

conventional broad-band singlet excitation, is also depicted in Figure 6 (dashed curve d). The temperature effect studies indicate that the electron-phonon coupling is stronger for the phenanthrene system than for the coronene system, in good agreement with the results previously derived from ZPL and PW structure analysis. Whereas the ZPLs can be observed at 70 K for coronene, they are no longer visible at 77 K for phenanthrene (Figure 6, curve b). At 300 K the PWs are so prominent that they mask all the vibronic features of the phosphorescence bands at 21 000-21 500 cm^{-1} (Figure 6, curve c).

A noteworthy difference between coronene and phenanthrene is the broadening of the RTP bandwidth in changing from monochromatic $T_1 \leftarrow S_0$ excitation to broad-band $S_1 \leftarrow S_0$ excitation. Whereas the bandwidths of the RTP spectra of coronene are similar with $T_1 \leftarrow S_0$ excitation (solid curve, Figure 5g) and $S_1 \leftarrow S_0$ excitation (dashed curve, Figure 5g), the bandwidth of the phenanthrene RTP spectrum significantly broadens and red shifts in changing from $T_1 \leftarrow S_0$ excitation (solid curve c, Figure 6) to $S_1 \leftarrow S_0$ excitation (dashed curve d, Figure 6). This feature indicates that intersystem crossing and/or thermal distribution in the triplet state at room temperature produces a wider distribution of triplet energies (and thus broader phosphorescence) in phenanthrene than in coronene. The results for phenanthrene demonstrates that the PLN technique can decrease the phosphorescence bandwidth of an organic compound adsorbed on paper even at room temperature.

Conclusion

This study provides the first observation of PLN spectra of organic compounds, such as phenanthrene and coronene, adsorbed on an analytically important cellulose substrate. Although these two compounds belong to the same family of homocyclic polyaromatic hydrocarbons, noticeable differences can be observed in their interaction, i.e., electron-phonon coupling, with the paper substrate. The strength of electron-phonon coupling is weak for coronene and moderately strong for phenanthrene. Narrow ZPL emission is successfully observed at 4 K for both compounds. The PLN spectra with the paper substrate and butyl bromide glass are similar. This result is of great interest since the filter paper can provide a practical substrate allowing fundamental studies of phosphorescence and related photophysical processes from low temperatures up to room temperature. Until now such a wide temperature range for phosphorescence studies is available only for organic compounds embedded in polymer matrices, which require more elaborate sample preparation procedures than do filter paper substrates. With regard to practical applications, the cellulose substrates can be used for routine, rapid and cost-effective analysis of environmental samples by RTP,² as well as for highly selective detection of specific PNA compounds in complex mixtures by laser-induced line narrowing spectroscopy at low temperatures.

Registry No. Phenanthrene, 85-01-8; coronene, 191-07-1; cellulose, 9004-34-6.

Quenching of Pyrene Fluorescence by Cesium Ions in Micellar Systems. Protection by Surface-Active Crown Ethers

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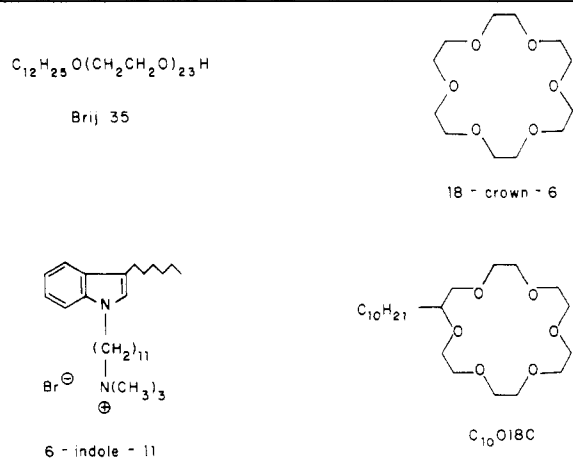
Cesium chloride is found to quench the first excited singlet state of pyrene with a rate constant of $9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solution. When pyrene is sequestered in micelles of a surface-active crown ether, nonionic Brij 35 micelles, or anionic SDS micelles the quenching efficiency depends critically upon the nature of the aggregate. Although cesium ions bind to the micelles of the crown ether, the pyrene singlet state is protected from the quencher in this system. Similar results are obtained for the quenching of the surfactant probe 6-indole-11. The quenching of the pyrene fluorescence was found to occur via heavy atom induced intersystem crossing to the triplet state.

