

On the effect of 2-propanol on phenol photonitration upon nitrate photolysis

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ABSTRACT

It is shown that the enhancement by 2-propanol of the nitration of phenol upon nitrate photolysis is compatible with the inhibition by the alcohol of in-cage recombination between $\bullet\text{O}^-$ and $\bullet\text{NO}_2$. This effect would increase the availability of $\bullet\text{NO}_2$ that is involved into phenol nitration, despite the enhancement by the alcohol of the production of superoxide that is a scavenger of $\bullet\text{NO}_2$. A kinetic model is proposed to describe the experimental data and to get insight into the processes involved. Kinetic calculations suggest that in the absence of 2-propanol less than 25% of cage $\bullet\text{O}^-$ and $\bullet\text{NO}_2$ would evolve into bulk species, the remainder undergoing recombination to nitrate. If reaction between cage $\bullet\text{O}^-$ and phenol were not negligible, the percentage of bulk species formation would be even lower. The data also show that most of the recombination between $\bullet\text{OH}/\bullet\text{O}^-$ and $\bullet\text{NO}_2$ would take place in the solvent cage instead of the solution bulk.

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The UV irradiation of nitrate produces $\bullet\text{OH}$ and $\bullet\text{NO}_2$, which can be involved into the transformation of dissolved compounds [1,2]. The hydroxyl radical is certainly the most reactive transient, but $\bullet\text{NO}_2$ can take part to photonitration reactions of aromatic molecules, yielding toxic and potentially mutagenic nitroderivatives [3]. Interestingly, $\bullet\text{NO}_2$ produced by nitrate photolysis and nitrite photooxidation induces significant nitration of chlorophenols (herbicide transformation intermediates) in flooded paddy fields and shallow lagoons [4, and references therein].

Early studies into phenol transformation upon nitrate photolysis have reported that $\bullet\text{OH}$ scavengers are able to enhance photonitration. Such an effect has been ascribed to the inhibition of recombination in the bulk between $\bullet\text{OH}$ and $\bullet\text{NO}_2$ [5]. However, it has been shown that the reaction between $\bullet\text{OH}$ and $\bullet\text{NO}_2$ in the solution bulk cannot be a significant sink for $\bullet\text{OH}$, *a fortiori* in the presence of dissolved organic substrates such as phenol [6]. Moreover, $\bullet\text{OH}$ scavengers such as formate and 2-propanol are able to increase the $\bullet\text{OH}$ quantum yield of nitrate photolysis [7]. A likely explanation is that photolytically generated $\bullet\text{O}^-$ (which later yields $\bullet\text{OH}$ upon protonation) and $\bullet\text{NO}_2$ are surrounded by a cage of water molecules, which favours their recombination to NO_3^- . Recombination can be inhibited by the reaction of the scavengers in excess with cage $\bullet\text{O}^-$, which increases the $\bullet\text{OH}$ quantum yield

measured from the reaction products of the scavengers [1,7]. For instance, acetone is formed by 2-propanol and $\bullet\text{OH}$. The formation rate of acetone was increased by about 3.8 times between 10^{-6} M and 0.1 M 2-propanol, which has been ascribed to the reaction between 2-propanol and cage $\bullet\text{O}^-$ [8]. Inhibition of the $\bullet\text{O}^- + \bullet\text{NO}_2$ cage recombination would enhance the generation of the nitrating agent $\bullet\text{NO}_2$. The purpose of the present work is to understand if the enhancement by 2-propanol of phenol photonitration upon nitrate photolysis can be accounted for by the cited cage process. This issue is relevant to photonitration reactions that take place in the environment [4], in natural waters rich in dissolved organic matter, and to advanced oxidation processes for wastewater treatment [1,9], which may use UV radiation and where organic compounds can be present in large amount.

Solutions (5 mL volume) containing phenol, nitrate and 2-propanol when relevant were placed in cylindrical Pyrex glass cells. For UVB irradiation it was adopted a Philips TL 01 lamp (incident photon flux $P_0 = 1.0 \times 10^{-6}$ Einstein $\text{L}^{-1} \text{s}^{-1}$ and maximum emission at 313 nm, near the 305-nm absorption maximum of nitrate [1]). Analysis after irradiation was carried out by liquid chromatography. 2-Nitrophenol (2NP) and 4-nitrophenol were formed as nitroderivatives. The former compound was present in larger amount, which allowed more accurate quantification; therefore, further discussion will concern 2NP only. The initial rates of 2NP formation were determined as the slopes for $t \rightarrow 0$ of the curves fitting the experimental data (see legend to Fig. 1). For further details concerning experimental set-up and data treatment see [4]. The reproducibility of repeated runs was 15–20%.

