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The Photochemistry of 1-Azaxanthone in Aqueous Solutions and in Micellar Environments

L. J. Martínez and J. C. Scaiano*

Department of Chemistry, University of Ottawa Ottawa, Ontario, Canada K1N 6N5

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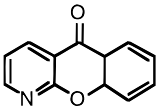
The reactivity and spectroscopic characteristics of the 1-azaxanthone triplet state in aqueous solutions indicate that inversion of states in the triplet manifold occurs in this solvent. Both the reactivity and spectroscopy of 1-azaxanthone suggest a predominantly π,π^* character for the lowest triplet state in aqueous solutions, in contrast with organic solvents where 1-azaxanthone has n,π^* character, even in polar media. The pH-dependent properties of the 1-azaxanthone triplet and its ketyl radical were examined. Despite the high reactivity of 1-azaxanthone toward photoreduction in organic solvents, in micellar systems the generation of ketyl radicals is inefficient. Studies of magnetic field effects on radical-pair behavior reveal similar characteristics to those observed with other carbonyl compounds, where geminate reaction and micellar exit are competing processes.

The photochemical behavior of aromatic compounds in aqueous solutions can sometimes be quite different from that observed in organic solvents. For example, photoionization becomes an important photochemical pathway in a highly polar environment such as water, and several aromatic compounds are known to yield hydrated electrons by either monophotonic or biphotonic mechanisms.[1−5] One major factor that limits photochemical studies of organic compounds in aqueous solutions is their poor solubility in this medium, despite its unique properties and obvious biological relevance.

We had previously reported the photochemical and photophysical properties of 1-azaxanthone in organic solvents.[6] Part of our interest in this ketone reflects its potential use as a probe to study guest/host interactions and radical-pair dynamics in supramolecular systems.



1-Azaxanthone

1-Azaxanthone proved to be efficiently photoreduced; its photoreduction rate is at least an order of magnitude faster compared to the rates of other related ketones such as xanthone or benzophenone.[6] Furthermore, it is sparingly soluble in water thus making it an attractive molecule for the study of radical-pair dynamics and magnetic field effects in micellar environments.

1-Azaxanthone has two basic sites (i.e., the pyridyl nitrogen and the carbonyl oxygen).[7] This allows for potential differences in the photochemical and spectroscopic properties of its different prototropic species; both factors are extremely important to consider when working in aqueous environments. We report here on the photochemical and photophysical properties of 1-azaxanthone in aqueous solutions and in micellar systems, as well as the entry−exit dynamics for micelles of different sizes. The photochemical properties of the protonated (i.e., pyridinium cation) form of 1-azaxanthone have also been examined. These studies provide the basis for its potential application in other supramolecular systems such as cyclodextrins, zeolites, or clays.

Experimental Section

1-Azaxanthone was purchased from Lancaster and recrystallized twice from ethanol. Water was purified through a Millipore Milli Q system and used for the preparation of all buffers and solutions. All other chemicals were of the highest purity available and used as received. The different buffers (25 mM) employed in these studies were acetate buffer (pH 3−4), citrate/phosphate buffer (pH 5−6), and phosphate buffer (pH 7−8). Sulfuric acid and sodium hydroxide were employed for the more acidic or basic range, respectively.

The laser system consists of a Surelite laser from Continuum for the 355 nm Nd:YAG wavelength and a Molectron UV-24 nitrogen laser for 337 nm. All pulse durations are <10 ns and typical pulse energies lie between 5 and 50 mJ. The signals from the monochromator/photomultiplier system are initially captured by a Tektronix 2440 digitizer and transferred to a PowerMacintosh computer that controls the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier.[8,9]

Fluorescence emission and excitation spectra were recorded with a Perkin-Elmer LS-50 spectrofluorimeter while absorption spectra were measured with a Cary 1E UV−visible spectrophotometer. Fluorescence lifetimes were determined at 90° excitation with the third harmonic (i.e., 355 nm) of a Continuum pulsed picosecond Nd:YAG laser and detection of the fluorescence using a Hamamatsu C-4334 Streak Camera. Further details can be found elsewhere.[10]