Introduction

It has been established that luminescence techniques can provide valuable information concerning the structure of aggregate systems in aqueous solutions.¹⁻³ In this regard pyrene and its derivatives have been among the more important of the fluorescent probes which have been used to determine properties such as the micropolarity, microviscosity, and aggregation number of many micellar systems.¹⁻³ The nature of the information which is obtained from such studies depends upon the physical location of the fluorescent species and quenchers in the microheterogeneous environment, which in turn depends upon the exact structure of the species involved. For example, very hydrophobic species tend to locate themselves in the hydrophobic interiors of the aggregate systems;⁴ whereas polar or ionic species tend either to stay in the polar exteriors of the aggregates or to be solubilized in the aqueous phase.⁴

In aqueous systems it is well-known that crown ethers can form complexes with cations,⁵ and recently it has been shown that long

CHART I: Structures of Compounds Used in the Present Study



alkyl chain substituted crown ethers form aggregates in water with the crown ether oriented toward the outer surface of the aggregate.⁶ In this work we describe the quenching of the fluorescence of pyrene and the surfactant probe 6-indole-11^{7,8} (Chart I) when

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TABLE I: Stern-Volmer and Rate Constants for Quenching of Pyrene and 6-Indole-11 by Cesium Chloride in Various Environments

	pyrene		6-indole-11 K_{SV}, M^{-1}
	K_{SV}, M^{-1}	$k_q, M^{-1} s^{-1}$	
water	11	9.7×10^7	4225
C ₁₀ O18C	2.1	1.3×10^7	4.6
SDS	305	1.8×10^9	272
SDS + 18-crown-6	260	1.4×10^9	50
Brij 35	1.3	6.1×10^6	1.2

these species are solubilized in micelles of the surface-active crown ether decyl 18-crown-6^{9,10} (C₁₀O18C, Chart I). The quenching behavior is compared to that observed in anionic micelles of sodium dodecyl sulfate (SDS), mixtures of SDS and 18-crown-6, and nonionic micelles of Brij 35 (Chart I). The fluorescence quenching measurements provide information concerning the ability of the metal ion to interact with the micellized fluorescent probes. Additionally, the results support previous suggestions as to the exact locations of the two fluorescent species in the micellar aggregates. The pyrene probe is generally thought to be solubilized in the outer core of an SDS micelle,^{11,12} whereas 6-indole-11 is usually assumed to be located toward the interior of micellar aggregate systems.^{7,8} The mechanism of the quenching of the pyrene fluorescence has been studied by the technique of laser flash photolysis.

Experimental Section

Pyrene (P) was recrystallized three times from ethanol. Sodium dodecyl sulfate (SDS, Bio Rad, electrophoresis grade), cesium chloride (CsCl, Alfa ultrapure grade), Brij 35 (Aldrich), and 18-crown-6 (Aldrich) were used as received. Decyl 18-crown-6 (C₁₀O18C) was a generous gift from Professor Mitsuo Okahara of Osaka University. 6-Indole-11 was available from previous studies.^{7,8}

Emission spectra were recorded on an SLM Instruments Model 8000 spectrometer. Single-photon-counting measurements were performed with a PRA instrument. The laser flash photolysis apparatus has been described previously.¹³

Experiments were performed with solutions of 2×10^{-3} M Brij 35 and C₁₀O18C and 5×10^{-2} M SDS. The concentrations of the fluorescent probes were 10^{-6} M for pyrene and 2×10^{-5} M for 6-indole-11.

