Modelling the natural photodegradation of water contaminants
A kinetic study on the light-induced aerobic interactions between riboflavin and 4-hydroxypyridine

Adriana Pajares [a], José Gianotti [a], Guillermo Stettler [a], Sonia Bertolotti [b], Susana Criado [b], Ariana Posadaz [b], Francisco Amat-Guerri [c], Norman A. García [b],*

[a] *Unidad Académica Río Gallegos, Universidad Nacional de la Patagonia Austral, Lisandro de la Torre 1070, 9400 Río Gallegos, Argentina*
[b] *Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina*
[c] *Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

Abstract

Within our current studies on the natural photodegradation of representative aquatic environmental contaminants, the visible light irradiation of the model compound 4-hydroxypyridine (4-OHP), in air-equilibrated aqueous solution and in the presence of riboflavin (Rf), has been studied employing stationary photolysis, polarographic detection of oxygen uptake, stationary and time-resolved fluorescence spectroscopy, and laser flash photolysis. The results indicate that 4-OHP — a compound inert towards the attack of singlet molecular oxygen ($O_2(^1\Delta_g)$) generated by Rose Bengal sensitization — quenches excited singlet and triplet states of Rf, with rate constants of $2.4 \times 10^9 \, M^{-1} \, s^{-1}$ and $1.2 \times 10^7 \, M^{-1} \, s^{-1}$, respectively. The photodecomposition of Rf, a known process taking place from triplet Rf, has been found to depend on the concentration of dissolved 4-OHP: at ≥ 20 mM limited photodecomposition occurs due to the quenching of excited singlet Rf, while at ca. 5 mM triplet Rf is photogenerated and subsequently quenched either by oxygen, giving rise to $O_2(^1\Delta_g)$, or by 4-OHP, yielding semireduced Rf through an electron transfer process. Superoxide dismutase inhibition of the oxygen uptake and flash photolysis data indicate that superoxide anion is generated, likely by the reaction of the anion radical from Rf with dissolved oxygen, also yielding neutral, ground state Rf. The final result is that both 4-OHP and Rf are photodegraded, probably through oxidation with superoxide anion. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The spontaneous photodegradation of pesticides in the aqueous environment under natural conditions is an important way of elimination of these contaminants. Since most common pesticides are transparent to natural daylight, the sensitized photooxidation in the presence of air and a daylight absorbing compound appears as a plausible alternative for their degradation, because these conditions are frequently fulfilled in surface waters.

We are currently studying the kinetics and mechanism of the photooxidation of compounds of environmental interest, or of molecules that can be considered their models, in a search directed towards the determination of the most efficient experimental conditions for their photodegrada-tion under visible light irradiation. In the particular cases of *N*-heteroaromatic compounds with the basic molecular structure of known pesticides [1], such as hydroxypyridines, hydroxyquinolines and hydroxypyrimidines, we have demonstrated that in the presence of Rose Bengal — the synthetic xanthene dye most frequently used as a sensitizer for singlet molecular oxygen ($O_2(^1\Delta_g)$) generation — [2] a $O_2(^1\Delta_g)$-mediated mechanism exclusively operates [3–5] with photooxidation quantum efficiencies for the reactive heteroaromatic compounds in the range 0.01–0.50. Regarding the three isomeric hydroxypyridines, the most susceptible one towards photooxidation in water is 3-hydroxypyridine (3-OHP), while 4-hydroxypyridine (4-OHP) does not react at all in this medium. The relatively low or total absence of reactivity of compounds with an OH group in the 4 position of the *N*-containing six-membered heterocycle has been interpreted as a consequence of the predominant, or exclusive, presence of the corresponding

* Corresponding author. Tel.: +54-358467233; fax: +54-358-4676157.
E-mail address: ngarcia@exa.unrc.edu.ar (N.A. García).

tautomeric 4-oxo forms [6,35], much less aromatic than the 4-hydroxy forms 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.

