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Ionization effects on the sensitized photooxidation of 2,3-dihydroxypyridine and 2,4-dihydroxypyridine: a kinetic study

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Abstract

The kinetics of the Rose Bengal (RB)-sensitized photooxidation of 2,3-dihydroxypyridine (2,3-DHP) and 2,4-dihydroxypyridine (2,4-DHP), two compounds profusely employed in multiple fields such as pesticides design, pharmacology, and clinical therapeutics have been studied in water at pH 5, 11 and 14, and in the mixture MeCN–water 4:1 (v/v) with and without 0.01 M KOH. These compounds present different ionization states, depending on the pH of the medium. Rate constants values in the range of 8×10^5–$6.80 \times 10^8\ M^{-1}\ s^{-1}$ for both overall (k_t) and reactive (k_r) singlet molecular oxygen, $O_2(^1\Delta_g)$, quenching processes were determined by time-resolved $O_2(^1\Delta_g)$ phosphorescence detection and by spectrophotometric, spectrofluorimetric and polarographic methods. The experimental evidence suggests a photooxidative process through a charge-transfer mediated mechanism involving an excited encounter complex. The ratios k_r/k_t indicate that the $O_2(^1\Delta_g)$ oxidation of both dihydroxypyridines is a relatively efficient pathway over an extended pH range, with respect to the same oxidation of the monohydroxypyridines. In a general sense, the increase of pH favours the overall interaction dihydroxypyridine–$O_2(^1\Delta_g)$, although this interaction does not correlate with the importance of the photooxidation reaction. In pH 5 medium or in the mixture MeCN–water, solvents where the respective un-ionized 2-pyridone forms predominate, only 2,3-DHP is photooxidized, whereas 2,4-DHP slightly deactivates $O_2(^1\Delta_g)$ only in a physical fashion. In pH 11 aqueous solution or in alkalinized MeCN–water, where the respective mono-ionized pyridone forms predominate, the highest k_r/k_t ratios are reached. In addition, in pH 14 water solution both di-ionized dihydroxypyridines show the highest k_t values, but lower relative reactivity than in the pH 11 solutions. All these results indicate that in aquatic environments containing these dihydroxypyridines or related aquatic pollutants, a simple change in the pH conditions of the medium could allow the switch between reactive and non-reactive $O_2(^1\Delta_g)$-mediated processes.

Keywords: 2,3-Dihydroxypyridine; 2,4-Dihydroxypyridine; Photooxidation; Photosensitization; Rose Bengal; Singlet molecular oxygen

1. Introduction

Hydroxylated N-heteroaromatic derivatives (OH–ND) and, in particular, hydroxypyridines (OHP) have attracted scientific interest in areas such as pesticides design [1,2], clinical therapeutics and pharmacology [3,4] among others. In relation to their use as pesticides and their natural disappearance from the environment, our group has studied the sensitized photooxidation of some OH–ND [5–10], with special emphasis on the behaviour of OHP, hydroxypyrimidines and hydroxyquinolines as physical and chemical quenchers of singlet molecular oxygen ($O_2(^1\Delta_g)$). In nature, the electrophilic and metastable agent $O_2(^1\Delta_g)$ is responsible for many photooxidations [11]. Scheme 1 shows its generation through visible-light absorption of a dye-sensitizer (S), as well as its main quenching processes [12]. $^1S^*$ and $^3S^*$ are the respective singlet and triplet excited states of S, and $O_2(^3\Sigma_g^-)$ is the ground-state molecular oxygen. $O_2(^1\Delta_g)$ is generated by energy transfer from $^3S^*$ to $O_2(^3\Sigma_g^-)$ (process (3)), and can be physically deactivated by collision with solvent molecules (process (4)), or with a quencher, Q, in the solution (process (5)), which can be transparent at the irradiation wavelength. Finally, $O_2(^1\Delta_g)$ can react with the quencher giving rise to oxidation products (process (6)).