Results

Steady-State Quenching. The fluorescence of water-solubilized pyrene is significantly quenched by the addition of 1 M CsCl ($I_0/I = 9.33$). However, this quenching efficiency is significantly changed when the pyrene is sequestered in the micellar aggregates. The C₁₀O18C micelles provide significant protection from quenching, as do the Brij 35 nonionic micelles ($I_0/I = 1.28$ and 1.13, respectively). The addition of 1 M CsCl to SDS resulted in the formation of a large amount of precipitate presumably due to an increase in the Kraft point for cesium dodecyl sulfate compared to sodium dodecyl sulfate.¹⁴ The surfactant redissolved at 40 °C and fluorescence measurements were made at this temperature. The I_0/I value observed under these conditions was 3.73.

A quantitative estimate of the extent of quenching was obtained by examining the I_0/I values as a function of concentration of added CsCl and assuming simple Stern-Volmer kinetics (Figure 1). The

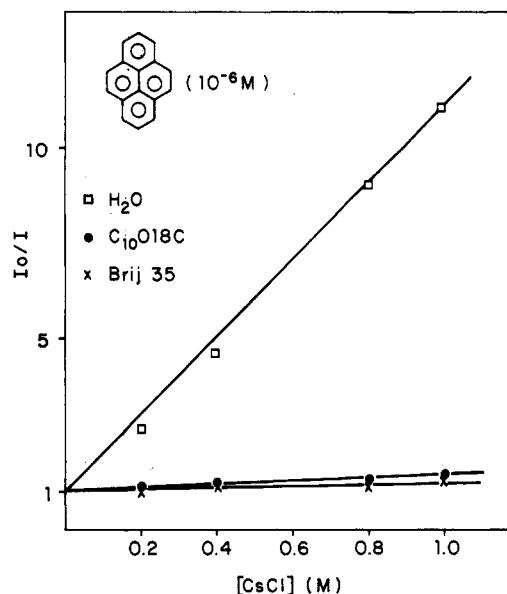


Figure 1. Stern-Volmer plots for quenching of pyrene fluorescence in water, C₁₀O18C, and Brij 35.

TABLE II: Lifetimes (ns) of Pyrene and 6-Indole-11 Singlet States in Aerated Solution, in the Absence and Presence of 1 M Cesium Chloride, and in Various Environments

	pyrene		6-indole-11, no salt
	no salt	+ CsCl	
water	113	18 (17) ^a	15
C ₁₀ O18C	162	135 (136)	9
SDS	175 (138)	— (53)	10
SDS + 18-crown-6	186	79 (79)	9
Brij 35	203	186 (188)	8

^a All measurements performed at 20 °C except those in parentheses which were performed at 40 °C.

appropriate Stern-Volmer constants (K_{SV}) are summarized in Table I. The value of K_{SV} for SDS is ca. 200 times greater than those for the nonionic micelles and ca. 20 times that observed in aqueous solution. The K_{SV} value for SDS was determined over a concentration range of $0-1 \times 10^{-2}$ M cesium chloride. At higher concentrations nonlinear behavior was observed with the I_0/I values increasing very slowly above ca. 0.05 M cesium chloride. The binding constant of cesium ions with SDS has been estimated to be ca. 10 000,¹⁵ which means that above 0.05 M quencher concentration almost every SDS molecule is associated with a cesium ion. In this concentration range, any further cesium ions which are added presumably do not contribute further to the quenching of the micellized probes. Interestingly, the value of I_0/I which is observed in this concentration range is ca. 3.5 which indicates that ca. 30% of the pyrene singlets are quenched inefficiently by CsCl. Those singlets whose fluorescence is quenched at lower concentrations of CsCl are in fact quenched more efficiently than in aqueous solution. The addition of 0.05 M 18-crown-6 to the SDS caused a slight decrease in the efficiency of quenching (Table I).

