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Kinetics of the dye-sensitized photooxidation of trihydroxybenzenes

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Abstract

The kinetics of the singlet molecular oxygen [$O_2(^1\Delta_g)$]-mediated photooxidation of the three isomeric trihydroxybenzenes (THBs), compounds of potential environmental significance as aquatic contaminants, has been studied in water solution as a function of pH and ionic strength, as well as in benzene and acetonitrile. Rate constants for chemical and overall interactions with $O_2(^1\Delta_g)$, determined by time-resolved IR phosphorescence detection and polarographic methods, are in the range 0.05×10^7–24.0×10^7 M^{-1} s^{-1}, depending on the medium and the particular compound. In water at pH 2, the photooxidation quantum efficiencies of 1,2,3-THB, 1,2,4-THB and 1,3,5-THB are 0.07, 0.07 and 0.19, respectively. The photooxidative processes are highly favored by the ionization of the OH groups, the increase of solvent polarity, and the presence of salts in the medium, strongly suggesting the participation of a polar encounter complex of the type [THB-$O_2(^1\Delta_g)$]. This kinetic behavior is similar to that observed in simple phenols and dihydroxybenzenes, although THBs are much easier photooxidizable, even in non-ionized form. These results possess environmental relevance, because they demonstrate that any THB in aqueous media undergoes spontaneous and fast solar-promoted photooxidation under practically any field condition. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photooxidation; Photosensitized oxidation; 1,2,3-trihydroxybenzene; 1,2,4-trihydroxybenzene; 1,3,5-trihydroxybenzene; Singlet molecular oxygen

1. Introduction

Polyhydroxybenzenes, including trihydroxybenzenes (THBs) are natural antioxidants and have been found dissolved in the surface microlayer of coastal waters [1], preferentially enriched with these compounds generally from terrestrial drainage delivers — which dissolve fulvic and humic material — and marine macroalgae exudates. Phloroglucinol (1,3,5-THB) is an integral structural component of flavonoids, and in its free form has been found in some eucalyptus and acacia species [2]. Many natural compounds found in higher plants, fungi, bacteria, insects, and marine organisms contain aromatic nucleus of the THB type, and pyrogallol (1,2,3-THB) and 1,3,5-THB are present with other phenols in wood tar distillates [3].

The photooxidation of the three THBs under direct irradiation with 254 nm light, in aqueous solution and in the presence of air, has been previously studied [4]. In the three cases, primary photochemical processes assisted by oxygen give rise to phenoxy radicals that eventually yield quinones through secondary processes. For 10^{-2} M solutions of 1,2,3-THB, hydroxyhydroquinone (1,2,4-THB) and 1,3,5-THB, the respective quantum efficiencies found for their disappearance by photooxidation were relatively low: 0.030, 0.033 and 0.022 [4]. The particular study of the photo-induced degradation under natural solar irradiation of phenol and 1,3,5-THB in surface microlayers and subsurface waters indicates that phenol decomposition is photochemical, rather than microbial, suggesting the involvement of photo-induced $O_2(^1\Delta_g)$ degradation for both compounds [5]. The same photodegradative pathway has also been proposed for the light-induced oxidation of 1,2,3-THB in alkaline media [6]. Nevertheless, to our knowledge no definitive evidences exist about the apparently intricate scheme of photochemical pathways in the sensitized photodegradation of THBs.

In the present work, we report the results of a kinetic study on the $O_2(^1\Delta_g)$-mediated photochemistry of the three isomeric THBs, looking for a better insight into the natural fading of this kind of compounds under field conditions, i.e. under the simultaneous presence of water, oxygen, visible light, and a dye sensitizer. In an effort to provide data for the controlled photodegradation of these potential contaminants, the kinetic parameters governing the photooxidation reactions under said conditions have been determined and

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related to the pH, ionic strength and polarity of the medium, and the possible reaction mechanism is discussed.

2. Materials and methods

2.1. Chemicals

The three THBs (Aldrich) were purified by recrystallization: 1,2,3-THB from benzene, 1,2,4-THB from diethyl ether, and 1,3,5-THB from distilled water. Rose Bengal (RB), perinaphthenone (PN), zinc tetraphenylporphyrine (ZntPP), sodium azide (NaN_3) and furfuryl alcohol (FFA) (all from Aldrich) were used as received, as well as benzene, acetonitrile (MeCN), diethyl ether (all Merck, spectroscopic grade), deuterium oxide 99.9% (D_2O) (Sigma), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl) (all Merck). Perinaphthenone-2-sulfonic acid (PNS) was a gift from Dr. S. Criado. Water was doubly distilled. All the measurements were carried out at room temperature and with freshly prepared solutions.

