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Modelling the occurrence and reactivity of the carbonate radical in surface freshwater

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Abstract

A model was developed to foresee the degradation kinetics of dissolved compounds for reaction with the carbonate radical in surface waters. It would contribute to the assessment of the environmental persistence of pollutants, therefore, allowing a better definition of the exposure of natural ecosystems and human communities to hazardous substances. The model is a function of the water chemical composition, the water column depth, and the second-order rate constant of the reaction between the relevant compound and the carbonate radical. A comparison between the reactivity of the carbonate and the hydroxyl radical shows that the latter would often play a more important role as reactive species, but the carbonate radical could prevail in carbonate-rich waters, giving the degradation of easily oxidisable molecules. ***To cite this article: D. Vione et al., C. R. Chimie 12 (2009).***

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1. Introduction

Photochemical reactions play an important role in the removal of biologically refractory pollutants from surface freshwater. They consist of the direct photolysis of sunlight-absorbing molecules and of a number of indirect photoreactions [1,2]. The latter can involve pollutants that do not absorb sunlight, and include the transformation processes photosensitised by dissolved organic matter (DOM), most likely through the excited triplet states (^{3}DOM*) [3,4], and the reaction with transient species such as ${}^{\bullet}$OH, $CO_3^{-\bullet}$, $^1O_2$, NO_2, and $Cl_2^{-\bullet}$ [5−9]. The cited transients can be produced upon irradiation by sunlight of photosensitisers such as DOM itself, nitrate, nitrite, and Fe(III). In some cases the interaction with inorganic anions such as bicarbonate, carbonate, chloride and nitrite is required. In many cases the transient species are consumed by natural scavengers, among which DOM is usually expected to play an important role [10]. Possible

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exceptions to the scavenging by DOM are the cases of $^1O_2$ and NO_2, for which deactivation by collision with water molecules [11] and hydrolysis [12], respectively, might be major removal pathways.

Recent research has enabled the modelling of the steady-state concentration of $^•OH$ in the surface layer of natural waters, as a function of the chemical composition of photoactive species. It is, therefore, possible to assess the lifetime of pollutants with known reaction rate constant with $^•OH$, from the values of NPOC (non-purgeable organic carbon, which quantifies DOM), $[NO_3^-]$, $[NO_2^-]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ [13]. Such a result was mainly allowed by the quantification of the role of DOM as photochemical $^•OH$ source. Interestingly the $^•OH$ radical is involved not only into the degradation of organic pollutants but also in the production of other reactive transients such as $CO_3^{-•}$ from carbonate and bicarbonate, and $^•NO_2$ from nitrite [14,15].

This work is focused on the modelling of the occurrence and reactivity of the carbonate radical in surface freshwater. The radical $CO_3^{-•}$ can be produced from $^•OH$ and CO_3^{2-} or HCO_3^- [16], from CO_3^{2-} and $^3DOM^*$ [17], and possibly also from irradiated Fe(III) oxides and CO_3^{2-} [18]:

$$^•OH + CO_3^{2-} \rightarrow OH^- + CO_3^{-•} \quad [k_1 = 3.9 \times 10^8\ M^{-1}\ s^{-1}] \qquad (1)$$

$$^•OH + HCO_3^- \rightarrow H_2O + CO_3^{-•} \quad [k_2 = 8.5 \times 10^6\ M^{-1}\ s^{-1}] \qquad (2)$$

$$^3DOM^* + CO_3^{2-} \rightarrow DOM^{-•} + CO_3^{-•} \quad [k_3 \approx 1 \times 10^5\ M^{-1}\ s^{-1}] \qquad (3)$$

The radical $CO_3^{-•}$ is less reactive than $^•OH$ toward the degradation of organic compounds [16,19], but in surface freshwaters it is also scavenged by DOM to a lesser extent [17]. The consequence is that $CO_3^{-•}$ can reach a higher steady-state concentration than the hydroxyl radical, which would compensate to a variable extent for the lower reactivity. It is generally believed that $CO_3^{-•}$ can be an important sink for water-dissolved phenolates and sulphur-containing compounds [17].

2. The model for carbonate radicals in surface waters

The present model is based on the formation of $CO_3^{-•}$ by $^•OH$ and $^3DOM^*$ (reactions (1)–(3)), and on its consumption by DOM itself (reaction (4)) and the pollutant(s) of interest.

$$DOM + CO_3^{-•} \rightarrow DOM^{+•} + CO_3^{2-} \quad [k_4 = 10^2 (mg\,C)^{-1}\ s^{-1}] \qquad (4)$$

The main issue with reaction (4) is that there is some disagreement among the values of k_4 reported in the literature, either 40 [20] or 280 ± 90 [17] (mg C/L)$^{-1}$ s^{-1}. The value adopted in the present paper can be regarded as a reasonable estimate based on those figures. To apply the model, it is also necessary to know the second-order rate constant for the reaction of the pollutant with $CO_3^{-•}$.

2.1. Production of $CO_3^{-•}$ from $^•OH$

As far as reactions (1) and (2) are concerned, it is essential to have an estimate of the formation rate of OH in the system ($R_{^•OH}^{tot}$) in order to derive the formation rate of the carbonate radical, $R_{CO_3^{-•}}$, from the concentration values of carbonate and bicarbonate. From the values of NPOC, $[NO_3^-]$ and $[NO_2^-]$ in the surface water layer, where most of the photochemical activity would occur [21], it is possible to derive the value of $R_{^•OH}^{tot}$ (in mol s^{-1}) under 22 W m^{-2} sunlight UV irradiance in a water volume $V = Sd$ [22]. $S = 1.26 \times 10^{-3}$ m^2 is the surface of the photoreactor adopted in the irradiation experiments that have been the experimental basis of the $^•OH$ model [22], and d is the water column depth best expressed as the average depth of the water body. All the calculations will be referred to the standard volume V (in litres), but it would be the same as referring them to the whole aquatic system. Another input datum for $R_{^•OH}^{tot}$ would be the absorption spectrum $A_1(\lambda)$ of the water over the optical path length $b = 1$ cm. However, in case where the spectrum is not available it would be possible to approximately model it from the NPOC value, as [22]:

$$A_1(\lambda) = 0.45\,\mathrm{NPOC}\,e^{-0.015\lambda} \qquad (5)$$

Eq. (5) depends on NPOC because DOM is by far the main radiation absorber in surface waters in the very vast majority of the cases of environmental significance [23].

The formation rate of the carbonate radical, accounted for by $^•OH$, is equal to $R_{^•OH}^{tot}$ times the fraction of the hydroxyl radicals that react with carbonate and bicarbonate (Eq. 6). It is expressed in mol s^{-1} in the volume $V = Sd$ ($S = 1.26 \times 10^{-3}$ m^2; d = average depth of the water body):