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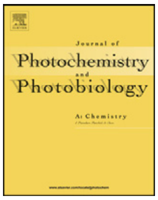

Influence of humic substances on the riboflavin photosensitized transformation of 2,4,6-trimethylphenol

Sofia Kouras-Hadef[a,b], Amina Amine-Khodja[b], Sabrina Halladja[b], Claire Richard[c,*]

[a] Clermont Université, Université Blaise Pascal, Laboratoire de Photochimie Moléculaire et Macromoléculaire (LPMM), BP 10448, 63000 Clermont-Ferrand, France
[b] Laboratoire des Techniques Innovantes de Protection de l'Environnement, Université Mentouri, 25000 Constantine, Algeria
[c] CNRS, UMR 6505, LPMM, F-63177 Aubière, France

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ABSTRACT

Humic substances are known to affect the fate of organic chemicals in the environment. While their capacity to produce reactive species upon irradiation has been intensively studied, their inhibiting properties have been much less investigated. In the present work, we studied the influence of various humic substances (humic acids, fulvic acids, natural organic matter) on the riboflavin photosensitized transformation of 2,4,6-trimethylphenol which takes place *via* oxidation of the phenol by the triplet excited state of riboflavin. Between 2 and 20 mg L^{-1} humic acids show an inhibiting effect on this reaction while below 2 mg L^{-1}, a small accelerating effect is generally observed. At 25 μM 2,6-dimethyl-1,4-benzoquinone also inhibits the photoreaction significantly. It is proposed that the quinone traps the superoxide anion produced in the course of the reaction yielding semiquinone radicals. The reduction potential of the quinone is low enough for making possible a subsequent reduction of 2,4,6-trimethylphenoxyl radical by semiquinone and a regeneration of 2,4,6-trimethylphenol. In the case of humic substances, the trapping of superoxide anion might be achieved by humic quinone moieties. In accordance, soil fulvic acids and aquatic natural organic matter which show a much lower electron accepting capacity than soil extracted humic acids do not show any inhibiting effect.

1. Introduction

Humic substances are ubiquitous natural compounds which are intensively studied owing their importance in the environment, especially in agriculture, in soil properties or in remediation. It has been shown that they affect the fate of organic micropollutants by promoting their phototransformation in sunlit aquatic environment [1,2]. This impact is however complex and not fully understood. Humic substances generate reactive species such as triplet excited states, $^1O_2$, HO·, oxy and peroxy radicals upon irradiation but also scavenge some of them in competition with the target micropollutants [3,4].

More recently new aspects of their complex reactivity were discovered. Canonica et al. [5,6] showed that dissolved organic matter (DOM) extracted from lakes or rivers is able to inhibit the benzophenone-4-carboxylate mediated phototransformation of a variety of organic micropollutants or model compounds (pharmaceuticals, phenols and anilines substituted by electroacceptor groups) while electron-rich phenols and phenylureas are not affected. To explain this, they postulated that the H-donor moiety of dissolved organic matter reduces the oxidation intermediates of the micropollutants and thus regenerate the parent compounds. They also observed that allochtonous aquatic DOM is more effective antioxidant than autochtonous aquatic DOM. Another interesting work was published by Pajares et al. [7]. These authors investigated the photosensitizing effect of a mixture humic acid (HA)–riboflavine (RF) on the photodegradation of 3-hydroxypyridine used as a model compound for hydroxyaromatic water contaminants. They demonstrated that at a level of 50 mg L^{-1} Aldrich HA inhibit the oxygen uptake. This effect was attributed to the catalytic decomposition of superoxide anion by HA.

In the present work, we aimed to investigate this inhibiting effect of humic substances (HS) more deeply, by varying their origin as well as their concentration. We focused on soil extracted HSs: HAs, the fraction soluble in basic medium and fulvic acids (FAs), the fraction soluble at all pH. An aquatic DOM was also investigated for comparison. This effect of HSs was investigated on the photosensitized oxidation of 2,4,6-trimethylphenol (TMP). RF was chosen as a sensitizer for several reasons. First, it is a well known sensitizer acting through electron and energy transfer as HSs do [8]. Second, due to its absorption at long wavelength (absorption maxima at

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[*] Corresponding author. Tel.: +33 473 40 71 42; fax: +33 473 40 77 00.
E-mail address: claire.richard@univ-bpclermont.fr (C. Richard).

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373 and 445 nm) it can be selectively excited in a spectral region where TMP does not absorb.

