particularly informative from a mechanistic point of view.

FUDGIT has another advantage aside from improved correlations. Suppose experimental data from another lactonization became available. It would be a simple matter for FUDGIT to reoptimize with *all* compounds and thereby improve predictive power if this were the primary goal. But since the Dorigo–Houk procedure, being burdened with assumptions, lacks such flexibility, data from this compound could cause a deterioration in the correlation. It would be possible, of course, to arbitrarily modify the parameter set (e.g., assume that force constants are 30% of their normal value rather than 50%), but then the method becomes equivalent in philosophy to the intellectually vacuous FUDGIT approach.

Conclusion

The claim by Dorigo and Houk that they have found an empirical method for predicting lactonization rates has been verified (although FUDGIT will do the job even better). Predictions do not depend, however, on the accuracy of the transition state, but rather on how closely the associated parameters coincide with one of many parameter sets (even "nonsense" sets) that happen to provide a good correlation.[11,14] Caution is advised in deducing from transition-state modeling any notions about chemical reactivity including transition-state structure and the relationship between rate and distance.

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Effect of Cyclodextrin Complexation on the Photochemistry of Xanthone. Absolute Measurement of the Kinetics for Triplet-State Exit[1]

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Abstract: The photochemistry of xanthone aqueous solutions has been examined in the presence of cyclodextrins (α-, β-, and γ-CD). From spectrophotometric measurements it is concluded that xanthone forms 1:1 inclusion complexes with all cyclodextrins and that association is most favored in the case of β-cyclodextrin. Laser flash photolysis studies provide valuable information on the association/dissociation kinetics of the inclusion process. Following excitation, the xanthone triplet relocates from the cyclodextrin cavity into the aqueous phase with exit rate constants of the order of 10^7 s^{-1}; we propose that this relocation is triggered by a change in dipole moment that leads to solubility changes between the ground and triplet states. The effect is most dramatic with β-cyclodextrin, reflecting the strong ground-state association between xanthone and this oligosaccharide.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides of α-D-glucose units produced by enzymatic degradation of starch; three distinct CDs are commonly available, consisting of six (α-CD), seven (β-CD), or eight (γ-CD) sugar units. Cyclodextrins have doughnut shapes and a relatively hydrophobic cavity. The most important property of these molecules is the ability to form inclusion complexes with organic or inorganic guests.[4-8] Thus, inclusion in the hydrophobic cyclodextrin cavity can affect photoprocesses that are sensitive to solvent polarity or dielectric properties.

While there is a large volume of data available on the complexation equilibrium between various cyclodextrins and numerous substrates, very little is known about the dynamics for the association/dissociation process.[9-12] Aromatic ketones are known to form complexes with cyclodextrins in aqueous media; in the case of benzophenone, the complex with β-cyclodextrin has a substantially higher association constant than in the cases of α- and γ-cyclodextrins.[13]

Dielectric loss experiments have shown that ketones with low-lying π,π^* triplet states frequently show large increases (e.g., $\Delta\mu = 1.35$ D for fluorenone and 4.9 D for 4-(dimethylamino)benzaldehyde) in dipole moment upon excitation into the triplet state.[14] We reasoned that such a triplet molecule would be more hydrophilic than its ground state and therefore excitation should promote dissociation of the complex. It is not sufficient to identify a ketone with a π,π^* triplet state, but in addition, the triplet state must have some property that changes significantly with changes in the media. Xanthone meets all the criteria mentioned above. Thus, in moderately polar media its triplet state has π,π^* character and has a relatively long lifetime as a result of the low reactivity frequently associated with $^3\pi,\pi^*$ states. Further, the triplet–triplet absorption spectra are quite intense and show considerable de-

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pendence on the polarity of the media. For example, λ_{max} = 615 nm in 2-propanol and 655 nm in carbon tetrachloride.[15] While the dipole moment of triplet xanthone has only been reported in nonpolar media (where the triplet has n,π^* character),[14] it is reasonable to expect a significant change relative to the ground state in moderately polar media where the triplet has well-defined π,π^* character. Earlier experiments in surfactant–polyelectrolyte aggregates seem to confirm this expectation.[16]

This report centers on the application of several spectroscopic techniques in the study of xanthone–cyclodextrin complexes. Several aspects center on β-CD simply because the relatively strong binding makes the studies simpler in this case. Laser flash photolysis has proven extremely valuable in the determination of dissociation (exit) rate constants.

