the cage, thereby enhancing the photochemistry of nitrate. We also studied the effect of bromide on the nitrate-induced photodegradation of organic compounds (phenol, tryptophan, nitrobenzene) with different reactivity toward the radical $Br_2^{-\bullet}$. The results provide novel insights into the photochemical effects of bromide and the $^{\bullet}OH$ scavengers in general toward the photolysis of nitrate, with implications for the photochemistry of the marine surface layer and of aqueous sea-salt particles.

2. Experimental

2.1. Reagents and materials

Phenol (purity grade 99%), catechol (>99%), 2-bromophenol (98%), 4-bromophenol (99%), tryptophan (>98%), nitrobenzene (>99%), 2-nitrophenol (98%), 3-nitrophenol (99%), 4-nitrophenol (98%), $NaNO_2$ (>97%) and 2,4-dinitrophenylhydrazine (97%) were purchased from Aldrich, $NaNO_3$ (99.5%) from VWR Int., NaBr (99%) from Fluka, acetonitrile (supergradient grade) from Scharlau. All reagents were used as received without further purification.

2.2. Experimental procedures

Irradiation experiments were carried out under a Philips TL01 lamp with emission maximum at 313 nm. The lamp irradiance was 5.6 W m^{-2}, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter and corresponding to 3.7×10^{-6} einstein L^{-1} s^{-1} in solution. The emission spectrum of the lamp is reported in Vione et al. (2008). Solutions for irradiation were placed into Pyrex glass cells (4.0 cm diameter, 2.3 cm height) and magnetically stirred during irradiation. After irradiation the solutions were analysed by High-Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD). The instrument used was a VWR-Hitachi chromatograph, equipped with L-2200 autosampler, L-2130 pump for low-pressure gradients, L-2300 column oven, L-2455 DAD detector, and a column Merck LiChroCART 125-4 (125 mm length by 4 mm diameter), packed with LiChrospher 100 RP18 (particle diameter 5 μm). Isocratic elution was carried out with a mixture of acetonitrile and phosphate buffer at 1.00 mL min^{-1} flow rate, and the column dead time was 0.9 min. Eluent composition and pH, detection wavelength (λ) and retention time (t_R) for the compounds of interest are all reported in Table 1.

Table 1. Chromatographic data relative to the compounds of interest in the present work.

Compound	% CH_3CN	pH	λ, nm	t_R, min
Phenol	30	3	276	3.12
Catechol	30	3	276	1.96
2-Bromophenol	30	3	200	6.65
4-Bromophenol	30	3	200	7.95
Tryptophan	4	6	280	5.50
Nitrobenzene	40	3	265	4.96
2-Nitrophenol	40	3	265	4.15
3-Nitrophenol	40	3	265	2.74
4-Nitrophenol	40	3	265	2.55

The quantification of nitrite was carried out following the procedure of Kieber and Seaton (1996). Pre-column derivatisation (10 min contact time) of nitrite with 2,4-dinitrophenylhydrazine in acidic solution by HCl yields an azide that can be detected by HPLC-DAD. Elution was carried out with a 50:50 mixture of acetonitrile: phosphate buffer (pH 3) at 1.00 mL min^{-1} flow rate, with detection at 307 nm. Under these conditions the retention time of the azide was 3.40 min and the column dead time 0.90 min. Note that 2,4-dinitrophenylhydrazine tends to get contaminated by the azide upon reaction with ambient nitrogen dioxide. To get a satisfactory detection limit for nitrite, the azide can be extracted from the reagent by CCl_4 (Kieber and Seaton, 1996).

The time evolution data of the substrates (phenol, tryptophan, nitrobenzene) were fitted with equations of the kind $[S]_t = [S]_0 \exp(-k\ t)$, where $[S]_t$ is the substrate concentration at the time t, $[S]_0$ the initial concentration, and k the pseudo-first order degradation rate constant. The initial degradation rate of S is given by $k\ [S]_0$. The degradation rates of the substrates are reported in Figure 2 (*vide infra*). The error bounds to the rates ($\mu \pm \sigma$) represent the goodness of the fit of the theoretical curves to the experimental data, and show the intra-series variability. The inter-series variability (repeated runs) was in the 5-15% range.

