Photosensitizing and Antioxidant Activities of Humic Substances: A case study of β2-adrenoceptor Agonist Terbutaline

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Abstract

Humic substances (HS) play an important role in the phototransformation of micro-pollutants in surface waters and a significant part of this reactivity is often attributed to oxidant triplet excited states ($^3$HS*). The present study aims to understand why $^3$HS* were found to be negligibly involved in the HS-mediated phototransformation of β2-adrenoceptor agonist terbutaline (TBL) while this chemical shows a high reactivity towards triplet 3-carboxybenzophenone ($^3$CBP*), a typical HS model sensitizer. To clarify this apparent discrepancy, several experiments were conducted. We first confirmed that TBL can be easily oxidized by triplet riboflavin ($^3$RF*), another sensitizer ($k = (1.7 \pm 0.4) \times 10^9$ M$^{-1}$ s$^{-1}$). Afterwards, we studied the effect of TBL on the HS-mediated phototransformation of 2,4,6-trimethylphenol (TMP), chosen for its high reactivity with $^3$HS*. TBL was found to enhance the rate of TMP loss. This result is rationalized by postulating that (i) TMP and TBL are both oxidized by $^3$HS* to yield the phenoxy radicals TMP$_{H^\bullet}$ and TBL$_{H^\bullet}$, respectively, and (ii) TBL$_{H^\bullet}$ is further reduced by TMP which generates additional TMP$_{H^\bullet}$. Fitting the experimental data gives $k = (1.8 \pm 0.5) \times 10^9$ M$^{-1}$ s$^{-1}$ for the reaction between $^3$HS* and TBL and DFT calculations further support the conclusion that TBL$_{H^\bullet}$ can be reduced by a lot of phenols. Hence, in the case of TBL, the oxidant effect of $^3$HS* is counterbalanced by the antioxidant properties of HS.

Key Words: Humic substances; Laser flash photolysis; Substituted phenols; Antioxidant; DFT calculation.

1. Introduction.

Humic substances (HS) that include humic and fulvic acids are ubiquitous in soils and natural waters, and can promote the degradation of organic micro-pollutants in illuminated aquatic environments [1, 2]. Their reactivity is however complex and not fully understood. Indeed, upon sunlit irradiation, HS is capable of generating various reactive species such as hydroxyl radical (OH) [3], singlet oxygen ($^1$O$_2$) [4], triplet excited states ($^3$HS*) [5], oxy and peroxy radicals [6], that can accelerate the decomposition of the organic micro-pollutants. Among all these reactive species, $^3$HS* have been found to play an
important role in the photochemical degradation of organic micro-pollutants, such as pesticides [7] and pharmaceuticals [8]. They are generally proposed to abstract electrons or H atoms from micropollutants and lead to their oxidation. However, it has been also reported that the sensitized-photodegradation of chemicals such as aniline and sulfonamide antibiotics can be inhibited by HS [9-11]. HS that contain phenolic/polyphenolic moieties in their complex structures [12, 13] could act as antioxidants, regenerating the starting micro-pollutants (reaction 1).

\[
\text{Aniline}_{\text{H}}^* + \text{HS} \rightarrow \text{Aniline} + \text{HS}_{\text{H}}^*
\]  

In a former study, the photodegradation of β2-adrenoceptor agonist terbutaline (TBL) in the presence of HS was reported [14]. Our results revealed that \(^3\text{HS}^*\) played a negligible role in the transformation of TBL, which seemed contradictory with the high reactivity of TBL with triplet \(^3\text{CBP}^*\), a typical HS model sensitizer [14]. We proposed a backwards reaction process to rationalize these observations. Specifically, TBL could be oxidized by \(^3\text{HS}^*\) at a significant rate, but the generated intermediary radical could also be reduced by HS itself to give back TBL.