Results and Discussion

A. Aqueous Solutions or Binary Solvent Mixtures. *Absorption, Fluorescence, and Phosphorescence Emission.* Small differences in the ground state absorption spectrum for 1-azaxanthone in water and acetonitrile were observed (spectra not shown). For example, in acetonitrile the absorption maxima were at 282 and 329 nm while in water they shifted to 284 and 335 nm. The absorption maxima in formamide coincided with those observed in aqueous solutions. We expected primarily an n,π^* character for the longer wavelength absorption of this ketone, but these results suggest considerable contributions and/or

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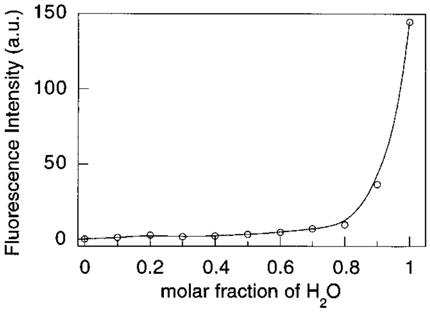

Figure 1. Changes in the fluorescence intensity (at 415 nm) of 1-azaxanthone in acetonitrile/water solvent mixtures. Excitation at 330 nm.

mixing with π,π^* transitions based on the polarity-dependent shifts for the absorption maxima.[11] In the binary (acetonitrile/water) solvent mixtures, the ground-state absorption spectrum at mole fractions of acetonitrile = 0.4 (spectra not shown) resembled that of the pure aprotic solvent.

We also examined the photophysical properties of the excited singlet state of 1-azaxanthone in solution using both steady-state and time-resolved fluorescence. No steady-state fluorescence emission was detected in acetonitrile while a broad, structureless band centered at 415 nm was observed in water (Φ_{flu} = 0.012).[12] The steady-state detection of fluorescence emission from 1-azaxanthone in water was shown to be partly due to the differences in τ_{flu} between water and organic solvents.[6] On the basis of the values obtained for the absorption extinction coefficients in aqueous vs organic solvents, a change in the oscillator strength for these transitions was proposed to account for the lack of fluorescence emission in organic solvents.[6]

Figure 1 shows the changes in the fluorescence intensity as a function of the mole fraction of water in acetonitrile/water solvent mixtures.[13] A fluorescence emission centered at 415 nm was detected in all the binary mixtures whose intensity increased linearly up to 0.8 mole fraction of water. A sharp increase in the intensity was observed in the water-rich region. The changes observed correlate with the changing polarizability for these solvent mixtures. The fluorescence lifetimes in water and D_2O were the same within experimental error and consistent with the proposal that specific solvent–solute interactions (i.e., specific H-bonding interactions between water and 1-azaxanthone) do not play a key role.

The absorption spectrum of 1-azaxanthone showed no significant changes within pH 2–10. The only spectral changes occurred in the region between 200 and 230 nm but the quality of the data gathered in this region did not allow us to determine the ground-state pK_a from absorption measurements. No shifts in the fluorescence maximum nor significant changes in the fluorescence intensity were observed within this pH interval. This was expected since in water τ_{flu} showed no variation with pH in the range from pH 2–11 [τ_{flu} = (216 ± 20 ps)].[14] However, under strongly acidic conditions (i.e., 1N H_2SO_4), we observed a 50% reduction in the emission intensity accompanied by a 25 nm red shift (i.e., λ_{max} = 430 nm; see Figure 2). This emission is assigned to the fluorescence from the pyridinium cation of 1-azaxanthone.

Delayed fluorescence and room-temperature phosphorescence are common phenomena for other ketones and benzoylpyridines.[15] The room-temperature emission of 1-azaxanthone decreases by ~50% in the presence of air. The low-temperature phosphorescence spectrum of 1-azaxanthone in a 2:1 ethylene glycol/water glass (Figure 3) suggests that the symmetry of the lowest triplet state has acquired a significant π,π^* character.[16] In fact, the carbonyl vibrational structure is somewhat lost and the lifetime of this phosphorescence emission has increased by more than 100-fold with respect to that observed in nonaqueous media.[17] Therefore, the well-known inversion of states that occurs for xanthone in moderately polar solvents is also observed with 1-azaxanthone although it seems to require far more polar conditions.[8,18] The polarity-dependent changes in the fluorescence intensity shown in Figure 1 imply that, in order to observe this inversion and/or mixing between n,π^* and π,π^* states in either the singlet or the triplet manifold (vide infra), the macroscopic dielectric constant must be >60. Therefore, we propose that in water the lowest triplet state of 1-azaxanthone has predominant π,π^* character. On the basis of the onset for the room-temperature fluorescence emission and low-temperature phosphorescence in aqueous media, we estimate an S–T energy gap of ~ 6 kcal mol^{-1}.