Although the addition of dyes such as Rose Bengal to environmental aqueous media can be envisaged as a way of promoting the programmed phototransformation of pesticides with structures related to the former *N*-heteroaromatic compounds, it is sure that the method would receive, in principle, justified ecological complains — an artificially rose river is evidently non-ecological — even taken into account that Rose Bengal is a non-toxic dye and, besides, that it could disappear from the water solution by photobleaching.

Another more *natural* alternative route for the photodegradation of said contaminants takes advantage of the presence of some natural dyes in surface waters, generally at low concentrations and, hence, almost unobservable. In particular, Riboflavin (Rf), a well known natural pigment present in waters of rivers, lakes and seas [7], has been postulated as a possible sensitizer for the natural photooxidative degradation of herbicides and related compounds [8,9].

We have recently studied the role of Rf in the visible light promoted decomposition of 3-OHP in water solution [10] looking for information on the physical and chemical interactions taking place in this and similar systems. The results support the existence of competitive reactions with $O_2(^1\Delta_g)$ and/or superoxide anion ($O_2^{\bullet-}$), the relative importance of which depends on the 3-OHP concentration. These reactions give eventually rise to the photooxidation of 3-OHP and the partial photostabilization of Rf.

In the present work we continue these studies investigating the Rf-sensitized photodegradation of 4-OHP, a compound inert towards $O_2(^1\Delta_g)$ attack. The results are discussed in the light of those formerly found for the easily photooxidizable isomer 3-OHP employing Rose Bengal and Rf as photosensitizers.

2. Experimental

2.1. Materials

3-Hydroxypyridine (3-OHP), superoxide dismutase (SOD) from bovine erithrocytes, Rf (all from Sigma) and sodium azide (Aldrich) were employed as received. 4-Hydroxypyridine (4-OHP) (Aldrich) was sublimed prior to use. All solutions were buffered with phosphate at pH 7.

2.2. Methods

The stationary quenching of the Rf fluorescence was studied with a RF 5301-PC Shimadzu spectrofluorimeter at $25 \pm 1°C$ in air-equilibrated solutions. Fluorescence lifetimes were measured with a time-correlated single photon counting technique on an Edinburgh FL-9000CD instrument. In both cases, excitation and emission wavelengths were 445 and 515 nm, respectively. Ground state absorption spectra were registered in a Hewlett Packard 8452A diode array spectrophotometer.

Nitrogen-saturated aqueous solutions of Rf (0.01 mM) were photolysed using a flash photolysis apparatus. A nanosecond Nd:YAG laser system (Spectron) at 355 nm was the excitation source, employing a 150 W xenon lamp as analysing light. The detection system comprised a PTI monochromator and a red-extended photomultiplier (Hamamatsu R666). The signal, acquired and averaged by a digital oscilloscope (Hewlett Packard 54504A), was transferred to a PC via an HPIB parallel interface, where it was analysed and stored.

Static aerobic photolysis of aqueous solutions containing 4-OHP (0.5 mM) and Rf (0.01–0.03 mM) were carried out in a PTI unit, provided with a high pass monochromator and 150 W Xe lamp, irradiating with 440 ± 10 nm, or in a home-made photolyser for non-monochromatic irradiation (150 W quartz-halogen lamp). In this case cut-off filters (400 nm) ensured that the light was only absorbed by the sensitizer.

The Rf-sensitized photooxygenation rates of 3-OHP (0.4 mM), 4-OHP (0.5–20 mM), and Rf (0.022 mM) were determined by evaluation of the initial slopes of oxygen consumption vs. irradiation time, employing a specific oxygen electrode (Orion 97-08).

Rf photodecomposition rates were determined by evaluation of the initial slopes of Rf consumption (decrease of absorbance at 446 nm) vs. irradiation time.