The time evolution data of the transformation intermediates were fitted with equations of the kind $[I]_t = k'\ [S]_0\ (k-k'')\ [\exp(-k''\ t) - \exp(-k\ t)]$, where $[I]_t$ is the concentration of the intermediate I at the time t, k' the pseudo-first order formation rate constant of I from S, and k" the pseudo-first order degradation rate constant of I. Some examples of fitting are given in Figures 1, 3, 4 (*vide infra*).

3. Results and Discussion

3.1. Effect of bromide on nitrite photogeneration

Looking more closely at reaction (3) one notices that, if bromide can react with $^{\bullet}OH$ inside the solvent cage it would inhibit the in-cage recombination between $^{\bullet}OH$ and $^{\bullet}NO_2$. A major consequence of this fact would be an enhancement of the transfer of $^{\bullet}NO_2$ out of the cage, into the solution bulk. Nitrogen dioxide undergoes

hydrolysis in aqueous solution (reactions 4,5), which is a major source of nitrite upon nitrate irradiation (Minero et al., 2007).

$$2\ {}^{\bullet}NO_2 \rightleftarrows N_2O_4 \qquad (4)$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2\ H^+ \qquad (5)$$

It could therefore be inferred that a solvent-cage effect of bromide on nitrate photolysis, such as that depicted in reaction 3 could enhance the formation of nitrite from irradiated nitrate. To test the solvent-cage hypothesis, we have studied the formation rate of nitrite upon irradiation of $NaNO_3$ in the presence of NaBr, and the results are shown in Figure 1. It is apparent from Figure 1 that the addition of bromide significantly enhances the generation of nitrite from nitrate. This finding is in agreement with the scavenging of ${}^{\bullet}OH$ by bromide inside the solvent cage. Also note that according to reactions (3-5) the formation rate of nitrite is proportional to that of ${}^{\bullet}NO_2$, which is in turn equal to that of ${}^{\bullet}OH + Br_2^{-\bullet}$. The cage reaction between ${}^{\bullet}OH$ and bromide would therefore consume ${}^{\bullet}OH$ but yield a higher amount of the radical $Br_2^{-\bullet}$.

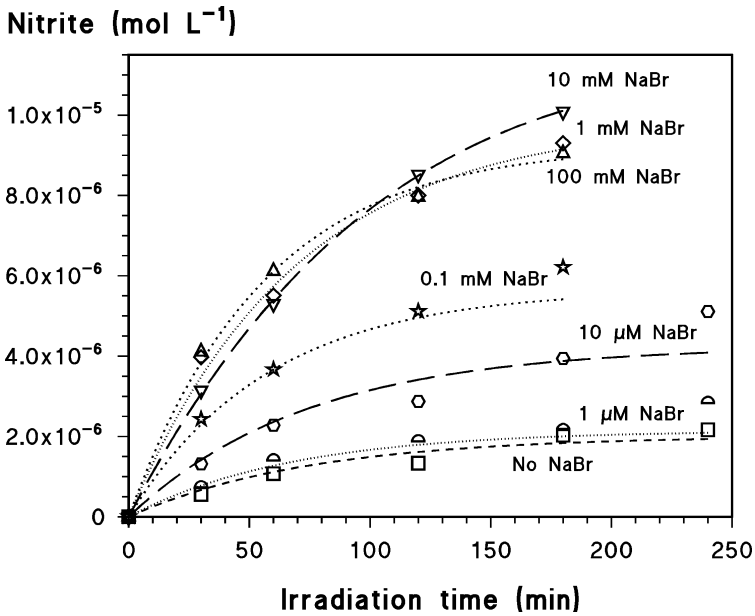


Figure 1. Time evolution of nitrite upon UVB irradiation of 0.10 M $NaNO_3$, in the presence of different amounts of NaBr. Note that nitrite photogeneration increases with increasing bromide.

This fact could have important but different consequences on the degradation kinetics of compounds with varied reactivity toward $Br_2^{-\bullet}$. An alternative explanation, that bromide can scavenge ${}^{\bullet}OH$ in the bulk and inhibit there the recombination between ${}^{\bullet}OH$ and ${}^{\bullet}NO_2$, is excluded by the results of previous numerical kinetic simulations. They show that the recombination rate of ${}^{\bullet}OH$ and ${}^{\bullet}NO_2$ in the solution bulk is negligible, and cannot control the availability of ${}^{\bullet}NO_2$ in the system (Minero et al., 2007). As a consequence, ${}^{\bullet}OH$ scavengers could not be able to enhance the photogeneration of nitrite via the bulk pathway.

