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Role of micellar inclusion in the photochemistry of 2-pyridyl phenyl ketone. A steady-state and laser flash photolytic study

F. Ortica, F. Elisei and G. Favaro*

Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy

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ABSTRACT: The photochemical behavior of the 2-pyridyl phenyl ketone was studied by stationary techniques in sodium dodecyl sulfate submicellar and micellar solutions. Nanosecond laser flash photolysis was employed to identify the primarily produced transients. The photochemistry is mainly due to fast intramolecular photocyclization, followed by photoaddition of water, with no competition by hydrogen abstraction from the surfactants by the triplet ketone. The intramicellar water molecules are more reactive in photoaddition than bulk water molecules. Transient absorption spectra and lifetimes were determined. By using quenchers which are solubilized in the micelle (biphenyl) or in the bulk water ($CuCl_2$), intra- and extra-micellar processes were characterized. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: 2-pyridyl phenyl ketone; photochemistry; micellar inclusion; steady state; laser flash photolysis

INTRODUCTION

2-Pyridyl phenyl ketone (2-PPK) has been the subject of previous investigations in homogeneous solutions because of its peculiar photochemical behavior[1,2] compared with the 3- and 4-PPK isomers.[3,4] By studying the photochemistry of this molecule in water, ethanol and other organic solvents of different polarity and hydrogen-bonding ability,[2] different photoreaction paths, leading to cyclization and reduction products, have been recognized. The relative contribution of the different pathways to the overall reactivity was found to be governed by the hydrogen-bonding ability of the solvent.

Like the other PPK isomers, 2-PPK can be solubilized in micelles; the partitioning constant between aqueous and micellar phase has been determined spectrophotometrically in sodium dodecyl sulfate (SLS) and Triton X-100 (TX-100) micelles. The values obtained (SLS 1.5×10^4 and TX-100 7.6×10^3 $dm^3\,mol^{-1}$) were very close to those determined for the other isomers.[5]

In this paper, the photochemistry of 2-PPK in micelles was investigated in order to obtain information about the role of inclusion in micelles on the intra- and intermolecular photoprocesses of this molecule and to gain further support for the reaction path proposed previously.

EXPERIMENTAL

Materials. 2-PPK was purchased from Aldrich and purified by recrystallization from light petroleum. $CuCl_2 \cdot 2H_2O$ (BDH) and biphenyl (J. T. Baker) were used without further purification. Trifluoroethanol (TFE) was a Fluka product. The surfactants sodium dodecyl sulfate (SLS) (BDH, specially pure) and Triton X-100 (TX-100) (Fluka) were used as supplied. Values of the critical micellar concentration, cmc (8.0×10^{-3} and 2.6×10^{-4} mol dm^{-3} for SLS and TX-100, respectively), and aggregation numbers, N (62 and 143), were taken from the literature.[6] Doubly distilled water was used.

Equipment and measurement conditions. Absorption spectra were measured on a Perkin-Elmer Lambda 16 spectrophotometer or on a Beckmann DU-7500 diode-array spectrophotometer.

For laser flash photolysis measurements, 347 nm radiation from a ruby laser (J. K. Lasers) was used. The laser energy was less than 10 mJ per pulse; the time resolution was about 20 ns. The expected accuracy in lifetime was within 10%. Spectral and kinetic measurements were carried out using a flow-through the cell system with a ketone concentration of the order of 1.5×10^{-3} mol dm^{-3}. Typically, measurements in micellar solutions were carried out with an occupancy number $n < 1$, in order to ensure preferential mono-occupancy, based on a Poisson distribution. However, some measurements were also carried out at submicellar

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*Correspondence to: G. Favaro, Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.

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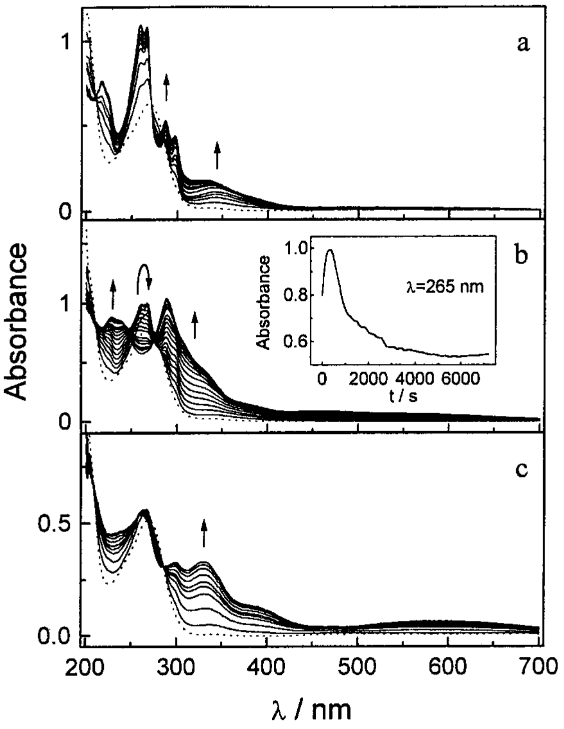


Figure 1. Irradiation time courses (full lines) of air-equilibrated 2-PPK solutions ([2-PPK] = 6.0 × 10^{-5} mol dm^{-3}, cell path 1 cm). (a) [SLS] = 5 × 10^{-3} mol dm^{-3} (submicellar concentration); (b) [SLS] = 2.5 × 10^{-2} mol dm^{-3} ($n = 0.22$); inset, absorbance changes at 265 nm under continuous irradiation; (c) [SLS] = 0.63 mol dm^{-3} ($n = 0.006$). Total irradiation time, 45 min. Dashed lines represent the spectrum before irradiation

surfactant concentration and in micellar solutions with $n > 1$.