3. Results

3.1. Rf-sensitized photooxygenation of 4-OHP

The Rf-sensitized photodegradation of 4-OHP was studied under experimental conditions that closely mimic the environmental ones [11], i.e. in air-equilibrated diluted aqueous solutions and under visible light ($\lambda > 400$ nm) irradiation. For comparative purposes 3-OHP was similarly irradiated in parallel experiments because its photooxidative behaviour with Rose Bengal or Rf as sensitizer is known [4]. The irradiations of the systems 4-OHP/Rf and 3-OHP/Rf (pyridine concentration ca. 0.5 mM) produced changes in the visible/UV absorption spectrum of the respective solutions (not shown), indicating chemical changes in both the pyridine and the dye, with simultaneous oxygen consumption. The initial rate of oxygen uptake by the system 4-OHP (5 mM)/Rf is 10 times slower than that of the system 3-OHP (0.4 mM)/Rf (lines (c) and (d), Fig. 1, respectively), even when the concentration of 4-OHP is ca. one order of magnitude higher.

The rate of oxygen uptake was greatly reduced, as compared to the one of the former system 4-OHP/Rf, in the aqueous aerobic irradiations of: (1) a solution of Rf (0.022 mM),
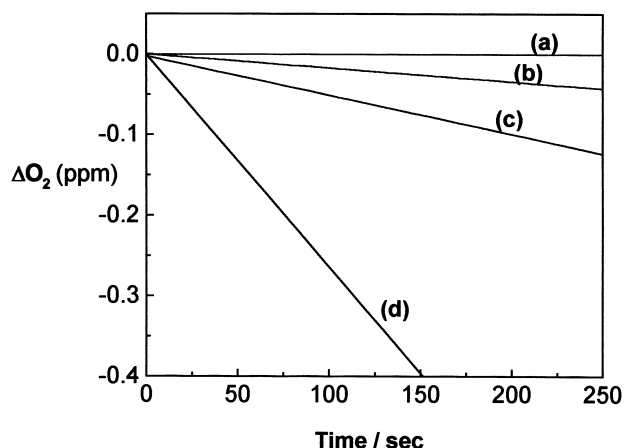
Fig. 1. Rates of oxygen uptake upon irradiation of air-equilibrated aqueous solutions containing: (a) Rf (0.022 mM), 4-OHP (0.5 mM) and NaN$_3$ (5 mM); (b) Rf (0.022 mM), 4-OHP (5 mM) and SOD (12 μg/ml); (c) Rf (0.022 mM) and 4-OHP (5 mM); (d) Rf (0.022 mM) and 3-OHP (0.4 mM). For the sake of clarity, experimental points have been omitted. The slope of each line is the mean value of three runs, differing <4%.

but in the absence of any pyridine (not shown); (2) a solution of 4-OHP (5 mM), Rf (0.022 mM) and sodium azide (1 mM) (line (a), Fig. 1); sodium azide is a well known selective physical quencher of O$_2$($^1\Delta_g$) [12]; (3) a solution of 4-OHP (5 mM), Rf (0.022 mM) and the enzyme SOD (12 μg/ml) (line (b), Fig. 1, compare with line (c)); a similar concentration of SOD has been previously used as an efficient quencher in O$_2^{\bullet-}$-mediated photooxidations [13–16]; (4) a solution of 4-OHP (20 mM) and Rf (0.022 mM) (not shown).

It is known that the photodegradation of Rf in water, in the absence of oxygen and under visible light irradiation, predominantly proceeds through the triplet state [17], and the rate of the process can be estimated by absorption spectroscopy. Comparative irradiations of nitrogen-saturated solutions of Rf (0.022 mM) in the absence and in the presence of 4-OHP (5 mM) showed that the photodegradation rate is higher in the latter case (Fig. 2, main), while no changes were detected in the absorption spectrum of 4-OHP. Ground state association between 4-OHP and Rf was not observed by absorption spectroscopy. The difference spectrum in the 380–600 nm range of Rf (0.022 mM) was not affected by the presence of 4-OHP (up to 10 mM).

It is evident that all the former results cannot be interpreted through a simple mechanism, and specific interactions of 4-OHP and oxygen with excited singlet and triplet Rf must be taken into account. The most important processes that can be operative when the system 4-OHP/Rf/oxygen is irradiated with visible light are shown in Scheme 1.