Experimental Section

Materials. Xanthone (Fluka) was recrystallized twice from ethanol (mp 176–7 °C). Potassium sorbate (Sigma) and $CuSO_4 \cdot 5H_2O$ (BDH) were used as received. Water was purified by passage through a Millipore Milli-Q system. α-, β-, and γ-cyclodextrins from Aldrich were used without further purification. While some batches of cyclodextrins are known to show weak impurity luminescence, the ones used here showed no detectable emission under the conditions (λ_{ex} = 355 nm) of our experiments.

For all the experiments, a saturated aqueous solution of xanthone was used. Saturation was achieved by vigorous magnetic stirring of the solid (in excess) for 2 h; the solutions were then filtered.

Steady-State Measurements. UV-absorption spectra were obtained on a HP-8451 A diode array spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter controlled by a PE-3600 data station, and fluorescence lifetimes were measured on a PRA singlet-proton-counting instrument employing a hydrogen lamp for excitation. Induced circular dichroism spectra were obtained on a Jasco J-600 spectropolarimeter interfaced to an IBM-AT computer. Experiments were performed at room temperature, and the solutions were deaerated for the fluorescence measurements.

Laser Flash Photolysis Studies. Solutions were deaerated by bubbling with oxygen-free nitrogen. Time-resolved measurements were performed in static cells or with a flow system. Static cells (constructed of 7 × 7 mm² Suprasil tubing) typically contained 2.5 mL of solution. For the flow experiments, the irradiation cell (built of the same tubing as the previous cells) was connected with Teflon tubing to a reservoir where the solutions were deaerated. The flow rate was adjusted to ensure the irradiation of a fresh portion of solution by each laser pulse.

The laser flash photolysis system at NRC has been described earlier.[15,17,18] The third harmonic of a pulsed frequency quadrupled Nd/YAG laser (355 nm, ≤100 mJ/pulse, ~12 ns) or a Lumonics TE 860 excimer laser operated with Xe/HCl/He mixtures (308 nm, ≤20 mJ/pulse, ~5 ns) were used for sample excitation. All the measurements were performed at room temperature.

Results

Evidence and Equilibrium Constants for Xanthone Complexation. Addition of cyclodextrins (α-, β-, or γ-CD) to aqueous solutions of xanthone causes changes in the absorption and fluorescence spectra of the latter. Furthermore, xanthone in the presence of cyclodextrins exhibits induced circular dichroism (icd) signals (vide infra). These results are attributed to the equilibrium of reaction 1, where X represents xanthone and X·CD is the association

$$X + CD \overset{K_A}{\rightleftharpoons} X{\cdot}CD \qquad (1)$$

complex between xanthone and a given cyclodextrin. The changes observed in the absorption, fluorescence, and circular dichroism spectra (ΔI) as a function of the cyclodextrin concentration ($[CD]_T \gg [X]_T$, where T refers to total concentration), can be related to the equilibrium of reaction 1 according to eq 2 where Δc is the

$$\Delta I = \frac{K_A \Delta c [X]_T [CD]_T}{1 + K_A [CD]_T} \qquad (2)$$

difference between the molar extinction coefficients, fluorescence quantum yields, or molar ellipticities for complexed and free xanthone (i.e., $\Delta c = c_{X \cdot CD} - c_X$), respectively.

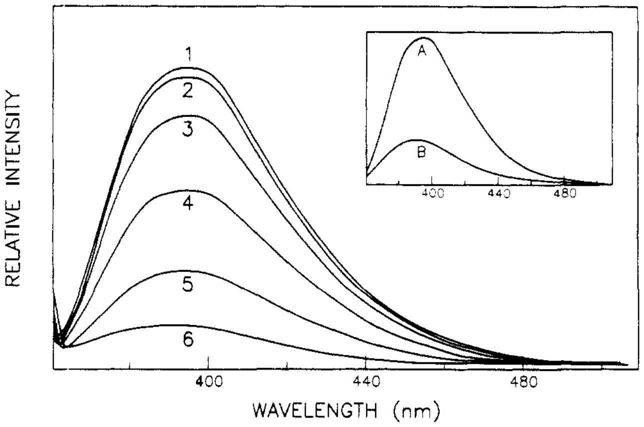

Figure 1. Fluorescence spectra of xanthone (≈3 × 10^{-5} M, water) in the presence of β-CD: 1, 0 mM; 2, 0.096 mM; 3, 0.24 mM; 4, 0.72 mM; 5, 2.4 mM; 6, 12 mM. Inset: xanthone fluorescence in water (A) and in 4:1 water/dioxane (v/v) mixture (B).