Steady-state irradiations of SLS submicellar and micellar solutions of 2-PPK were carried out using the 254 nm light from a low-pressure mercury arc (Mineral Light). The 2-PPK concentration was of the order of 6 × 10^{-5} mol dm^{-3}.

All experiments were performed at room temperature (20 ± 2 °C) using freshly prepared solutions; macroscopic homogeneity of the micellar solutions was obtained by sonication.

RESULTS

Steady-state photolysis

Steady-state photolysis of 2-PPK (6 × 10^{-5} mol dm^{-3}) was carried out in air-equilibrated aqueous solutions containing different amounts of surfactant, [SLS] = 5 × 10^{-3}, 2.5 × 10^{-2}, 0.1 and 0.628 mol dm^{-3}, corresponding to a submicellar concentration solution and micellar solutions with $n = 0.22$, 0.04 and 0.006, respectively (n represents the average of solutes per micelle). The measurement conditions are summarized in Table 1 along with the main-peak wavelengths at the end of irradiation. The spectral variations of 2-PPK solutions under continuous irradiation with 254 nm light were strongly dependent on the surfactant content of the solution. Examples are given in Fig. 1 where the time courses of the spectral changes of 2-PPK at three different SLS concentrations are reported (total irradiation time 45 min).

As can be seen from Figure 1(a) (submicellar SLS concentration), the intensity of the π,π^* band (269 nm) increased, changing into two double-peaked maxima (259–266 and 287–298 nm); two new bands appeared at 216 and 340 nm (broad). Clear isosbestic points were detected at 210, 271 and 285 nm.

In a micellar solution [$n = 0.22$, Fig. 1(b)], the spectral evolution first observed was in the same direction as that described above, but, after a short irradiation time, the isosbestic points were lost and the typical double-peaked bands disappeared. Therefore, in the 260 nm region, an initial increase in absorbance was followed by a decrease [see inset, Fig. 1(b)]. New bands grew at 228 and 288 nm. Moreover, a broad absorption in the visible region ($\lambda_{max} = 450$ nm), hardly detectable in the submicellar solution, increased in intensity.

At higher micellar concentration [$n = 0.006$, Fig. 1(c)], the spectrum showed the main increase in the 300–400 nm region (maxima at 298, 328 and 390 nm). A broad absorption in the visible region was centered at 595 nm.

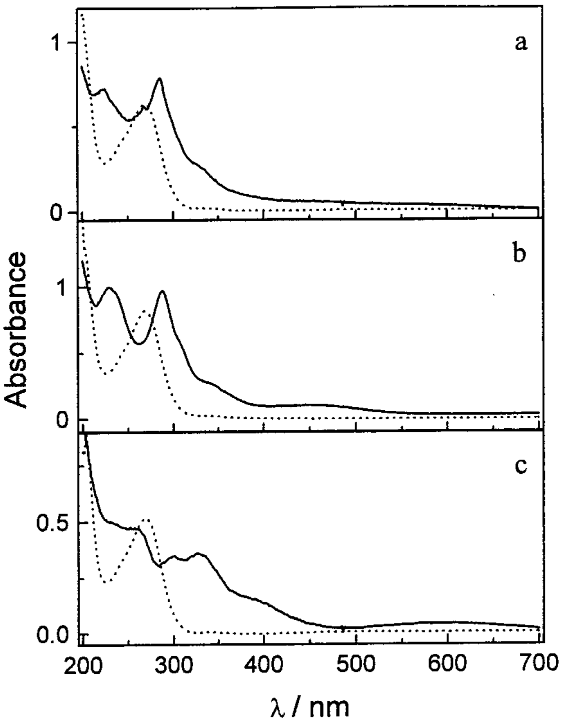


Figure 2. End-of-irradiation spectra (full lines) of air-equilibrated 2-PPK solutions ([2-PPK] = 6.0 × 10^{-5} mol dm^{-3}, cell path 1 cm). (a) [SLS] = 5 × 10^{-3} mol dm^{-3} (submicellar concentration); (b) [SLS] = 2.5 × 10^{-2} mol dm^{-3} ($n = 0.22$); (c) [SLS] = 0.63 mol dm^{-3} ($n = 0.006$). Total irradiation time, 4 h. Dashed lines represent the spectra before irradiation

Table 1. Steady-state irradiation: experimental conditions and end-of-irradiation characteristic peaks observed in aqueous solutions of 2-PPK (6×10^{-5} mol dm^{-3}) containing various amounts of SLS