The absorption of visible light promotes Rf to the electronically excited singlet (process (1)) and triplet (process (4)) states. Both states can either naturally decay (processes (2) and (5)) or be, respectively, quenched through processes (3) and (6)–(9). Triplet Rf can transfer its energy to ground state (triplet) molecular oxygen, O$_2$($^3\Sigma_g^-$), dissolved in the medium, yielding O$_2$($^1\Delta_g$) (process (9)), that can decay either by collision with surrounding solvent molecules (process (10)) or by physical or chemical interaction with 4-OHP (process (11) and type II photooxidation (12), respectively), or by reaction with Rf (reaction (13)). Triplet Rf can also react with 4-OHP (electron transfer reaction (8)), yielding the respective semireduced and semioxidized forms Rf$^{\bullet-}$ and
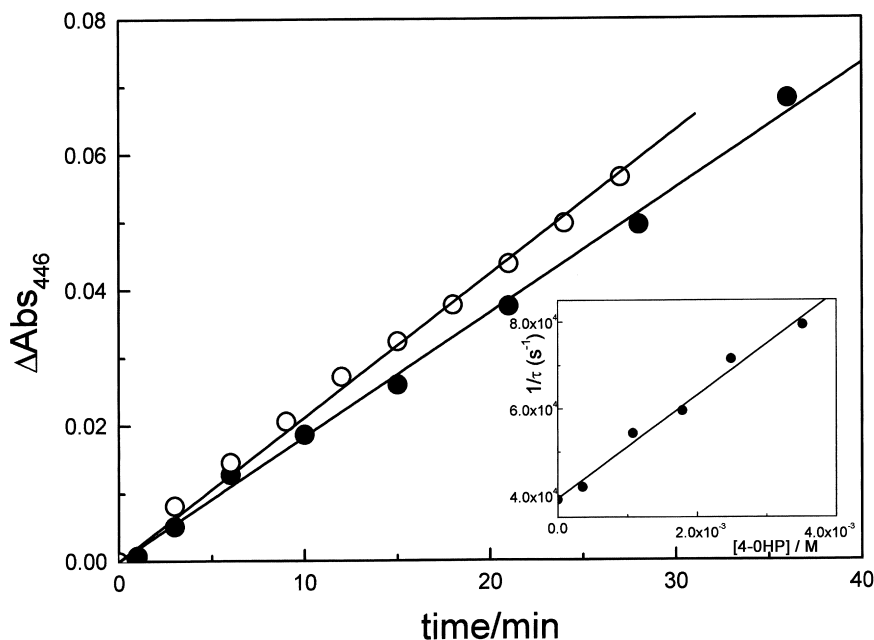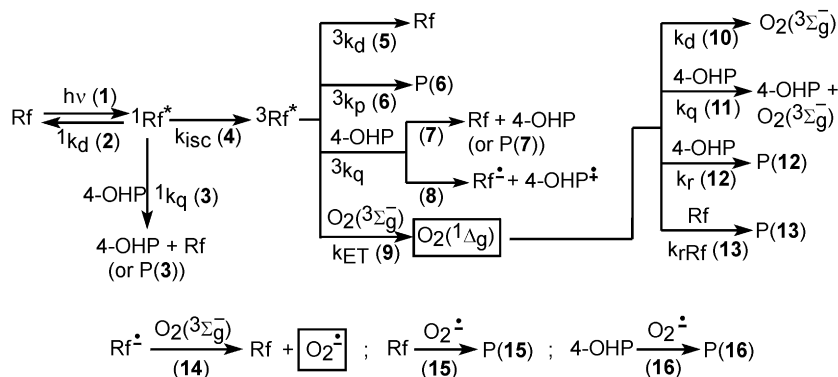

Fig. 2. Rates of Rf (0.022 mM) photodecomposition in the absence (●) and in the presence (○) of 4-OHP (5 mM), in argon-saturated water solutions. Inset: Stern–Volmer plot for the quenching of triplet Rf by 4-OHP.