Note that the reciprocal of eq 2 is in fact the linear Benesi–Hildebrand expression:[19]

$$\frac{1}{\Delta I} = \frac{1}{\Delta c [X]_T} + \frac{1}{K_A \Delta c [X]_T} \frac{1}{[CD]_T} \qquad (3)$$

Plots of the change in fluorescence intensities and icd signals according to eq 3 are linear (vide infra), indicating the formation of complexes with 1:1 stoichiometry.

Absorption Spectra. When increasing amounts of cyclodextrins are added to aqueous solutions of xanthone, a decrease in absorbance is observed, the magnitude of this decrease being in the order β-CD > γ-CD > α-CD. As the changes observed are small, we have preferred to apply a nonlinear fit directly to eq 2 because in this way the data are weighed in a manner that better reflects its quality. For β-CD we obtained a value of K_A = 1500 M^{-1} for studies at room temperature in the 10^{-2}–10^{-3} M β-CD range and for a concentration of xanthone of 3 × 10^{-5} M.

While absorbance changes were also observed for α-CD and γ-CD, their magnitude was smaller and thus the quality of the data inferior and a similar analysis was not justified; further, other techniques (vide infra) are available and more suitable in these cases.

Fluorescence Spectra. Xanthone fluoresces in aqueous solution with λ_{max} ~ 396 nm. Its fluorescence lifetime was estimated by use of time-correlated single photon counting and is smaller than 1.0 ns; a reliable value could not be obtained due to the poor resolution of the equipment for lifetimes shorter than 1.0 ns. However, in the presence of β-CD the decay is multiexponential with a major contribution of a species with a lifetime around 3.0 ns, confirming the formation of xanthone–cyclodextrin complexes. For α- and γ-CDs the long-lived species have lifetimes around 1.5 ns.

Addition of cyclodextrins causes a blue shift of the emission maximum and a substantial decrease of its intensity (Figure 1). Similar changes can be induced by addition of a solvent less polar than water, such as 1,4-dioxane, to aqueous solutions of xanthone (Figure 1, inset).

Plots of the change in emission intensity determined either at 396 nm or from the integrated spectra are nonlinear and approach

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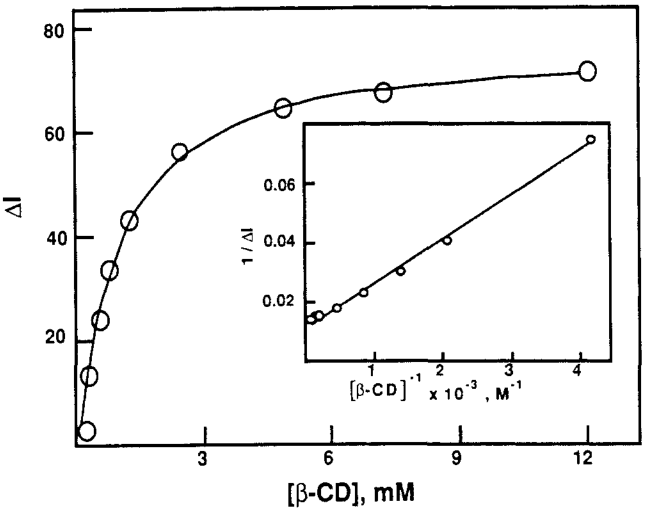

Figure 2. Dependence of the change in xanthone fluorescence intensity as a function of β-CD concentration ($[\text{xanthone}]_T \approx 3 \times 10^{-5}$ M). Inset: Benesi–Hildebrand plot.