Time-Resolved Measurements. In aerated water the lifetime which was obtained for the pyrene fluorescence was 113 ns. In each of the aggregate systems the pyrene singlet lifetime in aerated solution was increased with respect to water. The effectiveness of the protection from oxygen quenching, as given by the respective lifetimes, was Brij 35 > SDS > C₁₀O18C (Table II). The addition of 0.05 M 18-crown-6 to the SDS caused a slight increase in the pyrene singlet lifetime from 175 to 186 ns.

The lifetime of the pyrene singlet in aerated water in the presence of 1 M CsCl was determined to be 18 ns. The pyrene singlet was protected from quenching by the cesium by both the

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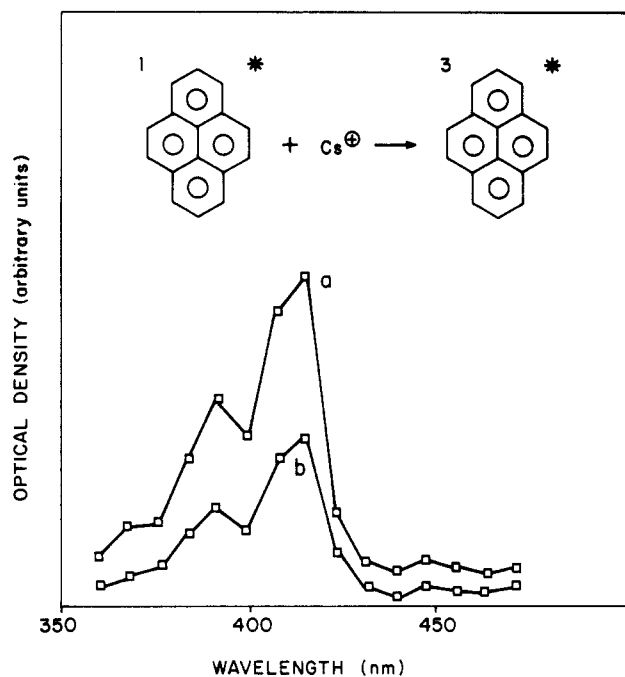


Figure 2. Transient absorption spectra observed upon laser flash photolysis of pyrene in water/ethanol (80/20) (a) in the presence of 1 M cesium chloride and (b) in the absence of added salt.

C₁₀O18C and Brij 35 micelles to a similar extent. In SDS with 1 M CsCl a lifetime of 53 ns was determined which presumably reflects the lifetime of the less efficiently quenched singlets as observed in the steady-state experiments (vide supra). In the presence of cesium the pyrene lifetime in each of the systems, except SDS for which no measurement could be made, was the same at 20 and 40 °C. The addition of 18-crown-6 to the SDS increased the lifetime somewhat from 53 to 79 ns.

From a combination of the lifetimes in the absence of quencher and the K_{SV} values shown in Table I, rate constants for quenching of pyrene singlet by cesium (k_q) in the different environments can be estimated. These data are summarized in Table I.

Quenching of 6-Indole-11. The fluorescence of this species is strongly quenched by cesium in aqueous solution and to a lesser extent in the micellar aggregates (Table I). The protection from CsCl quenching is greatest in C₁₀O18C and Brij 35 and least in SDS, although the quenching in this micelle is decreased compared to water. Again in SDS nonlinear Stern-Volmer behavior was observed at high CsCl concentrations. The addition of 18-crown-6 to SDS decreases the extent of quenching to a small extent.

The lifetime of the indole fluorescence in aerated solutions of the micelles (9 ns) was somewhat decreased with respect to water (15 ns), but no significant differences between the different aggregates could be detected.