Regarding the three isomeric OHP, we have demonstrated [5,6] that in the presence of Rose Bengal (RB)—the synthetic xanthene dye most frequently used as a sensitizer for $O_2(^1\Delta_g)$ generation [13]—an exclusive $O_2(^1\Delta_g)$-mediated

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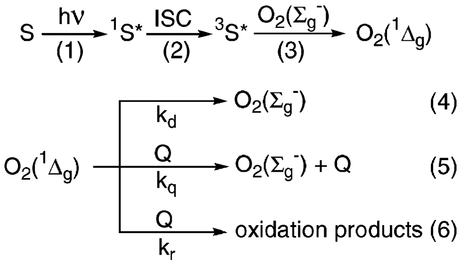


Scheme 1. Generation of $O_2(^1\Delta_g)$ by sensitization, and main quenching processes in solution. S, sensitizer; Q, quencher.

mechanism operates, being 3-hydroxypyridine (3-OHP) the isomer most susceptible towards photooxidation in water, while 4-hydroxypyridine (4-OHP) does not react at all in this medium (Table 1), and 2-hydroxypyridine (2-OHP) exhibits intermediate reactivity. The absence of reactivity of 4-OHP and, in general, of substituted 4-OHPs can be attributed to the predominant, or exclusive, presence of the corresponding tautomeric 4-keto forms [14,15], much less aromatic than the 4-hydroxy form and, hence, much less reactive towards the well-known electrophilic reagent $O_2(^1\Delta_g)$. On the contrary, in 3-OHP the OH-form is in equilibrium with the OH-ionized N-protonated zwitterionic tautomer, and the reaction with $O_2(^1\Delta_g)$ is much more efficient. As a continuation of these studies, we decided to explore the reactivity of dihydroxypyridines, relating it with the predominant form present in the medium and with its ionization state. Since some known pesticides include hydroxypyridine groups in their structure, the knowledge of the kinetics of photosensitized oxidations of the model compounds constitutes a meaningful assistance in the design of photodegradable molecules of controllable persistence in a given environment.

In the present paper we describe and discuss the kinetic behaviour of 2,3-dihydroxypyridine (2,3-DHP) and 2,4-dihydroxypyridine (2,4-DHP) upon RB-sensitized photooxidation conditions, in water buffered at different pH values and in the mixture acetonitrile–water 4:1 with or without added potassium hydroxide.

2. Experimental

2.1. Materials

2,3-DHP, 2,4-DHP, 9,10-dimethylanthracene (DMA), RB and sodium azide, all from (Aldrich), fluorescamine (Sigma) and furfuryl alcohol (FFA) (Riedel de Haën) were used without further purification. The following solvents were employed: D_2O (99.9% D, Sigma), acetonitrile (MeCN) (HPLC quality, Sintorgan) and triply distilled water. Water (H_2O–D_2O) solutions of different pH/pD values were prepared with phosphate buffers [16] (pH/pD 5 and 11) or by addition of potassium hydroxide (pH/pD 14). pH/pD values remained constant during the irradiations, as controlled with a pH-meter. The solvents MeCN–H_2O + KOH and MeCN–D_2O + KOH had an overall KOH concentration of 0.01 M. Along the experiments in the latter solvents some KOH-catalysed hydrolysis of MeCN cannot be discarded, although this process is far from efficient and normally requires vigorous basic conditions [17]. Anyway, the UV spectra of solutions of each dihydroxypyridine in MeCN–water + KOH remained unchanged when kept for weeks in the dark at room temperature. Solutions in D_2O or in MeCN–D_2O were employed in the time-resolved experiments.

Table 1
Rate constant values (±10%) for the overall (k_t) and reactive (k_r) quenching of $O_2(^1\Delta_g)$ by 2,3-DHP and 2,4-DHP, and k_r/k_t ratios[a]

Compound	Solvent	k_t ($\times 10^8$ M^{-1} s^{-1})	k_r ($\times 10^8$ M^{-1} s^{-1})	k_r/k_t
2,3-diOHP	Water, pH/pD 5	3.40	0.51	0.15
	Water, pH/pD 11	5.60	3.55	0.63
	Water, pH/pD 14	6.80	1.0	0.14
	MeCN–water	0.70	0.71	1.01
	MeCN–water + KOH	1.7	1.68	0.99
2,4-diOHP	Water, pH/pD 5	0.008	NR	
	Water, pH/pD 11	0.05	0.048	0.96
	Water, pH/pD 14	0.08	0.01	0.12
	MeCN–water	NQ	NR	
	MeCN–water + KOH	0.04	0.037	0.93
2-OHP (a)	Water, pH/pD 6[b]	NQ	NR	
	Water, pH/pD 11[b]	1.23	0.20	0.16
3-OHP (a)	Water, pH/pD 6[b]	0.39	0.26	0.67
	Water, pH/pD 11[b]	2.6	2.6	1.00
4-OHP (a)	Water, pH/pD 6[b]	NQ	NR	
	Water pH/pD 11[b]	NQ	NR	