$$Rf \underset{^1k_d\ (\mathbf{2})}{\overset{h\nu\ (\mathbf{1})}{\rightleftarrows}} {}^1Rf^* \xrightarrow{k_{isc}\ (\mathbf{4})} {}^3Rf^*$$

Processes from $^1Rf^*$ with 4-OHP, $^1k_q\ (\mathbf{3})$: 4-OHP + Rf (or P(**3**))

Processes from $^3Rf^*$:
- $^3k_d\ (\mathbf{5}) \rightarrow Rf$
- $^3k_p\ (\mathbf{6}) \rightarrow P(\mathbf{6})$
- ^3k_q with 4-OHP $(\mathbf{7}) \rightarrow Rf + 4\text{-OHP}$ (or P(**7**))
- $(\mathbf{8}) \rightarrow Rf^{\bullet -} + 4\text{-OHP}^{\bullet +}$
- $k_{ET}\ (\mathbf{9})$ with $O_2(^3\Sigma_g^-) \rightarrow O_2(^1\Delta_g)$

Processes from $O_2(^1\Delta_g)$:
- $k_d\ (\mathbf{10}) \rightarrow O_2(^3\Sigma_g^-)$
- $k_q\ (\mathbf{11})$ 4-OHP $\rightarrow 4\text{-OHP} + O_2(^3\Sigma_g^-)$
- $k_r\ (\mathbf{12})$ 4-OHP $\rightarrow P(\mathbf{12})$
- $k_r Rf\ (\mathbf{13})$ Rf $\rightarrow P(\mathbf{13})$

$$Rf^{\bullet -} \xrightarrow[(\mathbf{14})]{O_2(^3\Sigma_g^-)} Rf + O_2^{\bullet -} \quad ; \quad Rf \xrightarrow[(\mathbf{15})]{O_2^{\bullet -}} P(\mathbf{15}) \quad ; \quad 4\text{-OHP} \xrightarrow[(\mathbf{16})]{O_2^{\bullet -}} P(\mathbf{16})$$

Scheme 1. Possible important interactions in the visible light aerobic irradiation of 4-hydroxypyridine (4-OHP) in the presence of Rf. P denotes a reaction product.

4-OHP$^{\bullet +}$. Reaction (14) represents the generation of superoxide anion ($O_2^{\bullet -}$), which can react with Rf (reaction (15)) and/or with 4-OHP (reaction (16)).

3.2. Quenching of excited singlet Rf by 4-OHP

In air-equilibrated aqueous solution, Rf shows a fluorescence emission band centred at 515 nm with a fluorescence quantum yield of 0.25 [18]. In the presence of ≥ 10 mM 4-OHP, the quenching of the fluorescence from excited singlet Rf ($^1Rf^*$) is detectable as a decrease in the stationary emission intensity, but the shape of the emission spectrum does not change. Monitoring the fluorescence intensity of Rf in the absence (I_0) and in the presence (I) of different 4-OHP concentrations, the classical Stern–Volmer treatment ($I_o/I = 1 + {}^1K_{SV}[\text{4-OHP}]$) allows the determination of the Stern–Volmer constant ($^1K_{SV}$). Assuming that the fluorescence inhibition is a consequence of the quenching of $^1Rf^*$ by 4-OHP, the $^1K_{SV}$ value so obtained ($12.5\,M^{-1}$) will be equal to the ratio $^1k_q/^1k_d$, where ^1k_q and ^1k_d are the respective rate constants for the quenching of $^1Rf^*$ by 4-OHP, and for the thermal deactivation of $^1Rf^*$ (processes (3) and (2), respectively, Scheme 1). Time-resolved fluorescence measurements in the absence of 4-OHP yielded a ^1k_d value of $1.9 \times 10^8\,M^{-1}\,s^{-1}$ (corresponding to a Rf fluorescence lifetime, $^1\tau_0$, of 5.2 ns, in accord with published data [19]) and, consequently, a ^1k_q value of $2.4 \times 10^9\,M^{-1}\,s^{-1}$ could be deduced. This value is practically the same ($2.7 \times 10^9\,M^{-1}\,s^{-1}$) as that obtained by direct application of the Stern–Volmer equation ($^1\tau_0/^1\tau = 1 + (^1k_q/^1k_d)[\text{4-OHP}]$) to time-resolved fluorescence lifetimes of Rf in the absence ($^1\tau_0$) and in the presence ($^1\tau$) of 4-OHP.

