SUPPLEMENTARY MATERIAL

Inhibition by phenolic antioxidants of the degradation of aromatic amines and sulfadiazine by the carbonate radical ($CO_3^{\bullet -}$).

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Ani = aniline

3CA = 3-chloroaniline

4CA = 4-chloroaniline

3,4DCA = 3,4-dichloroaniline

PhOH = phenol

CBBP = benzophenone-4-carboxylate

2AN = 2-acetonapthone

HSDZ = sulfadiazine (amphoteric form)

SDZ^- = sulfadiazine (anionic form)

CDOM = chromophoric dissolved organic matter

TC = target compound (Ani, 3CA, 4CA, 3,4DCA, SDZ)

Text S1. List of Chemicals.

All chemicals in the following list were purchased from common commercial sources and used without purification. (A) Organic compounds: aniline (Sigma-Aldrich, ≥ 99.5%), 3-chloroaniline (Sigma-Aldrich, 99%), 4-chloroaniline (Sigma-Aldrich, 98%), 3,4-dichloroaniline (Sigma-Aldrich, 98%), 4-methylphenol (*p*-cresol, Fluka, > 99%), metoxuron (Sigma-Aldrich, Pestanal®, 99.5%), phenol (Fluka, ≥ 99.5%), sulfadiazine (Sigma, 99.0%), 4-carboxybenzophenone (Sigma-Aldrich, 99%). (B) Inorganic compounds: potassium persulfate ($K_2S_2O_8$, Fluka, ≥ 99.0%), sodium nitrate (Sigma-Aldrich, ≥ 99%), sodium bicarbonate ($NaHCO_3$, Aldrich, BioXtra, 99.5–100.5%), sodium hydroxide (Sigma-Aldrich, ≥ 97%), sulfuric acid (Aldrich, EMSURE for analysis, 98%). Ultrapure water (resistivity > 18 MΩ cm, organic carbon < 2 ppb) was obtained from a Barnstead Nanopure purification system or a Milli-Q system (Millipore) and used for all aqueous solutions and chromatographic analysis. Gradient-grade methanol for HPLC analysis was from VWR Chemicals BDH®.

The acidic stock solution of 4-carboxybenzophenone ($pK_a \sim 4.5$; NIST, 2004) was adjusted to pH 7.0 with NaOH 1 M, to keep the compound in the deprotonated form. Solution pH was measured with a 98100 Checker pH meter by Hanna Instruments.

Text S2. Chemical composition of the irradiated solutions for production of $CO_3^{\bullet -}$ by nitrate photolysis.

With the aim to investigate the back-reduction process during the degradation of TC by $CO_3^{\bullet -}$ ($TC^{\bullet +} + PhOH \rightarrow TC + PhO^{\bullet} + H^{+}$), it is necessary to minimize the pathways that compete with the formation of $CO_3^{\bullet -}$ from $HO^{\bullet}$, and with the reaction of TC with $CO_3^{\bullet -}$. This means that the fraction of $HO^{\bullet}$ that reacts with TC and PhOH ($\chi_{HO^{\bullet}}^{TC}$ and $\chi_{HO^{\bullet}}^{PhOH}$, respectively) should be negligible compared to the fraction that oxidizes bicarbonate/carbonate to $CO_3^{\bullet -}$ ($\chi_{HO^{\bullet}}^{NaHCO_3}$). Note that $\chi_{HO^{\bullet}}^{NaHCO_3} + \chi_{HO^{\bullet}}^{TC} + \chi_{HO^{\bullet}}^{PhOH} = 1$. Because a term in a sum can be neglected without significant errors if it is lower than 5% of the total sum (and 5% is also lower than the uncertainty of the results of the irradiation experiments), one can set $\chi_{HO^{\bullet}}^{TC} + \chi_{HO^{\bullet}}^{PhOH} < 0.05$, which means $\chi_{HO^{\bullet}}^{NaHCO_3} > 0.95$. By applying the same approach to the $CO_3^{\bullet -}$-scavenging pathways, one has that the majority of $CO_3^{\bullet -}$ should react with TC rather than with PhOH ($\chi_{CO_3^{\bullet -}}^{TC} > 0.95$).