3.2. Effect of bromide on substrate photodegradation

We studied the effect of bromide on the degradation of phenol, nitrobenzene, and tryptophan. It is reported that the second-order rate constants for reaction of phenol and tryptophan with $Br_2^{-\bullet}$ are 6×10^6 and 7×10^8 M^{-1} s^{-1}, respectively. In contrast, nitrobenzene does not react with $Br_2^{-\bullet}$ at a significant extent (Neta et al., 1988). Figure 2 reports the initial degradation rates of phenol, tryptophan and nitrobenzene, each of them at 0.1 mM initial concentration, in the presence of 0.10 M $NaNO_3$ and varying concentration values of bromide.

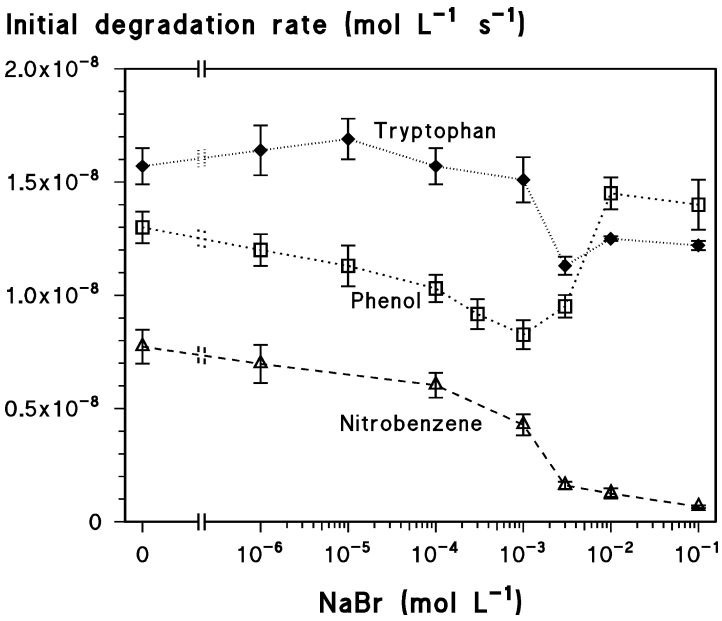


Figure 2. Initial degradation rates of phenol, nitrobenzene and tryptophan (initial concentration 0.1 mM) upon UVB irradiation of 0.10 M $NaNO_3$ and NaBr. Note that only nitrobenzene undergoes a steady inhibition of degradation by bromide.

In Figure 2 we show that the degradation of nitrobenzene is significantly inhibited by bromide. This is reasonable because Br^- scavenges $^\bullet OH$ and nitrobenzene reacts with $^\bullet OH$ (Buxton et al., 1988), but does not react with $Br_2^{-\bullet}$ at a significant extent (Neta et al., 1988). Additional support to this view comes from our finding that the initial formation of nitrophenols from nitrobenzene is inhibited by bromide (Figure 3). Indeed all the three nitrophenol isomers are formed upon reaction between nitrobenzene and $^\bullet OH$ (Chen et al., 2005), and the hydroxyl radical is consumed by the bromide ions.

