Photochemistry and Photophysics of 1-Azaxanthone in Organic Solvents

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The photochemical and photophysical properties of 1-azaxanthone have been studied to determine its usefulness as a probe for polarity, reactivity, and/or radical pair dynamics in supramolecular systems. Contrary to the behavior of xanthone, a structurally related ketone, the triplet−triplet absorption spectrum of 1-azaxanthone does not present polarity-induced shifts in its maximum despite its n,π* character. Self-quenching is a remarkably fast process that occurs at nearly diffusion-controlled rates. Nevertheless, the reactivity of 1-azaxanthone toward hydrogen atom abstraction in polar media is by far superior compared to the reactivities of other aromatic ketones. This property results from the unaltered n,π* triplet character as a consequence of the presence of a pyridine ring and makes it a convenient probe for the study of radical pair reactions and guest/host interactions in highly polar microheterogeneous systems.

Numerous carbonyl compounds have been employed as probes in organized and supramolecular systems.[1] Their spectroscopic properties and diverse photoreactions have allowed their use to test properties such as polarity, mobility, and reactivity of the host systems. Quite frequently, the use of ketones has also assisted the study of the behavior of free radicals in these environments.[1−6] Among the carbonyl compounds frequently used as probes, xanthone (**I**) has found a number of applications. Excitation of xanthone leads to a triplet state which can be easily monitored in laser flash photolysis experiments.[7,8] The triplet−triplet absorption spectrum of xanthone shifts significantly with changes in the solvent or environment polarity.[1,8] This characteristic has found a number of applications in the study of supramolecular systems.[1,9−11] In addition to the properties already mentioned, the xanthone triplet and the corresponding ketyl radicals show significant differences in their absorption spectra, in contrast with other systems, such as benzophenone, where the differences are much smaller.[12,13]

We have found in our work that aromatic ketones provide a convenient way of generating radical pairs through their photoreduction by either the host (e.g., the surfactant in the case of micelles) or an added hydrogen donor.[13] Radical pairs are a subject of continuing interest in supramolecular chemistry because the competition between separation and reaction of the geminate radical pair can determine the final products of the reaction.[2] Xanthone, being a convenient probe in other aspects, photoreduces very inefficiently in polar environments, as a result of a low-lying π,π* triplet state under these conditions.[8]

In the case of benzophenones, it is known that replacing a phenyl for a pyridyl ring can change and usually enhance their reactivities toward radical-like reactions, such as hydrogen abstraction.[14−18] We thought that if a similar structure dependence also applied to the xanthone moiety, it would be possible to develop a probe bearing some of the convenient properties that characterize xanthone, but with an enhanced reactivity toward hydrogen transfer. Thus, we reasoned that 1-azaxanthone (**II**) could be a good choice for this purpose.

I   **II**
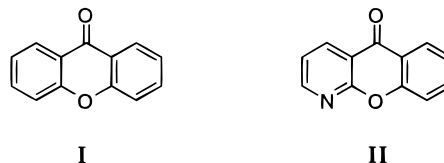
To our surprise, we were unable to locate any reports on the photophysics or photochemistry of 1-azaxanthone. Our results, which combine product studies, emission spectroscopy, and laser flash photolysis, confirm our expectation that the 1-azaxanthone triplet would be a good hydrogen abstractor; in fact, under most experimental conditions, it is an exceptionally efficient one. Further, some of its other physical properties, such as its modest solubility in aqueous solution and its ease of incorporation into supramolecular systems (such as zeolites), make it an attractive molecule for the study of guest/host interactions. While this article concentrates on a detailed report on the photochemistry and photophysics of 1-azaxanthone, much of this work has been stimulated by the potential applications of this molecule as a probe for other studies.

Experimental Section

1-Azaxanthone (Maybridge) was recrystalized from ethanol. Solvents were usually Omnisolv (spectro grade when available) and were used as received. All other chemicals (1-methylnaphthalene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, triethylamine, and tributyltin hydride, all from Aldrich) were of the highest purity available and were used as received.

