Inhibition by phenolic antioxidants of the degradation of aromatic amines and sulfadiazine by the carbonate radical (CO$_3^{•-}$)

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ABSTRACT

The carbonate radical CO$_3^{•-}$ and the excited triplet states of chromophoric dissolved organic matter play an important role in the photodegradation of some easily oxidized pollutants in surface waters, such as the aromatic amines. Anilines and sulfadiazine are known to undergo back-reduction processes when their degradation is mediated by the excited triplet states of photosensitizers (triplet sensitization). Back-reduction, which inhibits photodegradation, means that phenols or the antioxidant (mostly phenolic) moieties occurring in the natural dissolved organic matter of surface waters reduce, back to the parent compounds, the radical species derived from the mono-electronic oxidation of anilines and sulfadiazine. Here we show that a similar process takes place as well in the case of substrate oxidation by CO$_3^{•-}$. The carbonate radical was here produced upon oxidation of HCO$_3^{-}$/CO$_2^{•-}$ by either HO$^•$, generated by nitrate photolysis, or SO$_4^{•-}$, obtained by photolysis of persulfate. Back-reduction was observed in both cases in the presence of phenols, but at different extents as far as the details of reaction kinetics are concerned, and the occurrence of additional reductants might affect the efficacy by which phenols carry out the reduction process. In particular, when the carbonate radicals were produced by NO$_3$ photolysis in the presence of HCO$_3^{-}$/CO$_2^{•-}$, the numerical values of $[\text{PhOH}]_{1/2}$ (the phenol concentration that halves the photodegradation rate of the substrate) were 2.19 ± 0.23 µM for aniline, 1.15 ± 0.25 µM for 3-chloroaniline, 1.18 ± 0.26 µM for 4-chloroaniline, and 1.18 ± 0.22 µM for 3,4-dichloroaniline. In contrast, when CO$_3^{•-}$ was produced by photolysis of persulfate in the presence of HCO$_3^{-}$/CO$_2^{•-}$, the corresponding values were 0.28 ± 0.02 µM for aniline and 0.79 ± 0.10 µM for sulfadiazine. Back-reduction has the potential to significantly inhibit photodegradation by CO$_3^{•-}$ and excited triplet states in natural waters, and to comparatively increase the importance of HO$^•$-mediated degradation that is not affected by the same phenomenon.

1. Introduction

Photochemical reactions are important processes for the degradation of organic contaminants, especially biorecalcitrant compounds, in sunlit surface waters. Photoinduced processes consist of the direct photolysis, in which the contaminant absorbs sunlight and gets consequently transformed, and of indirect phototransformation. In the latter, absorption of sunlight by photosensitizers (such as the chromophoric dissolved organic matter – CDOM – nitrate and nitrite) yields reactive transient species, either directly or upon interaction with the water matrix (e.g., with the inorganic carbon species HCO$_3^{-}$ and CO$_2^{•-}$). These photochemically produced reactive intermediates (PPRIs) can react with the contaminants. The main PPRIs are the hydroxyl radical (HO$^•$), the triplet states of CDOM (CDOM$^*$), the singlet oxygen (O$_2$) and the carbonate radical (CO$_3^{•-}$) (Boreen et al., 2003; Remucal, 2014; Vialaton and Richard, 2002; Yan and Song, 2014).

The dissolved organic matter (DOM) and its chromophoric fraction (CDOM) play major roles in the photochemistry of natural surface waters. CDOM is a direct or indirect source of all the PPRIs, but it is also able to inhibit the direct photolysis processes by competing with the contaminants for sunlight irradiance. Furthermore, the DOM is a key scavenger of both HO$^•$ and CO$_3^{•-}$ (Vione et al., 2014; Yan et al., 2019). Therefore, the natural organic matter that occurs in surface waters is able to both inhibit and enhance the phototransformation reactions.

In addition to PPRIs scavenging, DOM can inhibit phototransformation through its antioxidant moieties (AOS, mostly phenolic). Indeed, it has been shown that the reactions between CDOM$^*$ and some contaminants (especially aromatic amines) yield partially oxidized...
intermediates, which can be back-reduced to the parent contaminants by DOM-AOs (Canonica and Laubscher, 2008; Wenk and Canonica, 2012).

This back-reduction process does not only affect reactions induced by 3CDOM+, but has recently been shown to occur for the reaction of the sulfate radical (SO4•−) with several anilines and sulfonamide antibiotics (Canonica and Schönenberger, 2019) as well as for the reaction of CO3•− with the cyanotoxin cylindrospermopsin (Hao et al., 2020). Since CO3•− is a typical one-electron oxidant (Neta et al., 1988) that reacts efficiently with a variety of aromatic amine compounds (Canonica et al., 2005; Hao et al., 2020), it is expected that such compounds are on the one hand significantly oxidized by CO3•− in the aquatic environment, and experience on the other hand back-reduction by DOM-AOs. Interestingly, occurrence of back-reduction has not been observed in the case of HO•, which undergoes addition to aromatic rings more easily than one-electron oxidation or H-atom abstraction (Wenk et al., 2011).

The present study has the goal of detecting and quantifying back-reduction by two phenols, used as DOM-AOs surrogates, in the reactions of CO•− with several anilines and the sulfonamide antibiotic sulfadiazine. The oxidation of HCO3−/CO32− to CO•− by strongly oxidizing radicals was carried out through two alternative methods (Huang and Mabury, 2000a; Neta et al., 1988). The first method is the photolysis of nitrate to yield HO• (Mack and Bolton, 1999), and the second is the photolysis of persulfate (S2O8•−) to form SO4•− (Criquet and Leitner, 2009). In addition, the effect of phenol on the transformation of two anilines photosensitized by a model aromatic ketone as a CDOM surrogate was also assessed, with the purpose of comparing the extent of back-reduction among different oxidation reactions.