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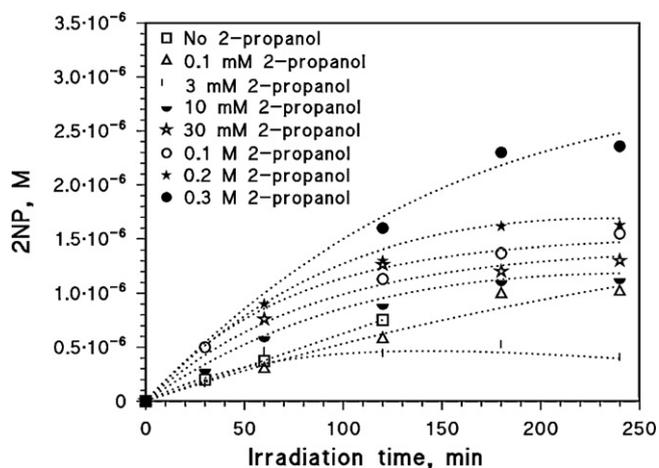


Fig. 1. Time evolution of 2NP upon UVB irradiation of 1 mM phenol and 0.1 M NaNO_3 (pH 6, phosphate buffer), in the presence of different initial concentrations of 2-propanol, in aerated solution. The time evolution data of 2NP are fitted with equations of the form $[2\text{NP}]_t = k_{2\text{NP}}^f \cdot [\text{PhOH}]_0 (k_{2\text{NP}}^d - k_{\text{PhOH}}^d)^{-1} [\exp(-k_{\text{PhOH}}^d \times t) - \exp(-k_{2\text{NP}}^d \times t)]$, where $[2\text{NP}]_t$ is the concentration of 2NP at the time t , $[\text{PhOH}]_0$ the initial phenol concentration, $k_{2\text{NP}}^f$ and $k_{2\text{NP}}^d$ the pseudo-first order rate constants for the formation and degradation of 2NP, and k_{PhOH}^d the pseudo-first order rate constant for the degradation of phenol.

Fig. 1 shows the time evolution of 2NP upon UVB irradiation of 1 mM phenol, 0.10 M nitrate and variable concentrations of 2-propanol. Phenol concentration was chosen to ensure that it scavenged a significant fraction of bulk $\bullet\text{NO}_2$ [4]. **Fig. 2** reports the initial formation rate of 2NP as a function of the alcohol concentration. The rate increased by 3.0 ± 1.2 times ($\mu \pm \sigma$) when passing from the absence of 2-propanol to the highest adopted concentration value (0.3 M). The data of **Fig. 2** are compatible with a reaction between 2-propanol and cage $\bullet\text{O}^-$, which would inhibit cage recombination and increase the availability of $\bullet\text{NO}_2$ [7,8]. A kinetic model was elaborated from the known reactions induced by nitrate photolysis, which can influence the photonitration of phenol [1,2,5,7,10–12] ($\text{PrOH} = 2\text{-propanol}$, $\text{PhOH} = \text{phenol}$, $A_{\text{NO}_3^-} = \text{nitrate absorbance}$):

