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(Article begins on next page)

05 May 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

ON THE EFFECT OF 2-PROPANOL ON PHENOL PHOTONITRATION UPON NITRATE PHOTOLYSIS

Davide Vione,[a,b,]* Babita Sur,[a,c] Binay K. Dutta,[d] Valter Maurino,[a] Claudio Minero [a]

[a] *Dipartimento di Chimica Analitica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy.*

[b] *Centro Interdipartimentale NatRisk, Università di Torino, Via L. Da Vinci 44, 10095 Grugliasco (TO), Italy.*

[c] *Department of Chemical Engineering, Calcutta University, 92 Acharya P. C. Road, Kolkata 700009, India.*

[d] *Chemical Engineering Department, The Petroleum Institute, Abu Dhabi, PO Box 2533, United Arab Emirates.*

* Corresponding author. Fax +39-011-6707615. E-mail: *davide.vione@unito.it*

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 $^\bullet O^-$ and $^\bullet NO_2$. This effect would increase the availability of $^\bullet NO_2$ that is involved into phenol nitration, despite the enhancement by the alcohol of the production of superoxide that is a scavenger of $^\bullet NO_2$. 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 $^\bullet O^-$ and $^\bullet NO_2$ would evolve into bulk species, the remainder undergoing recombination to nitrate. The data also show that most of the recombination between $^\bullet OH/^\bullet O^-$ and $^\bullet NO_2$ would take place in the solvent cage instead of the solution bulk.

Keywords: photochemistry; aromatic nitroderivatives; solvent cage; 2-nitrophenol; Chemical Kinetics Simulator.

The UV irradiation of nitrate produces $^\bullet OH$ and $^\bullet NO_2$, which can be involved into the transformation of dissolved compounds [1,2]. The hydroxyl radical is certainly the most reactive transient, but $^\bullet NO_2$ can take part to photonitration reactions of aromatic molecules, yielding toxic and potentially mutagenic nitroderivatives [3]. Interestingly, $^\bullet NO_2$ produced by nitrate photolysis and nitrite photoxidation 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 $^\bullet OH$ scavengers are able to enhance photonitration. Such an effect has been ascribed to the inhibition of recombination in the bulk between $^\bullet OH$ and $^\bullet NO_2$ [5]. However, it has been shown that the reaction between $^\bullet OH$ and $^\bullet NO_2$ in the solution bulk cannot be a significant sink for $^\bullet OH$, *a fortiori* in the presence of dissolved organic substrates such as phenol [6]. Moreover, $^\bullet OH$ scavengers such as formate and 2-propanol are able to increase the $^\bullet OH$ quantum yield of nitrate photolysis [7]. A

likely explanation is that photolytically generated $^\bullet O^-$ (which later yields $^\bullet OH$ upon protonation) and $^\bullet NO_2$ 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 $^\bullet O^-$, which increases the $^\bullet OH$ quantum yield measured from the reaction products of the scavengers [1, 7]. For instance, acetone is formed by 2-propanol and $^\bullet OH$. 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 $^\bullet OH$ [8]. Inhibition of the $^\bullet O^- + {^\bullet NO_2}$ cage recombination would enhance the generation of the nitrating agent $^\bullet NO_2$. 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 $P_o = 1.0 \cdot 10^{-6}$ Einstein L^{-1} 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→0 of the curves fitting the experimental data (see legend to Figure 1). For further details concerning experimental set-up and data treatment see [4]. The reproducibility of repeated runs was 15-20%.