To confirm our hypothesis according which HS oppose both photosensitizing and antioxidant activities, several experiments were conducted in this study. Laser flash photolysis (LFP) was applied to determine the reaction rate constant of TBL with triplet riboflavin (\(^3\text{RF}^*\)), which was selected as another HS model sensitizer. Moreover, we studied the HS-mediated transformation of 2,4,6-trimethylphenol (TMP) in the presence of TBL. TMP was chosen for its high reactivity with \(^3\text{HS}^*\) and used to confirm and evaluate the interaction between \(^3\text{HS}^*\) and TBL through competitive reactions [15-17]. Finally, density functional theory (DFT) calculations were performed to evaluate the antioxidant ability of a series of substituted phenols that could be potentially present in HS.

2. Experimental

2.1 Chemicals and reagents

Terbutaline hemisulfate (TBL, 98%), 2,4,6-trimethylphenol (TMP, 99%), riboflavin (RF, 98%) and humic acids (HS, reference number 53680) were purchased from Sigma-Aldrich. HPLC grade
acetonitrile (ACN) was supplied by Fisher Chemical. Other reagents were at least of analytical grade and used as received without further purification. Milli-Q water (18.2 MΩ cm) was obtained from a Millipore Milli-Q system.

### 2.2 Photodegradation experiments and analyses

A vertical cylindrical reactor (id = 14 mm) was used in this study. The air-saturated solutions were irradiated in a device equipped with three “black light” Mazda 125 W lamps (90 % of radiant energy emitted at 365 nm). The radiant flux was equal to $5 \times 10^8$ Einstein cm$^{-3}$ s$^{-1}$ which was measured directly using a VLC-3W radiometer. Aliquots of 1 mL were withdrawn after selected irradiation times and further analyzed by HPLC. The decay of TMP alone or in the presence of TBL was monitored until conversion extents comprised between 55 and 85%. The rates of TMP consumption were measured at conversion extents comprised between 12 and 30%. The concentration of TMP was measured by HPLC using a Waters HPLC apparatus equipped with a 2996 photodiode array detector (PAD), an auto sampler and a reverse-phase C$_{18}$ Nucleodur, Macherey-Nagel column (5 μm, 250×4.6 mm). The flow rate was set at 1 mL min$^{-1}$, and the mobile phase was a mixture of 60 % methanol and 40% water acidified with phosphoric acid (0.1%).

Laser flash photolysis (LFP) experiments were carried out using a Quanta Ray GCR 130-01Nd: YAG laser and an Applied Photophysics station previously described [18]. Solutions containing TBL and RF were irradiated at 355 nm, using the third harmonic of the laser. A red filter was placed between the cell and the photomultiplicator to avoid parasitic signals. The rate constant of reaction of TBL with $^3$RF* (absorbance of 0.5 at 355 nm) was measured by monitoring the decay of $^3$RF* at 650 nm. The rate of $^3$RF* disappearance in the absence of oxygen was equal to:

$$ -\frac{d[^3\text{RF*}]}{dt} = (k_d + k[TBL])[^3\text{RF*}] $$

(Eq 1)

where $k_d$ is the rate constant of desactivation of $^3$RF* and $k$ represents the bimolecular rate constant of reaction between TBL and $^3$RF*. $k_d + k[TBL]$ is the apparent first order decay rate constant of $^3$RF* that was obtained by fitting the experimental data using an exponential decay. The reactivity of the
phenoxyl radical issued from TBL with oxygen was studied by exciting TBL (10⁻³ M) at 266 nm. The phenoxyl radical decay was monitored over 940 µs at 440 nm, the maximum of absorption of the transient [19]. The solutions were saturated with air or with oxygen. The fitting of the transient decay was done between 50 and 400 µs.

2.3 Calculations

Density Functional Theory (DFT) calculations were performed using the Gaussian 09 software package [20]. The geometry optimization and frequency calculations were carried out by using B3LYP method and 6-311G* basis set. The obtained sums of electronic and thermal free energies were used to represent the Gibbs free energy of each chemical. The integral equation formalism polarized continuum model (IEFPCM), based on the self-consistent-reaction-field (SCRF) method, was used to consider the bulk solvent effect of water [21].