2. Materials and methods

The list of used chemicals is reported in Text S1 of the Supplementary Material, hereinafter SM. The main issue with the production of CO•− is that this radical is generated by oxidation of HCO3−/CO32−. Therefore, the production of CO•− requires a stronger oxidant than CO3•− itself which may, however, be able to compete with CO3•− for the degradation processes. Great care is thus to be taken to define the operational conditions, so that the chosen oxidant species is almost exclusively involved in the oxidation of inorganic carbon, while the generated CO•− reacts preferentially with the target substrate(s). In this work, two methods were used and compared for the generation of CO•−: (i) oxidation by HO•, produced by nitrate photolysis, and (ii) oxidation by SO4•−, produced by photolysis of persulfate (S2O8•−).

2.1. Formation of the carbonate radical (CO•−) by nitrate photolysis

The CO•− radicals were produced by irradiation of a mixture of NaN3 + NaHCO3 (pH 8.3), containing the aniline substrate (target compound TC) to be degraded as well as phenol (PhOH). In particular, TC = aniline (Ani), 3-chloroaniline (3CA), 4-chloroaniline (4CA), and 3,4-dichloroaniline (3,4DCA). Under UVB light nitrate photolyses and gives HO•, which then oxidizes HCO3−/CO32− to form CO•− and H2O/HO• (second-order rate constants for the corresponding reactions are defined in parenthesis) (Buxton et al., 1988).

\[
\begin{align*}
\text{NO}_3^- + h\nu + H^+ & \rightarrow \text{NO}_2 + \text{HO}^+ \quad (1) \\
\text{HCO}_3^- + \text{HO}^+ & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (2) \\
\text{CO}_3^{2-} + \text{HO}^+ & \rightarrow \text{CO}_2 + \text{HO}^+ \quad (3)
\end{align*}
\]

Photogenerated NO2 might interfere by reacting with some radical intermediates, but the use of H2O2 as alternative HO• source was ruled out because H2O2 also reacts with HO• producing the oxidant O2•−, which in turn has high potential to interfere with back-reduction processes (Canonica and Schönenberger, 2019).

In the system containing nitrate and bicarbonate under irradiation, both HO• and CO3•− could potentially react with TC and PhOH, causing their degradation. Because our aim was to assess the importance of back-reduction in the degradation of TC by CO3•−, the reactions involving HO• + TC, HO• + PhOH and CO3•− + PhOH had to be minimized (see Scheme 1). To achieve the above goals, photogenerated HO• should be almost exclusively involved in the oxidation of HCO3−/CO32− to produce CO•−.

In other words, the fraction of HO• that reacts with HCO3−/CO32− (\(k_{\text{HCO}_3^-/\text{CO}_2^{2-}}\)) should be > 95% (Eq. (4)). Note that \(k_{\text{HCO}_3^-/\text{CO}_2^{2-}}\) takes into account the HO• reaction with both bicarbonate and carbonate. At the same time, the majority of CO•− produced by HO• should react with TC (\(k_{\text{TC}}/k_{\text{HCO}_3^-/\text{CO}_2^{2-}} > 95\), Eq. (5); see also Text S2 in the SM).

\[
\begin{align*}
\chi_{\text{HCO}_3^-/\text{CO}_2^{2-}} &= \frac{k_{\text{HCO}_3^-/\text{CO}_2^{2-}}}{k_{\text{HCO}_3^-/\text{TC}} + k_{\text{TC}}/k_{\text{HCO}_3^-/\text{CO}_2^{2-}}} > 0.95 \\
\chi_{\text{TC}} &= \frac{k_{\text{TC}}}{k_{\text{TC}} + k_{\text{HCO}_3^-/\text{CO}_2^{2-}}} > 0.95
\end{align*}
\]

In Eqs. (4) and (5), \(k_j\) is the second-order rate constant of the reaction between the radical i (HO• or CO•−) and the species j (HCO3−/CO32−, TC or PhOH). Moreover, it is \(k_{\text{HCO}_3^-/\text{CO}_2^{2-}} = k_{\text{HCO}_3^-/\text{HO}_3^-} + a_1 k_{\text{HO}_3^-/\text{CO}_3^{2-}} + a_2 k_{\text{CO}_3^{2-}/\text{CO}_2^{2-}}\), where \(a_1\) and \(a_2\) are the molar fractions of HCO3− and CO32− at pH 8.3, computed taking into account the pKas of carbonic acid (pK\(_{a1}\) = 6.3 and pK\(_{a2}\) = 10.3; e.g., Millero et al., 2002). Finally, [TC], [PhOH] and cNaHCO3 are the respective molar concentrations of TC (fixed at 5 µM; Vione et al., 2018, Wenk and Canonica, 2012), PhOH and NaHCO3 (vide infra) added to the solution.

Being the values of \(k_j\) known (see Table S1 in the SM) Neta et al., 1988), Eqs. (4) and (5) can be solved for the variables [PhOH] and cNaHCO3. As a result, one gets the minimum value of cNaHCO3 (0.22–0.38 M, depending on substrate and conditions) and the maximum value of [PhOH] (5–8 µM) that should be used to allow for: (i) the reactions of HO• with HCO3−/CO32− to prevail over the reactions of HO• with TC and PhOH, and (ii) the reaction CO•− + TC to prevail over CO2•− + PhOH (Scheme 1). The complete chemical composition of the irradiated solutions is listed in Table S1 (SM).

To carry out the above experiments, synthetic aqueous solutions (5 mL) were magnetically stirred and irradiated in cylindrical Pyrex glass cells, under a Philips narrow band TL 20 W/01 lamp. The lamp mainly emits in the UVB wavelength range, with emission maximum at 313 nm. The spectral photon flux density (\(p(\lambda,\text{SM})\), Fig. S1, SM) was assessed by means of chemical actinometry with 2-nitrobenzaldehyde (Carena et al., 2019; Galbavy et al., 2016; Willett and Hites, 2000).