3.3. Quenching of triplet Rf by 4-OHP

Triplet Rf ($^3Rf^*$) was generated in water by a 355 nm laser pulse, and the $^3Rf^*$ disappearance was monitored from the first-order decay of the absorbance at 670 nm, a zone where the interference from other possible species is negligible. In the presence of 4-OHP, an appreciably decrease of the $^3Rf^*$ lifetime was observed, as shown for a typical case in Fig. 3, inset. The triplet decay was measured at low Rf concentration (typically 0.022 mM) and at low enough laser energy, in order to avoid self-quenching and triplet–triplet annihilation effects, respectively. As before, the Stern–Volmer treatment of the triplet quenching (Fig. 2, inset), using the expression $1/^3\tau = (1/^3\tau_0) + {}^3k_q[\text{4-OHP}]$ (where $^3\tau_0$ and $^3\tau$ are the experimentally determined lifetimes of ^3Rf in the absence and in the presence of 4-OHP, respectively), yielded a value for the bimolecular rate constant of the quenching of ^3Rf by 4-OHP (^3k_q, processes (7) and (8), Scheme 1) of $1.2 \times 10^7\,M^{-1}\,s^{-1}$.

The transient absorption spectrum of the Rf solution 1 μs after the laser pulse (Fig. 3, main, upper trace) is similar to the one reported for $^3Rf^*$ [20–23]. In the presence of 8 mM 4-OHP a different spectrum was observed (Fig. 3, main, lower trace), with a shape similar to that described [24] to account for electron transfer processes to $^3Rf^*$ from electron-donor substrates such as 2,6-dimethyphenol [25], aliphatic amines [22] and nucleotides [23], with the simultaneous generation of the well-known radical anion Rf$^{\bullet -}$ [22,23,26,27]. The described [24] transient spectrum for Rf$^{\bullet -}$ possesses a non-pronounced maximum in the range of 530 nm, a region where the absorption of triplet Rf is comparatively low, and a smooth decrease up to ca. 700 nm, which is, closely coincident with the lower trace (open circles) of Fig. 3, main.