The term $\chi_{HO^{\bullet}}^{NaHCO_3}$ can be expressed as the ratio between the sum of the rates of the reactions involving $HO^{\bullet} + HCO_3^{-}$ and $HO^{\bullet} + CO_3^{2-}$, and the total scavenging rate of $HO^{\bullet}$. Similarly, $\chi_{CO_3^{\bullet -}}^{TC}$ can be expressed as the ratio between the rate of the reaction between TC and $CO_3^{\bullet -}$, and the total scavenging rate of $CO_3^{\bullet -}$. By so doing, one gets **Eqs. S1,S2** that are the same as **Eqs. 4,5** in the main manuscript. Note that $\chi_{HO^{\bullet}}^{NaHCO_3}$ takes into account the reactivity of both bicarbonate and carbonate with $HO^{\bullet}$.

$$\chi_{HO^{\bullet}}^{NaHCO_3} = \frac{k_{HO^{\bullet}}^{NaHCO_3} \times C_{NaHCO_3}}{k_{HO^{\bullet},TC} \times [TC] + k_{HO^{\bullet},PhOH} \times [PhOH] + k_{HO^{\bullet}}^{NaHCO_3} \times C_{NaHCO_3}} > 0.95 \quad (S1)$$

$$\chi_{CO_3^{\bullet -}}^{TC} = \frac{k_{CO_3^{\bullet -},TC} \times [TC]}{k_{CO_3^{\bullet -},TC} \times [TC] + k_{CO_3^{\bullet -},PhOH} \times [PhOH]} > 0.95 \quad (S2)$$

In **Eq. S1**, $k_{HO^{\bullet}}^{NaHCO_3} = \left(k_{HO^{\bullet},HCO_3^{-}} \times \alpha_{HCO_3^{-}} + k_{HO^{\bullet},CO_3^{2-}} \times \alpha_{CO_3^{2-}}\right)$ where $\alpha_{HCO_3^{-}}$ and $\alpha_{CO_3^{2-}}$ are the molar fractions of bicarbonate and carbonate, respectively, at pH 8.3. Moreover, $k_{HO^{\bullet},HCO_3^{-}} = 8.5 \times 10^{6}\ M^{-1}\ s^{-1}$ and $k_{HO^{\bullet},CO_3^{2-}} = 3.9 \times 10^{8}\ M^{-1}\ s^{-1}$ (Buxton et al., 1988).

The solutions of **Eqs. S1,S2** with respect to C_{NaHCO_3} and $[PhOH]$ are the following:

$$C_{\mathrm{NaHCO_3}} > \frac{[TC]}{(1-0.95)\times k_{\mathrm{HO^\bullet}}^{\mathrm{NaHCO_3}}}\left[0.95 \times k_{\mathrm{HO^\bullet,TC}} + \frac{(1-0.95)\times k_{\mathrm{CO_3^{\bullet-},TC}} \times k_{\mathrm{HO^\bullet,PhOH}}}{k_{\mathrm{CO_3^{\bullet-},PhOH}}}\right] \tag{S3}$$

$$[PhOH] < \frac{(1-0.95)\times[TC]\times k_{\mathrm{CO_3^{\bullet-},TC}}}{0.95 \times k_{\mathrm{CO_3^{\bullet-},PhOH}}} \tag{S4}$$

Eqs. S3,S4 indicate, respectively, the minimum $NaHCO_3$ and the maximum phenol concentration values that should be added to the irradiated solutions in order to maximize the reaction between TC and $CO_3^{\bullet-}$, and that allow for appreciating the back-reduction process with negligible interference. We fixed the concentration of the organic substrate TC ($[TC]$) as 5 µM, as already done in previous works (Vione et al., 2018; Wenk and Canonica, 2012). **Table S1** lists the values of the second-order reaction rate constants used for the calculations (Buxton et al., 1988; Canonica et al., 2005; Carena et al., 2018; Neta et al., 1988; Wojnárovits et al., 2020), and the concentration values of $NaNO_3$ and $NaHCO_3$ chosen for the different irradiation experiments. The concentration of PhOH was varied in the range between 0 and the maximum value reported in the table.