[a] Values for monohydroxypyridines are included for comparison. $O_2(^1\Delta_g)$ generated through RB sensitization. MeCN–water 4:1 (v/v) mixtures. NQ, NR: no quenching or no reaction was observed.

[b] Values from Ref. [5].

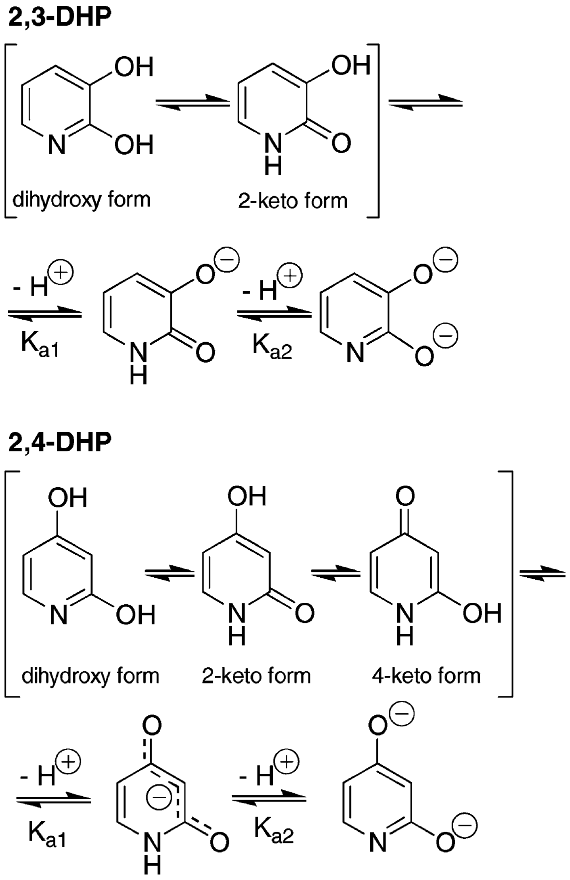
2.2. Determination of overall quenching rate constants, k_t

The overall rate constant for $O_2(^1\Delta_g)$ quenching (k_t) is defined as the sum of the rate constants of physical deactivation to ground-state molecular oxygen (k_q, process (5) in Scheme 1), and of chemical or reactive quenching (k_r), process (6). k_t values were determined by time-resolved phosphorescence detection (TRPD), using a laser kinetic spectrophotometer. A nanosecond Nd:YAG laser system (Spectron) at 532 nm was the excitation source. The emitted radiation (mainly 1270 nm) was detected at right angles with an amplified Judson J16/8Sp germanium detector, after passing through appropriate filters. The output of the detector was coupled to a digital oscilloscope and to a computer that allowed the processing of the signal. Sixteen shots were usually needed for averaging decay times, in order to get a good signal/noise ratio. The apparatus has been previously described [18].

The sensitizer RB, with a quantum yield of $O_2(^1\Delta_g)$ generation of 0.75 [13], was employed both in H_2O and D_2O at concentrations corresponding to absorbances at 532 nm in the range 0.4–0.5. $O_2(^1\Delta_g)$ lifetimes were evaluated in the absence (τ^0) and in the presence (τ) of each hydroxypyridine (10^{-4}–10^{-3} M), and the ratio τ^0/τ was plotted as a function of the quencher concentration, according to a simple Stern–Volmer treatment, using the expression $\tau^0/\tau = 1 + k_t\tau^0$ (DHP).

