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# The peroxyxynitrite pathway as a potentially important route for the photochemical generation of carbonate radicals in surface waters

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## Abstract

The carbonate radical ( $\text{CO}_3^{\cdot-}$ ) is a photoinduced transient species occurring in surface waters, which is involved in the transformation of electron-rich substrates such as anilines, phenols and organic sulphur compounds. Here we show that the reaction between peroxyxynitrite and carbon dioxide is a potentially significant source of  $\text{CO}_3^{\cdot-}$  in sunlit surface waters, and it could account for up to 10-15% of the total  $\text{CO}_3^{\cdot-}$  formation. The peroxyxynitrite pathway to  $\text{CO}_3^{\cdot-}$  would be most significant at pH 7-8, and its relative importance would be enhanced in waters with elevated nitrate and low alkalinity. Therefore, the proposed process could add to the known photochemical sources of  $\text{CO}_3^{\cdot-}$  in surface-water environments.

**Keywords:** Environmental photochemistry; indirect photolysis; modelling; sunlit waters; pollutant photodegradation.

## 1. Introduction

The carbonate radical ( $\text{CO}_3^{\cdot-}$ ) is a transient species that occurs in sunlit natural waters and can be involved in the transformation of natural compounds and man-made xenobiotics (Larson and Zepp 1988; Huang and Mabury 2000a), such as electron-rich anilines, phenols and sulphur-containing compounds (Huang and Mabury 2000b; Canonica et al. 2005; Bouillon and Miller 2005). The species  $\text{CO}_3^{\cdot-}$  is formed upon bicarbonate oxidation by the hydroxyl radical ( $\cdot\text{OH}$ ) and upon carbonate oxidation by  $\cdot\text{OH}$  and  $^3\text{CDOM}^*$  (the excited triplet states of chromophoric dissolved organic matter; Canonica et al. 2005). The scavenging of  $\text{CO}_3^{\cdot-}$  mainly occurs by reaction with the natural dissolved organic matter (DOM), which is also a major  $\cdot\text{OH}$  sink (Larson and Zepp 1988; Canonica et al. 2005). The formation rate of  $\text{CO}_3^{\cdot-}$  in natural waters is usually lower than that of  $\cdot\text{OH}$ , but the scavenging of  $\text{CO}_3^{\cdot-}$  by DOM is much slower than the corresponding  $\cdot\text{OH}$  process. As

a result,  $\text{CO}_3^{\bullet-}$  usually has higher steady-state concentration than  $\bullet\text{OH}$ , which may sometimes compensate for its lower reactivity (Sulzberger et al. 1997, Huang and Mabury 2000a).

The radical  $\text{CO}_3^{\bullet-}$  can also be formed by reaction between peroxyxynitrite ( $\text{ONOO}^-$ ) and dissolved  $\text{CO}_2$ . A possible formation route of  $\text{ONOO}^-$  is nitrate photoisomerisation (Thogersen et al. 2009), and nitrate is an important photoactive agent in surface waters (Chen et al. 2013). To our knowledge, the possible importance of this pathway for the formation of  $\text{CO}_3^{\bullet-}$  in surface waters has not been assessed so far. To fill this knowledge gap, a kinetic model was derived to describe the formation of  $\text{CO}_3^{\bullet-}$  via the reaction between  $\text{ONOO}^-$  and  $\text{CO}_2$ . The potential environmental significance of the process was then evaluated, by comparison with the known  $\text{CO}_3^{\bullet-}$  production pathways.