3. Results and discussion.

3.1 Reactivity of TBL towards ³RF*

It was previously shown that the photodegradation of TBL was significantly enhanced by HS [14]. Investigating the effect of sorbic acid and oxygen, two ³HS* scavengers, led to the conclusion that ³HS* played a negligible role in the HS-mediated photodegradation of TBL. However, this result was in contrast with the high reactivity of TBL towards triplet of 3-carboxybenzophenone (³CBP*), which is often regarded as a typical model sensitizer of HS.

To further verify the oxidability of TBL, another model sensitizer, riboflavin, was used in this work. The reaction rate constant of TBL with ³RF* was also determined by LFP as performed with CBP. Figure 1 shows the decay of ³RF* at 650 nm in the absence and presence of TBL (0-400 µM) in argon-saturated medium. TBL clearly accelerated the rate of ³RF* decay, the apparent first order decay rate constant of ³RF* increasing from 1.2×10⁵ s⁻¹ in the absence of TBL to 8.0×10⁵ s⁻¹ in the presence of 400 µM of TBL. Using a linear regression of the first order decay rate constant of ³RF* versus TBL
concentration, we could estimate the second order rate constant of reaction of TBL with $^3$RF$^*$ to $(1.7 \pm 0.4) \times 10^9$ M$^{-1}$ s$^{-1}$, which fits well with that found with $^3$CBP$^*$, $(2.7 \pm 0.3) \times 10^9$ M$^{-1}$ s$^{-1}$.

Figure 1. Decay of $^3$RF$^*$ monitored at 650 nm in the absence and presence of TBL under argon-saturated condition; the insert shows the linear relationship of the apparent first order decay rate constant of $^3$RF$^*$ versus the concentration of TBL.

3.2 HS-mediated photodegradation of the mixture TBL and TMP

Based on the reaction rate constants measured between TBL and $^3$CBP$^*$ or $^3$RF$^*$, we expected that TBL was able to be oxidized by $^3$HS$^*$. To confirm this hypothesis and to get a deeper insight into the reaction between HS and TBL, we investigated the effect of TBL on the HS-sensitized photodegradation of TMP. TMP was chosen because it readily can react with $^3$HS$^*$ and was often used as a probe molecule to quantify their contribution [15, 17]. On the first hand, TBL could compete with TMP for the reaction with $^3$HS$^*$ and potentially reduce its rate of photodegradation. On the other hand, as a good H-donor, TMP might reduce the phenoxy radicals issued from TBL (TBL-H$^*$), and regenerate TBL.