Table S1*. **(a)** Second-order rate constants (M^{-1} s^{-1}) for the reactions between $HO^\bullet/CO_3^{\bullet-}$ and the target compounds TC* (Buxton et al., 1988; Canonica et al., 2005; Carena et al., 2018; Neta et al., 1988; Wojnárovits et al., 2020) *and **(b)** the chosen bicarbonate, nitrate and (maximum) phenol concentrations (M). $k_{\mathrm{HO^\bullet,4CA}}$ was taken as the average of the $k_{\mathrm{HO^\bullet,TC}}$ values for Ani, 3CA and 3,4DCA.*

	Ani	3CA	4CA	3,4DCA	PhOH
			(a)		
$k_{\mathrm{HO^\bullet,TC}}$	1.5×10^{10}	1.4×10^{10}	1.4×10^{10}	1.3×10^{10}	1.4×10^{10}
$k_{\mathrm{CO_3^{\bullet-},TC}}$	5.0×10^{8}	4.3×10^{8}	6.2×10^{8}	4.8×10^{8}	2.0×10^{7}
			(b)		
$C_{\mathrm{NaHCO_3}}$	0.32	0.32	0.38	0.32	
$_{\max}[PhOH]$	5.0×10^{-6}	5.0×10^{-6}	8.0×10^{-6}	5.0×10^{-6}	
$[NaNO_3]$	1.0×10^{-2}	2.5×10^{-2}	2.5×10^{-2}	2.5×10^{-2}	

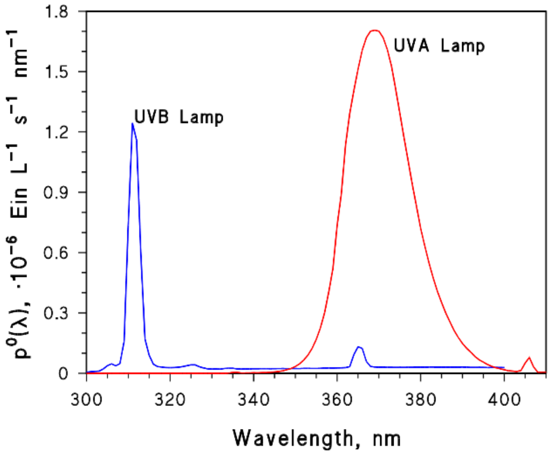


***Figure S1**. **Blue Curve**: spectral photon flux density ($p^0(\lambda)$) of the Philips narrow band TL 20W/01 lamp (2.9 ± 0.3 W m^{-2}) used in the irradiation experiments of $NaNO_3$ + $NaHCO_3$ + chloroanilines (UVB lamp). The relative standard deviation of $p^0(\lambda)$ is 10%. In the case of $NaNO_3$ + $NaHCO_3$ + aniline, the lamp irradiance was 4.2 ± 0.2 W m^{-2} and the reported $p^0(\lambda)$ has to be multiplied by 1.45. **Red Curve**: $p^0(\lambda)$ of the Philips TL-D 18 W lamp (42.6 ± 0.7 W m^{-2}) used in the irradiation experiments of CBBP + 3CA/3,4DCA (UVA lamp).*