2.2. Methods

The acidity constants (K_a) in water of each THB were determined by spectrophotometry, following methods already described [7,8], choosing as analytical wavelength that with maximum absorbance change with pH: 274 nm for 1,2,3-THB; 262 nm for 1,2,4-THB; and 278 nm (first ionization, Fig. 1, inset) and 350 nm (second ionization) for 1,3,5-THB. The ionic strength and the pH were adjusted by addition of NaCl and HCl or NaOH solutions, respectively. Ground state absorption spectra were recorded in a Hewlett-Packard 5482-A spectrophotometer.

The time resolved phosphorescence detection (TRPD) apparatus has been previously described [9]. The samples were irradiated with 15 ns pulses from a nitrogen laser at 337 nm or a Nd:YAG laser at 532 nm (Spectron). Typical decay signals are shown in Fig. 2, inset (see latter). The signals were fitted to monoexponential decay. The absorbance of the sensitizers for the dynamic measurement (ZnTPP in benzene, PN in MeCN, and PNS in D_2O, irradiation with 532 for the porphyrine and 337 nm for the perinaphthenone derivatives) was in the range 0.2–0.3 at the laser output. For each THB, the rate constant for the overall quenching process, k_t (equal to (k_r+k_q), k_r and k_q being the rate constants of chemical reaction and physical quenching, respectively), was determined by evaluation of the $O_2(^1\Delta_g)$ lifetimes in the absence (τ_o) and in the presence (τ) of THB, using TRPD. The ratio τ_o/τ was plotted as a function of THB concentration, according to a simple Stern–Volmer treatment (Eq. (1), Fig. 2), and the k_t value was deduced from the slope

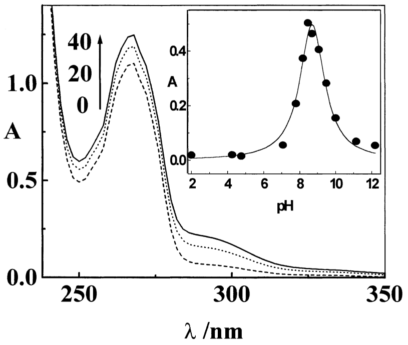

Fig. 1. Absorption spectrum changes during the sensitized photooxidation of 1,3,5-THB 2×10^{-3} M in pH 2 aqueous solution. Sensitizer: PNS ($Abs_{368\,nm}=0.8$). Numbers indicate irradiation times (min). Inset: changes with pH of the absorbance of the aqueous solution at 278 nm during the photooxidation of 1,3,5-THB.

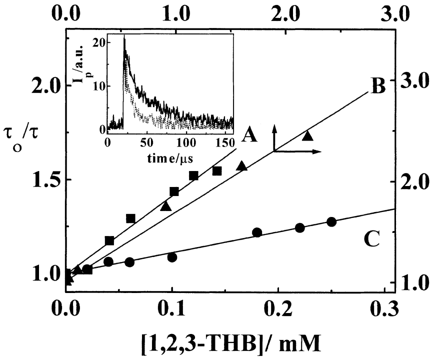

Fig. 2. Stern–Volmer plots for the quenching of $O_2(^1\Delta_g)$-phosphorescence lifetimes by 1,2,3-THB in: pD 6D_2O (A); acetonitrile (B); and pD 2D_2O solution (C). Inset: time resolved decay of the $O_2(^1\Delta_g)$ phosphorescence signal at 1270 nm in D_2O, pD 2 (upper trace) and in the presence of 1,2,3-THB 2.5×10^{-4} M (lower trace). Sensitizer: PNS ($Abs_{337\,nm}=0.2$).

$$\frac{\tau_o}{\tau} = 1 + k_t\tau_o[\mathrm{THB}] \qquad (1)$$

Rate constants k_r at pH 2 were determined in water solution by the method of Foote and Ching [10], employing FFA as a pH-independent reference [11], with $k_{r_R}=1.2\times10^8$ M^{-1} s^{-1} [12], and an excess of FFA or THB. It was assumed that the reaction $O_2(^1\Delta_g)$-FFA or $O_2(^1\Delta_g)$-THB is the only way of depleting oxygen concentration, and that the stoichiometry of this reaction under our working conditions is 1:1. In this case, the ratio between the first-order slopes of oxygen uptake by THB and FFA is equal to k_r/k_{r_R}. At pH values higher than 3–4, it was not possible to determine the respective k_r values due to additional oxygen consumption attributed to reactions that occur in the absence of irradiation involving the primary photochemical products.