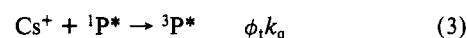
A combination of the lifetime and K_{SV} for quenching of the indole in aqueous solution leads to an apparent rate constant of $2.8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This is larger than the rate of diffusion in water and clearly implies static quenching of the fluorescence as a result of binding between the anionic indole and the cationic cesium ion. For concentrations of cesium up to 0.01 M (which corresponds to a value of I_0/I of > 20) no change in the lifetime of the indole fluorescence can be detected in aqueous solution. This result implies that for this concentration range the quenching is exclusively static in nature and thus the observed Stern-Volmer constant is equivalent to a binding constant.¹⁶

Laser Flash Photolysis. Laser flash photolysis of pyrene ($2 \times 10^{-5} \text{ M}$) in argon-purged ethanol/water (20/80) leads to a transient absorption signal with a maximum absorption at 415 nm which is assigned to the triplet state of this species (Figure 2).¹⁷ Under our experimental conditions only very small ab-

sorptions due to the pyrene radical cation (at 450 nm) could be observed.¹⁷ The triplet state grows in with a lifetime of 311 ns under these conditions which is equal to the singlet lifetime. Upon the addition of CsCl the growth lifetime of the triplet state decreases but the maximum absorption due to triplet, i.e., the triplet yield, increases (Figure 2). This result confirms that a product of the reaction of cesium ions with pyrene singlet is the pyrene triplet state. Similar results have been observed for quenching of pyrene singlets by other cations in SDS micelles.^{18a} Significantly, no increase in the amount of cation was observed upon addition of the salt, which would be expected if the mechanism of singlet quenching was electron transfer, as has been observed for other metal ions.^{18b}

Discussion

Mechanism of Quenching. The results of the laser flash photolysis experiments clearly indicate that the interaction of a cesium cation and a pyrene singlet results to at least some extent in the production of a pyrene triplet. The efficiency of the triplet production processes may be estimated by considering the following processes:



The rate constant k_d represents all of the processes which deactivate the singlet state of pyrene except intersystem crossing which is given by k_{isc} . The rate of singlet quenching by cesium cations is given by k_q , and the efficiency of formation of a triplet state for each quenching act is given by ϕ , which may have values between 0 and 1. Using this simple scheme, we may derive the following expressions for the quantum yield of triplet production in the absence (ϕ_0) and presence (ϕ_q) of cesium:

$$\phi_0 = k_{isc} \tau_0 \quad (5a)$$

$$\tau_0 = 1 / (k_{isc} + k_d) \quad (5b)$$

$$\phi_q = (k_{isc} + \phi_t k_q [Q]) \tau_q \quad (6a)$$

$$\tau_q = 1 / (k_{isc} + k_d + k_q [Q]) \quad (6b)$$

$$\frac{\tau_0 \phi_q}{\tau_q \phi_0} = 1 + \frac{\phi_t k_q [Q]}{k_{isc}} \quad (7)$$

The quantum yield for triplet formation (ϕ) is given by

$$\phi = \frac{[{}^3\text{P}^*]}{[{}^1\text{P}^*]_0} = \frac{A_T}{\epsilon l [{}^1\text{P}^*]_0} \quad (8)$$

Therefore, ϕ is directly proportional to A_T which is the transient absorbance at the end of the fluorescence. Thus

$$\frac{\tau_0 A_T(q)}{\tau_q A_T(0)} = 1 + \frac{\phi_t k_q [Q]}{k_{isc}} \quad (9)$$

In these equations τ_0 and τ_q represent the pyrene singlet lifetimes in the absence and presence of quencher. Thus a plot of the left-hand side of eq 9 vs. quencher concentration should be linear with an intercept of unity and a slope of $(\phi_t k_q / k_{isc})$. Such a plot is linear and yields a value of 8.9 ± 1.1 for $(\phi_t k_q / k_{isc})$. The quantum yield for intersystem crossing in 95% ethanol is known to be 0.38.¹⁹ The intersystem crossing yield in the current solvent system can be estimated by comparing the maximum optical