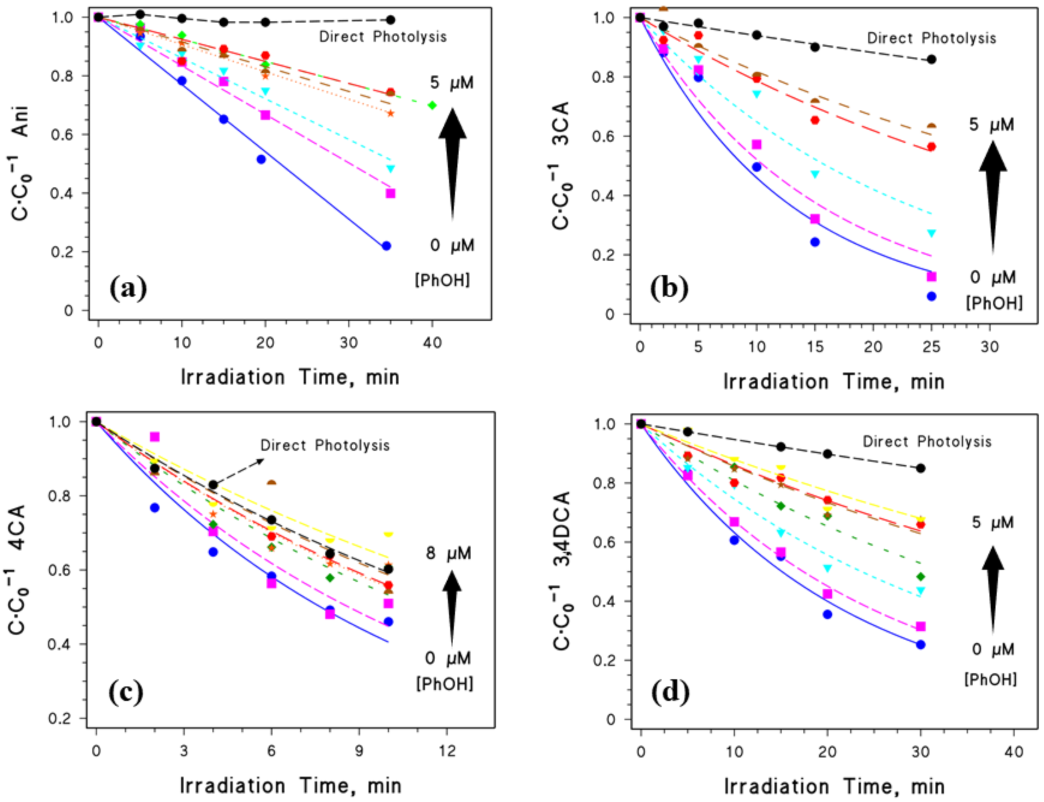


***Figure S2**. Degradation profiles (experimental data and associated fit curves) of **(a)** aniline, **(b)** 3-chloroaniline, **(c)** 4-chloroaniline and **(d)** 3,4-dichloroaniline, in the presence of $NaNO_3$ + $NaHCO_3$ + UVB light and different phenol (PhOH) concentrations. The phenol concentration values were those reported in **Fig. 1** (main manuscript). The direct photolysis data were obtained by irradiating anilines in the presence of $NaHCO_3$ only (no $NaNO_3$), under the UVB lamp.*

Text S3. Kinetic equations relevant to the carbonate radical-induced oxidation of a target compound and a reference compound (competitor) in competition kinetics experiments.

Basic assumption: the transformation of the target and reference compounds is caused exclusively by reaction with the carbonate radical ($CO_3^{\bullet-}$).

The rate equation for the depletion of a target compound (TC) induced by its reaction with $CO_3^{\bullet-}$ is given by the following expression:

$$\frac{d[\mathrm{TC}]}{dt} = -k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},TC}}[\mathrm{CO_3^{\bullet-}}][\mathrm{TC}] \tag{S5}$$

where square brackets refer to molar concentrations of the given species and $k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},TC}}$ is the second-order rate constant for the reaction of $CO_3^{\bullet-}$ with TC, leading to a permanent transformation (expressed by the superscript "tr") of TC under the conditions and time scale of the kinetics experiments. Rearrangement and integration of **Eq. S5** lead to **Eq. S6**.

$$\frac{1}{k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},TC}}}\ln\frac{[\mathrm{TC}]_0}{[\mathrm{TC}]} = \int[\mathrm{CO_3^{\bullet-}}]\,dt \tag{S6}$$