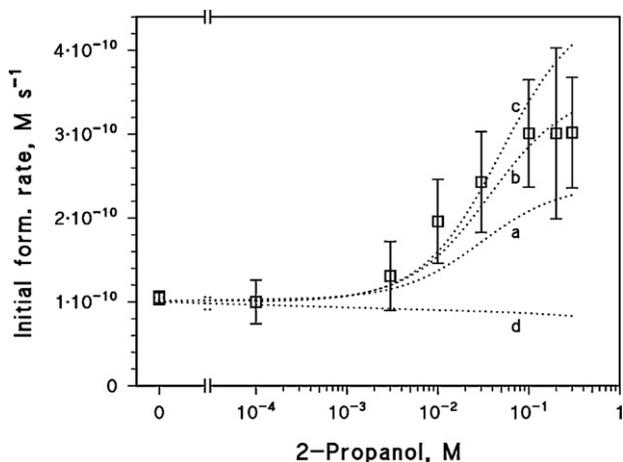
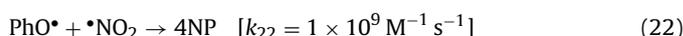
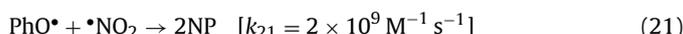
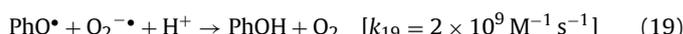
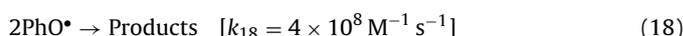
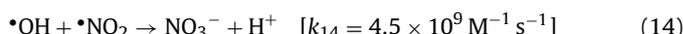
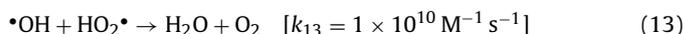
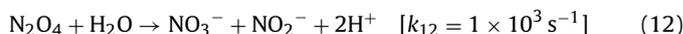
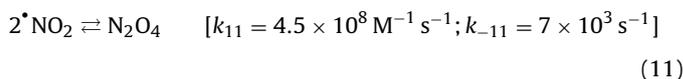
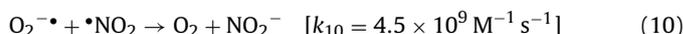
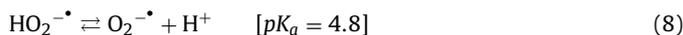
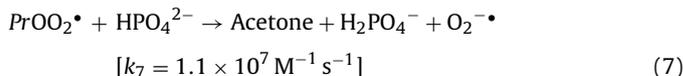
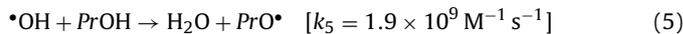
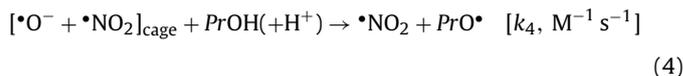
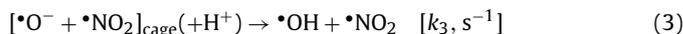
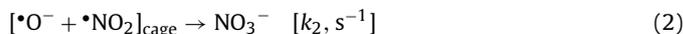


Fig. 2. Initial formation rate of 2NP upon UVB irradiation of 1 mM phenol and 0.1 M NaNO_3 , as a function of the concentration of 2-propanol. Note the logarithmic scale and the break in the X-axis. The dotted curves represent the trend foreseen by CKS calculations, on the basis of reactions (1–22), for $k_4 k_3^{-1} = 10^2 \text{ M}^{-1}$ (a–c) and $k_2 \times k_3^{-1} = 3$ (a), 5 (b) and 7 (c). Curve d was obtained by neglecting reaction (4) and with $k_2 \times k_3^{-1} = 5$. The experimental formation rates of 2NP were calculated as $R_{2\text{NP}} = k_{2\text{NP}}^f \cdot [\text{PhOH}]_0$. The error bounds associated to the rate data represent $\mu \pm \sigma$, derived from the fit of the experimental data reported in **Fig. 1** (intra-series variability).



The possible reaction between phenol and cage $\bullet\text{OH}$ was neglected because the trend with phenol concentration of the 2NP formation rate upon nitrate photolysis shows a plateau that can be accounted for by competition between reaction (20) and other $\bullet\text{NO}_2$ consumption processes in the solution bulk (see [4] and in the [supplementary material, Fig. S1](#)). A significant reaction between ~ 1 mM phenol and cage $\bullet\text{O}^-$ would enhance $\bullet\text{NO}_2$ generation and produce a further increase of the 2NP rate with phenol concentration that is not observed in [supplementary material, Fig. S1](#). If it were not negligible, the reaction between phenol and cage $\bullet\text{O}^-$ would further inhibit the recombination of $\bullet\text{O}^- + \bullet\text{NO}_2$ to nitrate. Furthermore, it was adopted $k_{21} = 2k_{22}$ because the formation rate of 2NP was about double compared to that of 4NP.