Emission spectra were recorded with a Perkin-Elmer LS-50 spectrofluorimeter. Fluorescence quantum yields were determined using 2-aminopyridine in 1 N H_2SO_4 as standard. Optically matched solutions at the excitation wavelength (i.e., 280 nm) having absorbances of less than 0.1 in a 1 cm^2 fluorescence cell were always employed. Fluorescence lifetimes were measured exciting with the third harmonic (i.e., 355 nm) of a YAG-pulsed picosecond laser system and a Hamamatsu Streakscope as detector. In most solvents the solutions had to
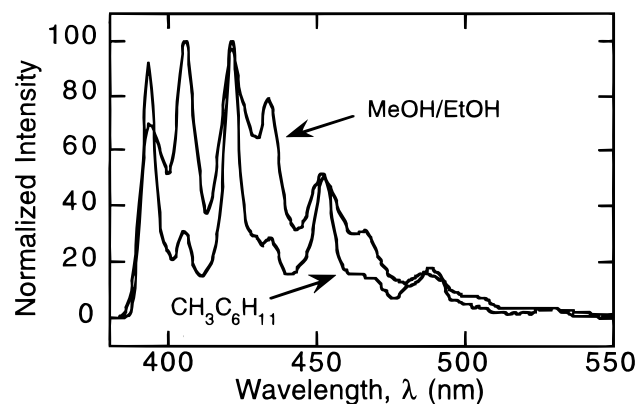
Photoproperties of 1-Azaxanthone in Organic Solvents

J. Phys. Chem. A, Vol. 102, No. 35, 1998 **6899**

Figure 1. Phosphorescence from 1-azaxanthone at 77 K in methylcyclohexane and methanol−ethanol glasses. Excitation was at 330 nm.

TABLE 1: Fluorescence Emission Parameters for 1-Azaxanthone in Different Solvents[a]

solvent	λ_{max} (nm)	τ_{flu} (ps)	Φ_{flu}
cyclohexane	395	<35	c
CHCl₃	b	b	b
acetonitrile	395	<35	c
methanol	395	<35	c
ethanol	395	<35	c
formamide	400	<35	c
H₂O	415	171 ± 7	0.012
D₂O	415	172 ± 7	0.011

[a] Emission spectra were recorded exciting at 280 nm, and excitation spectra were always measured at the fluorescence maximum in each solvent. [b] Fluorescence was not detected in this solvent even with picosecond time scale resolution. [c] With picosecond resolution, detection of a short-lived emission was achieved. However, since under steady-state conditions no fluorescence was detected, the quantum yields were not determined.
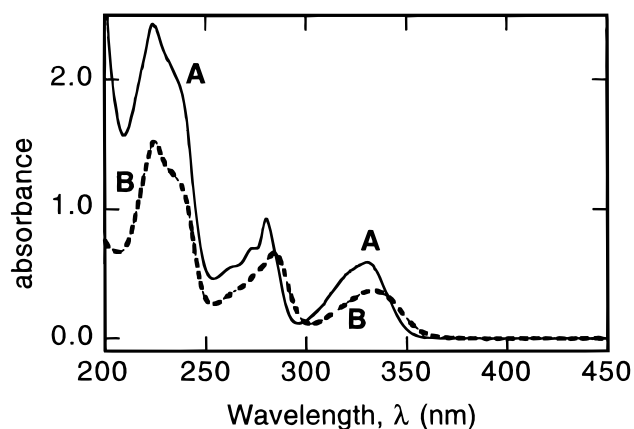
be flowed through a 7×7 mm² cell since the photoproducts resulting from the photoreduction of 1-azaxanthone were strongly fluorescent. Absorption spectra were measured with a Cary 1E spectrophotometer.

The nanosecond laser flash photolysis system used 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.[8,19]

Results

This section is divided according to the methodology employed in each case. When possible, the data are compared with those for xanthone.

Phosphorescence. The phosphorescence of 1-azaxanthone can be readily detected in glasses at cryogenic temperatures. Figure 1 shows the emission spectra recorded in methylcyclohexane and ethanol−methanol (4:1) glasses at 77 K. The characteristics of the spectra, such as their good vibrational resolution (corresponding to a carbonyl vibrational spacing of ~1670 cm⁻¹) and short lifetime (~2 ms in both glasses), are indicative of a low-lying n,π* state in both glasses. Surprisingly, there is no blue shift of the spectrum between nonpolar and polar media, a characteristic frequently observed for n,π* triplet states; it is possible that enhanced solvation at the pyridyl site in the excited state somewhat compensates for the usual shift. The 0,0 band at 393.5 nm corresponds to a triplet energy of 72.7 kcal/mol, a value quite similar to that for xanthone itself. Phosphorescence excitation spectra were in good agreement with the absorption spectra of 1-azaxanthone.