The direct photolysis can be an additional degradation pathway for TC and, although this process does not affect the branching ratios of the reactions involving HO• and CO3•−, it is still an experimental bias. Chloro-substituted anilines are known to undergo direct photolysis in the UVB range (Fig. S2, SM) (Carena et al., 2018). To minimize their direct photolysis rate, we used a higher NaN3 concentration (25 mM), exploiting the inner-filter effect of NaNO3, and a lower lamp irradiance (2.9 ± 0.3 W m\(^{-2}\)). In contrast, aniline did not show direct photolysis, which allowed for the use of lower nitrate (10 mM) and slightly higher lamp irradiance (4.2 ± 0.2 W m\(^{-2}\)).

2.1.1. Modeling TC degradation rate

The degradation rate (\(R_{\text{TC}}\)) of the organic substrate TC (Ani, 3CA, 4CA or 3,4DCA) upon UVB irradiation of a solution containing NaN3 + NaHCO3 + TC + PhOH is \(R_{\text{TC}} = R_{\text{TC}}^{\text{CO}_2^{2-}/\text{TC}} + R_{\text{HCO}_3^-/\text{TC}} + R_{\text{HCO}_3^-/\text{PhOH}}\), where \(R_{\text{CO}_2^{2-}/\text{TC}}, R_{\text{HCO}_3^-/\text{TC}}\) and \(R_{\text{HCO}_3^-/\text{PhOH}}\) are the rates of TC degradation by CO2•−, HO• and the direct photolysis, respectively. Based on the reactions reported in Scheme 1, \(R_{\text{CO}_2^{2-}/\text{TC}}\) and \(R_{\text{HCO}_3^-/\text{PhOH}}\) can be expressed as follows:
By introducing these steady-state concentration values in Eqs. (6) and (7) and by considering the definitions of \( \chi_{HCO_3} \), \( \chi_{CO_3} \) Eqs. (4) and ((5)) and \( \chi_{HO} \), (see Text S2, SM), one gets:

\[
R_{\text{RTC}} = R_{HCO_3} \times \chi_{HCO_3} \times \chi_{CO_3} \times \left( k_{\text{red}}^{\chi_{HO}} \times \frac{1}{1 + k_{\text{red}}^{\chi_{HO}} + k_{\text{red}}^{\chi_{HO}}} \right) + R_{f_p}
\]

(14)

where \( \chi_{HCO_3} = 0.965 - 0.985 \) and \( \chi_{CO_3} = 0.016 - 0.018 \) are the fractions of HO* that react with, respectively, bicarbonate/carbonate and the anilines (TC) under our experimental conditions (\( c_{HCO_3} = 0.32 \) – 0.38 M, pH 8.3, [TC] = 5 \( \mu \)M), while \( \chi_{CO_3} = 0.97 - 0.99 \) is the fraction of CO\(_3^{2-}\) reacting with TC. Note that the formation rate of CO\(_3^{2-}\) is \( R_{\text{CO}_3} = R_{HCO_3} \times \chi_{HCO_3} \times \chi_{CO_3} \approx R_{\text{RTC}} \). The quantity \( [\text{PhOH}]_s \) is operationally defined as the phenol concentration that halves the rate of TC degradation by CO\(_3^{2-}\), compared to the rate observed in the absence of phenol (when \( [\text{PhOH}] = 0 \), one has \( R_{\text{RTC}} \approx R_{HCO_3} + R_{f_p} \); when \( [\text{PhOH}] = [\text{PhOH}]_s \), one has \( R_{\text{RTC}} \approx 0.5 R_{HCO_3} + R_{f_p} \). The lower is \( [\text{PhOH}]_s \), the stronger is the inhibition of TC degradation by PhOH through the back-reduction process.

### 2.2. Formation of CO\(_3^{2-}\) by persulfate photolysis

The carbonate radical was also generated by photolysis of the persulfate anion in the presence of an excess of bicarbonate anion, according to Eqs. (15) and (16) (Huie and Clifton, 1990).

\[
S_2O_8^{2-} \xrightarrow{hv} 2 SO_4^{2-}
\]

(15)

\[
SO_4^{2-} + HCO_3^- \rightarrow SO_4^{3-} + CO_3^{2-} + H^+ (k_{SO_4\text{-HCO}_3} = 2.8 \times 10^6 \text{M}^{-1}\text{s}^{-1})
\]

(16)

Side-reactions of the sulfate radical anion (SO\(_4^{2-}\)) are discussed in the following. The carbonate anion (CO\(_3^{2-}\)) also reacts with SO\(_4^{2-}\) (\( k_{SO_4\text{-CO}_3} = 4.1 \times 10^6 \text{M}^{-1}\text{s}^{-1} \); Padmaja et al., 1993), but its contribution to CO\(_3^{2-}\) formation is only small (i.e., <1.5%) at pH 8.0, which was used in this study. Furthermore, no drawback of this reaction is expected, since no further reactive species than CO\(_3^{2-}\) are produced. The reactions of SO\(_4^{2-}\) with organic compounds used in this study are expected to be fast (second-order rate constants up to \(~5 \times 10^6 \text{M}^{-1}\text{s}^{-1} \); Neta et al., 1988). To reduce the transformation of these compounds due to direct reaction with SO\(_4^{2-}\), the concentrations of target compounds and the competitor were chosen to be a factor of 10\(^5\) smaller compared
to HCO$_3^-$, SO$_4^{2-}$ can also react with the substrate used for its production (i.e., S$_2$O$_8^{2-}$), but this reaction channel is estimated to be ~440 times lower compared to CO$_3^{2-}$ production. Owing to the low concentration of S$_2$O$_8^{2-}$ (~1 mM), possible products of this reaction are not expected to be relevant for the transformation of the used organic compounds. At the experimental pH, water is a further reactant to be considered for SO$_4^{2-}$ and leads to the formation of hydroxy radical (HO$^\bullet$) (Eq. (17) (Herrmann et al., 1995)).