2.3. Determination of photooxidation rate constants, k_r

The rate constants for the chemical reaction between OH–ND and $O_2(^1\Delta_g)$ were determined by different comparative methods [12], depending on the solvent used. In all the cases, the k_r value for the sensitized photooxidation of a reference compound must be known. In MeCN–water 4:1 (v/v) and in MeCN–water 9:1 (v/v) + 0.01 M KOH, the reference was DMA, with k_r values of 1.2×10^7 and $5.2 \times 10^7\ M^{-1}\ s^{-1}$, respectively, as determined by TRPD. The DMA disappearance was monitored by spectrofluorimetry in a Spex Fluoromax apparatus, with 395 and 450 nm as excitation and emission wavelengths, respectively. The disappearance of each pyridine was followed by absorption spectroscopy in a Hewlett Packard 8452A diode array spectrophotometer, reading absorbances at the wavelength of maximum absorption, in the range of 300–350 nm (depending on the substrate), where RB is practically transparent. In order to avoid interferences from possible photooxidation products, absorbance data for substrate conversions lower than 10% were employed, assuming much lower, or null, absorbances for said products at the analytical wavelength. In water, the reference was FFA, with $k_r = 1.2 \times 10^8\ M^{-1}\ s^{-1}$ [19], and the disappearance rates of substrate and reference upon sensitized irradiation were assumed equal to the rates of oxygen uptake of the respective solutions. This assumption is valid if the photooxidation reactions are the only oxygen-consuming processes. Oxygen uptakes were determined by the specific electrode Orion 97–08, only utilizable in solvents with more than 95% water.



Scheme 2. Accepted tautomeric and ionized forms of 2,3-DHP and 2,4-DHP.

3. Results

Both DHP can tautomerize to pyridone forms (Scheme 2). The main 2,3-DHP species present in water is the 2-keto form, and its successive ionizations produce the 3-ionized 2-keto form ($pK_{a1} = 8.7$) and the 2,3-di-ionized pyridine form. The second ionization is undetectable by spectroscopy or potentiometric titration [20,21]. The un-ionized 2-keto form also predominates in dimethylsulphoxide solution [22]. In water containing 20 mol% of ethanol, dimethylsulphoxide, or dioxane, both ionizations have been observed, with pK_{a1} and pK_{a2} in the ranges of 9.26–9.90 and 11.72–12.53, respectively [23]. In the case of 2,4-DHP (also known as 3-deazauracil), the 2-keto tautomer is present in the crystal structure [24], but in water solution other forms cannot be discarded. In this medium, the successive ionizations give rise to the corresponding 2-/4-keto ($pK_{a1} = 6.5$) and 2,4-di-ionized pyridine ($pK_{a2} = 13.0$) forms [25]. Monohydroxypyridines show similar tautomeric and ionization equilibria. In both aqueous and organic media, 2-OHP and