## 2. Methods

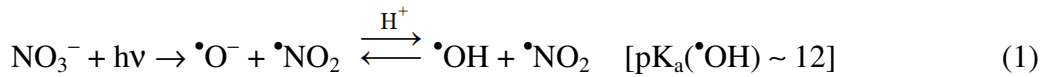
To carry out the comparison under conditions relevant to surface waters, it was used the software APEX (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) (Bodrato and Vione 2014). APEX predicts photochemical reactions (including the formation rates of transient species) based on water chemistry and depth, under summertime irradiation conditions. To get insight into the environmental significance of the process, a wide range of environmental conditions was obtained from the Global Environment Monitoring System (<http://www.GEMStat.org>), which reports the chemical composition of surface waters from many monitoring stations around the world. To have comparable values of sunlight irradiance, mid-latitude stations were chosen (40-50° N latitude) and, for each station for which summertime data of nitrate, DOC, inorganic carbon and pH were available (an issue that restricted the study zone to Europe), average values of these parameters were used. Summertime data were chosen because photochemical reactions are most important during the summer season (Tixier et al. 2002).

## 3. Results and Discussion

Peroxyxynitrite, together with its conjugated acid  $\text{ONOOH}$  (peroxyxynitrous acid), can be formed upon nitrate photoisomerisation. This process is quite efficient in the UVC range (Mark et al. 1996), while its occurrence at higher wavelengths is more controversial. There are reports excluding that the reaction occurs effectively above 280 nm under monochromatic irradiation (Goldstein and Rabani 2007), and findings that peroxyxynitrite can be formed by irradiation of basic nitrate solutions under a broadband UVB lamp (Borghesi et al. 2005). Possible reasons for this inconsistency are that nitrate has very low absorbance around 280 nm, and that the intensity of monochromatic radiation is usually quite low compared to broadband sources. Further evidence of the UVB-induced formation of  $\text{ONOOH}/\text{ONOO}^-$  from nitrate is the formation of 2-nitronaphthalene (and the lack of formation of 1-nitronaphthalene) upon UVB irradiation of naphthalene and nitrate. It would be difficult to

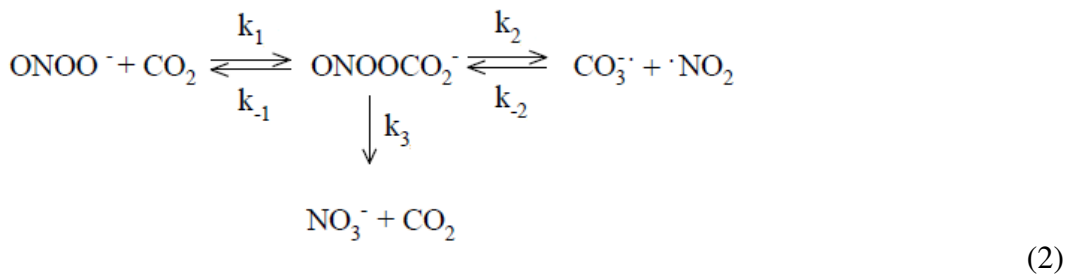
account for the occurrence of the 2-nitroisomer alone, without hypothesizing the occurrence of ONOOH/ONOO<sup>-</sup> as nitrating agent (Vione et al. 2005).

Peroxonitrous acid has pK<sub>a</sub> ~ 7, it is unstable and undergoes transformation to both NO<sub>3</sub><sup>-</sup> + H<sup>+</sup> (approximately 70% of the total) and •OH + •NO<sub>2</sub> (~30%) (Drexler et al. 1991; Coddington et al. 1999). In contrast, ONOO<sup>-</sup> transformation follows a completely different route (reaction with CO<sub>2</sub>, having rate constant k<sub>1</sub> = 3.0·10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>, without production of •OH) (Meli et al. 2002; Lyman and Hurst 1995; Pryor et al. 1997; Carballal et al. 2014). Direct formation of •OH from irradiated nitrate takes place *via* reaction (1), with quantum yield Φ<sub>1</sub> ~ 0.01. The •OH yield of this process could decrease with pH, but only around pH 12 (Warneck and Wurzinger 1988).