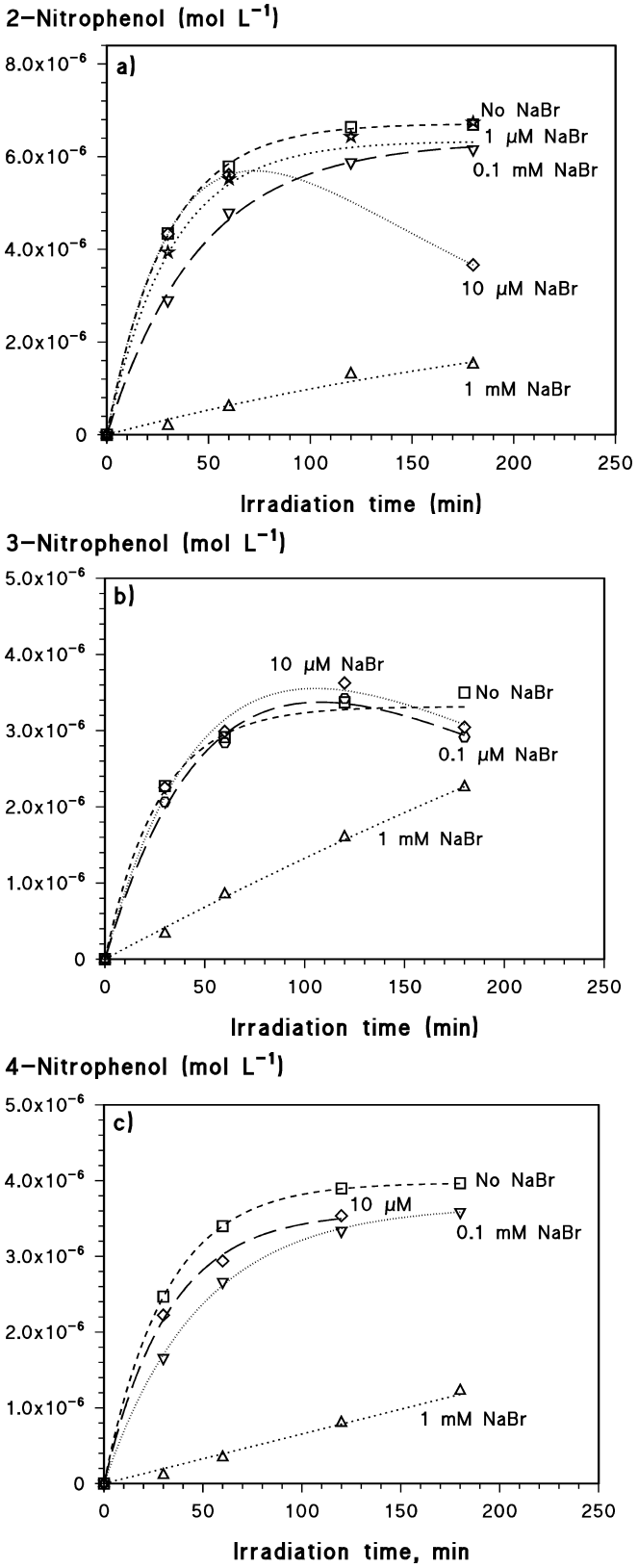


Figure 3. Formation of 2-, 3- and 4-nitrophenol from 0.10 mM nitrobenzene, upon UVB irradiation of 0.10 M $NaNO_3$ and varying concentration values of NaBr (reported near each curve). The time trend of nitrophenols reflects their formation/transformation budget, but bromide inhibits the initial formation of nitrophenols.

Figure 2 shows that the degradation of phenol decreases, although not substantially with increasing bromide up to 1 mM NaBr, after which is starts increasing with bromide. Above 10 mM NaBr the degradation rate of phenol is slightly higher than for the absence of bromide. The initial decrease of phenol degradation rate with bromide can be attributed to the scavenging of $^{\bullet}OH$ and to the lower reactivity of $Br_2^{-\bullet}$ compared to the hydroxyl radical. This is in agreement with our finding that the formation of catechol is inhibited and that of bromophenols enhanced by bromide (see Figure 4). Actually catechol is formed upon reaction between phenol and $^{\bullet}OH$, bromophenols from phenol and $Br_2^{-\bullet}$ (Vione et al., 2005; Vione et al., 2008).

The increase of phenol degradation rate above 1 mM NaBr can be attributed to the solvent-cage effect of bromide that enhances nitrate photochemistry. Indeed, the increase of the generation rate of $Br_2^{-\bullet}$ and the subsequent reaction between $Br_2^{-\bullet}$ and phenol would more than compensate for the scavenging of $^{\bullet}OH$.

The degradation of tryptophan is inhibited by sub-mM bromide at a far lesser extent than for phenol and nitrobenzene, probably because of the more elevated reactivity between tryptophan and $Br_2^{-\bullet}$. A certain increase of the degradation rate of tryptophan is also observed above 3 mM NaBr.

4. Conclusions

The present work provides evidence that bromide is able to scavenge the hydroxyl radicals inside the solvent cage, where they are formed upon the photolysis of nitrate. This finding is of substantial importance because the scavenging of the very reactive $^{\bullet}OH$ and the inhibition of the in-cage recombination between $^{\bullet}OH$ and $^{\bullet}NO_2$ result into an overall increase of the production of radical species in solution, especially $Br_2^{-\bullet}$. In the case of phenol the solvent-cage effect partially compensates, or more than compensates depending on the concentration of NaBr, for the scavenging of $^{\bullet}OH$ by bromide. Bromide around mM concentration as in seawater carries out a partial inhibition of the degradation of phenol. When the concentration is an order of magnitude higher as in aqueous sea-salt particles, the degradation rate of phenol is a bit higher than for the absence of bromide. In a similar way bromide does not inhibit significantly the degradation of tryptophan, also reactive with $Br_2^{-\bullet}$, in the presence of nitrate under irradiation. The situation is obviously different for more refractory compounds such as nitrobenzene, which reacts more selectively with $^{\bullet}OH$ and the photodegradation of which is inhibited by bromide.