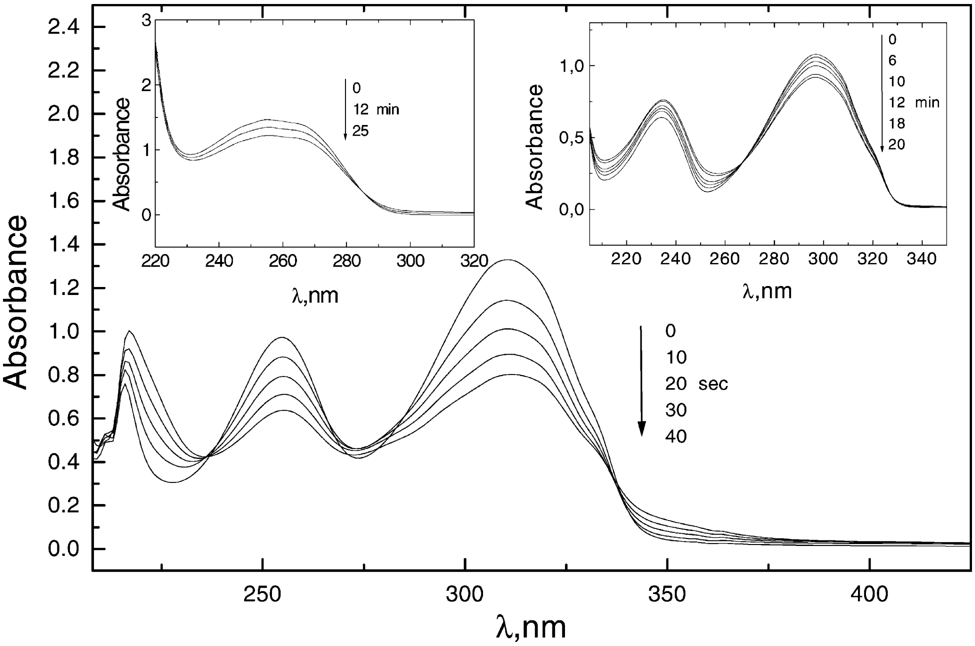


Fig. 1. Spectral evolution of dihydroxypyridines upon aerobic RB-sensitized photoirradiation. Main figure: 2,3-diOHP in pH 11 water. Right inset: 2,3-diOHP in pH 5 water. Left inset: 2,4-diOHP in pH 11 water. Numbers on the spectra represent irradiation time in minutes.

4-OHP stand as the corresponding 2-keto and 4-keto forms, and 3-OHP is mainly as the N-protonated zwitterionic tautomer, in equilibrium with the OH-form [14,15].

Consequently, the shapes of the absorption spectra of all these compounds strongly depend on the solvent and ionization state [26,27]. In the case of 2,3-DHP, its spectrum in pH 5 water solution was practically the same as in MeCN–H_2O 9:1, and that in pH 11 water solution was the same as in alkaline MeCN–H_2O 9:1. The same can be said for 2,4-DHP. Hence, it can be assumed that for each DHP the same predominant species is present in solutions with the same absorption spectrum.

The visible-light irradiation in the presence of RB of air-equilibrated solutions of 2,3-DHP in any of the sol-

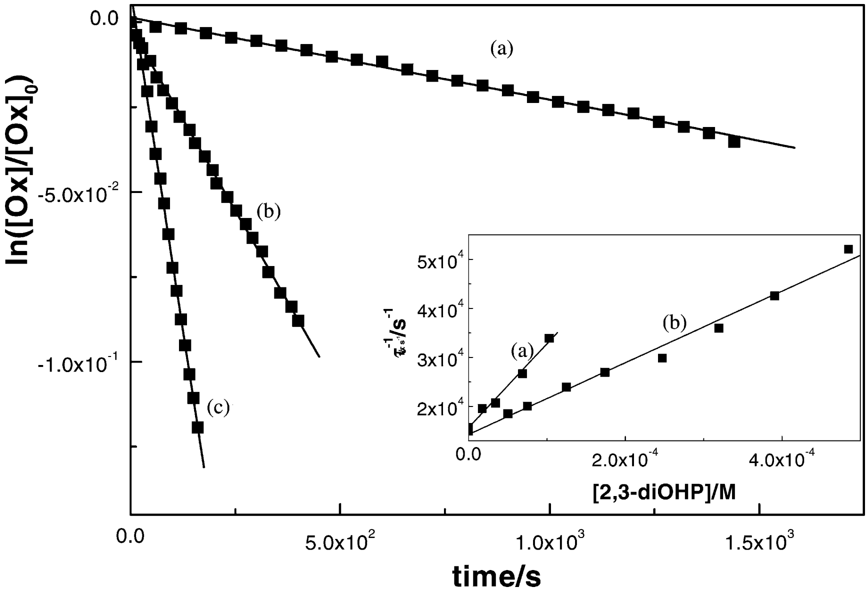


Fig. 2. First order plots for oxygen uptake upon RB photosensitized oxidation of (a) 2,4-diOHP, (b) furfuryl alcohol and (c) 2,3-diOHP; all 0.5 mM in pH 11 water. [Ox] and $[Ox]_0$ represent the dissolved molecular oxygen concentrations at time $t = t$ and $t = 0$, respectively. Inset: Stern–Volmer plots for the quenching of $O_2(^1\Delta_g)$ phosphorescence by 2,3-DHP in (b) MeCN–water 4:1 (v/v) and in (a) MeCN–water 4:1 (v/v) plus 0.01 M KOH.

vent herein used strongly modified the initial UV absorption spectra (Fig. 1). Although less pronounced, the same was observed for similar solutions of 2,4-DHP in water at pH 11, water at pH 14, and alkaline MeCN–H_2O 9:1. No spectral changes were detected for 2,4-DHP in water at pH 5 or in MeCN–H_2O 4:1, even after much longer irradiation times. The former spectral changes did not occur in nitrogen-saturated solutions, and were highly inhibited in the presence of 20 mM sodium azide, a well-known physical quencher of $O_2(^1\Delta_g)$ [12]. All these results indicate the existence of type II photooxidations, which were unambiguously corroborated by $O_2(^1\Delta_g)$-quenching experiments with TRPD.