Figure 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 $^\bullet NO_2$ [4]. Figure 2 reports the initial formation rate of 2NP as a function of the alcohol concentration. The rate increased by 3.0±1.2 times (μ±σ) when passing from the absence of 2-propanol to the highest adopted concentration value (0.3 M). The data of Figure 2 are compatible with a reaction between 2-propanol and cage $^\bullet O^-$, which would inhibit cage recombination and increase the availability of $^\bullet NO_2$ [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] (PrOH = 2-propanol, PhOH = phenol):

$$NO_3^- + h\nu \rightarrow [^\bullet O^- + {^\bullet NO_2}]_{cage} \qquad [R_1 \approx \Phi \cdot P_o \cdot (1\text{-}10^{-A_{NO3-}})] \qquad (1)$$

$$[^\bullet O^- + {^\bullet NO_2}]_{cage} \rightarrow NO_3^- \qquad [k_2, s^{-1}] \qquad (2)$$

$$[^\bullet O^- + {^\bullet NO_2}]_{cage} \xrightarrow{(+H^+)} {^\bullet OH} + {^\bullet NO_2} \qquad [k_3, s^{-1}] \qquad (3)$$

$$[^\bullet O^- + {^\bullet NO_2}]_{cage} + PrOH \xrightarrow{(+H^+)} {^\bullet NO_2} + PrO^\bullet \qquad [k_4, M^{-1} s^{-1}] \qquad (4)$$

$${^\bullet OH} + PrOH \rightarrow H_2O + PrO^\bullet \qquad [k_5 = 1.9 \cdot 10^9 M^{-1} s^{-1}] \qquad (5)$$

$$PrO^\bullet + O_2 \rightarrow PrOO_2^\bullet \qquad [k_6 = 4.5 \cdot 10^9 M^{-1} s^{-1}] \qquad (6)$$

$$\text{PrOO}_2{}^\bullet + \text{HPO}_4{}^{2-} \rightarrow \text{Acetone} + \text{H}_2\text{PO}_4{}^- + \text{O}_2{}^{-\bullet} \qquad [k_7 = 1.1 \cdot 10^7\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (7)$$

$$\text{HO}_2{}^\bullet \rightleftharpoons \text{O}_2{}^{-\bullet} + \text{H}^+ \qquad [pK_a = 4.8] \qquad (8)$$

$$\text{HO}_2{}^\bullet + \text{O}_2{}^{-\bullet} + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} \qquad [k_9 = 9.7 \cdot 10^7\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (9)$$

$$\text{O}_2{}^{-\bullet} + {}^\bullet\text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_2{}^- \qquad [k_{10} = 4.5 \cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (10)$$

$$2\ {}^\bullet\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \qquad [k_{11} = 4.5 \cdot 10^8\ \text{M}^{-1}\,\text{s}^{-1};\ k_{-11} = 7 \cdot 10^3\ \text{s}^{-1}] \qquad (11)$$

$$\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{NO}_3{}^- + \text{NO}_2{}^- + 2\ \text{H}^+ \qquad [k_{12} = 1 \cdot 10^3\ \text{s}^{-1}] \qquad (12)$$

$${}^\bullet\text{OH} + \text{HO}_2{}^\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2 \qquad [k_{13} = 1 \cdot 10^{10}\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (13)$$

$${}^\bullet\text{OH} + {}^\bullet\text{NO}_2 \rightarrow \text{NO}_3{}^- + \text{H}^+ \qquad [k_{14} = 4.5 \cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (14)$$

$$\text{PhOH} + {}^\bullet\text{OH} \rightarrow \text{Ph(OH)}_2{}^\bullet \qquad [k_{15} = 1.4 \cdot 10^{10}\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (15)$$

$$\text{Ph(OH)}_2{}^\bullet + \text{O}_2 \rightarrow \text{O}_2{}^{-\bullet} + \text{H}^+ + \text{Hydroxyderivatives} \qquad [k_{16}] \qquad (16)$$

$$\text{Ph(OH)}_2{}^\bullet \rightarrow \text{PhO}^\bullet + \text{H}_2\text{O} \qquad [k_{17}] \qquad (17)$$

$$2\ \text{PhO}^\bullet \rightarrow \text{Products} \qquad [k_{18} = 4 \cdot 10^8\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (18)$$

$$\text{PhO}^\bullet + \text{O}_2{}^{-\bullet} + \text{H}^+ \rightarrow \text{PhOH} + \text{O}_2 \qquad [k_{19} = 2 \cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (19)$$

$$\text{PhOH} + {}^\bullet\text{NO}_2 \rightarrow \text{PhO}^\bullet \qquad [k_{20} = 3 \cdot 10^3\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (20)$$

$$\text{PhO}^\bullet + {}^\bullet\text{NO}_2 \rightarrow 2\text{NP} \qquad [k_{21} = 2 \cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (21)$$

$$\text{PhO}^\bullet + {}^\bullet\text{NO}_2 \rightarrow 4\text{NP} \qquad [k_{22} = 1 \cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}] \qquad (22)$$