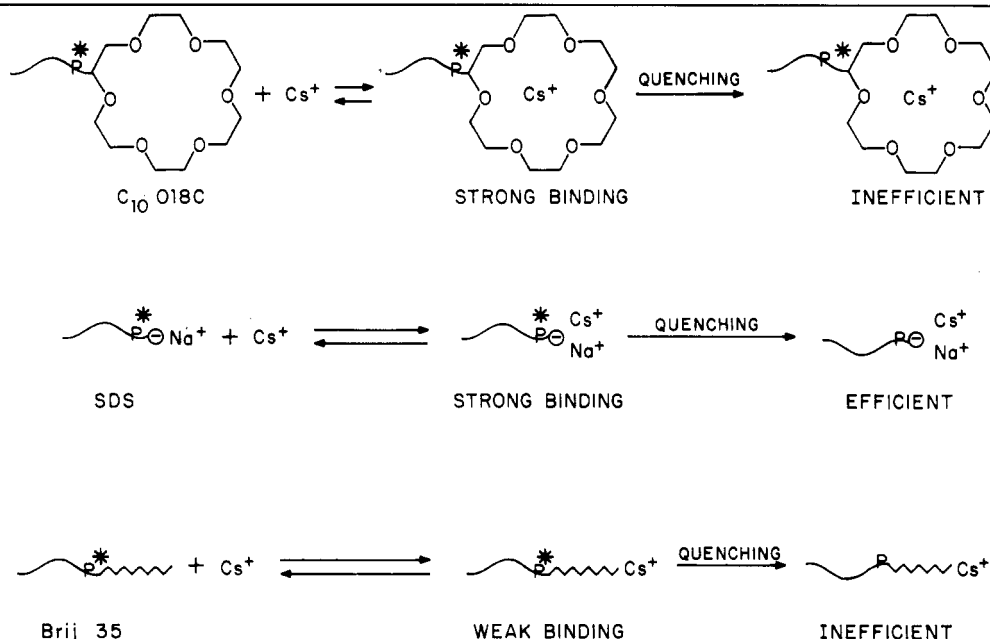
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SCHEME I: Schematic Representation Showing the Binding of Pyrene (P) to the Micellar Aggregates C₁₀O18C, SDS, Brij 35, and the Effectiveness of Quenching of the Fluorescence of Cesium Ions in Each Aggregate



densities of pyrene triplet observed for pulsed laser photolysis of solutions of equal optical density at the excitation wavelength, of pyrene in 95% and 20% ethanol. A value of the intersystem crossing value of 0.48, and thus a rate constant for k_{isc} of $1.6 \times 10^6 \text{ s}^{-1}$, is determined in this manner. The value of k_q is known in the present solvent system from the rate of triplet growth at each CsCl concentration and thus ϕ_i is determined to be 1.1 ± 0.2 . This result clearly shows that the mechanism of quenching of pyrene triplet by cesium ions is heavy atom induced intersystem crossing. This mechanism requires collisional contact between the pyrene excited state and the cation and thus defines the spatial requirements for quenching in the aggregate systems.

Quenching in Aggregate Systems. The pyrene singlet state is protected from quenching by oxygen, in comparison to aqueous solution, in each of the aggregate systems. Pyrene fluorescence is quenched more efficiently in SDS than homogeneous solution by cesium cations but less efficiently by the two nonionic micelles. The order of the quenching efficiency in each of the micelles is not the same for oxygen and CsCl. In the presence of oxygen the singlet lifetimes decrease in the order Brij 35 > SDS > C₁₀O18C, whereas for CsCl quenching we observe Brij 35 \approx C₁₀O18C > SDS. Clearly the role of the aggregate in determining the quenching efficiency is different in each case. The extent of cesium quenching is almost certainly related to the extent of complexation between the aggregate and the cesium cations. Ions which are held in close proximity to the micellized probes will be more efficient quenchers than those which are prevented from approaching the probes or exist as free cations in solution. As previously mentioned pyrene is thought to be located toward the outer layer of SDS micelles. We can obtain information concerning the location of the pyrene in the other aggregates from the nature of the pyrene fluorescence spectrum. The relative intensities of the first and third vibrational bands of pyrene fluorescence (I_1/I_3) depend upon the polarity of the environment in which the probe is solubilized.¹ The values of I_1/I_3 which are observed in water, SDS, and dodecane are 1.9, 1.2, and 0.6, respectively. In the micelles of C₁₀O18C and Brij 35 we observe values of 1.3 and 1.4. We interpret these results to indicate that the pyrene probe "sees" a similar environment in each micelle, and by analogy with SDS we assume that the pyrene probe is located close to the surfactant/water interface. For C₁₀O18C this means that the pyrene molecules are probably located close to the crown ether rings which make up the outer layer of these aggregates (Scheme I).^{6,9,10} Pyrene molecules solubilized in Brij 35 are likely to be located at the junction between the hydrophobic