4. Discussion

Flavins in general, and very specially Rf, are probably the most extensively studied biomolecules with respect to their complexation ability with other molecules of biological and environmental relevance, including hydroxyaromatic compounds [28]. However, no ground state interactions of Rf with 4-OHP were detected by absorption spectroscopy. Moreover, the excellent concordance between the values of the rate constant ^1k_q obtained for 4-OHP by both static and
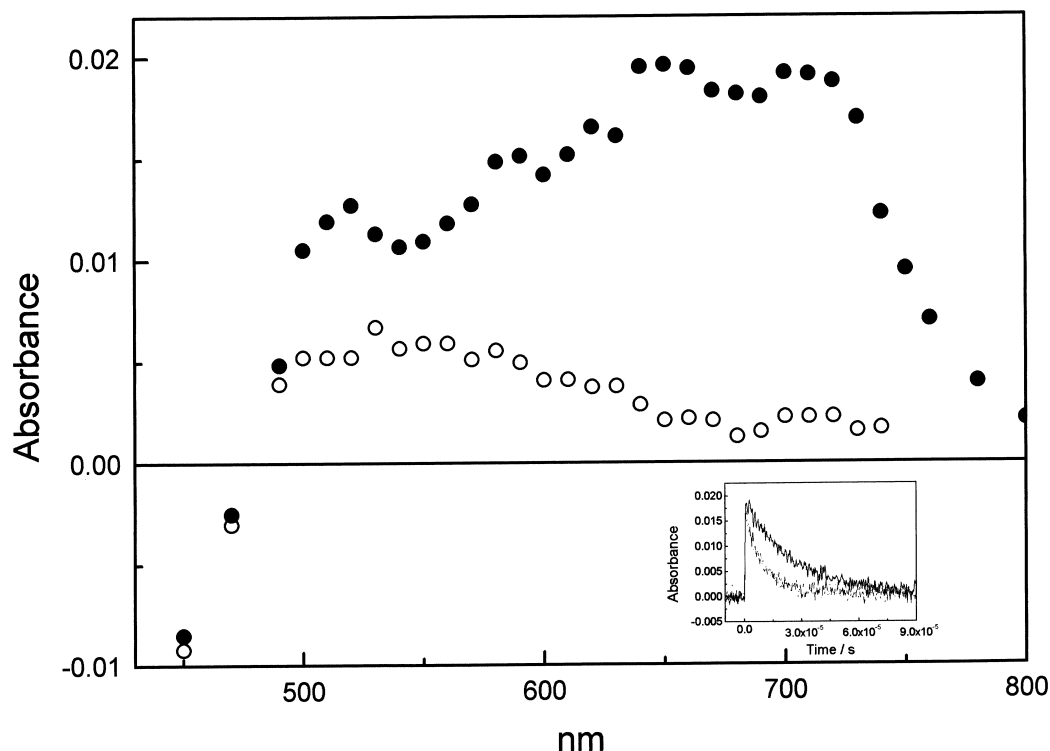
Fig. 3. Transient absorption spectra in the irradiation of Rf (0.01 mM) in argon-saturated aqueous solution, in the absence (●) and in the presence (○) of 4-OHP (8.2 mM), taken at 1 and 20 μs, respectively, after the laser pulse. Inset: transient absorption decay at 620 nm in the absence (upper curve) and in the presence (lower curve) of 4-OHP (3.6 mM).

time-resolved experiments on the quenching of the fluorescence of Rf (Table 1) corroborates that the only process involved is an interaction between $^1Rf^*$ and 4-OHP.

The spectral changes observed upon aerobic Rf-sensitized irradiation indicate the occurrence of chemical transformations. In addition, oxygen uptake experiments (Fig. 1) could be interpreted through the participation of reactive oxygen species in the photoprocesses. In principle, both excited singlet and triplet Rf can be directly or indirectly involved in the photodisappearance of 4-OHP. Although the interaction $^1Rf^*$/4-OHP (process (3), Scheme 1) occurs with a rate constant close to the diffusion limit (Table 1), relatively high concentrations of 4-OHP (80 mM, in order to quench 50%

Table 1
Rate constant values ($M^{-1} s^{-1}$) for the overall (k_t) and reactive (k_r) quenching of $O_2(^1\Delta_g)$ (from Rose Bengal sensitization), and for the quenching of excited singlet (^1k_q) and triplet (^3k_q) Rf, by 3-OHP and 4-OHP in water solution

Quencher	$O_2(^1\Delta_g)$ quenching		Excited Rf quenching	
	$k_t/10^9$	$k_r/10^9$	$^1k_q/10^{9a}$	$^3k_q/10^8$
3-OHP	0.03[b]	0.026[b]	5.9 (5.9)[c]	8.9[c]
4-OHP	nq[d]	–	2.4 (2.7)	0.12

[a] Determined by the single-photon-counting technique or (between brackets) static fluorescence.
[b] From Ref. [3].
[c] From Ref. [10].
[d] No quenching was observed.

$^1Rf^*$) are necessary to prevent triplet state population (process (4)).

Five main competitive pathways can occur from $^3Rf^*$ [29,30], three of them (reactions (6), (7) and (8)) with Rf and/or 4-OHP consumption, while the other two (processes (5) and (9)) are merely physical processes. The dominant mechanism will depend on the competition between O_2 and 4-OHP for the quenching of $^3Rf^*$. Under aerobic conditions the quenching of $^3Rf^*$ by O_2 occurs with a rate constant K_{ET} of $9 \times 10^8 M^{-1} s^{-1}$ (process (9)) [31]. As the reported quantum yield values for the generation of $O_2(^1\Delta_g)$ and $O_2^{•-}$ from $^3Rf^*$ are 0.47 and 0.009, respectively [32], it can be assumed that the direct generation of $O_2^{•-}$ by electron transfer from $^3Rf^*$ to O_2 — a reaction not included in Scheme 1 — must be negligible.