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{HO}^\bullet + \text{H}^+ \quad \left( k_{\text{HO}^\bullet, \text{n}_0} = 1.19 \times 10^4 \text{M}^{-1}\text{s}^{-1} \right) \quad (17)$$

The contribution of HO$^\bullet$ production from the reaction of SO$_4^{2-}$ with HO$^\bullet$ at pH 8 (HO$^\bullet$ = 1 pM) is about an order of magnitude smaller compared to water ([H$_2$O] ~ 55 M) (Canonica and Schönberger, 2019). At the bicarbonate concentration used in this study (0.10 M), HO$^\bullet$ formation rates are estimated to be ~390 times lower compared to SO$_4^{2-}$ formation rates. The formed HO$^\bullet$ reacts at pH 8 with both HCO$_3^-$ and CO$_3^{2-}$, leading to the formation of CO$_2^+$ (Eqs. (2) and (3)). The reactions of HO$^\bullet$ with the used organic compounds are expected to be fast (second-order rate constants up to ~1 $\times 10^5$ M$^{-1}$ s$^{-1}$; Buxton et al., 1988), but their importance for the transformation of these compounds is much lower compared to the aforementioned side-reactions of SO$_4^{2-}$, owing to the much lower formation rate of HO$^\bullet$ compared to SO$_4^{2-}$.

Therefore, the role of HO$^\bullet$ would be negligible in the frame of the used conditions.

### 2.2.1. Competition kinetics experiments

Aqueous solutions containing potassium persulfate (1.0 $\times 10^{-3}$ M), sodium bicarbonate (1.0 $\times 10^{-1}$ M), sulfuric acid (~0.8 $\times 10^{-3}$ M), a single target compound TC (aniline or sulfadiazine, 1.0 $\times 10^{-6}$ M), the phenylurea metoxuron (MET) as a competitor (1.0 $\times 10^{-6}$ M), and a variable concentration of either phenol or 4-methylphenol were prepared in quartz glass tubes (18 mm external diameter, 15 mm internal diameter) using appropriate stock solutions of the various components, with pH of 8.0 ± 0.1. This pH was achieved by 1:5 dilution of a sodium bicarbonate solution ($5.0 \times 10^{-1}$ M), a sodium oxalate solution (3% w/w) that was supplemented with two drops of a concentrated sulfuric acid solution (4.6 M). The tubes were closed with glass stoppers, shaken by hand, placed in a water bath and kept 15 min at a temperature of 25.0°C. They were then submitted to irradiation in a temperature-controlled (25.0 ± 0.2°C) DEMA (Hans Mangels GmbH, Bornheim-Roisdorf, Germany) model 125 merry-go-round photoreactor, which was equipped with a Heraeus Nobbliight model TQ718 medium-pressure mercury lamp operated at an input power of 500 W. The lamp was placed in a cooling jacket consisting of a quartz glass inner wall, a borosilicate glass outer wall and a UVW-55 glass filter (supplied by DEMA) in between.

The combination of these glasses resulted in a band-pass filter for the wavelength range of 308–410 nm. This setup was chosen, in analogy to previous studies (Canonica and Schönberger, 2019), to limit the direct phototransformation of the target compounds and the competitor while allowing for photolysis of persulfate, mainly induced by the 313 nm emission line of the mercury lamp. A more detailed description of the photoreactor and its operation is given elsewhere (Wegelin et al., 1994).

Samples (400 µL) were taken just before irradiation and during irradiation at regular time intervals, filled into vials and immediately transferred to the refrigerated autosampler (5.0°C) of the chromatographic equipment. All kinetic experiments were performed at least in duplicate. Control irradiation experiments were performed with persulfate-free solutions to check for possible interferences by direct or indirect phototransformation reactions of the target compounds and metoxuron (MET). Within the time range employed for competition kinetics experiments, such transformation rates were typically two orders of magnitude lower than the rates induced by CO$_3^{2-}$ in the absence of phenolic inhibitors, but became more important for the higher concentrations of inhibitor. These side-reactions were considered when fitting the data as explained in the Results and Discussion section.

### 2.2.2. Inhibitory effect of antioxidants on the second-order rate constant of the carbonate radical-induced oxidation of target compounds determined by competition kinetics

The previously elaborated one-channel model for the oxidation of TC inhibited by an antioxidant (AO) (Canonica and Laubscher, 2008; Wenk et al., 2011) is applied in this section to the derivation of the dependence of $k_{\text{TC,app}}$ on MET (see Text S3, SM for the definition of this second-order rate constant) on AO concentration (AO = phenol or 4-methylphenol), in an analogous manner as performed in the case of the sulfate radical as an oxidant (Canonica and Schönberger, 2019). We consider the case in which the transformation of TC is exclusively initiated by direct reaction with CO$_3^{2-}$ (i.e., side-reactions of TC can be neglected). The inhibitory effect of an AO on the oxidation of TC (TC = aniline or sulfadiazine) is rationalized in terms of the following reaction equations:

$$\text{CO}_3^{2-} + \text{TC} \rightarrow \text{CO}_3^{2-} + \text{TC}^+ \quad (19)$$

$$\text{TC}^+ \rightarrow \text{TC}_{\text{red}} \quad \left( k_{\text{TC,red}} \right) \quad (20)$$

$$\text{TC}^+ + \text{AO} \rightarrow \text{TC}_{\text{red}} + \text{AO}_{\text{ox}} \quad \left( k_{\text{TC,ox}, \text{AO}} \right) \quad (21)$$

where $\text{TC}^+$ is the reactive radical intermediate resulting from one-electron oxidation of TC, $k_{\text{TC,app}}$ is the second-order rate constant for the electron transfer (et) reaction between TC and CO$_3^{2-}$, $k_{\text{et}}$ is the first-order rate constant for the transformation of $\text{TC}^+$ to a stable oxidation product (TC$_{\text{red}}$), and $k_{\text{TC,ox}, \text{AO}}$ is the second-order rate constant for reaction of $\text{TC}^+$ with AO, which leads to $\text{TC}^+$ reduction back to TC and yields an oxidized antioxidant (AO$_{\text{ox}}$). The rate equations for TC and $\text{TC}^+$ can be expressed as follows:

$$\frac{d[T\text{C}]}{dt} = -k_{\text{TC,app}} \cdot [\text{CO}_3^{2-}] \cdot [\text{TC}] + k_{\text{TC,red}} \cdot [\text{TC}_{\text{red}}] \cdot [\text{AO}] \quad (22)$$

$$\frac{d[\text{TC}^+]}{dt} = k_{\text{TC,app}} \cdot [\text{CO}_3^{2-}] \cdot [\text{TC}] - k_{\text{TC,ox}, \text{AO}} \cdot [\text{TC}^+] \cdot [\text{AO}] - k_{\text{TC,ox}, \text{AO}} \cdot [\text{TC}^+] \quad (23)$$