Fluorescence. 1-Azaxanthone shows no steady-state fluorescence emission in organic solvents due to the extremely short lifetime of its excited singlet state (Table 1). A very weak fluorescence emission centered around 415 nm is observed only in aqueous solutions (spectrum not shown). The ground-state absorption spectra of 1-azaxanthone in ethanol and in water are shown in Figure 2. The extinction coefficients determined in ethanol solutions were $\epsilon_{329nm} = 6640$ L mol⁻¹ cm⁻¹ and $\epsilon_{280nm} = 10730$ L mol⁻¹ cm⁻¹. In water, both bands undergo a 4-nm red shift ($\epsilon_{333nm} = 3890$ L mol⁻¹ cm⁻¹ and $\epsilon_{284nm} = 6900$ L mol⁻¹ cm⁻¹). These results indicate a change in the oscillator strength for these transitions when the solvent is water. From

Figure 2. Ground-state absorption spectra for 1-azaxanthone in ethanol (A) and water (B).

these values, we determined that the radiative rate in aqueous solutions is ~40% slower compared to that in organic media. The fluorescence excitation and ground-state absorption spectra coincided in both H₂O and D₂O. Thus, in principle, the detection of fluorescence emission from 1-azaxanthone could be monitored and employed as a reporter of the microenvironment in which this probe is located when working in supramolecular systems, such as micelles, liposomes, unactivated zeolites and cyclodextrins.[20]

Laser Flash Photolysis. Among the laser wavelengths available in our laboratory, 308, 337, and 355 nm proved to be quite suitable for excitation of 1-azaxanthone in solution. Unless otherwise indicated, experiments were carried out with the 337-nm pulses from a nitrogen laser. Figure 3 shows spectra recorded in acetonitrile and in carbon tetrachloride, both solvents where the triplet state is rather long-lived. The triplet lifetimes determined for these and other solvents are listed in Table 2. The reported lifetimes correspond to those expected in the absence of self-quenching (vide infra), and we note that they depend strongly on the reactivity of the 1-azaxanthone triplet toward the solvents. In the case of xanthone, solvent changes lead to significant changes in the position of the triplet absorption maximum.[8] Such changes are not present in the case of 1-azaxanthone, although the spectral width changes (wider in nonpolar solvents) in much the same way as with xanthone.

Addition of hydrogen donors or excitation of 1-azaxanthone in hydrogen-donating solvents leads to a new spectrum which we assign to the corresponding ketyl radical, **III**. Figure 4
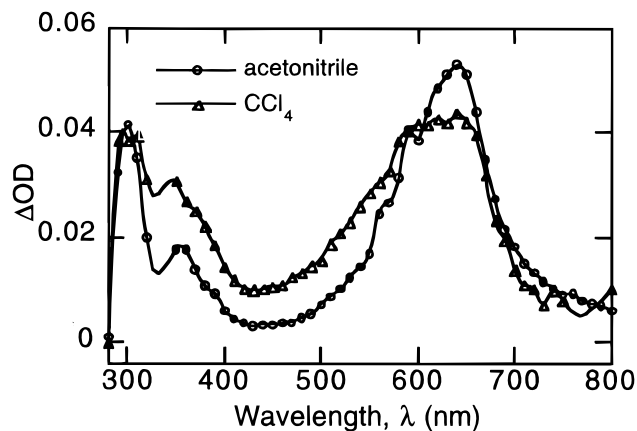
Figure 3. Triplet−triplet absorption spectra for 1-azaxanthone in acetonitrile and in carbon tetrachloride at room temperature. Laser excitation was at 337 nm.