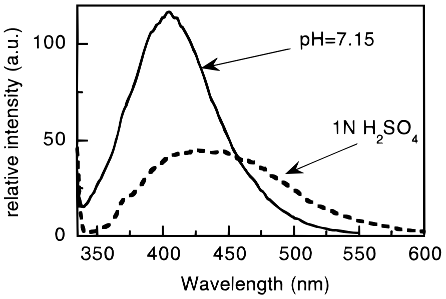

Figure 2. Fluorescence emission spectra of 1-azaxanthone in 25 mM phosphate buffer at pH 7.15 and in 1 N H_2SO_4. Excitation at 280 nm.

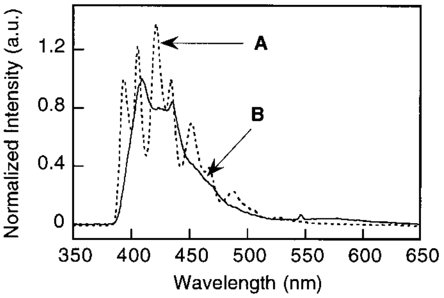

Figure 3. Low-temperature (77 K) phosphorescence emission of 1-azaxanthone in an (A) ethanol glass or in a (B) (2:1) ethylene glycol/water glass. Excitation at 330 nm.

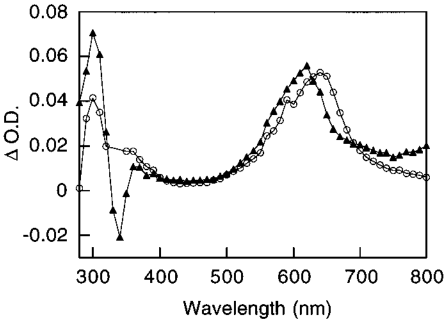

Figure 4. Transient absorption spectra for 1-azaxanthone in acetonitrile (○, 1.1 μs after the pulse) and in 25 mM phosphate buffer saline at pH 7 (▲, 1.3 μs after the pulse).

Laser Flash Photolysis. The T–T absorption spectra of 1-azaxanthone in acetonitrile (λ_{max} = 640 nm) and in 25 mM phosphate buffer saline at pH 7 (λ_{max} = 620 nm) are shown in Figure 4. In most hydroxylic organic solvents, the reactivity of the 1-azaxanthone triplet toward H-atom abstraction made its detection difficult with our nanosecond apparatus. Low-tem-

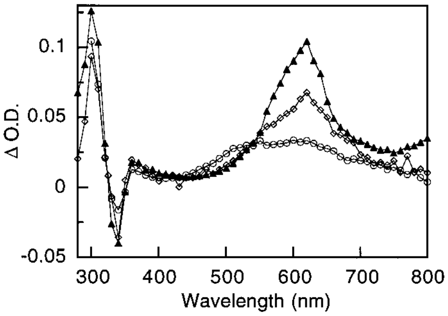

Figure 5. T-T absorption spectra for 1-azaxanthone at pH 2 (○, 72 ns after the pulse), pH 7 (▲, 0.56 μs after the pulse) and pH 12 (◇, 44 ns after the pulse).

perature phosphorescence measurements revealed that the lowest excited triplet state had n,π* character regardless of solvent polarity ($\epsilon \leq 36$) in contrast to the structurally related ketone, xanthone, which shows π,π* character in most media, except hydrocarbons and some halogenated solvents.[19] The large shifts in the T−T absorption spectra of xanthone with solvent polarity have been widely used as a sensor in supramolecular systems.[10,20] The T−T absorption of 1-azaxanthone does not show such large shifts except when working in aqueous media where the lowest triplet state has π,π* character (vide supra).