The irradiation setup, including the specific oxygen electrode (Orion 97-08), has been previously described [13]. Parallel experiments of oxygen consumption of the aqueous solutions containing the sensitizer (PNS, $Abs_{336\,nm}\cong0.5$) plus each THB at different pH values were run.

The quantum efficiency (φ_r) of the $O_2(^1\Delta_g)$-mediated photooxidation of each THB in 1 mM water solution at pH 2 was calculated by Eq. (2), where k_d is the rate constant of the $O_2(^1\Delta_g)$-decay by light emission and by collision with solvent molecules ($2.5\times10^5\ s^{-1}$ in water [14]).

$$\varphi_r = \frac{k_r[\mathrm{THB}]}{k_d + k_t[\mathrm{THB}]} \qquad (2)$$

3. Results

3.1. Determination of pK_a values

Only the first dissociation step of 1,2,3-THB and 1,2,4-THB could be evaluated by spectroscopy (respective pK_a^1 values found: 7.26 and 7.85), because the alkaline solutions of these compounds suffer spontaneous and irreversible dark oxidation. 1,3,5-THB has been considered as a dibasic acid because of the small difference between the pK_a values of the first and second ionizations ($pK_a^1 = 8.0$, $pK_a^2 = 9.2$, and $pK_a^3 \sim 14$) [2]. We have found similar values for the two first ionizations: $pK_a^1 = 8.08$ and $pK_a^2 = 9.04$.

3.2. Mechanism of sensitized photooxidations

The most important reactions of generation and quenching of $O_2(^1\Delta_g)$ in the system herein studied, and their respective rate constants, are shown in Scheme 1.

The absorption of light by the sensitizer (Sens) gives rise to the electronically excited singlet and triplet states (reaction (3)), and an energy transfer from this triplet to ground state molecular oxygen generates the excited oxygen species $O_2(^1\Delta_g)$ (reaction (4)). This can decay by light emission (phosphorescence) and by collision with surrounding molecules (typically the solvent, reaction (5)), or interact physically (reaction (6)) or chemically (reaction (7)) with a quencher.

The irradiation of each THB in the presence of oxygen with RB, PN or PNS as a photosensitizer produced spectral modifications. In Fig. 1 are shown the spectral changes observed for 1,3,5-THB, with absorbance increases along the range 240 and 350 nm.

These modifications were not observed in the dark, neither in the absence of sensitizer nor in the absence of oxygen (nitrogen saturated solutions), keeping constant the rest of the experimental conditions, pointing to a $O_2(^1\Delta_g)$-mediated photooxidation (Type II process [15]). The good linearity of the Stern–Volmer plots (Fig. 2) and the observed decrease in $O_2(^1\Delta_g)$ lifetime with the concentration of THB (Fig. 2, inset) offer an unambiguous evidence for the involvement of this type of process, as a consequence of the physical and chemical quenching reactions (6) and (7), respectively.

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1\mathrm{Sens}^* \xrightarrow{k_{\mathrm{ISC}}} {}^3\mathrm{Sens}^* \qquad (3)$$

$$^3\mathrm{Sens}^* + O_2(^3\Sigma_g) \xrightarrow{k_{\mathrm{ET}}} \mathrm{Sens} + O_2(^1\Delta_g) \qquad (4)$$

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g) \qquad (5)$$

$$O_2(^1\Delta_g) + \mathrm{THB} \xrightarrow{k_q} O_2(^3\Sigma_g) + \mathrm{THB} \qquad (6)$$

$$O_2(^1\Delta_g) + \mathrm{THB} \xrightarrow{k_r} \mathrm{products} \qquad (7)$$

Scheme 1.

Table 1
Rate constants for the removal of $O_2(^1\Delta_g)$ by THBs (k_t) and for the reaction of $O_2(^1\Delta_g)$ with THBs (k_r), and quantum efficiencies for the same reaction (φ_r)

Compound	k_t ($10^{-7}\ M^{-1}\ s^{-1}$ in solvent)[a]			k_r ($10^{-7}\ M^{-1}\ s^{-1}$ in H_2O at pH 2)[b]	φ_r[c]
	Benzene	MeCN	D_2O		
1,2,3-THB	0.06	0.83	5.0	1.9	0.07
1,2,4-THB	0.05	[d]	24.0	3.0	0.07
1,3,5-THB	0.10	0.11	2.5	5.5	0.19

[a] k_t values determined by Stern–Volmer treatment of singlet molecular oxygen lifetimes.
[b] k_r values determined by oxygen consumption.
[c] Determined in pH 2 aqueous solution.
[d] Spontaneous dark oxidation.