TABLE 2: Triplet State Lifetimes and Rate Constants for Self-Quenching of Xanthone and 1-Azaxanthone at Room Temperature

substrate	solvent	τ_0 (ns)	k_{sq} (M^{-1} s^{-1})	ref
I	acetonitrile	8300	4.5×10^8	8
I	methanol	1300	2.1×10^8	8
II	acetonitrile	7350 ± 20	$(1.55 \pm 0.07) \times 10^9$	this work
II	CCL$_4$	4400 ± 200	$(2.4 \pm 0.2) \times 10^9$	this work
II	methanol	60 ± 2	$(2.0 \pm 0.1) \times 10^{10}$	this work
II	ethanol	<10	a	this work
II	2-propanol	<10	a	this work
II	benzene	27 ± 5	$(2.5 \pm 0.2) \times 10^{10}$ ^{b}	this work
II	heptane	40 ± 5	c	this work
II	cyclohexane	<10	a	this work

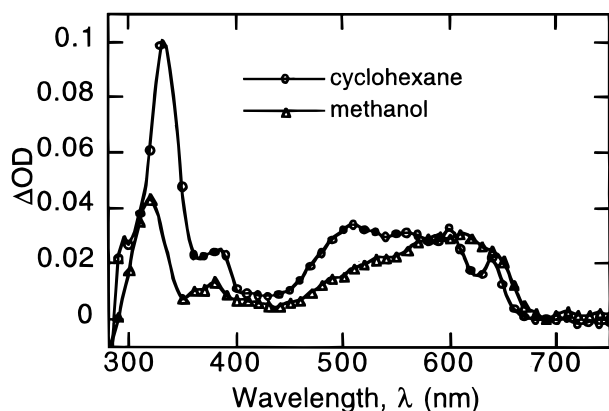^{a} Not measured. ^{b} Error could be as large as 30%. ^{c} See text.

Figure 4. Transient spectra recorded for 1-azaxanthone in cyclohexane and in methanol, 0.16 and 0.56 μs following 337-nm laser excitation. The signals are assigned to the ketyl radical **III**.

shows spectra recorded in methanol and in cyclohexane, both solvents in which the photoreduction occurs readily. For example, in the case of methanol
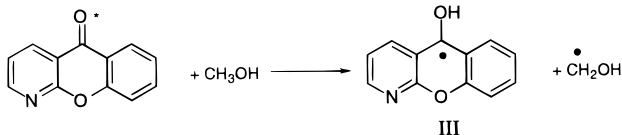
Interestingly, at around 680−700 nm ketyl radicals are transparent, while the ketone triplet (compare Figures 3 and 4)
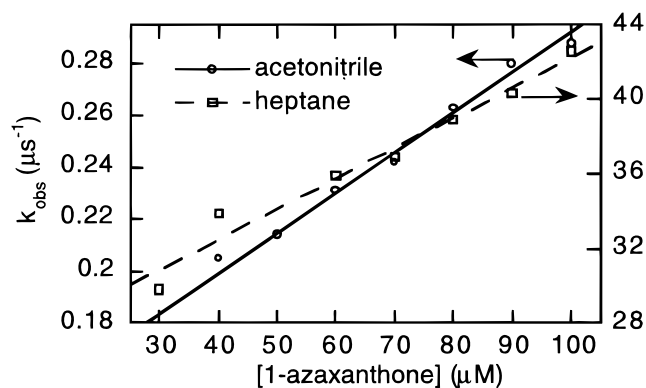

Figure 5. Self-quenching plot for 1-azaxanthone in *n*-heptane (□) and acetonitrile (○).

TABLE 3: Rate Constants for Energy Transfer between Triplet 1-Azaxanthone and Representative Energy Acceptors at Room Temperature

solvent	acceptor	k_q (M^{-1} s^{-1})
carbon tetrachloride	1,3-cyclohexadiene^a	$(7.6 \pm 0.1) \times 10^9$
acetonitrile	1-methylnaphthalene^b	$(1.50 \pm 0.04) \times 10^{10}$
acetonitrile	oxygen^c	1.2×10^{10}

^{a} Quencher concentration was varied from 0 and 1.3 mM. ^{b} Detection of the 1-methylnaphthalene triplet evidenced an energy-transfer process. Quencher concentrations in the range from 0 to 0.6 mM were employed. ^{c} This value was estimated on the basis of the known solubility of oxygen in acetonitrile.[36]

has a significant absorption. This permits the selective monitoring of the triplet state in this spectral region.[21]

We mentioned earlier that self-quenching can play an important role in determining the kinetics of triplet decay in unreactive solvents. To study this process, we examined the lifetimes of 1-azaxanthone triplets at low laser doses and as a function of the concentration of **II** (i.e., between 30 and 100 μM), as shown in Figure 5; the rate constants for self-quenching, k_{sq}, are given by the slopes of these plots. Low laser doses (i.e., less than 3 mJ/pulse at the sample holder) are preferred in order to minimize any interference from triplet−triplet annihilation. Table 2 compares self-quenching rate constants for xanthone and 1-azaxanthone in methanol and acetonitrile. We note that triplet lifetimes and rates of self-quenching are unusually large in some solvents (vide infra).