Applying the same procedure to the transformation of a reference compound (or competitor) R, present in the same solution as TC, one can derive **Eq. S7**.

$$\frac{1}{k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},R}}}\ln\frac{[\mathrm{R}]_0}{[\mathrm{R}]} = \int[\mathrm{CO_3^{\bullet-}}]\,dt \tag{S7}$$

Since the right-hand sides of **Eqs. S6,S7** are identical, one can equate the left-hand members of both equations which, after rearrangement, leads to **Eq. S8**, a classical competition kinetics expression.

$$\ln\frac{[\mathrm{TC}]_0}{[\mathrm{TC}]} = \frac{k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},TC}}}{k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},R}}}\ln\frac{[\mathrm{R}]_0}{[\mathrm{R}]} \tag{S8}$$

This equation is analogous to **Eq. 18** in the main paper with R = MET (metoxuron, which was used throughout this part of the study as a competitor). In the main paper, $k^{\mathrm{tr,app}}_{\mathrm{CO_3^{\bullet-},TC}}$ is used instead of $k^{\mathrm{tr}}_{\mathrm{CO_3^{\bullet-},TC}}$, in which the superscript "app" (for "apparent") was applied to allow for possible side-reactions in the transformation of TC.

Text S4. High-performance liquid chromatography / diode array detection (HPLC-DAD) analysis (nitrate photolysis and triplet-sensitized phototransformation experiments).

The quantification of anilines during the irradiation experiments was performed by means of HPLC-DAD. The HPLC-DAD instrument was a VWR-Hitachi LaChrom Elite chromatograph equipped with L-2200 autosampler (injection volume 60 μL), L-2130 quaternary pump for low-pressure gradients, Duratec vacuum degasser, L-2300 column oven (set at 40 °C), and L-2455 photodiode array detector. The column was a VWR LiChroCART 125-4 Cartridge, packed with LiChrospher 100 RP-18 (125mm×4mm×5μm), and the eluent flow rate was 1.0 mL min^{-1}. In the case of aniline, the column was a VWR Superspher® RP-18 HPLC Cartridge (250mm×4mm×5μm) and the flow rate was 0.8 mL min^{-1}. All the analyses were carried out in isocratic conditions. Methanol (A) and 10 mM phosphate buffer at pH 7.0 (B) were used as eluents. In particular, the elution conditions, retention times (t_r) and quantification wavelengths (λ_q) were as follows: 35% A and 65% B for Ani (t_r = 9.9 min, λ_q = 230 nm); 45% A and 55% B for 3CA (t_r = 5.2 min, λ_q = 245 nm); 35% A and 65% B for 4CA (t_r = 7.3 min, λ_q = 243 nm); 45% A and 55% B for 34DCA (t_r = 8.7 min, λ_q = 249 nm).

Table S2. HPLC analysis parameters for competition kinetics experiments (persulfate photolysis system). [a]

Compound (substrate, antioxidant or competitor)	**Eluent composition [vol %]** [b]			**Flow rate [mL min^{-1}]**	**Retention time [min]**	**Absorption wavelength [nm]** [c]	**Excitation / emission wavelength [nm]** [d]
	Methanol	Acetonitrile	Buffer				
Aniline		15 – 40	85 - 60 [e]	0.5	7.5		225 / 343
Sulfadiazine	10 – 35		90 – 65 [f]	0.7	6.6	270	
Phenol (in aniline solutions)		15 – 40	85 - 60 [e]	0.5	9.3		225 / 343
Phenol (in sulfadiazine solutions)	10 – 35		90 – 65 [f]	0.7	16.0		275 / 310
4-Methylphenol (in aniline solutions)		15 – 35	85 - 65 [e]	0.5	13.7		225 / 343
4-Methylphenol (in sulfadiazine solutions)	10 – 35		90 – 65 [f]	0.7	28.8		220 / 310
Metoxuron [g]						245	