[SLS] (mol dm^{-3})	n	% mic	$[2\text{-PPK}]_w$	$[2\text{-PPK}]_M/[2\text{-PPK}]_w$	λ_{max} (nm)
5×10^{-3}		0	6×10^{-5}		288
2.5×10^{-2}	0.22	78	1.3×10^{-5}	3.6	288, 450
0.1	0.04	95	0.3×10^{-5}	19	288, 450
0.63	0.006	99.3	0.04×10^{-5}	149	328, 590

If the irradiation was carried out for a longer time (4 h, Fig. 2), the concentrated micellar solution remained almost unchanged [Fig. 2(c)], while the submicellar and dilute micellar solutions tended to similar end-of-irradiation spectra characterized by a prominent peak at 288 nm. The rate of increase of this peak matched the absorbance decrease in the 260 nm region. Evolution in this direction was faster in the dilute micellar solution [Figs 1(b) and 2(b)] than in the submicellar solution [Figs 1(a) and 2(a)].

An absorption spectrum very similar to that in Fig. 2(c) was obtained when a concentrated micellar solution was added to the irradiated sample of Fig. 2(b). Upon 1:3 dilution with water of the irradiated sample of Fig. 2(c), the spectrum became that in Fig. 2(b). However, it was impossible to change the two-peaked spectrum in Fig. 1(a) or (b) into the spectrum of the irradiated micelle-concentrated solution by adding surfactant.

The photochemistry of 2-PPK in pure water was very similar to that at submicellar SLS concentration.

The photochemistry of 2-PPK in pure TFE resembled that in submicellar solution up to the transformation illustrated in Fig. 1(a); further irradiation left the double-peaked spectral pattern unchanged. Only when water was added did the spectrum change toward the end-of-irradiation spectrum with the maximum at 288 nm.

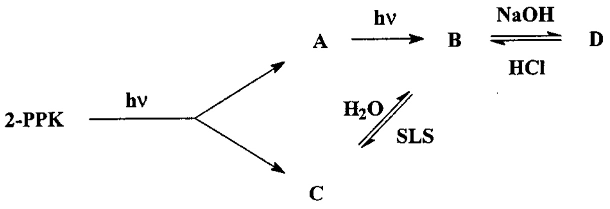
Summarizing, from the steady-state photolysis, three types of absorption spectra were obtained by irradiating 2-PPK in the presence of SLS:

(i) a two-peaked spectrum (A) which appeared in submicellar and dilute micellar solutions after a short irradiation period (also in water and in TFE);[2]

(ii) a spectrum characterized by the 288 nm peak (B), also showing absorptions at higher (228 nm) and lower (450 nm) energies (also in water but not in TFE), derived from the previous one;

(iii) a spectrum which appeared in concentrated micellar solution (C), extending in the UV and visible regions (characteristic peaks: 328 and 595 nm).

The molecular species corresponding to spectra A, B and C are related as shown in Scheme 1.



Scheme 1

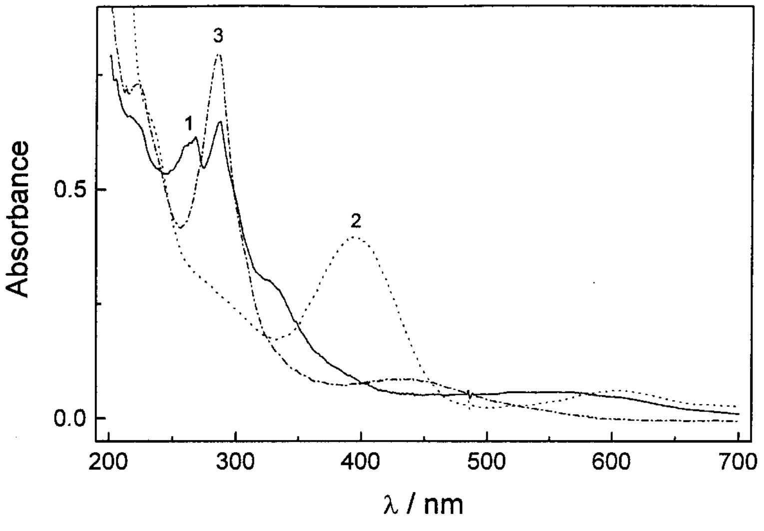


Figure 3. Effect of base and acid addition to a solution containing both A and B. (1) Starting irradiated solution; (2) after addition of concentrated NaOH; (3) after addition of concentrated HCl

Table 2. Spectral and kinetic characteristics of the transients obtained by flashing 2-PPK aerated solutions containing different SLS concentrations.

		T_1 (λ = 320–330 nm)		T_2 (λ = 390–490 nm)		T_3 (λ = 340 nm)
[SLS]	*n*	τ(μs)	k_{ox}(dm^3 mol^{-1} s^{-1})	τ(μs)	$k_{(CuCl_2)}$/(dm^3 mol^{-1} s^{-1})	τ(μs)[a]
0.63	0.15	0.27	3.3×10^9	93	1.3×10^7	
0.1	1.0	0.26		23		24
0.03	4.2	0.26		9.5		11
0.005	Submic.	0.35	2.8×10^9	800		
Water[b]		0.45	3.2×10^9	~600		

[a] Rise time.
[b] In oxygen-free solution; from Ref. 2.