The observation of a detectable fluorescence emission from 1-azaxanthone in aqueous solutions implied the possible reduction in its intersystem-crossing quantum yield (Φ_{isc}). Optically matched samples of benzophenone (for which $\Phi_{ISC} = 1.0$) and 1-azaxanthone in 20:80 (% by volume) acetonitrile/H_2O mixtures were used for the Φ_{isc} determinations.[21] 1-Naphthalenemethanol was used as a convenient water-soluble triplet energy acceptor by monitoring its T−T absorption at 420 nm. The concentration of acceptor employed (5 mM) was enough to ensure that >98% of the triplets were quenched by energy transfer. The Φ_{isc} values obtained in 80% aqueous solutions ($\Phi_{isc} = 0.80 \pm 0.02$) and organic media (in acetonitrile, $\Phi_{isc} = 0.82 \pm 0.04$) are the same within experimental error. The low Φ_{flu} value for 1-azaxanthone in aqueous solution showing just a 1.2% efficiency for this photoprocess (vide supra) is consistent with this result; the efficiency of intersystem crossing and/or internal conversion as deactivating channels for the first excited singlet of 1-azaxanthone are thus not significantly affected, although the relative rates of these deactivation pathways must vary in view of the longer excited singlet state lifetime in water.[22]

The triplet absorption spectra for 1-azaxanthone at different pH (Figure 5) showed considerable broadening upon protonation of the pyridyl nitrogen (pH < 2). At pH 2, the rate constants obtained from a biexponential fit of the triplet decay monitored at 600 nm were $k_1 = 1.0 \times 10^7$ s^{-1} and $k_2 = 3.5 \times 10^6$ s^{-1}; both the neutral and cationic forms of the 1-azaxanthone triplet contributed to the observed spectrum. In unbuffered aqueous solutions, the rate of decay of the 1-azaxanthone triplet was 50 times slower. The decay of the 1-azaxanthone triplet was monitored as a function of pH (Figure 6), allowing us to obtain a pK_a value of 2.3 for the 1-azaxanthone triplet state. For comparison, the triplet state pK_a of 3-benzoylpyridine has been reported to be 3.7.[23] The increase in the rate of decay at pH 2 must reflect the fast protonation of the triplet and the inherently short lifetime of the triplet pyridinium cation.

The triplet lifetime of ketones in solution can be controlled by self-quenching. We had previously shown that for 1-azaxanthone this process occurs at rates ~10^9 M^{-1} s^{-1} in organic solvents; similar rate constants have been observed for xanthone.[6,8] In aqueous solutions or binary solvent mixtures containing water as cosolvent, the rates of self-quenching (30 μM to 100 μM) were only 2-fold higher than those obtained in organic solvents (see Table 1). A plot of the rate of triplet decay vs increasing H_2O mole fraction in acetonitrile/water mixtures showed a nonlinear dependence upon reaching the water-rich region (Figure 7). The rate of triplet decay decreases upon increasing the concentration of water, which could be interpreted as resulting from protection of the triplet carbonyl by hydrogen-bonding interactions. Under all conditions the decay of the 1-azaxanthone triplet was monoexponential. We note, though, that the increase in the rate of triplet decay and increase in the fluorescence intensity occurred at the same molar fraction of water. It is likely that the 1-azaxanthone triplet lifetime is influenced by the changing polarizability of the medium in a similar way as the singlet state (vide supra); i.e., by increasing the mixing of states having n,π* and π,π* character.

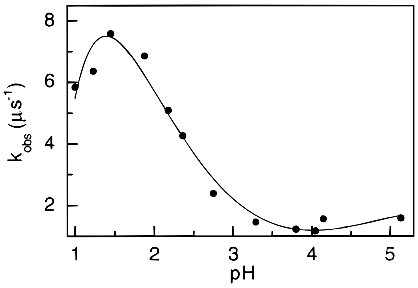

Figure 6. pH-dependence for the triplet lifetime of 1-azaxanthone in aqueous solutions.