Notes: [a] Column: COSMOSIL Packed Column 5C18-MS-II, 150 × 3 mm placed in a column oven that was maintained at a temperature of 25 °C. [b] Eluent composition ranges are given in the case gradient methods were used. [c] Absorbance measured using a photodiode array detector. [d] Emission measured using a fluorescence detector. [e] Composition: 10 mM phosphate buffer at pH 7 (disodium hydrogen phosphate (Merck, p.a.) and sodium dihydrogen phosphate (Merck, p.a.). [f] Composition: 0.675 mL of concentrated phosphoric acid (Fluka, puriss, p.a. ≥ 85%) per liter of ultrapure water, corresponding to a total phosphate concentration of 10 mM, pH 2.1. [g] Metoxuron was quantified in the same chromatograms used to quantify the target compounds and the phenolic antioxidants, therefore methods used and retention times vary.

Text S5. Assessment of $[PhOH]_{1/2}$ for the reaction of TC + ^{3}CBBP* (TC = 3CA/3,4DCA).

Fig. S3 shows the photodegradation trends of 3CA and 3,4DCA ($[TC]$ = 5 µmol L^{-1}), in the presence of 70 µmol L^{-1} CBBP under UVA light. The pH of the solution was ~7.0, and the direct photolysis of 3CA and 3,4DCA was negligible under UVA irradiation. Note that, differently from the runs involving $CO_3^{\bullet-}$ as reactive species, these experiments did not need any restriction on the chemical composition of the solutions. The potential transformation pathway of TC in our irradiated system is depicted in **Scheme S1**.

The degradation rate (R_{TC}) of TC = 3CA or 3,4DCA can be expressed as follows:

$$R_{\mathrm{TC}} = k_{3CBBP^*,\mathrm{TC}} \times [^3CBBP^*] \times [TC] - k^{\mathrm{red}}_{\mathrm{TC}^{\bullet+},\mathrm{AO}} \times [TC^{\bullet+}] \times [PhOH] \qquad \text{(S9)}$$

The steady-state concentration of $TC^{\bullet+}$ is $[TC^{\bullet+}] = f \times k_{\mathrm{3CBBP^*,TC}} \times [^3CBBP^*] \times [TC] \times \left(k^{\mathrm{red}}_{\mathrm{TC}^{\bullet+},\mathrm{AO}} \times [PhOH] + k^{\mathrm{ox}}_{\mathrm{TC}^{\bullet+}}\right)^{-1}$, where f is the fraction of TC that produces intermediates (in this case, $TC^{\bullet+}$) that are able to undergo back-reduction.