In the presence of HS (20 mg L$^{-1}$) and in air-saturated solution, TMP (5×10$^{-5}$ M) was photodegraded with an initial rate of 1.5×10$^{-8}$ M s$^{-1}$ (Figure 2). The addition of TBL in the range of 1×10$^{-4}$- 4×10$^{-4}$ M increased this rate until 3.7×10$^{-8}$ M s$^{-1}$ (Figure 2). To rationalize these data, we propose that reactions 2-8 take place. Specifically, $^3$HS$^*$ are formed after light absorption by HS and inter-system crossing (reaction 2), $\Phi_T$ is the quantum yield of $^3$HS$^*$ formation. Afterwards, $^3$HS$^*$ can undergo several decay
pathways: deactivation by reaction with oxygen (reaction 3), competitive oxidations of TBL (reaction 4) and TMP (reaction 5). Values of $k_3$ and $k_5$ were determined as $2 \times 10^5 \text{ s}^{-1}$ [17] and $2 \times 10^9 \text{ M s}^{-1}$ [15], respectively. Reaction 4 and 5 generate phenoxy radicals $\text{TBL}_\text{H}^\bullet$ and $\text{TMP}_\text{H}^\bullet$ that can potentially be involved in several reactions: they can react with oxygen, with TMP or TBL through addition or H-abstraction reactions, or with other radicals [22]. At low photon rate absorption as it is the case here, the phenoxy radicals concentration is low and radical/radical re-combinations should proceed at lower rates than radical/molecule reactions. Therefore, in this section, we consider that $\text{TBL}_\text{H}^\bullet$ and $\text{TMP}_\text{H}^\bullet$ will mainly react with molecules. The first possibility is a reaction with oxygen through reactions 6 and 7, respectively. To estimate the value of $k_6$, we generated $\text{TBL}_\text{H}^\bullet$ radicals by LFP of TBL (10$^{-3}$ M) and monitored their decay in different conditions. In air as in oxygen-saturated solutions, the decay of $\text{TBL}_\text{H}^\bullet$ was well fitted by a second order kinetics ($2k/\varepsilon = 3.2 \pm 0.3 \times 10^5 \text{ s}^{-1}$, Figure SI-1, Supporting Information), indicating that in these particular conditions where $\text{TBL}_\text{H}^\bullet$ concentration was very high, radical/radical reactions were dominant while reaction of $\text{TBL}_\text{H}^\bullet$ with both $\text{O}_2$ (2.6$\times 10^{-4}$ M or 1.3$\times 10^{-3}$ M) and TBL (10$^{-3}$ M) were negligible. The half-life of $\text{TBL}_\text{H}^\bullet$ being of 2$\times 10^{-4}$ s, the absence of oxygen effect on the radical decay indicates that the maximum value of $k_6[\text{O}_2]$ is about 370 s$^{-1}$, and $k_5$ smaller than 2.8$\times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The second possibility in the case of $\text{TBL}_\text{H}^\bullet$ radicals is a reaction with TMP (reaction 8). The exact nature of this reaction is not fully defined at this stage. It might be a H-atom transfer from TMP to $\text{TBL}_\text{H}^\bullet$, or some addition reaction of $\text{TBL}_\text{H}^\bullet$ on TMP. In both cases, reaction 8 constitutes an additional pathway of TMP consumption.

\[
\text{HS} + h\nu \rightarrow ^1\text{HS}^* \rightarrow ^3\text{HS}^* \quad \Phi_T \quad (2)
\]

\[
^3\text{HS}^* + \text{O}_2 \rightarrow \text{HS} + ^1\text{O}_2 \quad k_3 = 2 \times 10^5 \text{ s}^{-1} \quad (3)
\]

\[
^3\text{HS}^* + \text{TBL} \rightarrow \text{HS}^- + \text{H}^+ + \text{TBL}_\text{H}^\bullet \quad k_4 \quad (4)
\]

\[
^3\text{HS}^* + \text{TMP} \rightarrow \text{HS}^- + \text{H}^+ + \text{TMP}_\text{H}^\bullet \quad k_5 = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (5)
\]

\[
\text{TBL}_\text{H}^\bullet + \text{O}_2 \rightarrow \text{Radicals/Products} \quad k_6 \quad (6)
\]
In the absence of TBL, assuming the quasi stationaty state (q.s.s.) hypothesis, the steady state concentration of $\text{HS}^*$, $[\text{HS}^*]_{ss}$, is equal to:

$$[\text{HS}^*]_{ss} = I_a \Phi_T \frac{1}{k_3 + k_4[TMP]} \quad \text{(Eq 2)}$$

where $I_a$ is the light intensity absorbed by HS, $\Phi_T$, is the quantum yield of $\text{HS}^*$ formation and $[\text{TMP}]$ the concentration of TMP. The initial decay rate of TMP ($r_1$) is therefore equal to:

$$r_1 = \frac{d[TMP]}{dt} = I_a \Phi_T \frac{k_4[TMP]_0}{k_3 + k_4[TMP]_0} \quad \text{(Eq 3)}$$