The addition of NaOH to B produced a new absorption (D), characterized by a principal maximum at 393 nm and a weaker band at 605 nm, which reversibly converted to B when $HClO_4$ was added. As shown in Fig. 3 the addition of acid to the alkalinized solution completely suppressed the residual amount of A, present before alkalinization.

Experiments in TFE showed that water was necessary for the process A → B. Reversible conversion B ↔ C indicated that spectra B and C originated from the same chemical species in a different environment: B was in the bulk water, whereas C was enclosed in micelle. The unconvertibility of A to C (or vice versa) indicated that the species corresponding to A was probably a polar one, which, once it had escaped from the micelle, could not reenter to give spectrum C, but proceeded to B. The reversible conversion B ↔ D, when NaOH/HCl was added, indicated an acid–base equilibration.

Nanosecond laser flash photolysis measurements

2-PPK was investigated by nanosecond laser flash photolysis (λ_{exc} = 347 nm) in SLS anionic micelles. Some experiments were also carried out in TX-100 nonionic micelles, where the molecules experience a less polar environment.[5]

Measurements in SLS. Spectra and kinetics of the transients obtained upon flashing 2-PPK aqueous solutions ([2-PPK] = 1.5×10^{-3} mol dm^{-3}) in the presence of SLS were taken at submicellar surfactant concentration and in micelle solution at various micellar concentrations. Oxygen-free and air-equilibrated solutions were investigated. The spectral and kinetic data obtained are reported in Table 2. Time-resolved spectra of the transients obtained from an air-equilibrated micellar SLS solution ([SLS] = 0.03 mol dm^{-3}, *n* = 4.2) of 2-PPK ([2-PPK] = 1.5×10^{-3} mol dm^{-3}) are given in Fig. 4.

The spectral and kinetic behavior upon laser excitation of submicellar solutions ([SLS] = 5×10^{-3} mol dm^{-3}) of 2-PPK is similar to that previously found in pure water.[2] Two transients were observed (first-order decay), a short-lived one, T_1 (τ_1 = 420 ns at 330 nm in an oxygen-free solution, quenching by oxygen, $k_{ox} = 2.8 \times 10^9$ dm^3 mol^{-1} s^{-1}) and a longer-lived one, T_2 (rise-time = 380 ns at 520 nm), mainly absorbing in the visible region (λ_{max} = 400 and 490 nm, τ_2 = 800 μs), which was insensitive to oxygen.

The behavior upon laser excitation of 2-PPK in SLS micellar solution ([SLS] = 0.63 mol dm^{-3}, *n* = 0.15) was similar to that described in submicellar medium, but the lifetime of the longer-lived transient, T_2, was shortened (τ_2 *ca* 100 μs). The decay kinetics were also investigated in the presence of quenchers which were prevalently

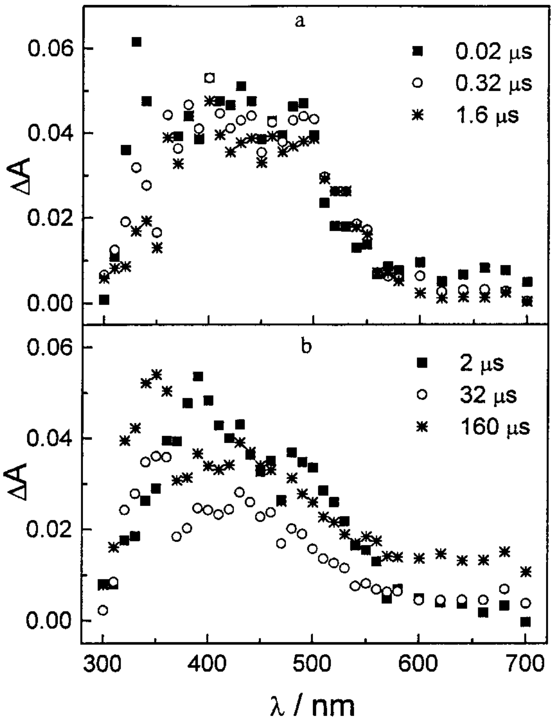


Figure 4. Time-resolved spectra of the transients obtained upon laser excitation (347 nm) of 2-PPK ([2-PPK] = 1.5×10^{-3} mol dm^{-3}) in an air-equilibrated SLS micellar solution ([SLS] = 0.03 mol dm^{-3}, *n* = 4.2). (a) ■, 0.02 μs; ○, 0.32 μs; ⋆, 1.6 μs. (b) ■, 2.0 μs; ○, 32 μs; ⋆, 160 μs