Applying the steady-state assumption for $\text{TC}^+$ leads to the following equation:

$$[\text{TC}^+] = \frac{k_{\text{TC,app}} \cdot [\text{CO}_3^{2-}] \cdot [\text{TC}]}{k_{\text{TC,red}} + k_{\text{TC,ox}, \text{AO}} \cdot [\text{AO}]} \quad (24)$$
Substituting \([TC^*}\) from Eq. (24) into Eq. (22) and rearranging yields Eq. (25):

\[
\frac{d[TC]}{dt} = - \frac{k_{ \text{CO}_2^*-TC}^{\text{app}}}{1 + \frac{k_{ \text{CO}_2^*-AO}^{\text{app}}}{k_{ \text{AO}^-}^{\text{app}}}} [CO_2^-] [TC]
\]  

(25)

Comparing Eqs. (SS) (see Text S3, SM) and (25) leads to the identity:

\[
k_{ \text{CO}_2^*-TC}^{\text{app}} = \frac{k_{ \text{CO}_2^*-TC}}{1 + \frac{k_{ \text{AO}^-}^{\text{app}}}{k_{ \text{CO}_2^*-AO}^{\text{app}}}} [AO]
\]  

(26)

Since AO is generally also transformed during the kinetic runs, \(k_{ \text{CO}_2^*-TC}^{\text{app}}\) from Eq. (26) is properly speaking not a kinetic constant. However, it can be approximated to a constant if \([AO]\) does not deviate strongly from \([AO]_0\) during irradiation. Note that in the case of \([AO] = 0\), \(k_{ \text{CO}_2^*-TC}^{\text{app}} = k_{ \text{CO}_2^*-TC}\).

2.3. Back-reduction processes in triplet-sensitized phototransformation

Additional experiments were carried out to investigate back-reduction by phenol (PhOH) during the degradation of TC = 3,4-dichloroaniline (3,4DCA) and 3-chloroaniline (3CA) with excited triplet states. Back-reduction is known to be operational in the degradation of aniline and 4-chloroaniline by \(\text{CDOM}^*\) (Canonica and Laubscher, 2008; Wenk and Canonica, 2012). The anionic form of 4-carboxybenzophenone (benzophenone-4-carboxylate, hereafter CBBP) was here used as CDOM proxy. Indeed, CBBP has already been employed for this purpose and to determine representative second-order rate constants for the reactions between organic substrates and \(\text{CDOM}^*\) (Carena et al., 2019; Vione et al., 2018). Solutions containing CBBP were irradiated under a UVA black light (Philips TL-D 18 W) with emission maximum at 369 nm, which produced a UV irradiance of 42.6 ± 0.7 W m\(^{-2}\) on top of the irradiated systems (Fig. S1, SM). A detailed description of this irradiation setup is reported in Carena et al. (2019). The initial concentrations of TC and CBBP were 5 and 70 \(\mu\)M, respectively, while PhOH was varied between 0 and 10 \(\mu\)M. The pH of the solutions was ~7 and did not vary significantly during irradiation. Buffers were not used in these experiments to avoid unwanted side-reactions. The direct photolysis of 3, 4DCA and 3CA was negligible under UVA irradiation during the experimental time interval (4 h irradiation).

2.4. Analytical methods

The concentration of target compounds during kinetic runs was followed by high-performance liquid chromatography (HPLC) using an Agilent 1100 system equipped with a quaternary low-pressure mixing gradient pump, a refrigerated autosampler, a temperature-controlled column compartment, a diode array detector and an Agilent 1200 fluorescence detector. Alternatively, an analogous Thermo Fisher Ultimate 3000 HPLC system or a VWR-Hitachi LaChrom Elite chromatograph (Text S4, SM) were used. A detailed list of HPLC analysis methods is given in Table S2, SM.

3. Results and discussion

3.1. Comparison of back-reduction in CO\(_2^*\)-induced (nitrile photolysis system) and triplet-sensitized transformation

The degradation of anilines by CO\(_2^*\) (produced upon oxidation of HCO\(_3^-\)/CO\(_2^*\)) by HO*generated by nitrate photolysis) was inhibited when increasing the concentration of added phenol (PhOH, Fig. S2, SM). The experimental conditions were chosen to minimize the scavenging of either CO\(_2^*\) or HO* by phenol, a process that would inhibit aniline degradation in a similar way as back-reduction. By excluding important scavenging of CO\(_2^*\)/HO*, it is possible to argueably assume that the observed inhibition by phenol was due to the reactions (back-reduction) between phenol itself and the one-electron oxidized intermediates formed upon transformation of the anilines (Scheme 1).

Assuming \(RT_c = R_{\text{CO}_2^*-TC} + R_{\text{PhOH}-TC} + R_{\text{PhOH}}\) as per Section 2.1.1 and taking into account the possible back-reduction process, \(RT_c\) can be expressed as Eq. (14) that was written in close analogy to the kinetic equations used in previous works, to describe back-reduction in the triplet-sensitized phototransformation of organic compounds (Vione et al., 2018; Wenk et al., 2011; Wenk and Canonica, 2012).