hydrocarbon and hydrophilic polyoxyethylene parts of the micelles (Scheme I).^{20,21} Information concerning the immediate micro-environment of 6-indole-11 is given by the wavelength of maximum fluorescence emission for this probe.^{7,8} In both C₁₀O18C and Brij 35 a maximum is observed at ca. 350 nm, which is similar to that observed in both ionic micelles and dodecane.^{7,8} This result confirms that 6-indole-11 "sees" a significantly more hydrophobic environment than pyrene in each of the aggregate systems.

For SDS micelles a high equilibrium concentration of cesium ions associated with the aggregate can result by exchange of cesium and sodium counterions. Indeed the estimated association constant of 10 000 for complexation between SDS and Cs cations¹⁵ probably accounts for the efficient quenching observed in these micelles. This effect is clearly observed by comparing the efficiency of pyrene quenching in SDS with that in Brij 35 (Table I). Association between the cation and the nonionic micelle is much less likely and so much less efficient quenching is observed.

The crown ether surfactant C₁₀O18C has been shown to form complexes with potassium cations with an efficiency defined by a binding constant of ca. 100 in aqueous solution at room temperature.²² This is almost identical with the same constant for complexation of potassium ions with unsubstituted 18-crown-6.²³ Therefore we assume that the association constant for cesium ions with 18-crown-6 (equal to 10 at room temperature²³) is a good estimate for the association constant for cesium ions and C₁₀O18C. Thus although the binding of the metal ions to this micelle is significantly less efficient than that to SDS, because of the low concentration of C₁₀O18C ($2 \times 10^{-3} \text{ M}$) and high concentrations of CsCl (up to 1 M) almost 100% of the crown ether molecules will be associated with a cesium cation. Thus although the quenching observed in C₁₀O18C is almost the same as that for the Brij 35 the mechanism of protection cannot be the same. Presumably the metal ions which are associated with the C₁₀O18C micelles are sequestered in the crown ether rings. Thus even if the fluorescent probe is in close proximity to the crown part of the micelle, contact between the probe and quencher is precluded by the presence of the crown ether ring. Thus the C₁₀O18C micelles provide an example of intramicellar protection from

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quenching due to the crown ether ring which imposes a strictly defined compartmentalization of the probe and quencher within the aggregate.

The results for the 18-crown-6/SDS mixtures are less well defined. 18-Crown-6 binds to both sodium and cesium cations with binding constants of 6 and 10, respectively.²³ In both cases the bound and unbound forms of the crown ether are very water soluble. For the mixed SDS and 18-crown-6 systems the most likely explanation for the reduced quenching efficiency compared to SDS is the removal of cesium ions from the micelle into the aqueous phase as complexes with the crown ether. However, these effects are unlikely to be large since the association constant for cesium with SDS is so much larger than that for 18-crown-6.