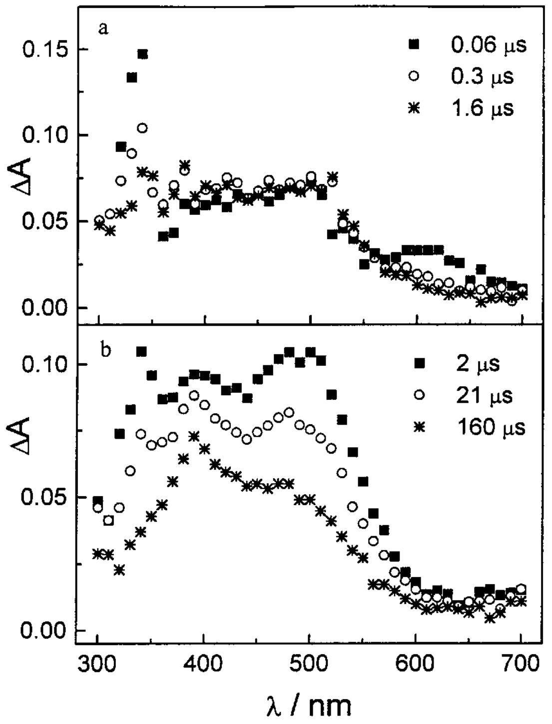


Figure 5. Time-resolved spectra of the transients obtained upon laser excitation (347 nm) of 2-PPK ([2-PPK] = 1.5 × 10^{-3} mol dm^{-3}) in an air-equilibrated TX-100 micellar solution ([TX-100] = 0.41 mol dm^{-3}, $n = 0.54$). (a) ■, 0.06 μs; ○, 0.3 μs; ✱, 1.6 μs. (b) ■, 2.0 μs; ○, 21 μs; ✱, 160 μs

solubilized in the micelle (biphenyl) or in the bulk water ($CuCl_2$) and were essentially transparent at the excitation wavelength (347 nm). Biphenyl, an efficient quencher of triplets,[7] resides predominantly in the micellar pseudophase[8] (>99% with [biphenyl] = 10^{-3}–10^{-2} mol dm^{-3} in a 0.6 mol dm^{-3} SLS solution).[9] The Cu^{2+} ion is an efficient quencher of radicals and dissolves in the water phase and the micellar surface.[10] The addition of biphenyl (3 × 10^{-3} to 10^{-2} mol dm^{-3}) to SLS micellar solutions ([SLS] = 0.63 mol dm^{-3}) of 2-PPK left the T_1 and T_2 lifetimes unchanged. However, sensitization of triplet biphenyl was indicated by the absorbance increase (ΔA) at 370 nm. The sensitization Stern–Volmer constant ($K_{sv} = 88$ dm^3 mol^{-1}), obtained from the relationship $\Delta A^{-1} = \Delta A_{max}{}^{-1}$ $(1 + 1/K_{sv}[\text{biphenyl}])$,[4] indicates a short-lived triplet sensitizer ($\tau \approx 10$ ns). The addition of $CuCl_2$ resulted in a decreased T_2 lifetime (but not ΔA) measured in the visible region ($k_q = 1.3 \times 10^7$ dm^3 $mol^{-1}s^{-1}$).

By decreasing the surfactant concentration in the micellar range, which implies an increased occupation number, a peculiar behavior was observed. The T_2 lifetime decreased further; this decrease was accompanied by an increased absorbance at 340–350 nm (T_3, rise-time matches τ_2), which was stable at least for 1 ms (long-lived transient or photoproduct).

Measurements in TX-100. The first transient, T_1, detected upon laser excitation in a TX-100 ([TX-100] = 0.41 mol dm^{-3}) micellar solution of 2-PPK ([2-PPK] = 1.5 × 10^{-3} mol dm^{-3}, $n = 0.52$) exhibited an absorption peak at 340 nm, an extended absorption within 360 and 510 nm and a low-intensity band at 610 nm. After a few hundred nanoseconds, the 340 and 610 nm bands decreased ($\tau_1 = 0.32$ μs), while the absorption slightly increased at 390 and 520–540 nm (rise-time *ca* 0.4 μs). The spectral evolution within 1.6 μs after the laser shot is illustrated in Fig. 5(a). The subsequent spectral changes [Fig. 5(b)] and kinetics indicated the presence of two other transients: a long-lived one (T_2, $\tau_2 = 120$ μs, $\lambda_{max} = 390$ nm) and a shorter-lived transient (T_3, $\tau_3 = 25$ μs), which absorbed in both the UV ($\lambda_{max} = 340$ nm) and visible ($\lambda_{max} = 490$ nm) regions. In the visible region the decay profile fits a bi-exponential law because the T_2 absorption overlapped the T_3 absorption. Even though it was barely measurable experimentally, the rise time of T_2 (390 nm) was of the same order of magnitude (*ca* 0.2 μs) as that of T_3 (530 nm) and very close to the T_1 lifetime. This means that both T_2 and T_3 originated from T_1. Owing to the shortness of τ_1, the spectra in Fig. 5(b) contained only the absorption contributions from T_2 and T_3; after 160 μs, the spectrum represented substantially the neat absorption of T_2. By subtracting this spectrum from that recorded after 2 μs (no contribution from T_1), the neat absorption of T_3 was obtained (Fig. 6). The T_3 spectrum showed two maxima at 340 and 500 nm. Both T_1 and T_3 were sensitive to oxygen ($k_{ox} = 2.9 \times 10^9$ and 4×10^8 dm^3 mol^{-1} s^{-1}, respectively). Both the T_2 and T_3 lifetimes were quenched by $CuCl_2$ with rate constants of 7.3 × 10^6 and 2.5 × 10^7 dm^3 mol^{-1} s^{-1}, respectively. Adding biphenyl did not affect τ or ΔA of the transients; a slight absorption increase was observed only at 370 nm with a decay time of *ca* 2 μs, presumably due to the biphenyl triplet.[11] The characteristics of the transients obtained are reported in Table 3.