3.3. Effect of the medium on k_t values

Regarding k_t values, although the values shown in Table 1 were determined in three solvents of different polarity and using different sensitizers (see Section 2.2), they can be straightforwardly compared because they do not depend on the interaction of the quencher with the electronically excited states of the sensitizer. The observed general trend is that k_t values increase with increasing dielectric constant values [16] of the solvent (see Fig. 5, latter).

We have correlated through the Hammett equation the former k_t values and those previously observed for 1,3-dihydroxybenzene and 1,4-dihydroxybenzene [17]. To obtain σ values [14], phenol was taken as the reference parent compound, and the parameters were calculated by adding the individual values for each additional OH group. Fig. 5, inset, shows that THB data fit to a straight line in the Hammett plot.

In aqueous solution, it is known that the overall interaction of $O_2(^1\Delta_g)$ with phenols increases with the proportion of OH-ionized form [18], and this effect has been also observed here in the case of THBs, with higher k_t values at alkaline pHs (Fig. 3). It can be noted that k_t values also increase with the ionic strength of the aqueous solution (Fig. 3, inset).

3.4. Effect of pH on k_r values

Using the specific oxygen electrode, the rates constants of oxygen uptake (k_r) by the irradiated THB solutions at pH 2 (Fig. 4, Table 1) have been measured under identical experimental conditions. At higher pH values, due to the exper-

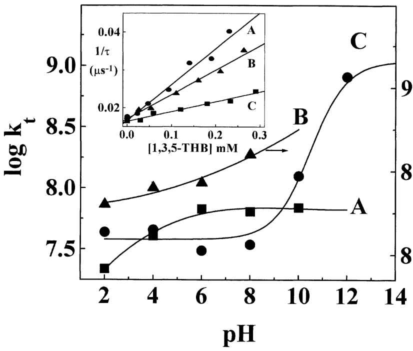

Fig. 3. Logarithm of the overall rate constant k_t as a function of pH for 1,2,3-THB (A); 1,2,4-THB (B); and 1,3,5-THB (C). Sensitizer: PNS ($Abs_{337\,nm}$=0.2). Inset: inverse of the $O_2(^1\Delta_g)$ lifetimes in D_2O solutions of 1,3,5-THB with different ionic strength (NaCl): 0.5 M (A); 0.2 M (B); and 0.0 M (C).

imental problems mentioned in Section 2.2, the respective relative initial rates of oxygen uptake (conversions lower than 10%) were compared. As expected, we have found that the higher the pH of the solutions the faster the photooxidation rate of the THB (Fig. 4, inset). This effect is more pronounced for 1,2,3-THB than for 1,3,5-THB. In the absence of THB or the sensitizer PNS, the irradiation under similar conditions did not give rise to a measurable oxygen uptake.

4. Discussion

The dye-sensitized photooxygenations of simple substituted phenols, hydroxybiphenyls and dihydroxybenzenes mainly involves singlet molecular oxygen [17,18], and the quenching of $O_2(^1\Delta_g)$ and, in particular, the chemical quenching, is only effective when the OH-ionized species are present. However, in the case of THBs, with three OH groups, we have found that their reactivity is high even at low pH values, where only the corresponding non-ionized form are present (Table 1). At intermediate pH values the kinetics of the photooxidation is more complex, because as much as four forms — non-ionized, monoanion, dianion and trianion — can be present in aqueous media. In the case of 1,3,5-THB — the only THB stable in alkaline medium — it can be easily deduced from its pK_a values that the maximum proportion of monoanion form exists at pH ca. 8.6 [19], so that it can be assumed that the only forms at pH 2 and at pH 12 are the non-ionized and the diionized forms, respectively. Therefore, the k_t values found at the latter pHs (4×10^7 and $8.3\times10^8\,M^{-1}\,s^{-1}$, respectively, see Fig. 3 main) practically correspond to these forms.

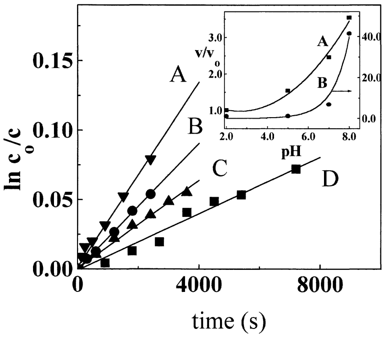

Fig. 4. Pseudo-first order plots for the rate of oxygen uptake of pH 2 aqueous solutions of FFA 5×10^{-4} M (A); 1,3,5-THB 7×10^{-4} M (B); 1,2,4-THB 1×10^{-3} M (C); and 1,2,3-THB 9×10^{-4} M (D) upon PNS sensitized irradiation. c and c_0 denote molar concentration of oxygen at times t=t and t=0, respectively. Inset: effect of pH on the relative rate of oxygen uptake by aqueous solutions of 1,2,4-THB (A); 1,3,5-THB (B); and 1,2,3-THB (C).