Where $[\text{TMP}]_0$ is the initial TMP concentration. When TBL is added to the solution, $[\text{HS}^*]_{ss}$ is equal to:

$$[\text{HS}^*]_{ss} = I_a \Phi_T \frac{1}{k_3 + k_4[TBL] + k_5[TMP]} \quad \text{(Eq 4)}$$

and the initial TMP loss rate ($r_2$) is equal to:

$$r_2 = \left(- \frac{d[TMP]}{dt}\right)_{\text{TBL}} = I_a \Phi_T \frac{k_4[TMP]_0}{k_3 + k_4[TBL]_0 + k_5[TMP]_0} + k_8[TMP]_0[TBL^{-\text{H}}]_{ss} \quad \text{(Eq 5)}$$

where $[\text{TBL}^{-\text{H}}]_{ss}$ represents the steady-state concentration of $\text{TBL}^{-\text{H}}$, which can be obtained by the following equation (Eq 6):

$$k_8[TMP][\text{TBL}^{-\text{H}}]_{ss} + k_6[O_2][\text{TBL}^{-\text{H}}]_{ss} = I_a \Phi_T \frac{k_4[TBL]}{k_3 + k_4[TBL] + k_5[TMP]} \quad \text{(Eq 6)}$$

and $[\text{TBL}^{-\text{H}}]_{ss}$ is equal to:

$$[\text{TBL}^{-\text{H}}]_{ss} = I_a \Phi_T \frac{k_4[TBL]}{k_3 + k_4[TBL] + k_5[TMP]} \times \frac{1}{k_6[O_2] + k_8[TMP]} \quad \text{(Eq 7)}$$
Finally, one gets:

\[
I_2 \Phi_T \times \frac{1}{k_3 + k_4[TBL]_0 + k_5[TMP]_0} \times \frac{k_8[TMP]_0 \times k_4[TBL]_0}{k_8[TMP]_0 + k_6[O_2]} \quad (Eq\ 8)
\]

Eq 8 confirms that if reaction 8 did not exist, TBL would decrease the rate of TMP loss due to the competition between TBL and TMP for the reaction with \(^3\)HS\(^*\), which is not confirmed experimentally. Therefore, reaction 8 needs to be considered in this study. Using Eq 8, we attempted to fit experimental data of Figure 2. For simplification, we first made the hypothesis that \(k_6[O_2]\) is negligible behind \(k_8[TMP]\). As \(k_6[O_2]\) is < 370 s\(^{-1}\), this implies that \(k_8[TMP]\) > 3700 s\(^{-1}\) and thus \(k_8\) > 7.3 \times 10^7 M\(^{-1}\) s\(^{-1}\), considering that \([TMP]_0 = 50 \mu M\). The experimental data were well fitted using \(k_4 = (1.8 \pm 0.5) \times 10^9 M^{-1} s^{-1}\) which is in accordance with the rate constant of reaction with \(^3\)CBP\(^*\) and \(^3\)RF\(^*\). If \(k_6[O_2]\) is not negligible behind \(k_8[TMP]\), then the consumption of TMP through reaction 8 is less important and \(k_4\) value has to be increased. The value of \((1.8 \pm 0.5) \times 10^9 M^{-1} s^{-1}\) is therefore a minimal value.

Concerning the nature of reaction 8, we postulated that the reaction is a H-atom transfer between TBL\(_{H}^*\) and TMP to yield TBL and TMP\(_{H}^*\) because TMP is a good H-atom donor. The H-atom transfer between TBL\(_{H}^*\) and TMP was further confirmed by DFT calculation estimating the difference of Gibbs free energies before and after this reaction (\(\Delta G\)). The result with \(\Delta G = -0.26\ eV\) <0 indicates the spontaneity of this reaction from the thermodynamic point of view, supporting our hypothesis that TBL\(_{H}^*\) can be reduced by TMP and induce its degradation.
Figure 2. Photodegradation of TMP in the presence of HS and different concentrations of TBL (A); Experimental and calculated decay rates of TMP (in M s\(^{-1}\)) under different conditions (B) ([TMP]\(_0\) = 50 \(\mu\)M, [HS]\(_0\) = 20 mg L\(^{-1}\), pH = 8.0, air-saturated condition).