The rate of TC direct photolysis (\(R_{\text{PhOH}}\)) was assessed by correcting the direct photolysis rate measured in ultrapure water (\(R_{\text{PhOH,exp}}\); see Fig. S2, SM for the experimental data) for the inner-filter effect of nitrate (the direct photolysis of TC is slower in the presence of nitrate, Eq. (27); Carena et al., 2018).

\[
R_{\text{PhOH}} = \frac{\int p(x) \times \left[\frac{\epsilon (\lambda) [TC]}{\epsilon (\lambda) [TC]} \times \left[1 - 10^{-\alpha (\lambda) [NO]^+} \times \alpha (\lambda) [TC] \right]\right] d\lambda}{\int p(x) \times \left[1 - 10^{-\alpha (\lambda) [NO]^+} \times \alpha (\lambda) [TC] \right] d\lambda}
\]

(27)

In Eq. (27), \(p(x)\) is the UVB lamp photon flux density incident over the solution, \(\alpha (\lambda)\) is a molar absorption coefficient (of TC or NO\(_3^-\)), and \(b\) is the solution optical path length (0.4 cm). The correction factor was ~0.94 (\(R_{\text{PhOH,exp}} \approx 0.94 R_{\text{PhOH}}\)). Note that \(R_{\text{PhOH}}\) was here considered not to vary with [PhOH], because the direct photolysis of chloroanilines should occur via loss of chlorine atoms rather than through photoionization of the amino group (Carena et al., 2018). Consequently, back reduction by PhOH should not affect the direct photolysis process.

Fig. 1 shows the experimental profiles of RTc vs. [PhOH] for the studied anilines. A very good fit to the experimental data was obtained with Eq. (14), which suggests that the kinetic model proposed for back-reduction matches the experimental findings. The calculated \(R_{\text{PhOH}}\) values (Eq. (27)) were 0.49 ± 0.03 nM s\(^{-1}\) for 3CA, 3.4 ± 0.5 nM s\(^{-1}\) for 4CA, and 0.44 ± 0.02 nM s\(^{-1}\) for 3,4DCA. Direct photolysis was negligible in the case of the Ani. The values of \(R_{\text{PhOH}}\) (Eq. (14)) obtained from data fit were 2.1 ± 0.1 nM s\(^{-1}\) for Ani, 6.3 ± 0.4 nM s\(^{-1}\) for 3CA, 4.3 ± 0.5 nM s\(^{-1}\) for 4CA, and 3.9 ± 0.3 nM s\(^{-1}\) for 3,4DCA. Data fit also yielded [PhOH]\(_{0}\) = 2.19 ± 0.23 \(\mu\)M for Ani, 1.15 ± 0.25 \(\mu\)M for 3CA, 1.18 ± 0.26 \(\mu\)M for 4CA, and 1.18 ± 0.22 \(\mu\)M for 3,4DCA.

Interestingly, Fig. 2 shows that the values of [PhOH]\(_{0}\) obtained for the degradation of the anilines by CO\(_2^*\) do not significantly differ from those observed in triplet-sensitized oxidation induced by the triplet states of benzophenone-4-carboxylate (\(\text{CBBP}^*\)) and 2-acetonaphthone (\(2\text{AN}^*\)). This finding suggests that CO\(_2^*\), \(\text{CBBP}^*\) and \(2\text{AN}^*\) produce the same intermediates upon aniline oxidation, which all undergo a similar back-reduction process in the presence of PhOH.

3.2. Back-reduction processes upon generation of CO\(_2^*\) by \(\text{SO}_4^*\) as reactive intermediate

Initially, competition kinetics experiments were performed for individual target compounds (TC), i.e., aniline and sulfadiazine, in the absence of phenolic inhibitors. Analogous experiments were also executed for phenol and 4-methylphenol as antioxidant compounds. These experiments yielded second-order rate constants for the reaction of TC with CO\(_2^*\) in the absence of additives, which are termed as \(k_{TC-\text{CO}_2^*}^{\text{app}}\) and provided in Table 1. The determined \(k_{TC-\text{CO}_2^*}^{\text{app}}\) values are within a factor of two compared to those known from the literature.

Interestingly, the determined CO\(_2^*\) rate constants for phenol and 4-methylphenol are at least 11 and 3 times lower, respectively, compared to the rate constants for aniline and sulfadiazine. This represents an obvious experimental advantage, since these phenols are more resistant to direct CO\(_2^*\)-induced transformation, and consequently expected to persist and exert their inhibitory effect during the whole course of TC.
transformation. Examples of kinetic runs showing the transformation of aniline as TC and metoxuron (MET) as competitor in the presence and absence of 0.5 μM phenol as inhibitor are provided in Fig. 3a, which also shows the transformation kinetics of phenol. All compounds exhibit zero-order kinetics, i.e., a linear decrease in their residual concentration with irradiation time. For the system with aniline and metoxuron without added phenol, this is an indication that aniline, which reacts much faster than metoxuron, is the major species responsible for the scavenging of CO$_3^{*\cdot}$ during the whole kinetic run, and that no reaction products significantly reacting with CO$_3^{*\cdot}$ are formed. Indeed, if $R_{CO3}$ is the formation rate of CO$_3^{*\cdot}$, if $R_{TC} = k_{TC}^{app} [TC] [CO_3^{*\cdot}]$ and if CO$_3^{*\cdot}$ mainly reacts with TC, it is $[CO_3^{*\cdot}] \cong R_{TC} \left(k_{TC}^{app} [TC]ight)^{-1}$ and $R_{TC} \cong R_{CO3}$, which means that $R_{TC}$ is independent of [TC] (zero-order kinetics).