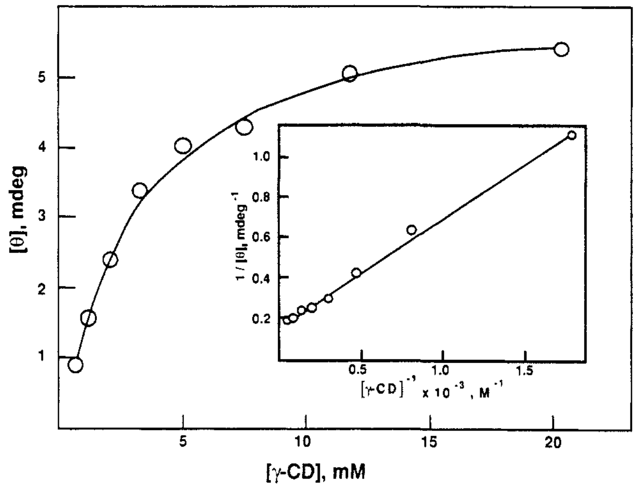

Figure 3. Dependence of the icd signal for xanthone as a function of γ-CD concentration ($[\text{xanthone}]_T \approx 3 \times 10^{-5}$ M). Inset: Benesi–Hildebrand plot.

Table I. Equilibrium Data for the Association of Xanthone with Cyclodextrins Obtained with Various Spectroscopic Techniques

	α-CD	β-CD	γ-CD
		Absorption	
K_A (M^{-1})		1500	
		Emission	
[CD] range (M)	0.05–0.1	1×10^{-4}–0.012	4×10^{-3}–0.02
K_A (M^{-1})	36	1000	200
		Circular Dichroism[a]	
[CD] range (M)	2.5×10^{-3}–0.11	8.2×10^{-5}–0.0137	5.6×10^{-4}–0.049
K_A (M^{-1})	50 ± 8	990 ± 30	290 ± 10

[a] Equilibrium constants were averaged for measurements at different wavelengths. The errors given correspond to the standard deviations.

asymptotically a plateau region, e.g., Figure 2. Nonlinear fitting of these data leads to the equilibrium values of Table I. While a nonlinear fit was preferred, the Benesi–Hildebrand plots are satisfactorily linear (Figure 2, inset) and the resulting K_A values are in agreement with those obtained from the nonlinear fitting.

Circular Dichroism. Xanthone in the presence of cyclodextrins exhibits induced circular dichroism signals. While xanthone itself is not optically active, inclusion in a chiral cavity induces optical activity.

Figure 3 shows a representative plot of ellipticity ([θ]) against the cyclodextrin concentration; the equilibrium constants obtained from these data have been included in Table I.

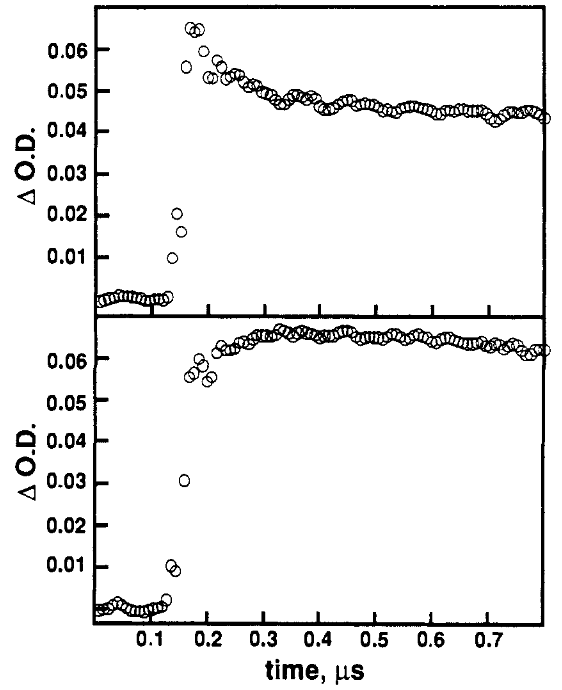

Figure 4. Triplet decay traces for xanthone (≈3×10^{-5} M) in the presence of 12.4 mM β-CD monitored at 570 nm (bottom) and 620 nm (top).