2. Experimental

2.1. Material

RF (99%) was purchased from Sigma–Aldrich and TMP (99.9%) from Fluka. Phosphate buffer was made of sodium hydrogenophosphate (Prolabo, 99.5%) and potassium dihydrogenophosphate (Prolabo, 99.5%). 2,6-Dimethylbenzoquinone (DMBP) (97%) was obtained from Janssen Chimica. The ultra-pure water used was obtained from a Millipore Milli-Q system. HSs were purchased from the International Humic Substances Society. Standard HA Elliott (1S102H), reference HA Waskish (1R107H) and standard HA Leonardite (1S104H) were extracted from soils, standard FA Elliott (2S102F) were also extracted from a soil. Standard HA Pahokee (1S103H) were extracted from a peat. The NOM Suwannee River (1R101N) was a dissolved natural organic matter extracted from the aquatic medium. Additional information on the samples is given on the website www.ihss.gatech.ed.

2.2. Methods

Experimental solutions consisted of RF (5.4 μM) in 1 mM phosphate buffer at pH 7. TMP was spiked at 0.1 or 0.05 mM, HAs and FA at 5 different concentrations ranging from 1 to 20 mg L^{-1}, and NOM Suwannee River was tested at 20 mg L^{-1}. DMBQ was spiked at 25 μM. The absorbance of DMBQ at 365 nm was measured in a cell of 5-cm path length: 0.018 ± 0.002. Solutions of DMBQ were made freshly just before each experiments. We checked by HPLC that the starting solutions did not contain 2,6-dimethylhydroquinone ($DMQH_2$). Experiments were mainly conducted in air-saturated medium. Some were also made at an oxygen concentration of 1.3 mM. For this, solutions were oxygenated by oxygen bubbling for 10 min prior to irradiations and the cuvette was capted by a septum after the oxygen bubbling.

Solutions were irradiated in a cuvette in parallel beam at 365 nm using a mercury high pressure lamp equipped with a Bausch and Lomb monochromator. The photon fluence rate was 1.13×10^{-6} Einstein $L^{-1}\,s^{-1}$ in average. It was measured periodically using potassium ferrioxalate as a chemical actinometer. Rates were normalized to this value. The absorbance of RF was 0.055 ± 0.003 at 365 nm. At this wavelength RF undergoes photolysis. The irradiation times were chosen to limit the percentage of RF photodegradation to 12%, while allowing a TMP photodegradation up to 15%. HSs also absorb at 365 nm; data were therefore corrected for the screen effect (see text). Calculations were based on the initial rates of consumption which were measured using conversion extents comprised between 5 and 15%. Experiments were made in duplicate or triplicate if necessary. UV–visible spectra were recorded on a Cary 3 spectrophotometer (Varian). The loss of RF, TMP and DMBP was monitored by HPLC by analytical HPLC using a Waters apparatus equipped with a photodiode array detector and a conventional reverse phase 5 μm column and a mixture of water with formic acid (0.3%)/methanol (40–60, v/v) as a mobile phase. The experimental setup for the transient absorption experiments has been described elsewhere [14]. Measurements were carried out using a frequency-quadrupled Nd:YAG laser (Quanta-Ray DCR-1, 266 nm, pulse duration 10 ns or Quanta-Ray GCR-130-1, 355 nm, pulse duration 9 ns). Solutions were deoxygenated or suroxygenated by bubbling argon or oxygen directly in the cuvette. The rate constants given are the average of five measurements.

3. Results and discussion

3.1. Photosensitized transformation of TMP by RF

The simplified mechanism of RF photolysis is summarized in Scheme 1. The triplet excited state, $^3RF^*$, is efficiently populated *via* inter-system crossing with a quantum yield, Φ_{isc}, equal to 0.375 ± 0.005 [9]. $^3RF^*$ deactivates (process 1, k_d) or undergoes photolysis through intramolecular hydrogen transfer yielding lumichrome (process 1′, k_i). In air-saturated medium, the quantum yield of RF photolysis is equal to 7.8×10^{-3} at pH 8 [10]. $^3RF^*$ is efficiently quenched by oxygen (process 2, k_{O_2}). A significant part of this reaction (80%) is energy transfer and yields singlet oxygen [11]. Last, $^3RF^*$ can react with chemicals through electron transfer. Many examples are reported in the literature [12,13].