The corresponding k_r values (Table 1) were graphically deduced either through the oxygen uptake in water or through the substrate consumption in MeCN–H_2O 4:1. On the other hand, oxygen consumption was detected in the RB-sensitized irradiation of 2,3-DHP in water at pH 5, 11 or 14, and of 2,4-DHP in water at pH 11 or 14, and in all the cases it was also totally inhibited by the presence of 20 mM sodium azide. The treatment of the TRPD data is shown in Fig. 2, as well as the $O_2(^1\Delta_g)$ phosphorescence decays in the absence and in the presence of 2,3-DHP (inset). Table 1 contains the respective k_t values. For comparative purposes, described kinetic data for 2-OHP, 3-OHP and 4-OHP in similar media have been also included.

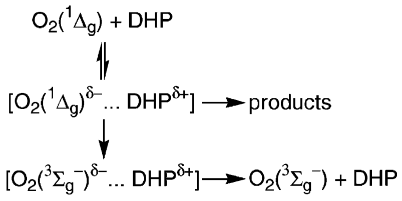
As it has been stressed before [28], no relevant information about the effectiveness of the actual photodegradation is obtained from the straightforward analysis of k_t and k_r values in $O_2(^1\Delta_g)$-mediated photooxidations. A simple and useful approach is the evaluation of the k_r/k_t ratio, which shows the fraction of overall quenching of $O_2(^1\Delta_g)$ that leads to chemical reaction. The values deduced for said ratio for 2,3-DHP, 2,4-DHP, and for the parent compounds 2-OHP, 3-OHP and 4-OHP, have been also included in Table 1.

4. Discussion

The kinetics of the $O_2(^1\Delta_g)$-mediated sensitized photooxidation of hydroxylated aromatic compounds and, in particular, of phenols and OHP has been extensively studied. Generally, speaking, the kinetic data found for these two families of compounds can be interpreted in a similar way. Thus, both phenols [28] and OHP [5–8] are efficient physical and/or chemical quenchers of $O_2(^1\Delta_g)$, and the opposite can be said about their respective non-hydroxylated parent compounds. The reactivity in phenols and OHP can be unambiguously related to the ionization state of the OH group, and the ionized forms always show much higher ability as $O_2(^1\Delta_g)$-scavenger [28]. Nevertheless, reported data on the $O_2(^1\Delta_g)$-mediated sensitized photooxidations of polyhydroxybenzenes [28] indicate that the presence of a second OH group in the aromatic nucleus produces kinetic and mechanistic effects that are not straightforwardly predictable from the available information for phenols. For example, hydroquinone is an efficient physical and chemical quencher of $O_2(^1\Delta_g)$ in water at pH 6, whereas in the same medium resorcinol and catechol behave as exclusive chemical and physical quenchers, respectively. The picture for trihydroxybenzenes is somewhat similar [29]; the three isomers are fairly good physical quenchers of $O_2(^1\Delta_g)$, and are easily photooxidizable even in water at pH 2, where the corresponding non-ionized forms are present. Turning to the hydroxypyridine family, and to OHP in particular, it has been demonstrated [5] that their interaction with $O_2(^1\Delta_g)$ increases with the ionization of the OH group, and decreases when keto forms prevails in the medium, as already mentioned in Section 1.

In the case of the two dihydroxypyridines herein studied, the kinetic data in Table 1 indicate an increase in the rate constants k_t and k_r with the ionization. This behaviour, common for other hydroxy-aromatic compounds [5,28], is attributed to the intermediate formation of an excited encounter complex of the type $[O_2(^1\Delta_g)\cdots \text{DHP}]$ with partial charge-transfer character (Scheme 3). Hence, the ionization of the OH groups and the polarity of the medium must favour the $O_2(^1\Delta_g)$–DHP interaction. A deeper analysis of the data accounts for the different species present in each medium, as follows.