TABLE 1: Triplet Lifetimes and Self-Quenching Rate Constants for 1-Azaxanthone in Aqueous Environments

solvent	τ_0 (ns)	k_{sq} (M^{-1} s^{-1})
acetonitrile	7350	1.5×10^9
acetonitrile/water (1:1)	13220	1.7×10^9
water	16620	2.0×10^9
water (pH 2)	154	negligible
water (pH 13)	<10	not measured
D_2O[a]	21570	2.5×10^9
0.2 M SDS	2230	5.9×10^9

[a] Solutions contained 5% by volume of acetonitrile.

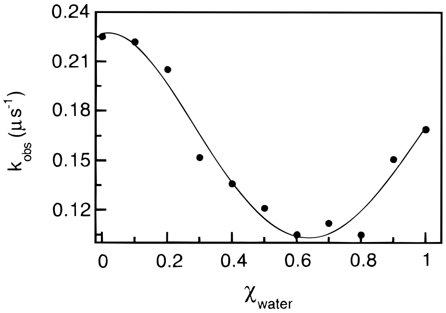

Figure 7. Dependence of the 1-azaxanthone triplet decay on solvent composition in acetonitrile/water mixtures.

One of the most remarkable properties of the 1-azaxanthone triplet is its high reactivity toward photoreduction in organic solvents. Changes in the polarity and protic character of the medium do not affect its efficiency to undergo energy transfer reactions. For example, quenching of the 1-azaxanthone triplet by sorbic acid or 1-naphthalenemethanol are only 3-fold lower compared to quenchers with the same functionality in organic solvents. However, its tendency to undergo photoreduction in aqueous solutions is considerably lower; the photoreduction of the 1-azaxanthone triplet by 2-propanol in water (5.2 × 10^5

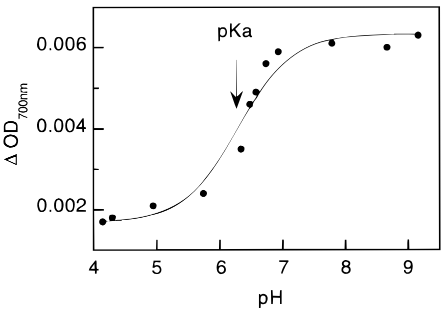

Figure 8. Changes in the transient absorption at 700 nm as a function of pH showing the pK$_a$ of the 1-azaxanthone ketyl radical.

M^{-1} s^{-1}) is 36-fold slower compared to acetonitrile and 2 orders of magnitude slower than in CCl_4. This correlates with the change in the nature of the lowest triplet state which changes from having n,π* character in solvents of low or intermediate polarity to having π,π* character in a very polar solvent like water. Charge-transfer quenching of the 1-azaxanthone triplet is also reduced by an order of magnitude.[24]

We attempted to examine the reactivity of the 1-azaxanthone pyridinium cation toward hydrogen-abstraction using 2-propanol as a hydrogen donor and H_2SO_4 to lower the pH. The presence of a protonated heterocyclic nitrogen should have the same effect as an electron withdrawing substituent, thus making the carbonyl site more electrophilic. The rate of triplet decay at pH 2 did not vary even at a 1 M concentration of 2-propanol which would suggest that the triplet pyridinium cation has little tendency toward H-atom abstraction. This supports the idea that the protonated 1-azaxanthone triplet also has π,π* character.

The equilibrium between the ketyl radical and ketyl radical anion resulting from the photoreduction of 1-azaxanthone was studied in solutions containing 2 M 2-propanol and monitoring at 700 nm where the ketyl radical anion has a stronger absorption.[6] A pK_a of 6.3 ± 0.3 was determined for the 1-azaxanthone ketyl radical (Figure 8). Our experimental approach was tested determining the pK_a of the ketyl radical of benzophenone obtaining a value of 9.4 ± 0.3, which is in close agreement with the value (i.e., 9.2) determined by pulse radiolysis.[25] We tried to determine the pK_a of the ketyl radical of xanthone using the same experimental approach, but the triplet carbonyl of xanthone was quite unreactive toward H-atom abstraction under these conditions, thus preventing us from generating and adequate radical concentration.