According to this, the RF-mediated photosensitized transformation of TMP may involve two different pathways: oxidation by $^3RF^*$ (process 3, k_{TMP}) or reaction with singlet oxygen (process 5, $k_{SO} = 6.2 \times 10^7\ M^{-1}\,s^{-1}$ for molecular TMP [15]). To clarify the mechanism, we undertook two series of experiments. In a first step, we measured the rate of TMP consumption upon steady-state irradiation of RF–TMP mixtures at 365 nm. The experimental rates of consumption of TMP, r_{TMP}, and of RF, r_{RF}, in air-saturated and oxygen-saturated solutions are given in Table 1. Increasing the oxygen concentration led to a decrease of r_{TMP} which is an evidence for the direct oxidation of TMP by $^3RF^*$ (process 3). The inhibiting effect of TMP on the photodegradation of RF is another evidence of the scavenging of $^3RF^*$ by TMP.

In a second step, we measured $^3RF^*$ reaction rate constants by laser flash photolysis at 355 nm. $^3RF^*$ is long-lived, and its decay can be selectively monitored at 670 nm because neither the reduced radical issued from RF nor the phenoxyl radical produced from TMP absorb in this wavelength range [16]. $^3RF^*$ is quenched by oxygen. The bimolecular rate constant was estimated to $k_{O_2} = (1.09 \pm 0.1) \times 10^9\ M^{-1}\,s^{-1}$ ($R^2 = 0.997$) by varying the oxygen concentration. This rate constant is in accordance with that reported in a previous works in methanol [17] and water [18]. The quenching of $^3RF^*$ by TMP was monitored for several concentrations of TMP ranging from 10^{-4} to 8×10^{-4} M in air-saturated solution. The plot of the pseudo first order rate constant against [TMP] is linear as expected from the relationship: $k = k_d + k_{O_2}[O_2] + k_{TMP}[TMP] + k_{dTMP}\,[TMP]$, where k_{dTMP} is the rate constant of $^3RF^*$ deactivation by TMP (process 3′). From the slope, one gets $k_{TMP} + k_{dTMP} = (2.3 \pm 0.2) \times 10^9\ M^{-1}\,s^{-1}$ ($R^2 = 0.971$).

r_{TMP} can be expressed by Eq. (1) and depends on $[^3RF^*]_{ss}$ and $[^1O_2]_{ss}$, the stationary concentrations of $^3RF^*$ and $^1O_2$, respectively. These latter are given by Eqs. (2) and (4) and obtained by postulating

$$RF \xrightarrow{h\nu} {}^1RF^* \xrightarrow{\Phi_{isc}} {}^3RF^*$$

$$^3RF^* \longrightarrow RF \qquad p1$$

$$^3RF^* \longrightarrow \text{radicals} \qquad p1'$$

$$^3RF^* + O_2 \longrightarrow RF + {}^1O_2 \text{ or } O_2 \qquad p2$$

$$^3RF^* + TMP \longrightarrow RF^{-\cdot} + TMP^{+\cdot} \qquad p3$$

$$^3RF^* + TMP \longrightarrow RF + TMP \qquad p3'$$

$$^1O_2 \longrightarrow O_2 \qquad p4$$

$$TMP + {}^1O_2 \longrightarrow \text{products} \qquad p5$$

Scheme 1. Formation and reactivity of $^3RF^*$.

Table 1

Compared experimental (exp) and calculated (calc) initial rates of TMP and RF consumption upon 365 nm-irradiation of neutral aqueous TMP–RF mixtures. [RF] = 5.4 μM, $A_{365} = 0.055$, $I_0 = 1.1 \times 10^{-6}$ Einstein $L^{-1}\ s^{-1}$.

[TMP]/mM	$[O_2]$/mM	r_{RF} exp/M s^{-1}	r_{RF} calc/M s^{-1}	r_{TMP} exp/M s^{-1}	r_{TMP} calc/M s^{-1}
0	0.26	$(9.0 \pm 1.0) \times 10^{-9}$	1.1×10^{-8}		–
5×10^{-2}	0.26	$(8.0 \pm 1.0) \times 10^{-9}$	0.83×10^{-8}	$(1.1 \pm 0.1) \times 10^{-8}$	1.2×10^{-8}
5×10^{-2}	1.3			$(4.5 \pm 0.1) \times 10^{-9}$	0.41×10^{-8}
10^{-1}	0.26	$(7.0 \pm 1.0) \times 10^{-9}$	0.73×10^{-8}	$(1.8 \pm 0.1) \times 10^{-8}$	1.9×10^{-8}
10^{-1}	1.3			$(1.1 \pm 0.1) \times 10^{-8}$	0.81×10^{-8}

that for both intermediates the rate of formation equals the rate of disappearance.