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 Figure SM1 in the Supplementary Material). 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 which is not observed. Furthermore, it was adopted $k_{21} = 2\ k_{22}$ 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 (more details about the software settings are reported as Supplementary Material). 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 the range from 1 to $10^{10}\ \text{M}^{-1}\,\text{s}^{-1}$, and a conventional value of $10^7\ \text{M}^{-1}\ \text{s}^{-1}$ was adopted. From the equilibrium reaction (8) it was derived $[\text{HO}_2{}^\bullet] = 6.3 \cdot 10^{-2}\ [\text{O}_2{}^{-\bullet}]$ at pH 6, and the reactions (9) and (13) were 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 $k_4 = 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$. Figure 2 shows the comparison between experimental data and model results for $k_4\ k_3{}^{-1} = 10^2\ \text{M}^{-1}$ and different values of $k_2\ k_3{}^{-1}$: 3 (*a*), 5 (*b*) and 7 (*c*). No good agreement with the experimental data can be obtained for $k_2\ k_3{}^{-1}$ outside the 3-7 range, or for $k_4\ k_3{}^{-1}$ values that are significantly different from $10^2\ \text{M}^{-1}$. This means that geminate recombination of $[{}^\bullet\text{O}^- + {}^\bullet\text{NO}_2]_{\text{cage}}$ would occur in the nanosecond-time domain. It is slower than the recombination kinetics of the two ${}^\bullet\text{OH}$ produced by H_2O_2 photolysis [14], but ${}^\bullet\text{NO}_2$ formed upon nitrate photolysis is considerably less reactive than ${}^\bullet\text{OH}$. Values of $k_2\ k_3{}^{-1}$ in the 3-7 range mean

that, in the absence of 2-propanol, less than 25% of $[^{\bullet}O^- + {}^{\bullet}NO_2]_{cage}$ would evolve into bulk radical species, the remainder undergoing recombination to nitrate.

In the absence of reaction (4) the model foresees a slight inhibition by 2-propanol of the formation of 2NP (curve *d* in Figure 2), possibly due to the enhanced production of $O_2^{-\bullet}$ in the presence of the alcohol. Indeed, $O_2^{-\bullet}$ is able to scavenge ${}^{\bullet}NO_2$ in reaction (10). Reaction (4) followed by (5-7) should significantly increase the formation rates of both ${}^{\bullet}NO_2$ and $O_2^{-\bullet}$: the former is expected to enhance and the latter to inhibit phenol nitration. Both species undergo dismutation (reactions 11-12 and 9) and the respective dismutation rates are proportional to $[{}^{\bullet}NO_2]^2$ and to $[O_2^{-\bullet}]^2$ (because $[O_2^{-\bullet}] [HO_2^{\bullet}] \sim \alpha_{HO2\bullet} [O_2^{-\bullet}]^2$). The rates of reactions (9) and (11-12) grow thus very fast with increasing $[{}^{\bullet}NO_2]$ and $[O_2^{-\bullet}]$, but while reactions (11-12) are considerably slower than (20-22) in the presence of 1 mM phenol, reaction (9) is a significant $O_2^{-\bullet}$ sink. Therefore, formation of both ${}^{\bullet}NO_2$ and $O_2^{-\bullet}$ in reactions (4-7) would enhance the consumption rate of $O_2^{-\bullet}$ more than that of ${}^{\bullet}NO_2$, leaving an excess ${}^{\bullet}NO_2$ that would enhance nitration.