It is known that the rate constants k_t of the $O_2(^1\Delta_g)$-mediated photooxidation of phenols in aqueous medium undergo a jump when the pH of the solution coincides with the pK_a value of the phenol [18]. For the symmetric compound 1,3,5-THB, the plot log k_t versus pH shows a single inflection point in the range pH 2–pH 12, at pH ca. 10 (Fig. 3), possibly because the pK_a values of the first and the second ionizations — 8.08 and 9.04 — are too close to be individually reflected by the k_t values. Said plots are different for 1,2,3-THB and 1,2,4-THB, with a continuous increase in k_t values with the pH (Fig. 3), indicating small differences in k_t values for neutral, mono- and diionized forms. A similar behavior has been reported for the rate constant k_r, as a function of pH in the case of the phenol derivative Trolox, a water soluble model compound for Vitamin E [20].

Regarding the mechanism of these photooxidative processes, we propose as intermediate an encounter complex of the type $[THB\cdots O_2(^1\Delta_g)]$, with partial charge transfer character, as previously postulated for the bimolecular reactions of $O_2(^1\Delta_g)$ with indoles, amines, sulfides, phenols, and dihydroxybenzenes [18]. Several characteristics of the kinetics of the THB photooxidation under different experimental conditions can be satisfactorily attributed to the intermediacy of this complex, such as: (a) the overall rate constants, k_t, clearly increase with the solvent polarity (Fig. 5), indicating the involvement of a polar transition state [13]; (b) the observed effect of the ionic strength on

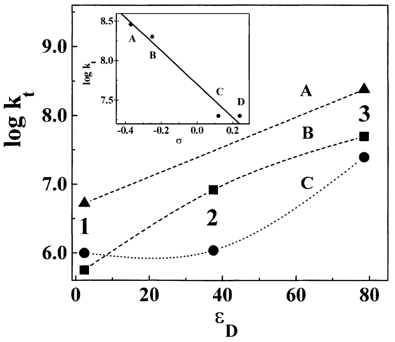

Fig. 5. Logarithm of k_t vs. the dielectric constant of the solvent (ε_D) for 1,2,4-THB (A); 1,3,5-THB (B); and 1,2,3-THB (C) in benzene (1), MeCN (2) and D_2O (3). Inset: Hammett plot (see text) for 1,4-dihydroxybenzene (A); 1,2,4-THB (B); 1,3-dihydroxybenzene (C); and 1,3,5-THB (D). Points A and C were taken from [17].

the k_t values can be explained by the stabilization of said encounter complex by the added electrolyte, because both the $O_2(^1\Delta_g)$ quantum yield and the $O_2(^1\Delta_g)$ lifetimes are barely modified by salt addition [21,22]; (c) both k_t and k_r are significantly higher when the $O_2(^1\Delta_g)$ quenching is exerted by the ionized species, with higher electron-donating capability, suggesting that the rate determining step of the encounter complex formation includes an electron transfer process; and (d) the slope of the Hammett plot (Fig. 5, inset) ($\rho=-2.11\pm0.27$), similar to that found for other phenols [23], indicates that electron-donating groups must increase the quenching constant k_t [24], and again, that a moderate charge transfer takes place in the quenching step.

A final comment on the reactivity exhibited by THBs at pH 2 should be done. At this pH value 1,2,3-THB, 1,2,4-THB and 1,3,5-THB are in their non-ionized form, and their corresponding photooxidation quantum efficiencies are 0.07, 0.07 and 0.17 (Table 1). In the cases of dihydroxybenzenes in aqueous solution, high φ_r values, similar to the former ones, are only reached when the totally OH-ionized species predominate [18]. If the interaction THB-$O_2(^1\Delta_g)$ proceeds through an intermediate with a certain charge transfer component, it is clear that the introduction of a third OH group in the benzene nucleus remarkably enhances the electron-donor ability of the aromatic ring.

5. Conclusions

All the experimental evidences in this work confirm that the aerobic dye-sensitized oxidation of THBs in aqueous solution is mediated by $O_2(^1\Delta_g)$, and the efficiency of the oxidation is relatively high over an extended pH range. Hence, the photodegradation of THBs constitutes a viable, useful and attainable photochemical process practically under any field condition, in stored THB-containing solutions or in natural water courses contaminated with these compounds, being the only requirement a source of visible light and a visible light-absorber pigment present in the air-saturated medium.

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