$$r_{TMP} = k_{TMP}[TMP][^3RF^*]_{ss} + k_{SO}[TMP][^1O_2]_{ss} \tag{1}$$

$$[^3RF^*]_{ss} = I_a \Phi_{isc} \frac{1}{k_d + k_i + k_{O_2}[O_2] + k_{TMP}[TMP] + d_{dTMP}[TMP]} \tag{2}$$

$$\Phi_{SO} = \Phi_{isc} \cdot \frac{0.8 k_{O_2}[O_2]}{k_d + k_i + k_{O_2}[O_2] + k_{TMP}[TMP] + k_{dTMP}[TMP]} \tag{3}$$

$$[^1O_2]_{ss} = I_a \cdot \Phi_{SO} \frac{1}{k'_d + k_{SO}[TMP]} \tag{4}$$

These expressions are supposed to be valid provided that [RF] and [TMP] vary by less than 15% and that the oxygen concentration is constant. I_a is the rate of photon absorption by RF at 365 nm, it was equal to 1.34×10^{-7} Einstein $L^{-1}\ s^{-1}$. $[^1O_2]_{ss}$ depends on Φ_{SO} (Eq. (3)). In this equation, k'_d is the rate constant of singlet oxygen deactivation in water ($2.5 \times 10^5\ s^{-1}$). Using [11], we assume that the reaction of $^3RF^*$ with oxygen yields $^1O_2$ with a yield of 80%. Combining Eqs. (1), (2) and (4) gives r_{TMP} (Eq. (5)).

$$r_{TMP} = I_a \Phi_{isc} \frac{k_{TMP}[TMP]}{k_d + k_i + k_{O_2}[O_2] + k_{TMP}[TMP] + k_{dTMP}[TMP]} + I_a \Phi_{SO} \frac{k_{SO}[TMP]}{k'_d + k_{SO}[TMP]} \tag{5}$$

The rates of RF photolysis in the absence and in the presence of TMP, r_{RF} and $(r_{RF})^{TMP}$, are described by Eq. (6) by Eq. (7), respectively.

$$r_{RF} = I_a \cdot \Phi_{isc} \frac{k_i}{k_d + k_i + k_{O_2}[O_2]} \tag{6}$$

$$(r_{RF})^{TMP} = I_a \cdot \Phi_{isc} \frac{k_i}{k_d + k_i + k_{O_2}[O_2] + k_{TMP}[TMP] + k_{dTMP}[TMP]} \tag{7}$$

To calculate r_{TMP} and r_{RF}, we made two assumptions in a first approach. We neglected the second term of Eq. (5) using that r_{TMP} was much slower in oxygen than in air saturated solution. We also postulated that process 3′ is negligible with respect to process 3. Values obtained in these conditions are reported in Table 1. They are very close to experimental ones confirming the validity of Scheme 1 and the assumptions made.

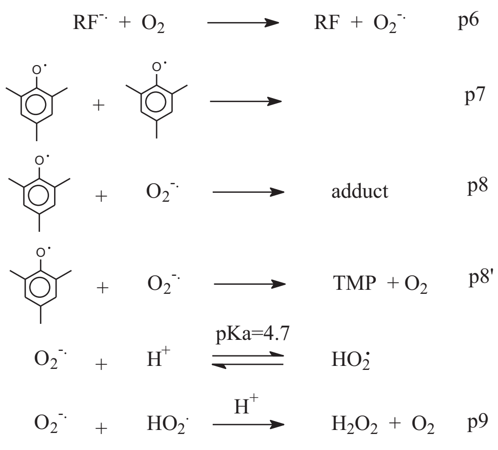
In this first part, we have not considered the fate of formed radicals. The radical anion $RF^{\bullet-}$ is highly expected to reduce oxygen by electron transfer yielding superoxide anion (process 6) [19]. In the same time, the radical cation issued from 2,4,6-trimethylphenol deprotonates [20] yielding the phenoxyl radical ($\Phi O^\bullet$) which can react through several reactions: with itself (process 7, $k_7 = 2 \times 10^7\ M^{-1}\ s^{-1}$ [21]), and with $O_2^{\bullet-}$ (processes 8 and 8′, $k_8 + k_{8'} = 1.2 \times 10^9\ M^{-1}\ s^{-1}$ [21]). This latter reaction may yield photoproducts and/or regenerate TMP [22]. The very good agreement between experimental and calculated data indicates that TMP regeneration by process 8′ is negligible, otherwise the experimental rates would be lower than the calculated one. The reaction between phenoxyl radical and oxygen is not taken into account because it is generally very slow for highly substituted phenoxyl radicals [23]. Moreover, $O_2^{\bullet-}$ can react with $HO_2^\bullet$, its protonated form (process 9, $k_9 = 9.7 \times 10^7\ M^{-1}\ s^{-1}$ [24]). Given this and postulating that $\Phi O^\bullet$ and $O_2^{\bullet-}$ are produced at similar rates, rate of process 8 is much higher than those of processes 7 and 9, and process 8 will be considered to be the main route of $\Phi O^\bullet$ and $O_2^{\bullet-}$ losses (Scheme 2).