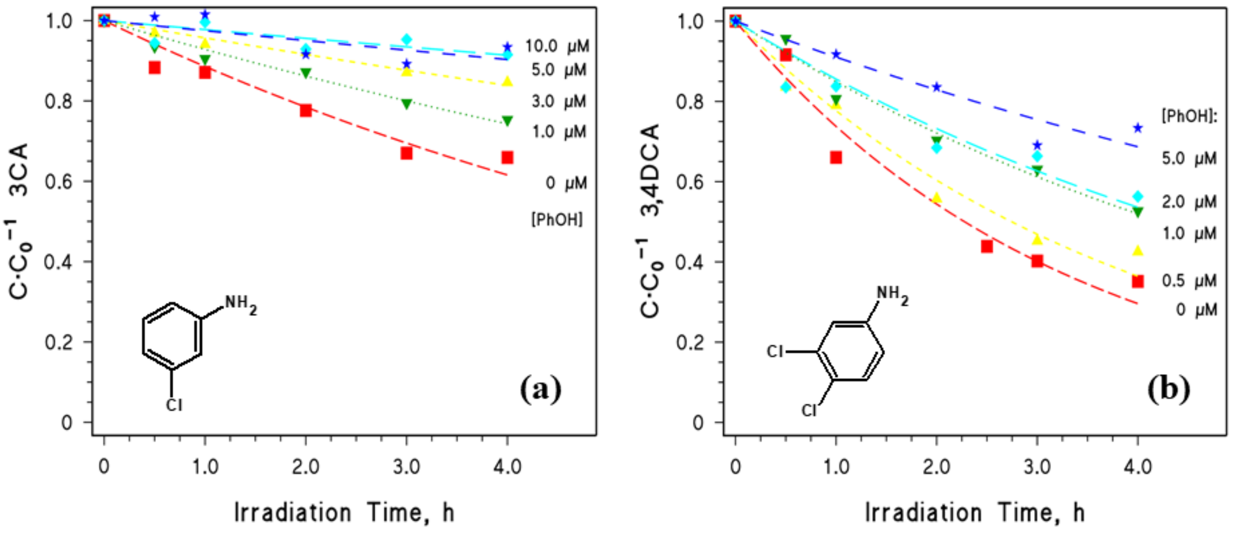
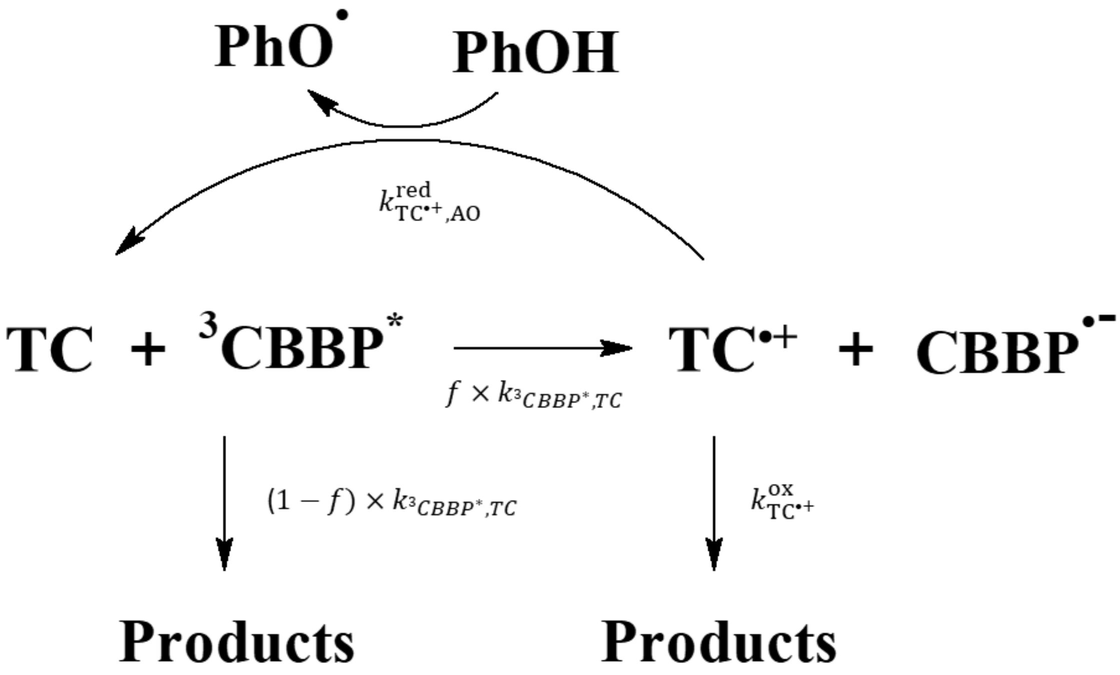


***Figure S3**. Degradation profiles (experimental data and associated fit curves) of **(a)** 3CA and **(b)** 3,4DCA, (C_0 = 5 µM in both cases), in the presence of CBBP (70 µM) + UVA light and different phenol (PhOH) concentrations. The phenol concentration values are reported next to the fit curves. No significant direct photolysis of 3CA or 3,4DCA was observed under the chosen irradiation conditions (UVA lamp).*



Scheme S1. *Simplified scheme showing the possible reactions taking place in our irradiated solutions, which can be used for the assessment of the back-reduction processes during the degradation of TC by* ^{3}*CBBP*. Modified from Wenk and Canonica (2012).*