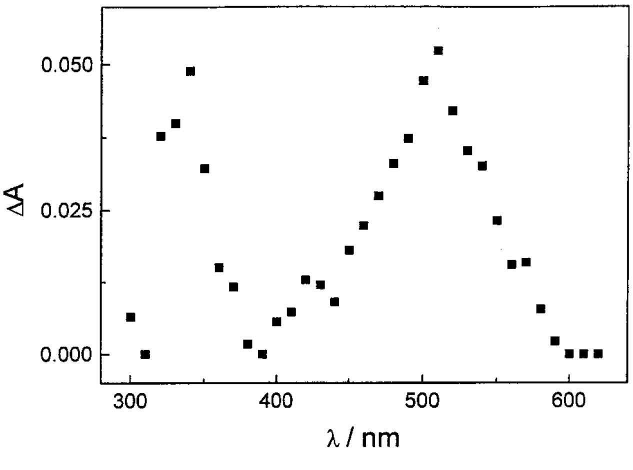


Figure 6. Absorption spectrum of T_3 obtained by subtraction of spectra in Fig. 5(b) (see text)

Table 3. Spectral and kinetic characteristics of the transients obtained by flashing an aerated TX-100 micellar solution ([TX-100] = 0.41 mol dm^{-3}, $n = 0.52$) of 2-PPK

Transient	λ_{max} (nm)	τ (μs)	Effect of quenchers
T_1	340	0.32	$k_{ox} = 2.9 \times 10^9$ dm^3 mol^{-1} s^{-1}
T_2	390	120	$k_{(CuCl_2)} = 7.3 \times 10^6$ dm^3 mol^{-1} s^{-1}
T_3	340	26	$k_{ox} = 4.6 \times 10^8$ dm^3 mol^{-1} s^{-1} $k_{(CuCl_2)} = 2.9 \times 10^7$ dm^3 mol^{-1} s^{-1}
	490	23	$k_{ox} = 3.8 \times 10^8$ dm^3 mol^{-1} s^{-1} $k_{(CuCl_2)} = 2.0 \times 10^7$ dm^3 mol^{-1} s^{-1}

DISCUSSION

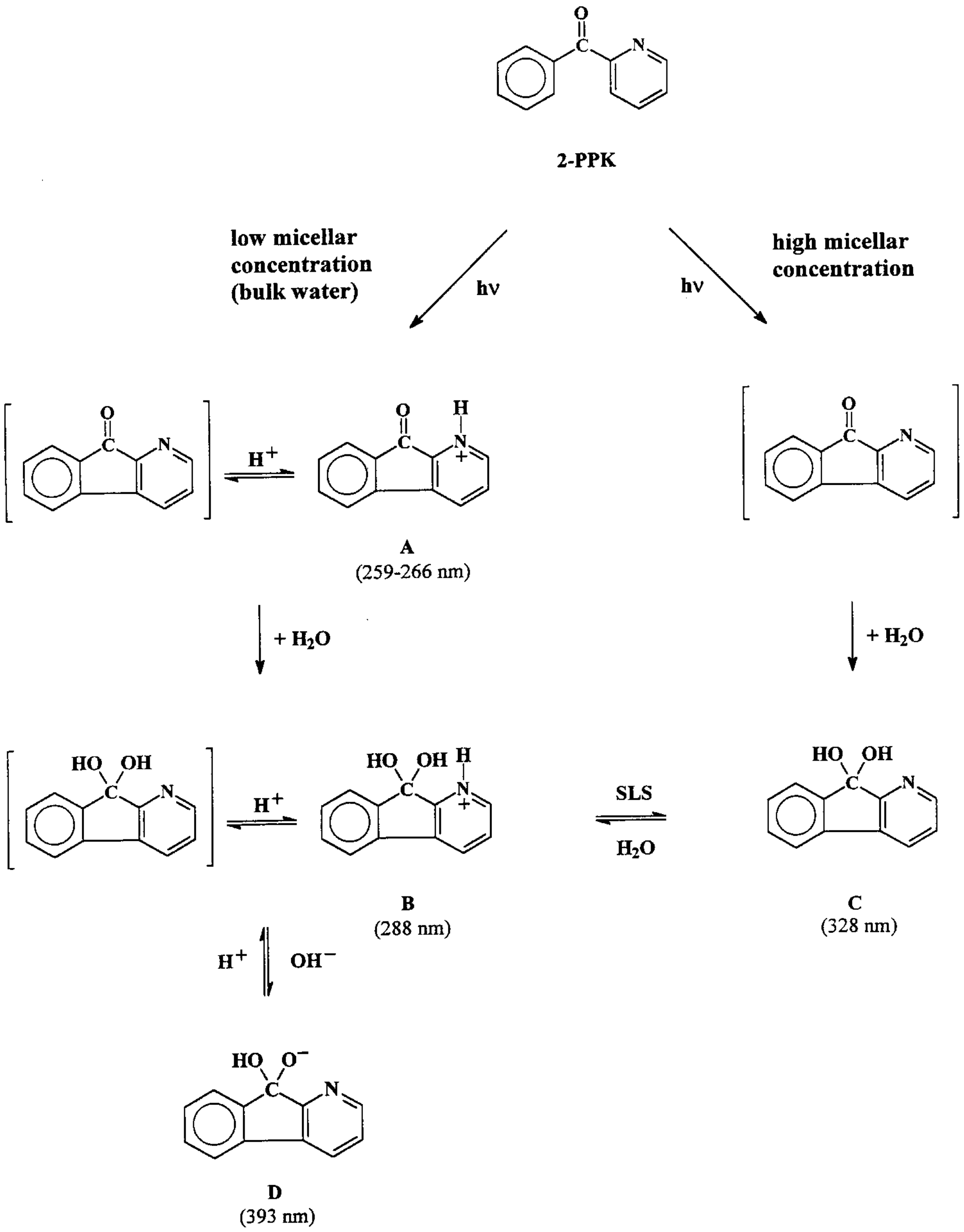
Micellar solutions used in the steady-state experiments were so diluted in 2-PPK (Table 1) as to exclude intramicellar bimolecular interactions. In the flash photolysis experiments, owing to irradiating on the weak n,π^* transition, higher 2-PPK concentrations were used, and therefore the occurrence of bimolecular interactions within the micelle could not be ruled out. The photoreactivity, and therefore the spectral changes, were mainly determined by the distribution of the molecules between the aqueous and micellar phases and the dynamics of entry and exit from the micelle of the species produced.