B. Micellar Systems. *Absorption and Fluorescence Emission.* Our studies in binary solvent mixtures served as the basis for understanding the photophysical properties of 1-azaxanthone in supramolecular systems. The values reported for the effective dielectric constant of SDS micelles varies from 32 to 51, depending on the location of the probe molecule employed for these determinations.[26] Even if alcohol/water mixtures provide a better model for the micellar interface, the efficient photoreduction of the 1-azaxanthone triplet by simple alcohols did not allow us to employ these binary systems. We chose to work in acetonitrile/water mixtures since the dielectric constant also changes within the range of 32−80.[26]

The ground-state absorption spectra for 1-azaxanthone in aqueous solutions and in 0.1 M SDS were identical confirming the lack of specific interactions between the surfactant and the ground state of this ketone. The fluorescence emission of 1-azaxanthone was not affected by the surfactant if its concentration was kept below the CMC. A decrease in the emission intensity was observed at concentrations of SDS above its CMC; this was clearly related to the aggregation of the surfactant to form micelles and the incorporation of the ketone into these structures. In fact, the fluorescence lifetime determined in 0.1 M SDS was 78 ps. The decrease in τ_{flu} is ascribed to a change in the location of 1-azaxanthone into regions of lower local microscopic polarity. The τ_{flu} value in the SDS micelles is lower compared to τ_{flu} in aqueous solutions but larger than the one obtained in organic solvents, suggesting that this probe could localize preferentially at the micellar interface (i.e., Stern layer), or that entry rates are competitive with singlet decay.

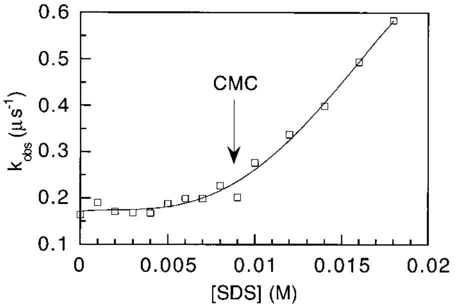

Figure 9. Decay of the 1-azaxanthone triplet as a function of surfactant concentration.

TABLE 2: Quenching of the 1-Azaxanthone Triplet by Different Donors/Acceptors in Aqueous Solutions

quencher	solvent	k_q (M^{-1} s^{-1})
sorbic acid	water	3.7×10^9
1-naphthalenemethanol[a]	water	5.0×10^9
oxygen	water	1.9×10^9
2-propanol	water (pH 7)	5.2×10^5
SDS	water	(8.4×10^6)[b]
CTAC	water	(4.2×10^7)[b]
biphenyl[a]	0.2 M SDS	(2.1×10^9)[b]
1,4-cyclohexadiene	0.2 M SDS	(8.1×10^8)[b]

[a] Triplet state of the quencher was detected. [b] The system is microheterogeneous.

Laser Flash Photolysis. We were initially discouraged by the lower reactivity of 1-azaxanthone toward photoreduction in aqueous solutions and by the fact that the T−T absorption maximum was not shifted in the presence of micelles, a property that makes xanthone a very useful probe.[10,27] Nonetheless, the triplet decay was affected by micelle formation suggesting that this probe could reside and/or interact with the micelle (Figure 9) and that this interaction leads to quenching of the excited triplet state. We used hydrophobic quenchers that would localize preferentially inside the micelle to probe in this way the accessibility of 1-azaxanthone triplet into these supramolecular systems.

The data in Table 2 clearly show that 1-azaxanthone is able to sensitize the formation of the biphenyl triplet efficiently and must therefore be present somewhere in the micelle. Furthermore, the apparent rate of self-quenching of the 1-azaxanthone triplet in the SDS micelles is almost 3-fold larger compared to aqueous solutions (Table 1) which points out to a redistribution favoring the micellar phase as previously suggested. Interestingly, the lifetime of the 1-azaxanthone triplet extrapolated to zero ketone concentration is considerably shorter than for xanthone but considerably longer compared to benzophenone.[28] We attribute this result to a larger mobility for this probe which probably exchanges between the aqueous and micellar phases (vide infra).