Indeed, it is known that chloroanilines can react with the excited triplet states of proxy molecules for CDOM, undergoing transformation pathways that form at least in part hardly reducible by-products, such as dechlorinated compounds (Carena et al., 2018; Wenk and Canonica, 2012). Note that the reaction between TC and $CO_3^{\bullet-}$ would only yield $TC^{\bullet+}$, thus the factor *f* was not introduced in the relevant kinetic model (**Text S4**). By rearranging **Eq. S9** and considering that $[PhOH]_{1/2} = k^{\mathrm{ox}}_{\mathrm{TC^{\bullet+}}} \times \left(k^{\mathrm{red}}_{\mathrm{TC^{\bullet+},AO}}\right)^{-1}$, one gets (Wenk and Canonica, 2012):

$$R_{\mathrm{TC}} = R^{0}_{\mathrm{TC}} \times \left(\frac{f}{1+\frac{[PhOH]}{[PhOH]_{1/2}}} + 1 - f \right) \qquad \text{(S10)}$$

$R^{0}_{\mathrm{TC}} = k_{^3CBBP^*,\mathrm{TC}} \times [^3CBBP^*] \times [TC]$ is the degradation rate of TC measured in the absence of phenol, which was 0.17 ± 0.01 nM s^{-1} for 3CA and 0.45 ± 0.03 nM s^{-1} for 3,4DCA. **Eq. S10** was used to fit the experimental data reported in **Fig. S4**. The value of $[PhOH]_{1/2}$ was obtained as a floating variable of the fit, together with *f*. In particular, for 3CA, $[PhOH]_{1/2}$ = 1.31 ± 0.17 µM and *f* = 0.93 ± 0.07; for 3,4DCA, $[PhOH]_{1/2}$ = 1.27 ± 0.32 µM and *f* = 0.87 ± 0.17.

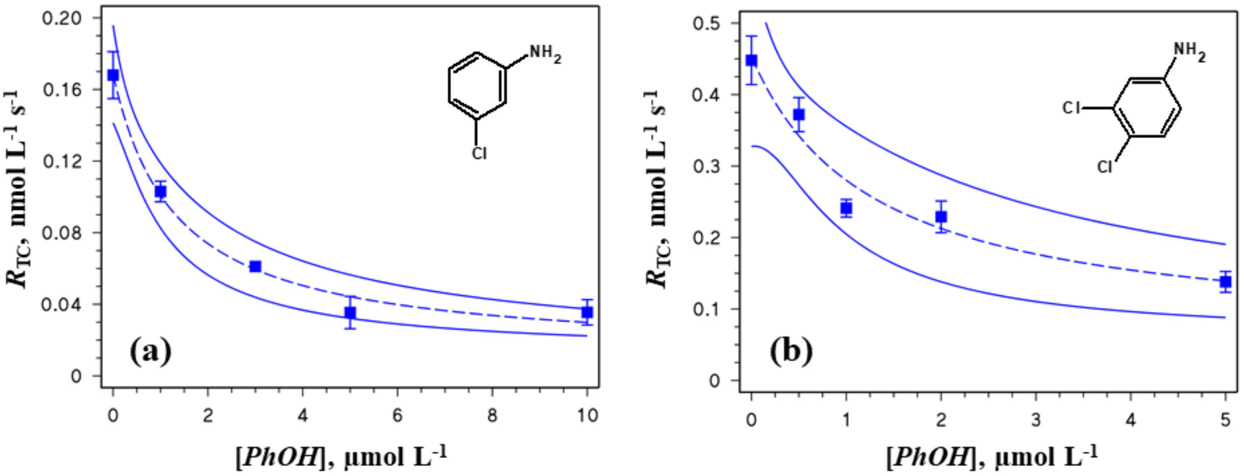


Figure S4. *Experimental degradation rates of* ***(a)*** *3CA and* ***(b)*** *3,4DCA, as a function of the added phenol concentration. The dashed curves represent the fitting curves (****Eq.S10****), while the solid curves delimit the 95% confidence band of the fit.*

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