It can be concluded that bromide could inhibit the nitrate-induced photodegradation of easy-to-oxidise substrates to a much lesser extent than could be foreseen by its ability to scavenge $^{\bullet}OH$. In some cases the inhibition could not be observed (such as for phenol), or a degradation enhancement could be operational (such as in the case of dimethyl sulphide; Bouillon and Miller, 2005). These findings prompt for a reconsideration of the role of bromide in saltwater photochemistry.

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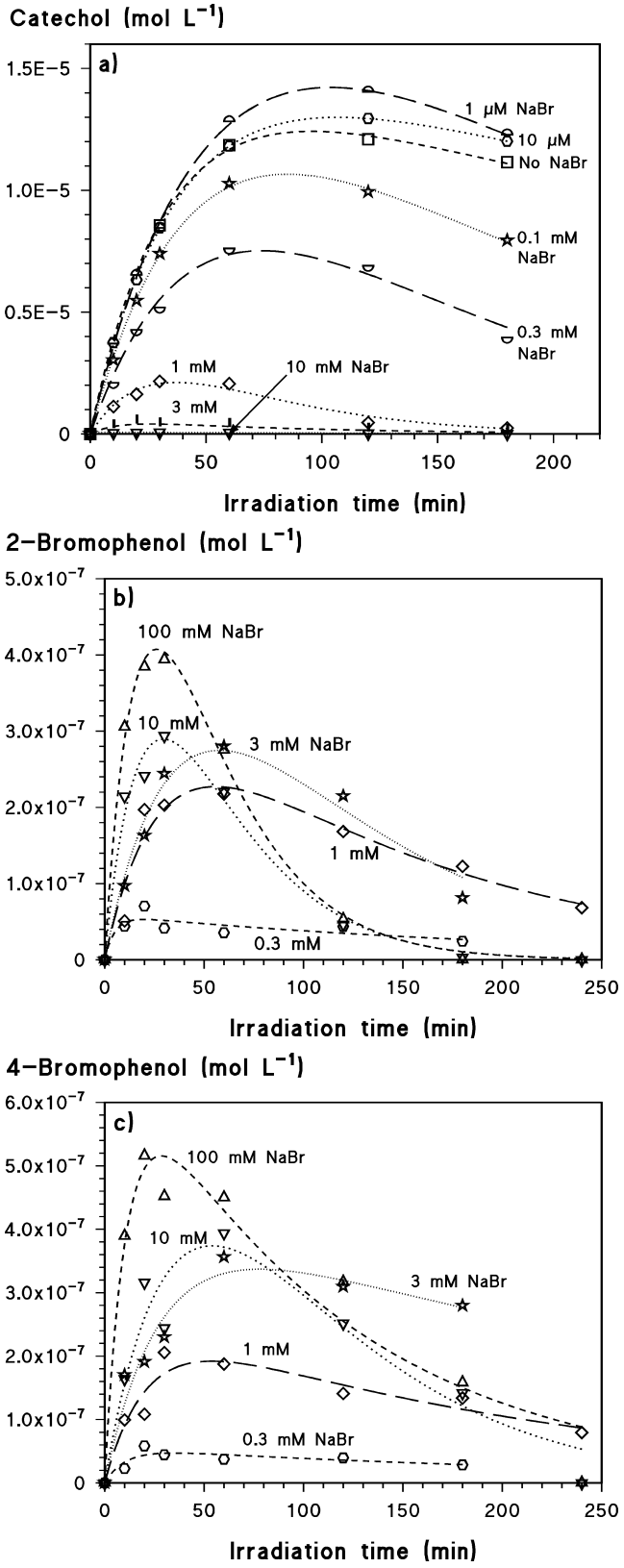

Figure 4. Formation of catechol and of 2- and 4-bromophenol from 0.10 mM phenol, upon UVB irradiation of 0.10 M $NaNO_3$ and varying concentration values of NaBr (reported near each curve). Note that bromide inhibits the formation of catechol and enhances that of bromophenols.

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