In all the studied media, the values for the rate constants k_t and k_r of 2,3-DHP are one to two orders of magnitude higher than the respective ones of 2,4-DHP. This suggests that a condition for reaching high overall reactivity towards $O_2(^1\Delta_g)$ is the presence of an OH group in position 3, as has also been observed in the three OHP [5,6] (Table 1). This condition is particularly evident in water at pH 5 and in MeCN–water 4:1, solvents where only 2,3-DHP is photooxidized. According to the data, the efficiency of the photooxidation process, measured as the ratio k_r/k_t, is low (0.15) in the pH 5 medium, but is very efficient (a value close to the unity) in the mixture MeCN–water 4:1. A similar dependence, with higher photooxidative efficiency in a less polar solvent (MeCN–water 4:1 mixture, as compared to water) has been already observed for other hydroxyaromatic derivatives, being interpreted in terms of the evolution of the suggested excited encounter complex [28]. On the contrary, the overall quenching process is favoured in more polar solvents. The balance between physical and chemical quenching of $O_2(^1\Delta_g)$ could be assimilated to those cases previously hypothesized for the hydroxy-aromatic com-



Scheme 3. Generation and evolution of the encounter excited complex between $O_2(^1\Delta_g)$ and a dihydroxypyridine.

pounds α-tocopherol [30], poly-alkylphenols [31] and some tyrosine-containing peptides [32,33]. This balance has been previously described as a sensitive function of spin–orbit coupling properties and entropy factors within the encounter complex, as supported by the observed flat enthalpy profile along the reaction coordinate in experiments at different temperatures [31].

Regarding 2,4-DHP in water at pH 5, the non-ionized keto forms mainly present in the medium have demonstrated to be extremely poor quenchers of $O_2(^1\Delta_g)$, exhibiting only a physical quenching component ($k_t = k_q = 8 \times 10^5\,M^{-1}\,s^{-1}$). According to the kinetic data, relatively high concentrations of 2,4-DHP (ca. 30 mM) are necessary to intercept $O_2(^1\Delta_g)$ under competitive conditions with its natural environmental decay ($k_d = 2.5 \times 10^4\,s^{-1}$) [12]. In water at pH 11 and in alkaline MeCN–water 4:1, where both DHP are mainly in their respective mono-ionized pyridone forms, the k_r/k_t ratios reach the highest values.

Finally, in water at pH 14 the di-ionized forms of both DHP behaved in a particular fashion. Even when in this medium the rate constants for the overall $O_2(^1\Delta_g)$ quenching process, k_t, were higher than those found at pH 5 or 11, the respective k_r values were, in relative terms, very low, indicating that most $O_2(^1\Delta_g)$ is deactivated by physical processes. This is an experimental evidence of the high nucleophilicity of the DHP di-ionized species, which favours the formation of the encounter complex with $O_2(^1\Delta_g)$.

In conclusion, all this experimental evidence indicates that the aerobic dye-sensitized photooxidation in aqueous solution of 2,3-DHP or 2,4-DHP, a photoreaction mediated by $O_2(^1\Delta_g)$, is a relatively efficient degradation pathway over an extended pH range. This photodegradation was observed previously in some other polyhydroxylated aromatic compounds, but not in the corresponding monohydroxylated parent compounds OHP. Even though the pH increase favours the overall interaction $O_2(^1\Delta_g)$–DHP, this increase is not sufficient for increasing the photooxidation rate, and the highest photodegradative efficiencies have been observed in moderate-to-high alkaline media, where the two DHP stands as their respective mono-ionized pyridone forms. Besides, in an acidic medium, where the corresponding un-ionized forms are present, only 2,3-DHP is photooxidized, while in a highly alkaline medium, where both DHP are as di-ionized forms, their relative chemical reactivities are low.

Regarding the natural photo disappearance of pesticides related with DHP, all these results indicate that a simple change in the environmental conditions, such as a sudden alteration of pH, could allow the switch between reactive and non-reactive situations. The knowledge of the related experimental facts constitutes an imperative requisite when programmed or natural field photodegradations of aquatic pollutants are considered. This includes the cheap and efficient *lagooning* method [34,35], i.e. degradation by the combined action of spontaneous physical, chemical and biological processes taking place in lagoons in the simple presence of oxygen and sunlight.

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