The rate constants for triplet energy transfer between 1-azaxanthone and representative triplet quenchers were determined from the slopes of plots of the rate constants for triplet decay as a function of quencher concentrations. These plots were linear and led to the rate constants given in Table 3; the values are fully consistent with energy transfer, as is the detection of triplet 1-methylnaphthalene[22,23] by laser flash photolysis. Similarly, in the case of oxygen quenching,[24] singlet oxygen phosphorescence (vide infra) was detected, as expected for a triplet sensitizer.

Quenching of excited triplets by oxygen leads to variable yields of singlet oxygen ($^1\Delta_g$) formation. These quantum yields (Φ_Δ) can be determined by monitoring the phosphorescence from singlet oxygen at 1.27 μm. In this case, we monitored this emission for oxygen-saturated solutions of **I** and **II** in acetonitrile, using phenazine, for which the yield of singlet oxygen is well established, as a reference.[25] Further details on the technique can be found elsewhere.[26] The results obtained, along with literature values for other representative carbonyl compounds, have been included in Table 4. These quantum

Photoproperties of 1-Azaxanthone in Organic Solvents

J. Phys. Chem. A, Vol. 102, No. 35, 1998 **6901**

TABLE 4: Quantum Yields for Singlet Oxygen Formation in the Quenching of Carbonyl Triplets by Oxygen in Acetonitrile

compound	Φ_Δ	S_Δ	ref
xanthone	0.26	0.27	this work
1-azaxanthone	0.30	0.36	this work
benzophenone	0.35	0.35	25
phenazine[a]	0.83	0.98	26

[a] Reference compound.
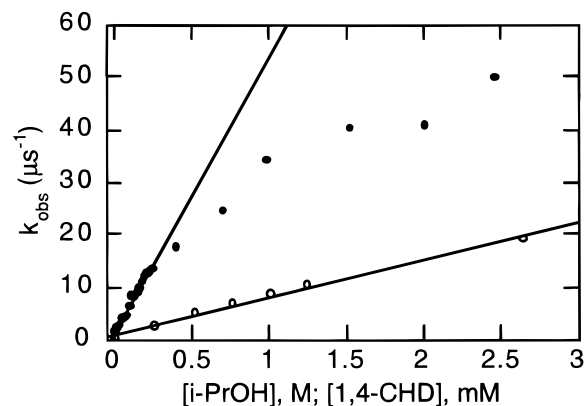
Figure 6. Effect of hydrogen atom donor concentration on the decay of the 1-azaxanthone triplet. (○) 1,4-CHD, (●) 2-propanol.

yields can be transformed into efficiencies (S_Δ) with which the triplet states produce singlet oxygen if the quantum yields of intersystem crossing (Φ_{ISC}) are known, eq 1.

$$S_\Delta = \Phi_\Delta/\Phi_{ISC} \tag{1}$$

The corresponding values of S_Δ are also given in Table 4. In the case of 1-azaxanthone, where Φ_{ISC} was not known, it was determined as indicated below.

The quenching of triplet 1-azaxanthone by 1-methylnaphthalene leads to the detection of the triplet state of the latter. These signals were monitored at 420 nm (near the absorption maximum) and are proportional to Φ_{ISC} if the experiment is carried out under conditions of near-quantitative triplet quenching by the acceptor. From the data in Tables 2 and 3, it can be calculated that 0.01 M 1-methylnaphthalene should be sufficient to intercept >98% of the triplets in acetonitrile. The signals due to triplet 1-methylnaphthalene were compared with those for samples containing 1-azaxanthone and benzophenone (as sensitizers) of matched absorbance at the laser wavelength (337 nm) and containing 0.01 M 1-methylnaphthalene. Since Φ_{ISC} = 1.0 for benzophenone, the value for other sensitizers can be determined. For 1-azaxanthone, we obtained $\Phi_{ISC} = 0.82 \pm 0.04$ in acetonitrile.