Quenching of 6-Indole-11. Since 6-indole-11 is located in a very hydrophobic environment in each aggregate, the quenching of this species could be different than that observed for pyrene. Additionally this probe does provide slightly different information than the pyrene probe since the "Stern-Volmer" analysis leads to association constants rather than dynamic quenching constants. The order of quenching efficiency in the aggregate systems is the same as that observed for pyrene (SDS > C₁₀O18C ≈ Brij 35). However, the Stern-Volmer constant for SDS is smaller than the corresponding value in aqueous solution and thus quenching is observed to be less efficient. For the pyrene probe a higher quenching efficiency is observed in SDS compared to homogeneous solution. Although solubilization within an SDS micelle results in a higher effective cesium concentration for pyrene, the effective

concentration for the indole is evidently lower than that possible in homogeneous solution. The most likely reason for this is that the indole is located in the hydrophobic layer of the micelle and thus is protected from quenched by the cations which are associated with the outer layer. The quenching efficiency in both nonionic micelles is lower than in SDS presumably for the same reasons that pyrene is quenched less efficiently.

Conclusions

the quenching of the fluorescence of pyrene by cesium cations occurs via heavy atom induced intersystem crossing to the triplet state of this species. The efficiency of quenching is increased in SDS micelles compared to homogeneous solution for most of the pyrene singlets, and significantly decreased for C₁₀O18C and Brij 35. The quenching protection observed in C10O18C is due to an intramicellar sequestering of the cation which prevents contact between the probe and quencher, whereas the protection in Brij 35 is due to a simple lack of association between the micelle and cation. Similar results are obtained for 6-indole-11 after the effect of location of the probe within the aggregate is taken into account.

Acknowledgment. The authors thank the National Science Foundation and the Army Office of Research for their generous support of this research.

Registry No. 6-Indole-11, 51097-79-1; C₁₀O₁₈C, 60742-60-1; SDS, 151-21-3; 18-crown-6, 17455-13-9; Brij 35, 9002-92-0; cesium chloride, 7647-17-8; pyrene, 129-00-0; water, 7732-18-5.

Photochemistry and Photophysics of Small Heterocyclic Molecules: 1. Multiphoton Ionization and Dissociation of *N*-Isopropylidimethyloxaziridine¹

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The resonantly enhanced visible multiphoton ionization spectrum of *N*-isopropylidimethyloxaziridine has been recorded over the wavelength region from 375 to 600 nm. Rydberg series have been observed and assigned to *ns*, *np*, and *nd* transitions, with *n* spanning the range from 3 to 6. These transitions are accompanied by changes in the vibrational energy of a ring deformation mode. The ionization potential for this molecule is estimated to be 8.84 eV from both the Rydberg series limits and the spectral changes accompanying the transition from a three- to a four-photon requirement for ionization. Preliminary gas-phase photochemical results indicate a sharp energy dependence in the mechanism for dissociation. A one-photon pathway leads primarily to simple ring opening and an amide final product, while a second, multiphoton channel leads exclusively to the severing of two bonds and an acetone fragment. These results are compared with earlier theoretical predictions and experimental results. The unique advantages of multiphoton photochemistry for the production of novel species are discussed.

I. Introduction

Prompted largely by practical considerations, inquiry into the chemistry of strained ring compounds has a rich history in the field of organic chemistry.² One reason for the interest in these molecules is their inherent instability, which enables them to be sources of highly reactive intermediates. The chemistry of heterocyclic compounds is equally interesting for its theoretical implications.² Due, in part, to a dipole moment created by the presence of one or more heteroatoms in the ring, small ring heterocycles exhibit physical properties distinct from their alkane analogues such as cyclopropanes and cyclobutanes.³ Hindered by the increased complexity of the heterocyclic systems in comparison to the hydrocarbon analogues, physical chemists were slow to systematically examine the intra- and intermolecular interactions associated with these molecules. However, a considerable body of data in such areas as reaction mechanism, bonding, equilibrium

thermodynamics, and polymerization is now available for the single heteroatom molecules.⁴

We have begun a systematic study of the laser-driven, photochemical dissociation dynamics of small rings containing at least two heteroatoms. The goal of this research is a detailed understanding of the dependence of the reaction rate and dynamics on the nature of the heteroatoms and the quantum state of the molecule. Due to the lack of critical data, these goals will also require an examination of the electronic structure of the molecules from both experimental and theoretical viewpoints. Initial studies will concentrate on heterocycles in the gas phase at low pressures.

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