### 3.3 Antioxidant ability of phenolic moieties

To explain the negligible involvement of \(^3\)HS\(^*\) in the HS-mediated photodegradation of TBL, we postulate that like TMP, HS may have the capacity to reduce TBL\(_{1H}^*\), as described in reaction 9,

\[
\text{TBL}_{1H}^* + \text{HS} \rightarrow \text{TBL} + \text{HS}_{1H}^*  \tag{9}
\]

The mentioned antioxidant properties of HS have been documented in the case of compounds such as aniline and sulfonamide antibiotics [9-11]. They are linked to H-atom donor properties, and mainly attributed to HS phenolic and polyphenolic moieties [12, 13, 23]. Janssen et al. have used mono- and dihydroxylated cinnamic acids as proxies of some of the hydroquinonic and phenolic moieties in HS [24]. They found that these analogues of redox-active moieties could suppress the indirect photolysis of tryptophan with rate constants ranging from \(9.7 \times 10^6\) to \(2.6 \times 10^9\) M\(^{-1}\)s\(^{-1}\). After the H-atom abstraction, HS will undergo irreversible follow-up reactions [25].

Table 1. DFT calculation results for the possibilities of H-abstraction reactions of different substituted phenols with TBL\(_{1H}^*\) (\(\Delta G_1\)) and SAL\(_{1H}^*\) (\(\Delta G_2\)).
To further support our conclusion of HS’s antioxidant properties on TBL-H•, DFT calculations were performed to evaluate the reaction of a series of substituted phenols with TBL-H• (Scheme 1), as listed in Table 1. These results suggest that many substituted phenols moieties in HS are potentially able to reduce TBL-H• (ΔG₁ <0), depending on the substituted groups and their positions. For instance, all the three methyl-phenols could reduce TBL-H•. Moreover, similar calculations were also conducted in the case of salbutamol (SAL), a structurally related chemical of TBL, to verify the reliability of the proposed reduction mechanism. As reported previously [14], SAL that exhibited relative high reactivity towards \(^3\)HS* (>10⁹ M⁻¹ s⁻¹) was photodegraded much faster than TBL in the same experimental conditions ruling out a significant importance of the reduction of SAL-H•. As expected, calculation results (ΔG₂ in Table 1) reveal that most of the selected phenols are not able to reduce

<table>
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<th>Substituted phenol</th>
<th>Position</th>
<th>ΔG₁ (eV)</th>
<th>ΔG₂ (eV)</th>
<th>Substituted phenol</th>
<th>Position</th>
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to SAL, indicating that such process was less favourable, in accordance with former conclusions [14].

\[
\begin{align*}
\text{OH} + \text{H}^\bullet & \rightarrow \text{OH}^\bullet + \text{H}^\bullet \\
\text{R} & \quad \text{R}
\end{align*}
\]

\[
\begin{align*}
\text{OH} + \text{H}^\bullet & \rightarrow \text{OH}^\bullet + \text{H}^\bullet \\
\text{R} & \quad \text{R}
\end{align*}
\]

Scheme 1. Proposed reduction pathways of TBL-H• and SAL-H• by phenols.

4. Conclusion.

The present study was designed to answer why \( ^3 \text{HS}^\bullet \) appeared to be negligibly involved in the photochemical transformation of TBL while TBL readily reacts towards \( ^3 \text{CBP}^\bullet \), a typical HS model sensitizer. Studying the HS photosensitized degradation of TBL/2,4,6-trimethylphenol revealed that TBL accelerated the photodegradation of the phenolic probe. This behavior was rationalized by postulating a set of reactions in which \( ^3 \text{HS}^\bullet \) oxidized both TBL and TMP while the radical issued from TBL reacts with TMP, regenerating TBL and consuming TMP. In addition, DFT calculation results further confirmed that TBL-H• can be reduced by a lot of phenols via H abstraction. The results obtained in this work could explain the poor photodegradation of TBL in the presence of HS, which would be mainly due to the regeneration processes of TBL by the phenol moieties of HS. The present study provides very useful information about the photochemical behavior of TBL in natural waters containing HS, and would also help us to understand the photosensitivity and antioxidant activities of HS.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 21806037).
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