In the absence of phenol, the depletion of both aniline and MET is faster than in its presence, but the reduction in depletion rate is more important for aniline. Fig. 3b displays competition kinetics examples for the same compounds and different concentrations of added phenol. The slope of the regression lines (defined above as $a$ and given numerically in the graph as a function of the concentration of added phenol) decreases with increasing phenol concentration, indicating a concomitantly decreasing $k_{TC}^{app}$; aniline. The trend in $a$ shown in Fig. 3b clearly demonstrates the inhibitory effect of phenol on the transformation of aniline induced by CO$_3^{*\cdot}$. Based on Eq. (26), we define here the inhibition factor, IF, in analogy to previous studies as the ratio between $k_{TC}^{app}$, and $k_{TC}^{app}$; TC, where the latter is the second-order rate constant for the transformation of TC induced by CO$_3^{*\cdot}$ determined without antioxidant addition.

$$IF([AO]) = \frac{k_{TC}^{app};TC}{k_{TC}^{app};AO}$$

Substituting the right-hand term of Eq. (26) into Eq. (28) yields:

$$IF([AO]) = \frac{1}{1 + \left(\frac{k_{TC}^{app};AO}{k_{TC}^{app};AO} \times [AO]\right)}$$

With $[AO]_{1/2} = k_{TC}^{app};AO / k_{TC}^{app};AO$, Eq. (29) transforms to:

$$IF([AO]) = \frac{1}{1 + [AO] / [AO]_{1/2}}$$

Series of competition kinetics experiments were performed for the two target compounds, namely aniline and sulfadiazine, using phenol and, alternatively, 4-methylphenol as antioxidants. The results of these experiments are shown in Fig. 4 in terms of inhibition factor as a function of AO concentration. For all four target compound/antioxidant pairs, a decrease in IF with increasing [AO] is observed. The four IF data series were fitted to the following Eq. (31), which is a slightly modified
M). For sulfadiazine, fitted values for phenol (0.28 ± 0.01 M), aniline (0.10 µM initial concentration) as competitor, for several different phenol concentrations indicated numerically. The intensity of the filling of the markers increases (i.e., second order rate constants for the reaction of the carbonate radical with target compounds, determined in this study by competition kinetics at pH 8.0 were obtained from experiments carried out at very similar pH values (8.0 ± 0.1). The average values from at least two independent experiments are given. The errors represent 95% confidence intervals obtained from linear regression and by applying Gaussian error propagation.

\[ k_{TC}^{\text{MET}} \times \text{M} \text{phenol (gray filled squares). The lines represent linear regressions.} \]

\[ \text{Sulfadiazine} \ 6.80 ± 0.10 \ M \]

\[ \text{Phenol} \ 0.435 ± 0.008 \ M \]

\[ 4\text{-Methylphenol} \ 1.58 ± 0.03 \ M \]

\( \alpha \) is the fraction of TC reacting through the main pathway that is inhibited by antioxidants. For aniline (An: AnH+/An; b) for sulfadiazine (SD): SD/SD (H-), second pK\(_a\) or pK\(_{sd}\) for the phenols (R-PhOH): R-PhOH/R-PhO-.

\[ \text{Slope} \ \alpha \ \ldotp \ \text{slope of the competition kinetics plots according to Eq. (18), obtained by linear regression, and corresponding to } k_{TC}^{\text{MET}} \times k_{\text{MET}}^{\text{MET}} \text{. The average values from} \]

\[ \text{Slope} \ \alpha \ \text{is shown numerically as a function of } \frac{[\text{AO}]}{[\text{AO}]}_1/2 \text{ and } (1-f). \]

Here \( f \) is the fraction of TC reacting through the main pathway that is inhibited by antioxidants. For aniline, \( f \) fits yielded identical \([\text{AO}]/[\text{AO}])_1/2\) values for phenol (0.28 ± 0.02 µM) and 4-methylphenol (0.28 ± 0.04 µM). For sulfadiazine, fitted \([\text{AO}]/[\text{AO}])_1/2\) values were 0.79 ± 0.10 µM for phenol and 0.67 ± 0.06 µM for 4-methylphenol, and therefore higher compared to aniline by a factor of 2.4 and 2.8, respectively. Obtained \( f \) values were high, namely 0.78 for the pair sulfadiazine/phenol and >0.92 for all other TC/AO pairs, indicating the minor importance of side-reactions not subject to inhibition by AO.

In the case of aniline, it is interesting to observe that the value of [PhOH] \(_i\) (AO = phenol) is lower by an order of magnitude compared to the value obtained when CO\(_3^+\) was produced by nitrate photolysis (see Section 3.1). It is also an order of magnitude lower compared to the values determined for triplet-sensitized aniline transformation, conducted using CBBP and 2-AN as photosensitizers (Canonica and Laubscher, 2008; Wenk and Canonica, 2012). All these [PhOH] \(_i\) values were obtained from experiments carried out at very similar pH values (8.0 ± 8.3). Therefore, the slight changes in speciation of the various species involved in the back-reduction process are probably not the cause of the differences in [PhOH] \(_i\).

Anilines (Ar-NH\(_2\)) undergo mono-electronic oxidation by CO\(_3^+\) \((\text{Elango et al., 1984; Huang and Mabury, 2000a; Jonsson et al., 1994; Liu et al., 2018; Wojnárovits et al., 2020})\) and by the triplet states of 2-acetonaphthone (\(^2\text{2AN}\)) and benzophenone-4-carboxylate (\(^2\text{CBBP}\)) (Canonica and Laubscher, 2008; Vione et al., 2018; Wenk and Canonica,
forming radical cations (Ar-NH$_2^+$) that easily deprotonate to produce Ar-NH$^\bullet$. Previous works have shown that phenolic compounds including phenol (PhOH) can act as antioxidants for the species Ar-NH$^\bullet$ (Canonica and Laubscher, 2008; Vione et al., 2018; Wenk and Canonica, 2012). Therefore, the following reactions should take place in the studied systems (where T$^*$ represents an excited triplet state, such as that of $^3$2AN$^*$):

\[
\text{Ar-NH}_2 + \text{CO}_3^{2-} \rightarrow \text{Ar-NH}_2^++ \text{CO}_3^{2-} \quad (32)
\]

\[
\text{Ar-NH}_2 + T^* \rightarrow \text{Ar-NH}_2^+ + T^{**} \quad (33)
\]

\[
\text{Ar-NH}_2^+ \rightleftharpoons \text{Ar-NH}^\bullet + H^+ \quad (34)
\]

\[
\text{Ar-NH}^\bullet \rightarrow \text{oxidized products} \quad (35)
\]

\[
\text{Ar-NH}^\bullet + \text{PhOH} \rightarrow \text{Ar-NH}_2 + \text{PhO}^\bullet \quad (36)
\]