The experimental pH trend of •OH photoproduction upon nitrate photolysis showed a ~50% decrease between pH 6 and 8 (Vione et al. 2009), which might be due to the occurrence of •OH-producing ONOOH at pH 6, and of ONOO<sup>-</sup> at pH 8. If this is the case, at pH 6 the ONOOH pathway would produce about as much •OH as reaction (1). From the •OH yield of ONOOH (η~0.3) and with Φ<sub>1</sub> ~ 0.01, one estimates Φ<sub>ONOOH</sub><sup>NO<sub>3</sub><sup>-</sup></sup> ~ Φ<sub>1</sub> η<sup>-1</sup> ~ 0.03 as the formation quantum yield of ONOOH from irradiated nitrate.

ONOO<sup>-</sup> might react with ONOOH, H<sub>2</sub>S and nitrite. However, given the reaction rate constants and the typical concentrations of the relevant species in surface waters, these processes can be safely neglected compared to the CO<sub>2</sub> reaction (Kissner and Koppenol 2002; Molina et al. 2013; Gupta et al. 2009; Verma et al. 2015; Maurer et al. 2003; Carballal et al. 2011). The latter process yields ONOOCO<sub>2</sub><sup>-</sup>, which can evolve into either nitrate and CO<sub>2</sub> or the radicals CO<sub>3</sub><sup>-•</sup> and •NO<sub>2</sub> (see scheme (2) below) (Drexler et al. 1991; Coddington et al. 1999). The production of •NO<sub>2</sub> might account for the formation of phenol nitroderivatives upon UVB irradiation of nitrate and bicarbonate (Chiron et al. 2009).



The equilibrium ONOO<sup>-</sup> + CO<sub>2</sub> ⇌ ONOOCO<sub>2</sub><sup>-</sup> is likely shifted to the right, because CO<sub>2</sub> significantly inhibits the nitration reactions induced by ONOO<sup>-</sup> (Denicola et al. 1996), thereby excluding a significant back transformation of ONOOCO<sub>2</sub><sup>-</sup> into ONOO<sup>-</sup> + CO<sub>2</sub>. The recombination of the radicals CO<sub>3</sub><sup>-•</sup> + •NO<sub>2</sub> is also little likely, because of their low steady-state concentrations and of the fast hydrolysis of •NO<sub>2</sub> in aqueous solution (Logager and Sehested 1993). Finally, the

reaction yields of  $\text{NO}_3^- + \text{CO}_2$  and of  $\text{CO}_3^{\bullet-} + \bullet\text{NO}_2$  have been determined as, respectively,  $\sim 95\%$  and  $\sim 5\%$  (Meli et al. 2002). With these approximations and considering a steady-state  $[\text{ONOOCO}_2^-]$ , the generation rate of  $\text{CO}_3^{\bullet-}$  from  $\text{ONOO}^- + \text{CO}_2$  would be  $R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} = k_1 k_2 (k_2 + k_3)^{-1} [\text{ONOO}^-] [\text{CO}_2]$ , where  $k_2 (k_2 + k_3)^{-1} = 0.05$ .

The formation rate of  $\text{ONOO}^-$  upon nitrate photolysis is  $R_{\text{ONOO}^-}^{\text{NO}_3^-} = \Phi_{\text{ONOO}^-}^{\text{NO}_3^-} P_a^{\text{NO}_3^-} \alpha_{\text{ONOO}^-}$ , where  $\Phi_{\text{ONOO}^-}^{\text{NO}_3^-} \sim 0.03$  (see above),  $P_a^{\text{NO}_3^-}$  is the photon flux absorbed by nitrate, and  $\alpha_{\text{ONOO}^-}$  is the peroxyxynitrite fraction resulting from the acid-base equilibrium with  $\text{ONOOH}$  (where  $\alpha_{\text{ONOOH}} + \alpha_{\text{ONOO}^-} = 1$ ). When considering the reaction with  $\text{CO}_2$ , the steady-state  $[\text{ONOO}^-]$  can be expressed as:  $[\text{ONOO}^-] = R_{\text{ONOO}^-} (k_1 [\text{CO}_2])^{-1} = \Phi_{\text{ONOO}^-}^{\text{NO}_3^-} P_a^{\text{NO}_3^-} \alpha_{\text{ONOO}^-} (k_1 [\text{CO}_2])^{-1}$ . Therefore, one gets:

$$R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} = k_2 (k_2 + k_3)^{-1} \Phi_{\text{ONOO}^-}^{\text{NO}_3^-} P_a^{\text{NO}_3^-} \alpha_{\text{ONOO}^-} \quad (3)$$