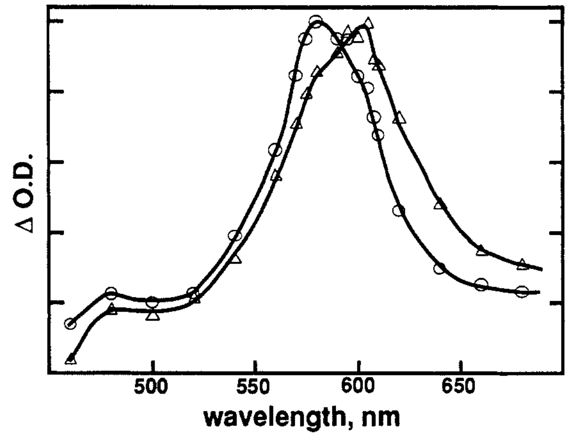

Figure 5. Normalized triplet–triplet absorption spectra for xanthone in the presence of 5 mM β-CD recorded 30 ns (Δ) and 500 ns (O) after laser excitation.

The equilibrium constants obtained by different techniques agree and compare well with those reported by Monti et al. for benzophenone–cyclodextrin complexation.[13]

Laser Flash Photolysis Experiments. T-T Spectroscopy and Lifetimes. Upon laser excitation, xanthone shows an intense and readily detectable triplet–triplet (T–T) absorption spectrum. Experiments in water lead to $\lambda_{max} \sim 580$ nm, and in carefully deaerated solutions the lifetimes are normally >15 μs and incorporate a considerable contribution from second-order processes that can be attributed to triplet–triplet annihilation. In the presence of cyclodextrins it was clear that the samples deteriorated upon laser excitation. This made the use of a flow system essential. Under these conditions each laser shot excites a fresh portion of solution; however, the quality of degassing is not the same, and traces of oxygen usually reduce the triplet lifetime to 3–4 μs.

The traces obtained upon 355-nm laser excitation of xanthone solutions containing β-CD are very dependent upon the monitoring wavelength. Thus, at λ < 600 nm (e.g., 570 nm) the trace shows a growth profile that then decays with the lifetime mentioned above (Figure 4, bottom). In contrast, at λ > 600 nm (e.g., 620 nm) we observe fast and slow decay processes (Figure 4, top); the former is concurrent with the growth process mentioned before (Figure 4, bottom).[20] The lifetimes recorded for the fast processes

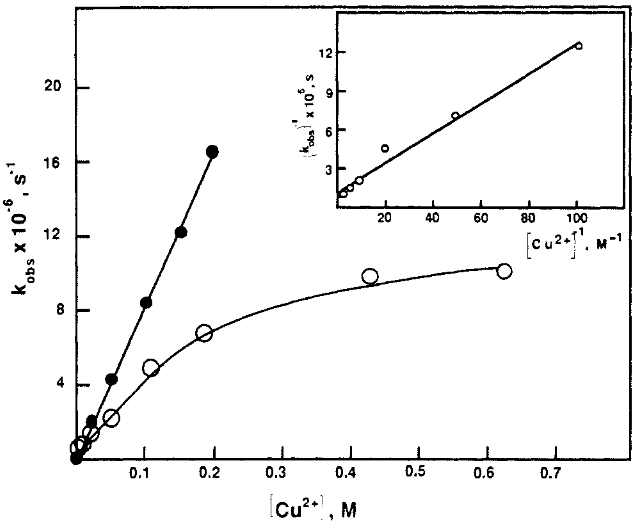

Figure 6. Quenching of xanthone triplet by Cu^{2+} in aqueous solution (●) and in the presence of 13.9 mM of β-CD (○). Inset: double-reciprocal plot for the quenching by Cu^{2+} in the presence of β-CD. Only representative data have been included for $[Cu^{2+}] < 0.1$ M.

observed at 570 and 620 nm are 90 ± 20 ns and are independent of the cyclodextrin concentration.

Naturally, the fact that the shape of the traces depends on the monitoring wavelength also implies that the transient spectra change as a function of the delay following the laser pulse. Figure 5 shows the T–T spectra for xanthone in β-CD excited with a 308-nm laser pulse recorded 30 and 500 ns after laser excitation. The two spectra present λ_{max} at 602 and 580 nm, respectively. This shift parallels that observed in homogeneous solutions when the solvent is changed from a nonpolar to a polar one.[15]

Similar experiments were carried out in α- and γ-CD, but they were not as conclusive. In both cases it is possible to detect a fast decay at $\lambda > 600$ nm with a lifetime of 50 ± 10 ns for α-CD and 160 ± 50 ns for γ-CD, but no growth trace could be obtained at shorter wavelengths. Perhaps this is not surprising; examination of the data in Table I shows that the α-CD and γ-CD complexes are much weaker than in the case of β-CD. Thus, there is more room for change in the degree of complexation in the case of β-CD than in any other cyclodextrin examined.