The triplet state of 1-azaxanthone proved to be an excellent hydrogen abstractor. For example, 1,4-cyclohexadiene, a good hydrogen donor, quenches the triplet state with a rate constant of 9.6×10^9 M^{-1} s^{-1} in acetonitrile. Figure 6 shows plots of the rate constants for triplet decay as a function of hydrogen donor concentrations; the rates of hydrogen abstraction are given by the slopes of these plots. The measurements were performed at 700 nm, where the triplet signals, while weak, can be monitored without interference from the ketyl radical absorptions (vide supra). The spectrum recorded in the presence of 1,4-cyclohexadiene following triplet decay agrees well with that for the ketyl radical (see Figure 4), thus confirming that quenching involves hydrogen transfer to the carbonyl group.[27]

TABLE 5: Rate Constants for the Quenching of 1-Azaxanthone Triplets by Various Hydrogen/Electron Donors at Room Temperature

quencher	solvent	k_q (M^{-1} s^{-1})
1,4-cyclohexadiene	acetonitrile	$(9.6 \pm 0.5) \times 10^9$
2-propanol	water	$(5.2 \pm 0.2) \times 10^5$
2-propanol (c → 0)	acetonitrile	$(1.9 \pm 0.1) \times 10^7$
2-propanol	CCl$_4$	$(5.3 \pm 0.3) \times 10^7$
cyclohexane	acetonitrile	$(1.03 \pm 0.02) \times 10^7$
cyclohexane	CCl$_4$	$(1.88 \pm 0.04) \times 10^7$
Bu$_3$SnH	acetonitrile	$(2.8 \pm 0.3) \times 10^9$
triethylamine	acetonitrile	$(1.07 \pm 0.05) \times 10^{10}$
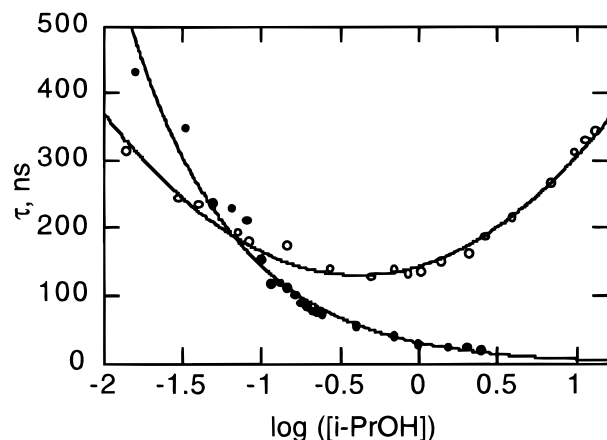
Figure 7. Effect of solvent composition on the lifetime of the triplet state of xanthone (○) and 1-azaxanthone (●) in carbon tetrachloride/2-propanol mixtures.

Several other hydrogen donors were also examined, and the corresponding rate constants are listed in Table 5. We note that several of the short lifetimes listed in Table 2 (particularly those for alcohols) are also controlled by hydrogen abstraction from the solvent.[28]

In the case of xanthone, we reported an unusual effect in the triplet quenching by 2-propanol in carbon tetrachloride.[8] At low alcohol concentrations, addition of 2-propanol leads to a decrease in the triplet lifetime; however, as more alcohol is added, the effect reverses and eventually the lifetime of triplet xanthone gets longer with further increases in the quencher concentration. The lifetime reaches a minimum at ca. 0.6 M 2-propanol; this relationship is reproduced in Figure 7 and detailed experimental results are available in an earlier publication.[8] A similar set of experiments was performed with 1-azaxanthone, but in this case no inversion is observed, although the plot is linear for 2-propanol only at concentrations below 0.25 M (see Figures 6 and 7). The rate constant given in Table 5 corresponds to the value at very low concentrations, as illustrated in Figures 6 and 7.