The value of  $P_a^{\text{NO}_3^-}$  depends on the irradiation wavelength(s), on nitrate concentration and on the occurrence of other radiation-absorbing species in solution. Under conditions relevant to surface waters,  $P_a^{\text{NO}_3^-}$  can be assessed with APEX. The software also calculates  $R_{\text{CO}_3^{\bullet-}}^{\text{no ONOO}^-}$ , namely the formation rate of  $\text{CO}_3^{\bullet-}$  via the "traditional" production processes (reaction between  $\bullet\text{OH}$  and  $\text{HCO}_3^-$ ,  $\bullet\text{OH}$  and  $\text{CO}_3^{2-}$ , and  ${}^3\text{CDOM}^*$  and  $\text{CO}_3^{2-}$ ). In this context, the fractional contribution of peroxyxynitrite to the total formation rate of  $\text{CO}_3^{\bullet-}$  is  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} = R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} (R_{\text{CO}_3^{\bullet-}}^{\text{no ONOO}^-} + R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-})^{-1}$ .  $R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  is determined with equation (3), and the total formation rate of  $\text{CO}_3^{\bullet-}$  is  $R_{\text{CO}_3^{\bullet-}}^{\text{tot}} = R_{\text{CO}_3^{\bullet-}}^{\text{no ONOO}^-} + R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$ .

Figure 1 reports the fractions of  $\text{CO}_3^{\bullet-}$  produced by the different processes, as a function of pH. Used water conditions are 0.1 mM nitrate, 2 mgC L<sup>-1</sup> dissolved organic carbon (DOC), 0.5 m depth, and 1.7 mM inorganic carbon (dissolved  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ). The figure reports the fractions of  $\text{CO}_3^{\bullet-}$  formation, while the total formation rate  $R_{\text{CO}_3^{\bullet-}}^{\text{tot}}$  increases with increasing pH because the  $\text{CO}_3^{2-}$  reactions are more effective than the  $\text{HCO}_3^-$  ones. The  $\bullet\text{OH} + \text{HCO}_3^-$  process is the most important at pH < 8.5, while  $\bullet\text{OH} + \text{CO}_3^{2-}$  prevails at higher pH. Interestingly,  $\bullet\text{OH}$  has a major role in the production of  $\text{CO}_3^{\bullet-}$ , despite the  $\bullet\text{OH}$  scavenging carried out by DOM (here quantified as the water DOC). The  $\text{ONOO}^-$  process would be most important at pH 7-8, where it could account for around 10% of  $R_{\text{CO}_3^{\bullet-}}^{\text{tot}}$  under the assumed water conditions. Interestingly, the pH range 7-8 is very common in surface waters (Polesello et al. 2006). At pH < 7 the importance of the peroxyxynitrite pathway would decrease because of the decreasing  $\alpha_{\text{ONOO}^-}$  fraction ( $\text{ONOO}^-$  is protonated to  $\text{ONOOH}$ ). At pH < 6, however, the decreasing  $\alpha_{\text{ONOO}^-}$  is compensated for by the protonation of  $\text{HCO}_3^-$  (Martell et al. 1997), with the consequence that  $R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  and  $R_{\text{CO}_3^{\bullet-}}^{\text{tot}}$  undergo a parallel decrease. Therefore,  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  stabilises at around 5%. At pH > 8 both  $\alpha_{\text{ONOO}^-}$  and  $R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  are approximately constant, but  $R_{\text{CO}_3^{\bullet-}}^{\text{tot}}$  increases with pH and  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} = R_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-} (R_{\text{CO}_3^{\bullet-}}^{\text{tot}})^{-1}$  decreases as a consequence. A final comment concerns the reaction of  ${}^3\text{CDOM}^*$  with  $\text{CO}_3^{2-}$ : it is less important

than the  $\bullet\text{OH}$  reactions under most conditions, but its importance would be higher than shown (and the role of  $\bullet\text{OH}$  correspondingly lower) at more elevated DOC values (Canonica et al. 2005).