A possibility to account for differences in the [PhOH]$_{1/2}$ values observed in different systems is to assume that antioxidant compounds are produced even in the absence of added PhOH, thereby providing a baseline level of back-reduction (Canonica and Schönenberger, 2019). Such a process would decrease the steady-state [Ar-NH$^\bullet$] with the consequence that, the higher the baseline reductants, the higher is the concentration of PhOH (quantified as [PhOH]$_{1/2}$) required to obtain the same IF value. Therefore, different systems could show varying levels of baseline back-reduction and provide different values of [PhOH]$_{1/2}$. A potential photogenerated reductant is superoxide, O$_2^{\bullet-}$, which is for instance produced by reaction between T$^*$ and dissolved oxygen (Canonica and Schönenberger, 2019; Huber et al., 2003). Moreover, the one-electron oxidation of anilines is well known to produce phenolic intermediates (Bossmann et al., 1998) that might act as baseline antioxidants.

As far as back-reduction in sulfadiazine transformation is concerned, the [PhOH]$_{1/2}$ value found in this study (0.79 ± 0.10 µM) is well matched with [PhOH]$_{1/2}$ = 0.86 ± 0.10 µM that was obtained for the transformation of sulfadiazine photosensitized by CBBP at pH 8.5 (Vione et al., 2018), but four times lower than a previously determined value (3.2 ± 0.8 µM) for triplet-sensitized transformation at pH 8.0 (Wenk and Canonica, 2012). Therefore, for sulfadiazine the presence of possible baseline antioxidants appears to play a less important role than in the case of aniline.

### 3.3. Environmental significance

To assess the role of back-reduction on the phototransformation of water pollutants, the photochemical fate of aniline was modeled in a lake-water scenario by means of the APEX software (Fig. 5) (Vione, 2020).

Aniline was chosen here because two alternative values of [PhOH]$_{1/2}$ were obtained in this work for this compound, which could be observed under different conditions as far as transformation by CO$_3^{\bullet-}$ is concerned. Aniline does not undergo direct photolysis to a significant extent, but it reacts with HO$^\bullet$ (second-order rate constant $k_{\text{HO}^\bullet, \text{Ani}} = 1.4 \times 10^{10}$ M$^{-1}$ s$^{-1}$; Buxton et al., 1988), CO$_3^{\bullet-}$ ($k_{\text{CO}_3^{\bullet-}, \text{Ani}} = 5 \times 10^8$ M$^{-1}$ s$^{-1}$, etc.)
would prevail at low DOC and would play a comparable role as CDOM* at high DOC. In the case of aniline (Wenk and Canonica, 2012). In the case of aniline equivalents as DOC (this work) and CDOM* (k_{CDOM,Anil}^{\text{tr}} = 4 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}; estimated from values published by Erickson et al. (2015), for several anilines using methylene blue as model photosensitizer). In the case of natural waters, the natural organic matter is the provider of phenolic antioxidant moieties. The experimental [PhOH]_j values can be translated into DOC_j equivalents as DOC_j (mg C L^-1) = 0.4 \times [PhOH]_j (µM), as reported by Vione et al. (2018) (see also Leresche et al., 2016). In the case of aniline + HO*, no back-reduction is expected (Wenk et al., 2011). In the case of aniline + CDOM*, one has [PhOH]_j = 2.8 µM ⇒ DOC_j = 1.1 mgC L^-1 (Wenk and Canonica, 2012). In the case of aniline + CO_3^{2-} (this work), one has either [PhOH]_j = 0.28 µM ⇒ DOC_j = 0.11 mgC L^-1, or [PhOH]_j = 2.2 µM ⇒ DOC_j = 0.88 mgC L^-1.

Here, three different scenarios are considered. In the first (Scenario 1), no back-reduction is supposed to be operational with either CDOM* or CO_3^{2-}. In Scenario 2, we used DOC_j = 1.1 mgC L^-1 for the CDOM* process and DOC_j = 0.88 mgC L^-1 for CO_3^{2-} (moderate back-reduction for CO_3^{2-}). In Scenario 3, we used again DOC_j = 1.1 mgC L^-1 for CDOM* but DOC_j = 0.11 mgC L^-1 for CO_3^{2-} (strong back-reduction for CO_3^{2-}).

Fig. 5 shows that, in the absence of back-reduction (5a), CO_3^{2-} would be the main aniline photodegradation process at low DOC while CDOM* would prevail at high DOC (indeed, CO_3^{2-} is very efficiently scavenged by DOM; Yan et al. 2019). Reaction with HO* always plays a secondary role. The back-reduction processes increase the relative role of HO*, and the HO* reaction becomes a very important if not the main pathway of aniline phototransformation. In the most extreme back-reduction scenario (Scenario 3, Fig. 5c), the reaction with HO* would prevail at low DOC and would play a comparable role as CDOM* at high DOC. The back-reduction processes also slow down significantly the photodegradation kinetics of aniline, with an important increase in the relevant lifetimes.

4. Conclusion

- Back-reduction by phenolic compounds is operational in the case of the CO_3^{2-}-mediated photodegradation of anilines and sulfadiazine.
- The observed similarities concerning back-reduction for CO_3^{2-}-induced and triplet-sensitized degradation suggest that the same reaction intermediates are involved in both cases.
- The operational conditions by which CO_3^{2-} is photogenerated (photolysis of nitrate or persulfate) affect the experimental values of [AO]_j for aniline, presumably as a consequence of the different formation of additional reducing species in different systems.
- In sunlit surface waters scenarios, back-reduction decreases the contributions of both CO_3^{2-} and CDOM* to aniline photodegradation. In the absence of back-reduction, HO* would always be a secondary process and aniline photodegradation would be dominated by CO_3^{2-} at low DOC and by CDOM* at high DOC. In contrast, HO* and CDOM* play comparable roles at high DOC with back-reduction. Moreover, in the strongest back-reduction scenario for the CO_3^{2-} process, aniline photodegradation at low DOC would be dominated by HO*.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

References