$^3Rf^*$ is quenched by 4-OHP (reactions (7) and (8)) with a global ^3k_q value of $1.2 \times 10^7 M^{-1} s^{-1}$. As suggested by laser flash photolysis experiments, reaction (8) would yield the radical anion $Rf^{•-}$. In the presence of oxygen, this process could compete with the generation of $O_2(^1\Delta_g)$ (process (9)), and for identical concentrations of 4-OHP and dissolved molecular oxygen the rate of $O_2(^1\Delta_g)$ production will be much higher than the rate of the quenching of $^3Rf^*$ by 4-OHP. However, reactions (7), (8) and (9) will have about the same importance at 4-OHP concentrations in the range 5–10 mM, which is a reasonable concentration range for contaminants in the aquatic environment. Consequently, under air saturated conditions, i.e. with a concentration of

dissolved oxygen approximately equals to 0.26 mM [33], $O_2^{\bullet-}$ could be formed by electron transfer from $Rf^{\bullet-}$ to O_2 (reaction (14)). For this recognized efficient reaction, which regenerates ground state Rf, a rate constant value of $1.4 \times 10^8 \, M^{-1} \, s^{-1}$ has been recently reported [23]. $O_2^{\bullet-}$ is a key intermediate in the oxygen redox chemistry of a number of biological and organic substrates [34]. Hence, the oxygen consumption by 4-OHP in the Rf-sensitized process could be mediated by a $O_2^{\bullet-}$ mechanism. Indirect evidence in support of this participation was provided by the SOD inhibition of the oxygen uptake (Fig. 1), as well as by the already commented results from flash photolysis experiments.

As we have demonstrated before [4], 4-OHP does not react at all with $O_2(^1\Delta_g)$ generated with RB as a sensitizer, whereas 3-OHP is photooxidized under the same conditions with a quantum yield of ca. 0.1. This difference is also reflected in the higher rate of oxygen uptake exhibited by 3-OHP, with regard to 4-OHP. The inhibitory effect on the oxygen uptake observed in the irradiation of the system 4-OHP/Rf/NaN$_3$ (line (a), Fig. 1) possibly obeys to the known quenching of $^3Rf^*$ by the azide anion [23], and/or to the quenching of $O_2(^1\Delta_g)$-photooxidation of the own Rf (reaction (13)), for which a rate constant $k_{rRf} = 6 \times 10^7 \, M^{-1} \, s^{-1}$ has been reported [26].

5. Conclusions

The visible light irradiation of 4-OHP in air-equilibrated aqueous solution and in the presence of Rf triggers a complex picture of competitive processes involving $^3Rf^*$ that eventually produce chemical transformations in both Rf and 4-OHP. The rate of Rf disappearance depends on the concentration of 4-OHP: at concentrations ≥20 mM limited photodegradation occurs due to the quenching of excited singlet Rf, while at ≤5–10 mM triplet Rf is photogenerated and, then, quenched by oxygen, with the concomitant production of $O_2(^1\Delta_g)$, or by 4-OHP, yielding semireduced Rf $Rf^{\bullet-}$ through an electron transfer process. Then, the reaction of $Rf^{\bullet-}$ with dissolved oxygen can produce $O_2^{\bullet-}$ and ground state Rf. As a final result, both 4-OHP and Rf are photodegraded. 4-OHP disappears by oxygenation, and no decomposition was observed in the absence of oxygen. On the contrary, under these conditions Rf photodegradation is favoured, because Rf regeneration via $O_2^{\bullet-}$ production is precluded. Finally, the present results demonstrate that contaminants with the group 4-hydroxypyridine in their structures can be susceptible to photodegradation under usual environmental conditions and in the presence of the dye Rf.

Acknowledgements

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