Quenching by triethylamine is also quite rapid, as shown by the rate constants in Table 5. In nonpolar solvents the behavior parallels that of 1,4-cyclohexadiene and other hydrogen donors; i.e., on the nanosecond time scale, one detects formation of ketyl radicals that appear to occur concurrently with triplet decay. In contrast, in polar media, such as acetonitrile, triplet decay leads to the formation of a new transient with absorptions at longer wavelengths, as illustrated in Figure 8. These spectral observations are characteristic of aromatic ketone radical anion formation. These intermediates are usually red-shifted with respect to the corresponding triplet states and ketyl radicals. It is very likely that a similar process takes place in nonpolar solvents
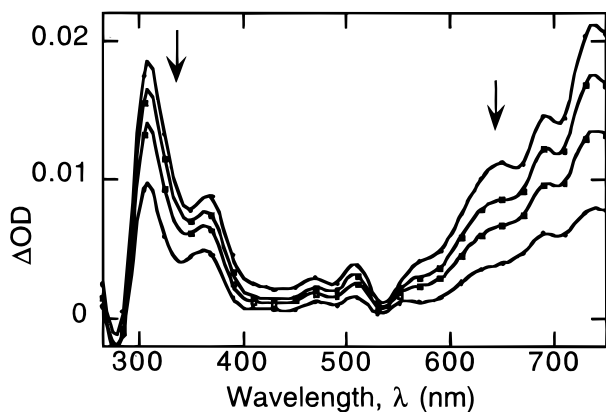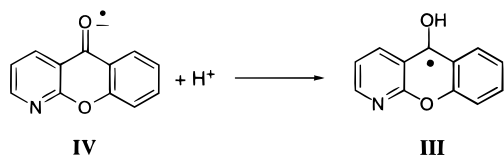
6902 *J. Phys. Chem. A, Vol. 102, No. 35, 1998*

Scaiano et al.

Figure 8. Transient spectra following 337-nm excitation of 1-aza-xanthone in acetonitrile containing 0.12 mM triethylamine. The different spectra correspond to 5, 18, 34, and 68 μs following laser excitation.

where it is likely followed by rapid proton transfer to yield the corresponding neutral ketyl radical,

Discussion

It is interesting to compare the similarities and differences between xanthone and 1-azaxanthone. Such differences are reflected in their spectroscopy and reactivity and will clearly influence their applications as probes or radical photoinitiators.

Xanthone has a highly reactive n,π* triplet state only in extremely nonpolar media, such as in dry alkanes, where it abstracts hydrogen atoms readily. In polar media, hydroxylic or not, or in supramolecular systems such as micelles,[29] cyclodextrins,[9,11,30] or zeolites,[31] xanthone has a low-lying π,π* triplet with little tendency toward hydrogen abstraction. In contrast, 1-azaxanthone shows an n,π* triplet state in polar and nonpolar media. For example, the phosphorescence spectra and lifetimes (see Figure 1) are fully consistent with this assignment, including a vibrational spacing of $\sim$1670 cm^{-1}, consistent with a C=O vibrational frequency.[32] In this sense, 1-azaxanthone resembles benzophenone more than xanthone.

1-Azaxanthone shows fluorescence emission under steady-state conditions only in aqueous solutions. In organic solvents, the very short lifetime of its fluorescence emission prevents its steady-state detection. In addition, the spectral shifts and changes in extinction coefficients determined in water and organic media suggest that radiative rates are slower in aqueous solutions. Recently, the polarity-dependent ultrafast intersystem crossing kinetics of xanthone were reported.[33] For this ketone, solvent polarity affects the relative energies of the $\pi\pi$* electronic states and this in turn controls both the rates of internal conversion and intersystem crossing. Although for 1-azaxanthone there is no solvent-dependent state inversion in the triplet manifold, we hypothesize that a similar stabilization of the $\pi\pi$* transitions in a highly polar solvent like water could affect the relative contribution of these two nonradiative processes to the decay of the 1-azaxanthone singlet excited state.

The reactivity of the 1-azaxanthone triplets toward hydrogen donors (see Table 5) usually exceeds that of benzophenone, frequently by about an order of magnitude. This characteristic is probably a reflection of the higher excitation energy of

1-azaxanthone, coupled with the reactivity enhancement antici-pated by introducing a pyridine ring.