Acknowledgements

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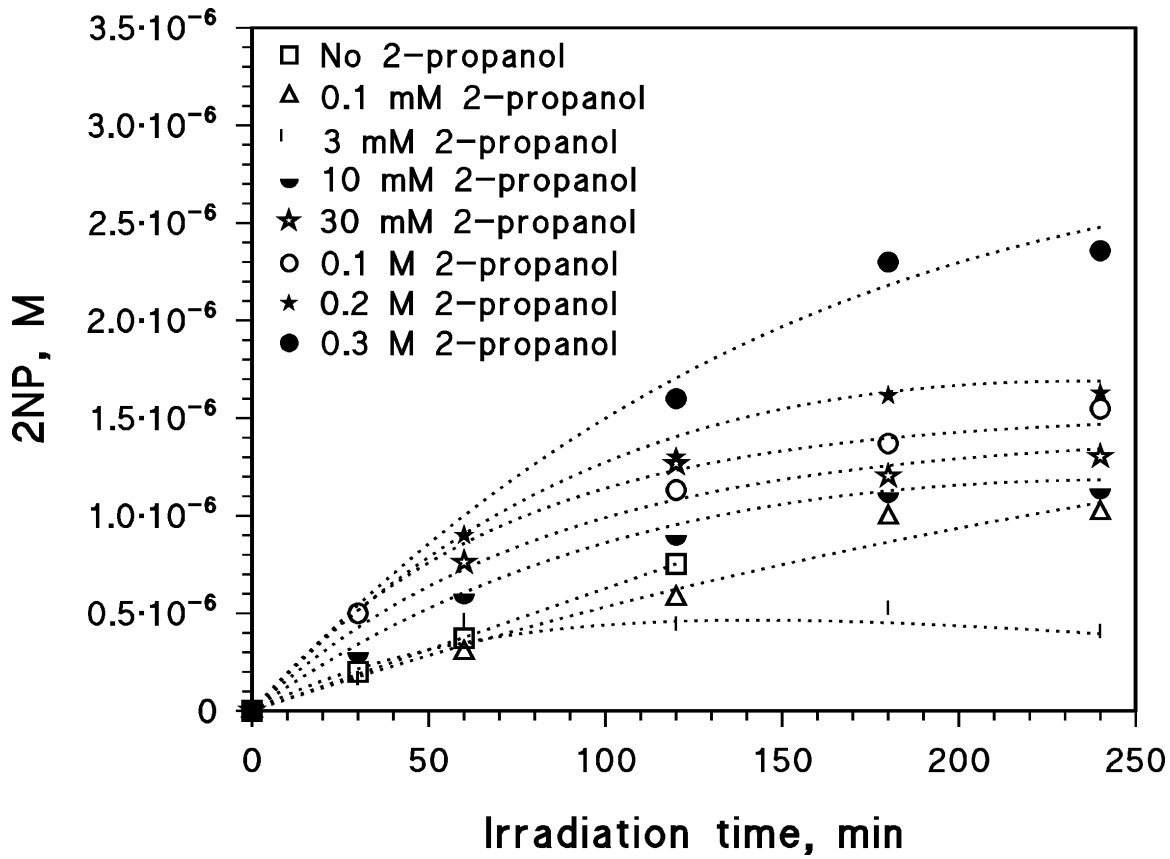
Figure 1. Time evolution of 2NP upon UVB irradiation of 1 mM phenol and 0.1 M NaNO₃ (pH 6, phosphate buffer), in the presence of different initial concentrations of 2-propanol, in aerated solution. The time evolution data of 2NP are fitted with equations of the form $[2NP]_t = k^f_{2NP} [PhOH]_0 (k^d_{2NP} - k^d_{PhOH})^{-1} [exp(-k^d_{PhOH} t) - exp(-k^d_{2NP} t)]$, where $[2NP]_t$ is the concentration of 2NP at the time t, $[PhOH]_0$ the initial phenol concentration, k^f_{NP} and k^d_{NP} the pseudo-first order rate constants for the formation and degradation of 2NP, and k^d_{PhOH} the pseudo-first order rate constant for the degradation of phenol.