An assignment of photoproducts is proposed in Scheme 2; species which were not spectrally detected are enclosed in square brackets. As shown in Scheme 2 the most important process was the fast intramolecular reaction of 2-PPK. In this scheme, spectrum A (typical two-peaked band), observed upon a short irradiation of an air-equilibrated submicellar SLS solution or even of a low micelle-concentration solution of 2-PPK, similar to that also found in pure water, was previously assigned to a cyclic ketone.[2] This species is probably in the protonated form when in bulk water, but is deprotonated in the less polar environment of the micelle. Fluorenone-like heterocyclic ketones have in fact been found to exhibit absorptions spreading in the visible region, strongly dependent on pH and solvent.[12] Hydrogen abstraction from the surfactant by the n,π^* triplet ketone, which was found very efficient for the 3- and 4-PPK isomers,[4] was not detected here. This indicates an efficient competition of the intramolecular fast reaction with the bimolecular interaction of the short-lived (picosecond time-scale in water)[2] triplet of 2-PPK.

The subsequent spectral evolution observed in both submicellar and low micelle concentration solutions (spectrum B, 288 nm peak) was also observed in water after a longer irradiation time, but not in neat TFE, indicating that water is involved in the photoreaction. We suggest that B derives from the photoaddition of one water molecule to the carbonyl (Scheme 2). The difference between submicellar and dilute micellar solutions is a faster rate (about fivefold) of B formation in the micellar solution than in the submicellar one (and much more than in water). In a more concentrated SLS solution ([SLS] = 0.63 mol dm^{-3}, $n = 0.006$), where the micellization is 99% and the 2-PPK concentration in the bulk water is of the order of 10^{-7} mol dm^{-3} (as calculated from the partitioning constant, 1.5×10^4 dm^{3}mol^{-1}),[5] the evolution to spectrum C of the irradiated 2-PPK is apparently different. However, the conversion of C to B by dilution with water and of B to C by adding surfactant indicates that the same species is photoproduced in both micelles and water and the spectral differences are due to the different environments. Photoaddition of water to the photoproduced cyclic ketone in micelles, which probably occurs on the unprotonated form, is so fast that the species spectrally detectable is directly the addition product C. While it may be surprising that water adds more easily in the micelle than in the bulk, we believe that water molecules, penetrating into the micelle,[13] are more reactive than bulk water molecules because of the hydrogen-bonded structure in the bulk. This means that the ketone is located in the aqueous Stern region, near the water–micelle interface. In fact, near the micellar surface, a certain ‘porosity’ exists where water molecules penetrate very deeply,[13] up to a distance of four to six carbon atoms.[14] Thus, ‘free’ water molecules can easily add to the carbonyl in the micelle cage. Similarly, the faster rate in submicellar solution than in pure water can be attributed to the ‘structure-breaker’ role played by the surfactant.

The reversible effect of acid/base addition to the irradiated solutions and the new spectrum D observed in very alkaline solution support the hypothesis of the photoproduct structure bearing two basic functions. It can also be observed that in the aqueous (pH $\approx$ 5) irradiated systems (spectrum 1 in Fig. 3), A (259–266 nm) and B (288 nm) are both present with a shoulder at 328 nm; after alkalinization (pH $>$ 10) and re-acidification (pH $<$ 3), the 328 nm absorption disappears. This behavior supports the assignment of the 328 nm peak to a species of intermediate basicity between B and D. This is probably the adduct C which dominates the spectral pattern in SLS concentrated solution [Fig. 2(c)].