We interpret the changes above in terms of the relocation of xanthone triplets from the cyclodextrin cavity to the bulk aqueous phase; we propose (vide infra) that this is triggered by dipole moment changes between the ground and triplet states that lead to differences between their association constants and, hence, to a displacement of the equilibrium position. Several of the experiments described in following text were designed to test this hypothesis.

Effect of β-CD on the Quenching of Xanthone Triplets. Cupric ions (added as $CuSO_4$) are excellent quenchers of xanthone triplets; on the other hand, at least in the concentration range examined, there is no indication of singlet quenching. Only dynamic quenching is observed, as indicated by the fact that addition of Cu^{2+} has no effect on the "initial" optical density due to T–T absorption by xanthone in the absence or in the presence of β-CD. The xanthone triplet decay was monitored at 600 nm, where free and complexed xanthone triplets show an isosbestic point. Figure 6 shows the corresponding quenching plots in aqueous solution and in the presence of 0.0139 M β-CD. The former is linear and leads to $k_q^{water} = (8.6 \pm 0.5) \times 10^7$ M^{-1} s^{-1}. In the case of β-CD solution, the plot is not linear, but rather approaches a plateau level at sufficiently high Cu^{2+} concentration. The rate constant obtained from the slope when $[Cu^{2+}] \rightarrow 0$ is $(8.1 \pm 0.1) \times 10^7$ M^{-1} s^{-1}, i.e., within experimental error the same value obtained in water.

Table II. Exit Rate Constants of Triplet Xanthone from Cyclodextrins Determined from the Triplet Decay or from the Triplet Quenching by Cupric Ions[a]

	exit rate constants × 10^{-7} (s^{-1})		
	kinetic analysis		
cyclodextrin	growth	decay	quenching by Cu^{2+}
α-CD		1.9 ± 0.4	2.2 ± 0.4
β-CD	1.0 ± 0.1	1.2 ± 0.1	0.9 ± 0.2
γ-CD		0.6 ± 0.2	1.5 ± 0.2

[a] See text.

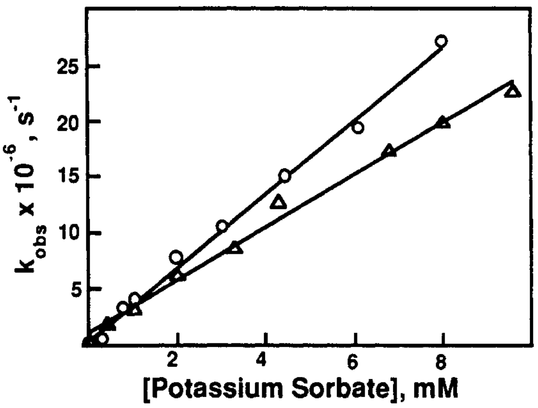

Figure 7. Quenching of xanthone triplet by potassium sorbate in aqueous solution (○) and in the presence of 1.25 mM β-CD (△).

The rate constant for triplet decay in the plateau region can be obtained from the intercept of a double-reciprocal plot (Figure 6 inset). Significantly, the value obtained [$(9 \pm 2) \times 10^6$ s^{-1}] agrees well with the lifetime of 90 ± 20 ns determined from traces in Figure 4 (Table II).

The same approach, quenching of xanthone triplet by cupric ions, was used for α- and γ-CD. In the case of α-CD the limiting rate constant agrees well with the one determined from the time-resolved experiment, whereas for γ-CD a higher limiting rate is observed from the quenching experiment (Table II).