3.2. Influence of HSs on the TMP–RF photolysis

We first measured r_{TMP} when TMP is irradiated in the presence of HSs spiked at 20 mg L^{-1}, the highest concentration investigated here. The time of irradiation was chosen equal to that achieving a photodegradation of TMP of 15% in the RF–TMP mixture. After this irradiation time, no TMP degradation was observed in the HS–TMP mixtures. Actually, HSs are able to photosensitize the degradation of TMP, but they need an irradiation time 10–20-fold longer than RF for an equal amount of TMP loss. Then, we investigated the effect of each HS at a concentration comprised between 1 and 20 mg L^{-1} on the rate of TMP photolysis in the presence of RF in air-saturated medium. Fig. 1 shows the ratio $r_{TMP}/(r_{TMP})^{HS}$ against the HS concentration, where $(r_{TMP})^{HS}$ represents the rate of TMP phototransformation in the presence of both RF and HS. Data were corrected for the screening effect of HSs using the relationship of Eq. (8).

$$\frac{I_a}{I_a^{HS}} = \frac{1 - 10^{-A_{RF}}}{1 - 10^{-(A_{RF}+A_{HS})}} \frac{A_{RF} + A_{HS}}{A_{RF}} \tag{8}$$

where I_a^{HS} was the photon absorbance of RF in the presence of HS, A_{RF} and A_{HS} were the absorbance of RF and HS at 365 nm. The highest screening effect was measured at 20 mg L^{-1} of HS and was of 34%. FA had not visible effect on r_{TMP}, just as the NOM of Suwannee river added at 20 mg L^{-1}. In contrast, HAs affected r_{TMP}. HA Pahokee exhibited an inhibiting effect for a concentration >5 mg L^{-1}. The inhibiting effect reached 53% at 20 mg L^{-1}. HA Elliott, HA Waskish and HA Leonardite had a small accelerating effect at low concentration and an inhibiting effect at higher concentration. The inhibiting effect started between 2 and 5 mg L^{-1} of HA Waskish, between 5



Scheme 2. Reactivity of produced radicals.

Table 2
Effect of DMBQ (25 μM) on the rates of TMP consumption upon irradiation of TMP (0.1 mM)–RF (5.4 μM) mixtures.

Conditions	r_{DMBQ}/M s^{-1}	r_{TMP}/M s^{-1}	Δ[TMP]/M after 15 min of irradiation
DMBQ	$(6.3 \pm 0.5) \times 10^{-9}$	–	
DMBQ + RF	$(3.9 \pm 0.5) \times 10^{-9}$	–	
RF + TMP	–	$(1.8 \pm 0.1) \times 10^{-8}$	1.6×10^{-5}
DMBQ + RF + TMP	$(3.6 \pm 0.5) \times 10^{-9}$	$(8.9 \pm 0.5) \times 10^{-9}$	8.1×10^{-5}

and 10 mg L^{-1} of HA Elliott and between 10 and 20 mg L^{-1} of HA Leonardite. The inhibiting effects reached 60% for HA Elliott, 50% for HA Waskish and 22% for HA Leonardite.