The kinetic system made up of reactions (1)–(22) was treated numerically by means of the Chemical Kinetics Simulator (CKS [13]) software package, which makes use of Monte Carlo techniques to solve complex kinetic systems (more details about the software settings are reported as [supplementary material](#)). Reactions (13) and (14) can be safely neglected because reactions (5) and (15) would be by far the main $\bullet\text{OH}$ sinks in the system. Concerning the unknown rate constants, no change of the modelled 2NP formation rate was observed by varying the values of k_{16} and k_{17} in a wide

range, from 1 to 10^{10} ($M^{-1} s^{-1}$ or s^{-1} as applicable), and a conventional value of 10^7 was adopted. The value of k_{17} is probably some orders of magnitude lower [14], but a modification would not change the calculation results. From the equilibrium reaction (8) it was derived $[HO_2\cdot] = 6.3 \times 10^{-2} [O_2^{\cdot-}]$ at pH 6, and reaction (9) was modified accordingly. The CKS results are independent of the actual values adopted for k_2 , k_3 and k_4 , they rather depend on their ratios. Anyway, it was hypothesised $k_4 = 10^{10} M^{-1} s^{-1}$. Fig. 2 shows the comparison between experimental data and model results for $k_4 \times k_3^{-1} = 10^2 M^{-1}$ and different values of $k_2 \times k_3^{-1}$: 3 (a), 5 (b) and 7 (c). No good agreement with the experimental data can be obtained for $k_2 \times k_3^{-1}$ outside the 3–7 range, or for $k_4 \times k_3^{-1}$ values that are significantly different from $10^2 M^{-1}$. This means that geminate recombination of $[O\cdot^- + \cdot NO_2]_{cage}$ would occur in the nanosecond-time domain. It is slower than the recombination kinetics of the two $\cdot OH$ produced by H_2O_2 photolysis [15], but $\cdot NO_2$ and the unprotonated $O\cdot^-$ formed upon nitrate photolysis should be less reactive than $\cdot OH$ [10]. Values of $k_2 \times k_3^{-1}$ in the 3–7 range mean that, in the absence of 2-propanol, less than 25% of $[O\cdot^- + \cdot NO_2]_{cage}$ would evolve into bulk radical species, the remainder undergoing recombination to nitrate. In case of a significant reaction between phenol and cage $O\cdot^-$, the percentage of $[O\cdot^- + \cdot NO_2]_{cage}$ that would evolve into bulk species would be even lower.

In the absence of reaction (4) the model foresees a slight inhibition by 2-propanol of the formation of 2NP (curve *d* in Fig. 2), most likely due to the enhanced production of $O_2^{\cdot-}$ in the presence of the alcohol (reactions (5)–(7)). Indeed, $O_2^{\cdot-}$ is able to scavenge $\cdot NO_2$ in reaction (10), which is the main sink for both $O_2^{\cdot-}$ and $\cdot NO_2$. Reaction (4) followed by (5)–(7) should significantly increase the formation rates of both $\cdot NO_2$ and $O_2^{\cdot-}$: the former is expected to enhance and the latter to inhibit phenol nitration. A simplified kinetic system made up of reactions (1)–(7) and (10) would be a null cycle for both $O_2^{\cdot-}$ and $\cdot NO_2$ and would compensate for their enhanced formation rates, because all the surplus superoxide and nitrogen dioxide would disappear in reaction (10). Therefore, the effect of 2-propanol on the formation of 2NP would be explained by the additional, secondary processes that involve $O_2^{\cdot-}$ and $\cdot NO_2$. Both species undergo dismutation (reactions (11) and (12) and (9)) and the respective dismutation rates are proportional to $[\cdot NO_2]^2$ and to $[O_2^{\cdot-}]^2$ (because $[O_2^{\cdot-}][HO_2\cdot] \sim \alpha_{HO_2} [O_2^{\cdot-}]^2$). The rates of reactions (9) and (11) and (12) would thus grow very fast with increasing $[\cdot NO_2]$ and $[O_2^{\cdot-}]$, but reactions (11) and (12) are considerably slower than (20)–(22) in the presence of 1 mM phenol, while reaction (9) is a significant $O_2^{\cdot-}$ sink. Considering that reactions (20)–(22) are first order in $\cdot NO_2$, the formation of both $\cdot NO_2$ and $O_2^{\cdot-}$ in reactions (4)–(7) would enhance the consumption rate of $O_2^{\cdot-}$ more than that of $\cdot NO_2$, leaving an excess of $\cdot NO_2$ (see also the supplementary material) that would enhance nitration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.09.008.

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