Another quencher examined is potassium sorbate. No evidence for static quenching is observed either in the absence or in the presence of β-CD. The case of potassium sorbate contrasts with that of Cu^{2+} in that the quenching plots are linear both in the absence and in the presence of β-CD (Figure 7); further, the rate constant in the presence of β-CD [$(2.3 \pm 0.2) \times 10^9$ M^{-1} s^{-1} for 1.25 mM β-CD] is significantly smaller than the value of $(3.3 \pm 0.2) \times 10^9$ M^{-1} s^{-1} measured in water. Increase of the cyclodextrin concentration by a factor of ~10 led to only a minor change in the rate constant for quenching (i.e., 2.0×10^9 M^{-1} s^{-1} for 0.012 M β-CD). Potassium sorbate quenching reduces the triplet lifetime well below the value of ~90 ns derived from Figure 4.

Discussion

Inclusion of xanthone in cyclodextrin has a significant effect on virtually all spectroscopic properties, as suggested by the changes observed in absorption, emission, and transient spectra. In addition, inclusion in the cyclodextrin cavity induces chirality in the otherwise achiral xanthone.

Xanthone triplets have n,π^* character only in highly nonpolar solvent but acquire π,π^* character in even mildly polar media.[15] All our evidence indicates that the environment sensed in the cyclodextrin cavity is sufficiently polar for xanthone to retain predominant π,π^* character and thus would be rather unreactive toward typical carbonyl reactions such as hydrogen abstraction.

The equilibrium constant values for the association of xanthone with cyclodextrins (reaction 1) are very close to those reported for benzophenone by Monti et al.[13] based on circular dichroism studies (50, 1500, and 170 M^{-1} for α-, β-, and γ-CD, respectively). From the data in Table I, we estimate that in the case of 0.01 M β-CD at least 90% of the ketone would be associated with cyclodextrin, while for 0.001 M about 50% would be complexed.

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[20] These traces were analyzed for two consecutive first-order processes by use of the fitting procedure previously described: Bohne, C. B.; Abuin, E. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4226.

Excitation of xanthone leads to its readily detectable triplet state. The initial spectrum in β-CD shows λ_{max} 605 nm; the value of λ_{max}, which is very sensitive to the polarity of the media, compares well with those obtained in alcohols,[15] such as 2-propanol. As already indicated (see Figures 4 and 5), the spectrum shifts with time and the maximum is located at ~580 nm after the fast decay of Figure 4 is complete. The position of λ_{max} and general spectral characteristics at this point are identical with those recorded in water.

We propose that the explanation for the observations of Figures 4 and 5 is that, following the photoinduced change in dipole moment, triplet xanthone exits from the cyclodextrin cavity into the aqueous phase. In other words, we anticipate that triplet xanthone will have a higher dipole moment than its ground state,[21] and as a result the value of K_A will be smaller for the triplet state. Xanthone triplet exits from the β-CD cavity with a rate constant of 1.1×10^7 s^{-1}; the rate constants appear to be independent of cyclodextrin concentration, indicating that dissociation is largely irreversible. To the best of our knowledge, this is the first time that an exit (or dissociation) rate constant for a cyclodextrin complex has been determined directly by time-resolved techniques taking advantage of property differences between different electronic states. As pointed out earlier, a few values were obtained by other methods[9,10,12] including an example of triplet quenching,[11] which also provides excited-state mobilities. On the other hand, the rates of dissociation/exit of the cyclodextrin–triplet xanthone complexes are quite similar to the value obtained for the exit (1.1×10^7 s^{-1}) of the same triplet from surfactant–polyelectrolyte aggregates. It should be noted, however, that with our data it is not possible to distinguish which of the driving forces for complex formation (e.g., hydrophobic interactions or breakdown of water structure)[4] is dominant. We simply attribute the relocation of xanthone to differences between its ground- and excited-state polarity.