The efficiencies of singlet oxygen formation by energy transfer (see Table 4) are in line with typical values for ketones in this range ($\sim$70 kcal/mol) of triplet energies.[24] The fact that the values for xanthone and 1-azaxanthone are quite close confirms that the nature of the excited state (n,π* or π,π*) is not the key factor controlling the singlet oxygen generation efficiencies.[24,34] We note also that the rate of quenching by oxygen is extremely fast, approximately corresponding to the maximum 4/9 of diffusion-controlled limit, consistent with singlet and triplet encounters leading to triplet-state deactivation.

Triplet quenching by typical energy acceptors, such as 1,3-cyclohexadiene and 1-methylnaphthalene, are in line with rate constants measured for other ketones, typically falling slightly below the diffusion limit.

Self-quenching is a remarkably fast process, even in com-parison with xanthone (see Table 2). In most organic solvents, the triplet lifetimes were very short (i.e., in *n*-heptane $\tau_0 = 40$ ns and in cyclohexane it could not be resolved with our nanosecond system). The determination of self-quenching rates and τ_0 values was complicated by the short lifetime and the contribution from the absorption of the ketyl radical generated. The low triplet lifetimes and high rates of self-quenching observed in some organic solvents are attributed to the high reactivity of 1-azaxanthone toward hydrogen atom abstraction. We were initially puzzled by this remarkable efficiency and interpreted it in the following way. It is known that xanthone is quenched by many aromatic solvents (e.g., the triplet lifetime in benzene is 71 ns).[8] Experiments comparing benzene and pyridine show that the latter is a better quencher.[35] It is thus not unreasonable to expect 1-azaxanthone to be a better (self) quencher than the parent xanthone. The nature of these self-quenching interactions probably involves charge transfer and remains to be fully understood in xanthone and in numerous other systems.

The solvent-induced spectral shifts that are well established in the case of xanthone[8] do not occur for 1-azaxanthone; clearly those shifts are related to the polarity-dependent triplet state inversion (i.e., n,π* vs π,π*) that occurs for xanthone. Although no inversion of states is observed for 1-azaxanthone, the reactivity of its excited triplet state is still dependent on solvent polarity and proticity. Using 2-propanol as a hydrogen donor, we determined the rates of photoreduction of the 1-azaxanthone triplet by this alcohol in water, acetonitrile, and CCl$_4$ (5.2 $\times$ 10^5 M^{-1} s^{-1}, 1.9 $\times$ 10^7 M^{-1} s^{-1} and 5.3 $\times$ 10^7 M^{-1} s^{-1}, respectively). It is obvious that, by increasing the polarity of the solvent, the reactivity of the 1-azaxanthone triplet toward hydrogen atom abstraction is decreased. A reasonable explana-tion for this behavior would be an increase in the mixing between the n,π* and π,π* states in the triplet manifold resulting from the stabilization of the π,π* states and destabilization of the n,π* states as the solvent polarity increases. Again, even if the effect is not as pronounced in 1-azaxanthone as to induce a state inversion in organic solvents, it might still be enough to affect the reactivity of the triplet toward hydrogen atom abstraction if the lowest triplet state acquires some π,π* character with increasing solvent polarity. The results shown in Figure 6 could just reflect the increase in the macroscopic medium polarity with the addition of 2-propanol to CCl$_4$.

To establish if hydrogen bonding interactions could also be responsible for the saturating effect shown in Figure 6, the same experiment was done using water as solvent instead of CCl$_4$. In water, hydrogen bonding interactions are maximized and the

Photoproperties of 1-Azaxanthone in Organic Solvents

J. Phys. Chem. A, Vol. 102, No. 35, 1998 **6903**

saturating behavior upon increasing the 2-propanol concentration is not observed. In addition, when the quencher is not able to participate in hydrogen bonding interactions with 1-azaxanthone (i.e., cyclohexane), there is no saturating effect either. It therefore seems that both polarity and proticity affect the reactivity of the 1-azaxanthone triplet.

The differences in reactivities and spectroscopic properties between xanthone and 1-azaxanthone provide the researcher with two useful probes for the study of polarity-dependent phenomena and dynamics of radical reactions. Obviously, the researcher has the choice of employing xanthone as a probe for polarity, mobility, and reactivity in supramolecular systems by taking advantage of the polarity-induced spectral shifts of its excited triplet state. On the other hand, the enhanced reactivity of 1-azaxanthone toward hydrogen atom abstraction makes it an attractive probe to study the dynamics of radical pairs in more polar environments.

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