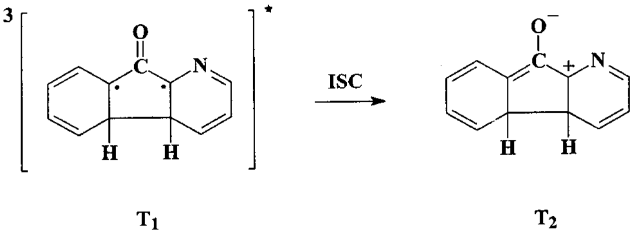
Laser flash photolysis experiments are not easily related to steady-state irradiation experiments, for two reasons. First, owing to experimental requirements, the 2-



Scheme 2

PPK concentration differs by more than two orders of magnitude. Second, the transients detected upon laser excitation, which are the precursors of the species (intermediates and/or final photoproducts) observed under continuous irradiation, may exhibit different affinities towards micelles and may relocate during their lifetime.

The close similarity of the photobehavior of a water solution and a dilute micellar solution at the earliest irradiation times (spectrum A) allows one to hypothesize a reaction mechanism analogous to that proposed in water.[2] The photochemistry originates from the short-lived triplet n,π^* state, which is here revealed indirectly by biphenyl sensitization occurring in the micelle. Sensitization of biphenyl occurs since the triplet energies of 2-PPK[15] and biphenyl[16] match ($E_T \approx 65.5$ kcal mol^{-1}) but the exciting light is only absorbed by 2-PPK. Of the directly detected transients, only T_1 (Table 2) in its kinetics and spectral behavior corresponds well to the transient found in water, which has been assigned to the triplet dihydro derivative (Scheme 3). This species, because of its insensitivity to $CuCl_2$ addition, resides in micelle. By crossing to the singlet state, it yields the dipolar species T_2. However, as shown in Table 2, the lifetime of this transient is much shorter in the micellar solution than in water (which, in turn, is close to a submicellar solution). Since such a dipolar structure would exist almost exclusively in the aqueous pseudo-phase, shortening of its lifetime could be due to some quenching process occurring on (or before) exit from micelle. As shown in Table 2, the quenching is operative in the micellar solutions and becomes more efficient when the micelle concentration decreases (occupation number increases). The increased quenching with decreased micelle concentration can be explained by assuming a quenching process of T_2 by unreacted ground-state ketone in the micelle cage. As the occupation number increases, this process becomes more and more probable, thus reducing the T_2 lifetime. T_3, which clearly derives from T_2, is the quenching (unidentified) byproduct, which is undetectable in concentrated micelle solutions because it is produced in small amounts, but it is indirectly revealed by the ΔA (330 nm) decrease when $CuCl_2$ is added. In the submicellar medium, where the cage effect does not occur, the T_2 lifetime is of the same order of magnitude as in the absence of surfactant.



Scheme 3

The behavior in TX-100 shows some analogies, even if not supported by results under continuous irradiation, since steady-state irradiation experiments were not performed owing to the appreciable absorption of the 254 nm light by the surfactant. The first transient T_1 is the same as in previous cases, that is, a triplet species, as proven by oxygen quenching. Subsequently, the production of T_3 (typical absorption with two maxima at 340 and 490 nm, $\tau \approx 25\ \mu s$), which has previously been assigned to a radical derived from TX-100,[4] indicates an interaction of the surfactant with T_1. Since T_1 is a triplet, hydrogen abstraction from the surfactant is the process most likely to occur. We recall that TX-100 is a more efficient hydrogen donor than SLS,[4] where this process was not detected.

CONCLUSIONS

The peculiar behavior of 2-PPK, compared with the 3- and 4-PPK isomers, is demonstrated by the results of this work. The surfactant concentration in submicellar medium, which was high enough to cause interaction with the 3- and 4-PPK triplets yielding hydrogen abstraction,[4] has no effect on either the photochemistry or the dynamics of the transients involved in the 2-PPK photolysis, apart from a slight reduction in the time required for the water photoaddition reaction. Even in micellar solution, where the interaction of the triplet ketone with the surfactant should increase because of the vicinity effect, the monomolecular process is by far preferred.

The photochemistry of 2-PPK in the presence of surfactant does not substantially differ from the photochemistry in water. This is due to the very strong reactivity of its n,π^* triplet state in hydrogen-bonding media which competes efficiently with other photophysical processes or bimolecular interactions. Thus, the first reaction step is the same in micellar medium as in water, because the ketone is enclosed in a micellar site where the carbonyl is exposed to interaction with water. The effect of the microheterogeneous system is mainly reflected in the decay dynamics of the transients which are photoproduced and the rate of water photoaddition. The cage effect is responsible for the quenching process observed in micelles and is particularly evident under the high occupation number conditions of the laser experiments. The interstitial water affects the rate of photochemistry by rapid addition to the first observed metastable species.

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