Another way to examine the partitioning of 1-azaxanthone between the micelles and the external aqueous medium is by looking at the dynamics for micellar exit and the association constant of the triplet excited molecule with micelles of different

TABLE 3: Kinetic and Equilibrium Parameters for the Exit and Entry of 1-Azaxanthone in Different Micelles

surfactant[a]	k_- (s^{-1})	k_+ (M^{-1} s^{-1})	K_{assoc} (M^{-1})
SDeS (0.2 M)	9.0×10^6	1.0×10^{10}	1160
SDS (0.2 M)	9.6×10^6 5.5×10^{6b}	3.4×10^{10}	3500
SDS (0.5 M)[c]	5.5×10^6	8.6×10^9	1550
STDS (0.01 M)	4.3×10^6	5.0×10^{10}	11630
CTAC (0.05 M)	2.4×10^6	2.0×10^{11}	82000

[a] Abbreviations: SDeS, sodium decyl sulfate; SDS, sodium dodecyl sulfate; STDS, sodium tetradecyl sulfate; CTAC, cetyl hexadecylammonium chloride. [b] Value determined using a micellized quencher (biphenyl), see text. [c] At this SDS concentration the micelles formed are rod shaped, not spherical.

sizes. Our approach consisted in using a water-soluble quencher (i.e., $NaNO_2$ for negatively charged micelles and $CuSO_4$ for positively charged micelles) under conditions that would make the exit of the triplet 1-azaxanthone the rate-limiting step.[10,28] The results presented so far suggest that 1-azaxanthone is locating in the micelle (vide supra), thus the following kinetic scheme applies:

$$AZX_M \xrightarrow{h\nu} {}^1AZX_M \xrightarrow{ISC} {}^3AZX_M \tag{1}$$

$$^3AZX_M \xrightarrow{1/\tau_0\ (k_0)} AZX_M \tag{2}$$

$$^3AZX_M \underset{k_+}{\overset{k_-}{\rightleftharpoons}} {}^3AZX_W + M \tag{3}$$

$$^3AZX_W + Q_W \xrightarrow{k_q} AZX_W + Q_W \tag{4}$$

where AZX is 1-azaxanthone, the subscripts M or W are used to specify the location of the probe in the aqueous phase or the micelle, and Q is the water-soluble quencher. The observed rate of decay of the 1-azaxanthone triplet will then be given by eq 5.

$$k_{exp} = k_0 + \frac{k_- k_q[Q]}{k_q[Q] + k_+[M]} \tag{5}$$

The conventional approach for the determination of the association constants and rates of micellar entry and exit is by rearranging eq 5 into its reciprocal form (eq 6).

$$\frac{1}{k_{exp} - k_0} = \frac{1}{k_-} + \frac{k_+[M]}{k_- k_q[Q]} \tag{6}$$

Plots of $(k_{exp} - k_0)^{-1}$ vs [Q] at a given surfactant concentration were linear, and the results obtained using this approach with water-soluble quenchers are listed in Table 3 for surfactants of various chain lengths and charges at the polar headgroup. It can be seen that there is good correlation between the rate of micellar exit and the size of the micelle. The large k_- values compared to other ketones indicate that this probe is very dynamic and that, in the absence of any quenching event, the 1-azaxanthone excited triplet state is able to visit several micelles before decaying. The known limitations in the use of an aqueous quencher to estimate exit rate constants[28] prompted us to employ an alternate method using the triplet energy transfer to biphenyl as the acceptor. This approach assumes that the quenching of the 1-azaxanthone triplet occurs when the probe "visits" the micelle and therefore energy transfer will occur with a 100% probability. Using this method[29] we obtained an exit rate constant of 5.5×10^6 s^{-1} from the SDS micelles. Combining this value with the known τ_0 of the triplet 1-azaxanthone, one can estimate that the 1-azaxanthone triplet will on the average visit ∼10 micelles before decaying, thus emphasizing the dynamic nature of this probe.