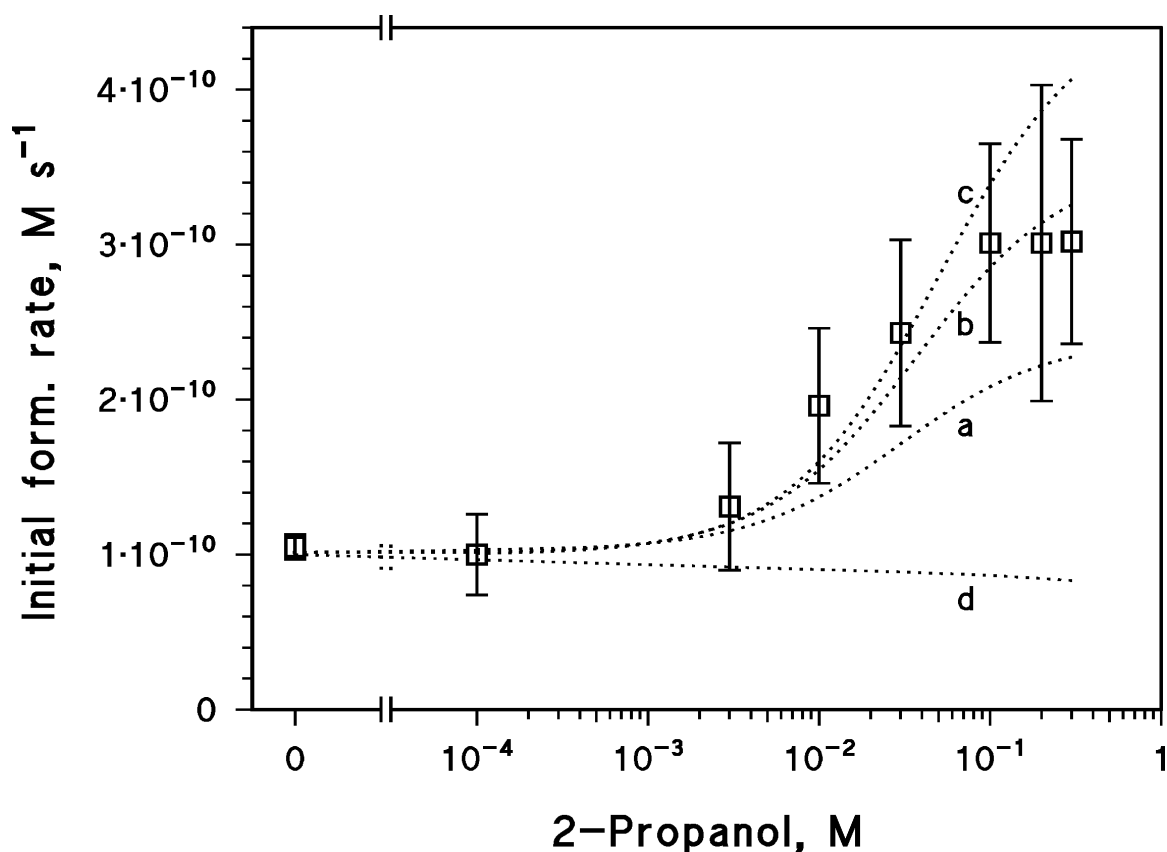
Figure 2. Initial formation rate of 2NP upon UVB irradiation of 1 mM phenol and 0.1 M $NaNO_3$, as a function of the concentration of 2-propanol. Note the logarithmic scale and the break in the X-axis. The dotted curves represents the trend foreseen by CKS calculations, on the basis of reactions (1-22), for $k_4 \, k_3^{-1} = 10^2 \, M^{-1}$ (*a-c*) and $k_2 \, k_3^{-1} = 3$ (*a*), 5 (*b*) and 7 (*c*). Curve *d* was obtained by neglecting reaction (4) and with $k_2 \, k_3^{-1} = 5$. The experimental formation rates of 2NP were calculated as $R_{2NP} = k^f_{2NP} \, [PhOH]_0$. The error bounds associated to the rate data represent $\mu \pm \sigma$, derived from the fit of the experimental data reported in Figure 1 (intra-series variability).