A wider geographical outlook was obtained from the data of the Global Environment Monitoring System. On this basis, the APEX software could compute  $R_{\text{CO}_3^\bullet}^{\text{no ONOO}^-}$  and  $P_a^{\text{NO}_3^-}$ , from which  $R_{\text{CO}_3^\bullet}^{\text{ONOO}^-}$ ,  $R_{\text{CO}_3^\bullet}^{\text{tot}}$  and  $f_{\text{CO}_3^\bullet}^{\text{ONOO}^-}$  were derived as explained above. Figure 2a reports the ratio  $f_{\text{CO}_3^\bullet}^{\text{ONOO}^-} = R_{\text{CO}_3^\bullet}^{\text{ONOO}^-} (R_{\text{CO}_3^\bullet}^{\text{tot}})^{-1}$  for the different stations, which are represented by their respective pH values to enable a direct comparison with Figure 1. The ONOO<sup>-</sup> process could account for ~10% (and up to 20%) of CO<sub>3</sub><sup>•-</sup> photoproduction at 7.4 < pH < 8.6, in overall agreement with Figure 1. Interestingly, the highest value of  $f_{\text{CO}_3^\bullet}^{\text{ONOO}^-}$  (almost 25%) was obtained at pH ~ 6.9 that is quite far from the optimum pH conditions. The reason is that, in the relevant sample, the nitrate concentration was quite high (~0.17 mM) and its absorbed photon flux ( $P_a^{\text{NO}_3^-}$ ) was also elevated. Moreover, the low alkalinity (that is, low carbonate and bicarbonate) at pH ~ 6.9 would limit the role of  $\bullet\text{OH}$  as source of CO<sub>3</sub><sup>•-</sup>. All these issues would offset the relatively low  $\alpha_{\text{ONOO}^-}$  at that pH value. Figure 2b shows the geographic distribution of the sampling stations. Most of the useful data were from Belgium and Switzerland, with slightly higher values of  $f_{\text{CO}_3^\bullet}^{\text{ONOO}^-}$  in the latter country.

#### 4. Conclusions

The reaction between ONOO<sup>-</sup> and CO<sub>2</sub> could account for a significant fraction of the CO<sub>3</sub><sup>•-</sup> formation in surface waters, in the pH interval 7-8 and/or in the presence of elevated nitrate/low alkalinity (~10% of  $R_{\text{CO}_3^\bullet}^{\text{tot}}$  in the tested scenarios, and in one case even up to ~25%). Therefore, it is a potentially novel route to CO<sub>3</sub><sup>•-</sup> in surface-water environments. The present assessment was based on a formation quantum yield of ONOO<sup>-</sup> from nitrate ( $\Phi_{\text{ONOO}^-}^{\text{NO}_3^-} \sim 0.03$ ) that was indirectly estimated from experimental data under UVB irradiation, and on the hypothesis that CO<sub>2</sub> is the main ONOO<sup>-</sup> sink. The latter issue is very reasonable under physiological conditions, but the occurrence of additional ONOO<sup>-</sup> sinks (*e.g.* dissolved organic matter) in surface waters is presently unknown.