3.3. *Possible involvement of quinone moieties*

To resume, HAs exhibited a small accelerating influence at low concentration and an inhibiting effect at higher concentration while FA and NOM had little accelerating effects at low concentration and no inhibiting effects at higher concentration. These results confirm that the sensitized phototransformation of electron-rich phenolic compounds is not inhibited by aquatic NOM [5,6]. In addition, it shows that soil extracted HAs inhibit TMP phototransformation. To better understand this inhibiting effect, we undertook some additional experiments.

a. We investigated the possible reactivity of HAs with $^3RF^*$. This was made by laser flash photolysis. As Pajares et al. did not see any effect of HA Aldrich on $^3RF^*$ decay [7], we did not see any effect of HAs. It can be deduced that HAs are not able to reduce $^3RF^*$.
b. The previous observation of Pajares et al. that HS led to a reduction of oxygen consumption [7], gave us the idea that HS might oxidize $O_2^{\bullet-}$. Moreover, catalyzed superoxide decay was also observed in a variety of humic and fulvic acid samples and suggested as possibly occurring through quinone functionalities [25]. To confirm this, we replaced HS by a quinone. Indeed, quinones are known to scavenge $O_2^{\bullet-}$ yielding oxygen back [26], and HS are known to contain quinonic moieties [27,28]. Dimethylbenzoquinone (DMBQ) (0.025 mM) was irradiated alone, in the presence of RF, and in the presence of RF and TMP at 365 nm. Data are reported Table 2. Unless a very low absorbance (<0.004 at 365 nm), DMBQ was slowly photolysed due to a quantum yield of photolysis close to 1. This reaction gives an equimolar mixture of $DMBQH_2$ and dimethylhydroxybenzoquinone [29]. In the presence of RF, DMBQ loss was reduced by 39%. This inhibition is likely due to the oxidation of $DMBQH_2$ by $^3RF^*$ to give DMBQ. In the case it occurred, this reaction was only partial as $DMBQH_2$ was still observed by HPLC. The rate of RF loss remained the same in the presence and in the absence of DMBQ. Last, when TMP was irradiated in the presence of the RF–DMBQ mixture r_{TMP} was divided by a factor of 2 while the rate of DMBQ was the same as in the presence of RF alone. These results are rationalized as follows.

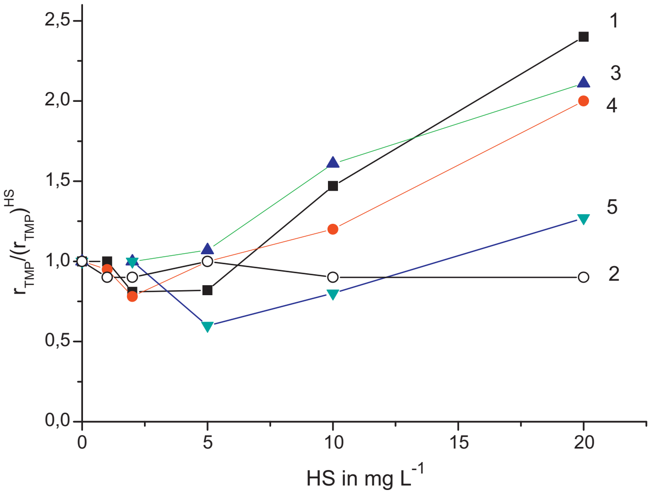
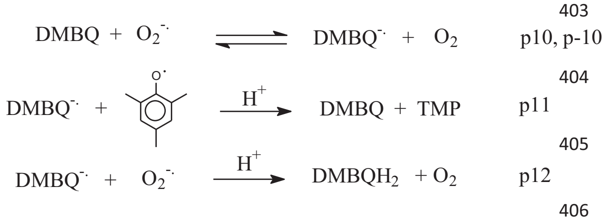


Fig. 1. Effect of HSs on the rates of TMP consumption upon irradiation of TMP–RF mixtures. [RF] = 5.4 μM, A_{365} = 0.055, $I_0 = 1.1 \times 10^{-6}$ Einstein L^{-1} s^{-1}. (1) HA Elliott; (2) FA Elliott; (3) HA Pahokee; (4) HA Waskish; (5) HA Leonardite.