Just as in the case of benzophenone, the ketyl radical yield derived from hydrogen abstraction from the surfactant was very low. The transient absorption spectra in micellar systems revealed the formation of another species absorbing between 350 and 450 nm which did not decay within the detection limits of our nanosecond system (∼200 μs).[30] The absorption maximum for this long-lived intermediate could not be determined due to the overlapping ground-state photobleaching of 1-azaxanthone. This transient probably results from ring coupling products, of the type frequently described as LATs (for light-absorbing transients).[31]

The behavior of triplet-derived radical pairs in micelles is normally controlled by the competition between micellar exit and geminate reaction.[31−34] The rate determining step of the latter is spin evolution to a singlet radical-pair that can yield nonradical products in a fast (spin allowed) process. Application of an external field leads to splitting of the triplet sublevels and as a result a slow of intersystem crossing. As a consequence of this, radical exit from the micelle is favored by external fields.

To study the magnetic field dependent radical-pair dynamics, the usual approach is to add a hydrogen donor (e.g., 1,4-cyclohexadiene) to increase the yield and rate of formation of ketyl radicals and easily monitor their absorption either in the UV or visible region.[31] For 1-azaxanthone in 0.2 M SDS, the triplet lifetime in the absence of an added hydrogen donor is 570 ns. By adding 50 mM of 1,4-cyclohexadiene (an excellent hydrogen donor),[35] the triplet lifetime of 1-azaxanthone decreased to 32 ns. However, this was accompanied by a decrease in the absorption of the triplet suggesting that the diene could also be quenching the excited singlet state. Time-resolved experiments revealed that the lifetime of the excited singlet state of 1-azaxanthone was not altered by the presence of 1,4-cyclohexadiene (i.e., ∼78 ps in 0.2 M SDS with or without added diene) but the intensity of the emission was significantly decreased suggesting that static quenching was occurring. We hypothesize that the 1,4-cyclohexadiene is effectively quenching that fraction of the probes localized within the micelle at the time of excitation and this will show up experimentally as "static" quenching, therefore affecting the intensity but not the lifetime of its fluorescence emission. This would explain the decrease in the intensity of the T−T absorption and the small yield of ketyl radicals generated even in the presence of an added H-atom donor. Hydrogen abstraction would then predominantly involve triplet states that enter the micelle after intersystem crossing.

We monitored the absorption of the small fraction of ketyl radicals generated at 550 nm. Our results show that upon application of an external magnetic field the amount of ketyl radicals that are able to escape from the micelle increases (Figure 10). In the absence of an external field, the sum of the rates of escape and ISC was obtained from the decay part of the trace for the signal monitored at 550 nm yielding a value of 7.0×10^6 s^{-1}, which, based on the usual kinetic analysis, leads to a rate of escape of 2.4×10^6 s^{-1} and an intersystem-crossing rate of 4.6×10^6 s^{-1} for the 1-azaxanthone ketyl-cyclohexadienyl radical-pair.[31] These results demonstrate that the dynamics of the radical-pair resulting from the photoreduction of the 1-azaxanthone triplet in SDS micelles shows a similar behavior

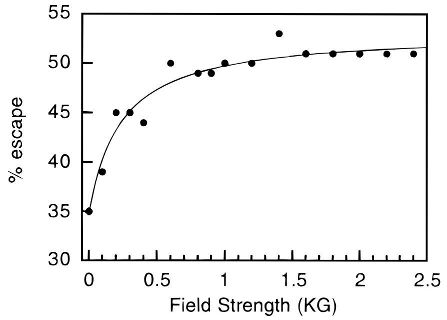

Figure 10. Fraction of 1-azaxanthone ketyl radicals that escape geminate recombination as a function of external magnetic field strength.

as other carbon-centered radicals in the presence of an external magnetic field, with competing exit and spin evolution processes.

Conclusions

Polarity dependent inversion of states in the singlet and triplet manifold of 1-azaxanthone has been observed in aqueous solvents mixtures with a large macroscopic dielectric constant ($\epsilon > 60$). This inversion results in a lower reactivity for the primarily π,π^* triplet state of 1-azaxanthone in aqueous solutions. 1-Azaxanthone fluoresces significantly only in aqueous solvents, a property that may be useful as a probe in aqueous supramolecular systems. The reactivity toward hydrogen abstraction is considerably moderated in water, reflecting an inversion of states leading to a π,π^* triplet state for aqueous media with dielectric constants above 60.

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