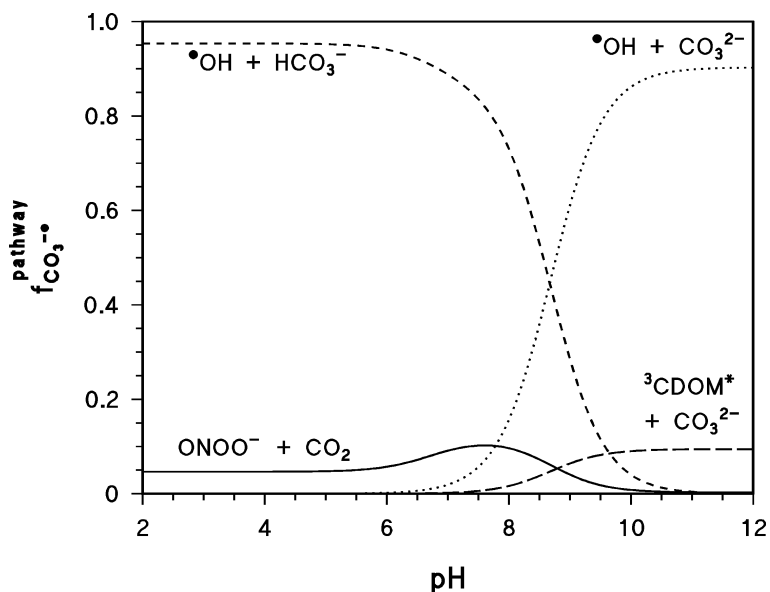
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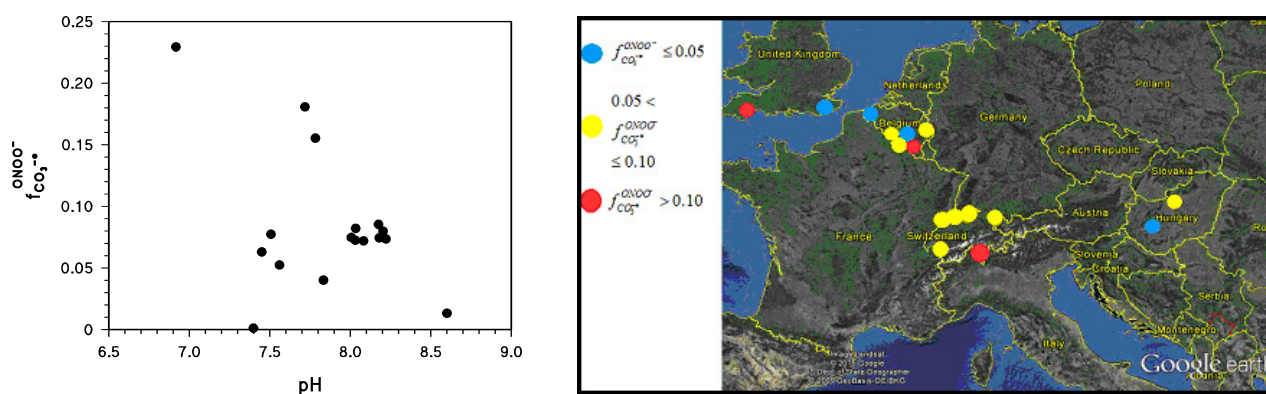
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**Figure 1.** Fractions of  $\text{CO}_3^{\bullet-}$  formation accounted for by the different pathways, as a function of pH. Water conditions: 0.1 mM nitrate, 2 mgC L<sup>-1</sup> DOC, 0.5 m depth, 1.7 mM total carbonates (dissolved  $\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$ ). Note the important role of the  $\bullet\text{OH}$  reactions and the maximum of  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  between pH 7.5 and 8.



**Figure 2. Left:** Fraction of  $\text{CO}_3^{\bullet-}$  formation accounted for by the  $\text{ONOO}^-$  pathway ( $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$ ), as a function of pH. Water chemistry data were taken from the Global Environment Monitoring System database (<http://www.GEMStat.org>), for a water column depth of 0.5 m. Overall, there is an optimum  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  at pH values between 7.5 and 8, coherently with Figure 1 data. **Right:** Map showing the geographic distribution of the relevant sampling stations and of the associated  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  values. Note the relatively elevated  $f_{\text{CO}_3^{\bullet-}}^{\text{ONOO}^-}$  in Swiss rivers.