One can of course ask if the xanthone triplet has truly relocated from the complex into the water or if the modes of inclusion of the ground and the triplet states are simply different, with the latter being more exposed to the aqueous phase. Recent work by Bright et al.[22] with several anilinonaphthalenesulfonates included in β-CD showed that the fluorescence behavior of the complexed probes could be interpreted on the basis of lifetime distributions corresponding to various cyclodextrin-cavity environments. Our data are not inconsistent with the coexistence of several environments or intracavity sites for the cyclodextrin-bound fraction. However, the spectroscopic and kinetic behavior observed here can only be explained in terms of triplet-state exit directly and fully into the aqueous phase due to the following: (a) The delayed triplet spectrum is *identical* with, not just similar to, that in water. (b) The quenching of the triplet state by low Cu^{2+} concentrations occurs with the same rate constant as in aqueous solution; this is particularly significant since Cu^{2+} quenching is much slower than diffusion controlled and therefore one could anticipate considerable selectivity if the species quenched were different. (c) The fact that the quenching plot is curved (see Figure 6) and reaches a plateau indicates the presence of two types of triplets, one that is readily quenchable and the other that is unquenchable. It is straightforward to explain these results on the basis of an exit model, particularly given the excellent agreement between the plateau and the fast decay rate observed, but it is hard to see what kind of intracavity motion would cause such a dramatic effect on the rate of Cu^{2+} quenching. For α- and β-CD the exit rate constants obtained from the analysis of the triplet decay kinetics agree well with the limiting quenching rate by cupric ions. The smaller equilibrium constant and faster exit rate indicate that the cavity of α-CD is too small to accommodate the xanthone. In the case of γ-CD the exit rate obtained from the triplet decay (6×10^6 s^{-1}) is smaller than the one estimated from the plateau region of the quenching plot (1.5×10^7 s^{-1}). Besides, the equilibrium constant for xanthone inclusion in γ-CD is smaller than that in β-CD. The less efficient complexation is probably due to the bigger cavity of γ-CD when compared to β-CD, making it possible to accommodate a greater amount of water around the included xanthone. Thus, Cu^{2+} ions have a better "access" to the triplet xanthone, this being the reason for a shorter limiting lifetime obtained in the quenching experiments with γ-CD. The slower exit of triplet xanthone from γ-CD (6×10^6 s^{-1}) when compared to β-CD (1.1×10^7 s^{-1}) can also be explained by the presence of more molecules of water in the γ-CD cavity. Thus, the difference between the ground- and triplet-state equilibrium constants is smaller for γ-CD than for β-CD. On the other hand, the presence of a greater amount of water in γ-CD complexes would also be indicated by the smaller changes observed in the transient spectra when compared with those observed in the presence of β-CD. The intermediate-size cavity of β-CD offers the best protection of xanthone from bulk water. Reducing the cavity size, such as in α-CD, leads to a poor fit and therefore some exposure to water; on the other hand, xanthone is not sufficiently big to completely fill the γ-CD cavity and as a result even the included molecule is exposed to water molecules with which it probably shares the cavity.

The observation that quenching by sorbate ion does not reach a plateau is readily explainable since we expect sorbate to include in the cyclodextrin cavity; in fact, even substantially more polar molecules and ions do include in these cavities.[9,10] Thus, the fact that sorbate can include suggests that it may be able to access xanthone even in the cavity. The slower sorbate quenching in the presence of β-CD reflects the decrease in the rate constant for quenching upon complexation of sorbate, a process that causes a decrease in its mobility and accessibility. Even when a large fraction of the xanthone is in the aqueous phase, the rate constant observed is lower than in water, indicating sorbate inclusion. That is, sorbate complexation reduces its availability as "free" sorbate in the aqueous phase. Thus, even if the xanthone triplet has exited into the water, the quencher remains largely included. The small but noticeable effect of cyclodextrin concentration may be due to incomplete inclusion of the sorbate at the lower concentrations.

In principle, the dipole moment of the fluorescent state of xanthone, i.e., its singlet, should be different from that of the ground state. However, as the singlet lifetime is extremely short, we can anticipate that relocation will be slow compared with fluorescence decay, so that it is legitimate to use fluorescence of xanthone to determine "ground-state" complexation parameters.

Finally, we have shown that the association constant for xanthone in cyclodextrins is strongly dependent upon the electronic state involved; i.e., while its ground state forms a rather stable complex with β-CD, the triplet state has a strong preference for the aqueous phase. Thus, in any system where the excited-state lifetime competes with the association or dissociation rate constants, one must keep in mind that the properties measured by photochemical techniques, such as those employed here, are those of the excited electronic state, not the ground state.

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(21) Excitation to a π,π^* state in aromatic carbonyls involves promotion of the ring π electrons so that the electrons on the oxygen are repelled even farther away from the ring increasing the dipole moment.[14]

(22) Bright, F. V.; Catena, G. C.; Huang, J. *J. Am. Chem. Soc.* **1990**, *112*, 1343.