Data of Table 2 show that 8.1×10^{-6} M of TMP have been lost after 15 min of irradiation in the presence of RF and DMBQ against 1.6×10^{-5} M in the presence of RF alone. Therefore, 8.1×10^{-6} M of TMP are regenerated in the presence of DMBQ. This regeneration could be explained by the reduction of $\Phi O^\bullet$ by $DMBQH_2$ or by $DMBQ^{\bullet-}$ (process 11) (Scheme 3). This latter process is possible because the reduction potential of the couple $DBMQ/DMBQ^{\bullet-}$ is −0.08 V against 0.49 for the couple $\Phi O^-/\Phi O^\bullet$ [20,30]. $DMBQ^{\bullet-}$ can be produced by process 10 which is equilibrium with process −10 (Scheme 3). Rate constants k_{10} and k_{-10} for reduction of DMBQ by $O_2^{\bullet-}$ and for oxidation of semiquinone anion $DMBQ^{\bullet-}$ by O_2 are known: $k_{10} = 3.4 \times 10^8$ M^{-1} s^{-1} and $k_{-10} = 5 \times 10^6$ M^{-1} s^{-1} [26]. Based on the concentrations of DMBQ and O_2, on computes that the ratio $[O_2^{\bullet-}]/[DMBQ^{\bullet-}]$ is equal to 0.15. This means that the concentration of $O_2^{\bullet-}$ is drastically reduced by DMBQ, decreasing the rate of process 8 and changing the relative contributions of termination reactions. The observed regeneration of TMP is rationalized as soon as a part of phenoxyl reacts through process 11.

The reduction of phenoxyl can also be due to $DMBQH_2$. The contribution of this pathway depends on the amount of $DMBQH_2$ produced in the system. This is quite difficult to evaluate because $DMBQH_2$ is formed by DMBQ photolysis and in process 12 whereas it disappears through reaction with $^3RF^*$. The importance of process 12 is probably limited because of the low $O_2^{\bullet-}$ concentration. Moreover, the formation of $DMBQH_2$ through DMBQ photolysis is necessarily less than 3.5×10^{-6} M, the total amount of transformed DMBQ. Thus, it seems reasonable to estimate that a significant part of TMP is regenerated through process 11.

According to this, the inhibiting properties of HAs could be due to the reactivity of quinonic moieties with $O_2^{\bullet-}$. This capacity of HAs to act as electron transfer agents has been already mentioned in the literature [28,31]. The electron accepting capacity of a broad



Scheme 3. Redox processes involving DMBQ.

Table 3
Inhibiting effect of HSs at 20 mg L^{-1} *vs.* ^{13}C aromaticity, C/H mass ratio and electron accepting capacity [29].

HS	$r_{TMP}/(r_{TMP})^{HS}$	^{13}C aromaticity/%	C/H	Electron accepting capacity/μmol$_{e-}$ g$_{HS}^{-1}$
HA Elliott	2.4	50	15.80	1962
HA Waskish	2.0	42	13.54	
HA Pahokee	2.1	47	14.75	1684
HA Leonardite	1.27	58	17.24	1711
FA Elliott	0.80	30	11.71	704
NOM Suwannee river	0.90	23	12.52	

spectrum of terrestrial and aquatic HSs has been evaluated, among them some of the HSs tested here [31]. The authors found out that the electron accepting capacity is highly connected with high C/H ratio and high aromaticity. HSs showing high electron accepting capacity are expected to be the more efficient in $O_2^{\bullet-}$ scavenging. Data are given Table 3. For HA Elliott, the electron accepting capacity is equal to 1962 μmol per g of HA, this HA shows the highest inhibiting effect in our experiments. In a solution at 20 mg L^{-1}, this electron accepting capacity gives a concentration of oxidant of 36 μM close to the one of DMBQ for which a close inhibiting effect was observed. With 1684 μmol per g of HA, HA Pahokee is only little less inhibiting than HA Elliott. FA Elliott that is not inhibitor has an electron accepting capacity much lower (704 μmol per g of FA). All these results are consistent. In contrast HA Leonardite which shows a rather high electron accepting capacity (1711 μmol per g of HA) and should be as inhibitor as the other HAs, fails to do this. The accelerating effect observed at low HA Leonardite concentration is quite pronounced, more than that of the other HAs and probably counterbalances the inhibiting effect. The accelerating effect which was also observed by other authors [5,6] is not really understood. It may result from a radical induced oxidation of HA yielding to an overconsumption of TMP acting as an antioxidant.

4. Conclusion

HSs play an effect on the fate of organic micropollutants not only through their photochemical properties but also probably by their redox properties. These latter effects occur at rather low concentration and should be more systematically taken into account when the HS-mediated phototransformation of micropollutants are investigated. We propose in this work that the inhibiting effect is due to reduction of quinonic moieties by reaction intermediate superoxide anions. The accelerating influence would also deserve to be studied in more details.

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