

Finally, while the electron-transfer products have lifetimes of <5 ns, we have shown that it is possible to compete with recombination by using TEOA as a sacrificial donor. We are presently studying complexes in which we have incorporated both diquat-modified ligands and electron donor species (e.g., phenothiazine) into a tris(bipyridine)ruthenium chromophore.

**Acknowledgment.** Support for this work by the National Science Foundation (CHE-8214299) is gratefully acknowledged. Also, we thank Dr. John S. Connolly of the Solar Energy Research Institute, Golden, CO for performing the photophysical measurements reported.

**Registry No. 1.** 96897-04-0; 2(PF<sub>6</sub>)<sub>2</sub>, 96897-06-2; 2<sup>+</sup>, 96897-13-1; 2 (neutral), 96897-14-2; 2<sup>-</sup>, 96947-74-9; 3(PF<sub>6</sub>)<sub>2</sub>, 96897-08-4; 3<sup>+</sup>, 96897-15-3; 3 (neutral), 96897-16-4; 3<sup>-</sup>, 96947-75-0; 4(PF<sub>6</sub>)<sub>4</sub>, 96897-18-6; 4<sup>2+</sup>, 96897-30-2; 4<sup>3+</sup>, 96897-37-9; 4<sup>2+</sup>, 96897-43-7; 4<sup>+</sup>, 96913-25-6; 4 (neutral), 96897-56-2; 4<sup>-</sup>, 96913-27-8; 5(PF<sub>6</sub>)<sub>4</sub>, 96897-19-7; 5<sup>2+</sup>, 96410-78-5; 5<sup>3+</sup>, 96897-38-0; 5<sup>2+</sup>, 96897-44-8; 5<sup>+</sup>, 96897-49-3; 5 (neutral), 96897-

57-3; 5<sup>-</sup>, 96897-63-1; 6(PF<sub>6</sub>)<sub>4</sub>, 96897-21-1; 6<sup>5+</sup>, 96897-31-3; 6<sup>3+</sup>, 96897-39-1; 6<sup>2+</sup>, 96897-45-9; 6<sup>+</sup>, 96897-50-6; 6 (neutral), 96897-58-4; 6<sup>-</sup>, 96897-64-2; 7(PF<sub>6</sub>)<sub>4</sub>, 96897-23-3; 7<sup>5+</sup>, 96897-32-4; 7<sup>3+</sup>, 96897-40-4; 7<sup>2+</sup>, 96897-46-0; 7<sup>+</sup>, 96897-51-7; 7 (neutral), 96897-59-5; 7<sup>-</sup>, 96897-66-4; 8(PF<sub>6</sub>)<sub>4</sub>, 96897-25-5; 8<sup>5+</sup>, 96897-33-5; 8<sup>3+</sup>, 96897-41-5; 8<sup>2+</sup>, 96897-47-1; 8<sup>+</sup>, 96897-52-8; 8 (neutral), 96897-60-8; 8<sup>-</sup>, 96897-65-3; 8<sup>2-</sup>, 96897-70-0; 8<sup>3-</sup>, 96897-72-2; 9(PF<sub>6</sub>)<sub>4</sub>, 96897-27-7; 9<sup>5+</sup>, 96897-34-6; 9<sup>3+</sup>, 96897-42-6; 9<sup>2+</sup>, 96897-48-2; 9<sup>+</sup>, 96897-53-9; 9 (neutral), 96913-26-7; 9<sup>-</sup>, 96897-67-5; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>3+</sup>, 96897-35-7; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>+</sup>, 96897-54-0; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>-</sup>, 96897-61-9; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>-</sup>, 96897-68-6; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>3+</sup>, 96897-36-8; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>2</sub>, 96897-29-9; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>+</sup>, 96897-55-1; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>-</sup>, 96897-62-0; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>-</sup>, 96897-69-7; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>2-</sup>, 96897-71-1; [Ru]([COOEt]<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>3-</sup>, 96897-73-3; Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, 15746-57-3; Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub>, 11070-19-2; Me<sub>2</sub>bpy, 1134-35-6; Me<sub>2</sub>-2DQ<sup>2+</sup>, 96913-23-4; Me<sub>2</sub>-2DQ<sup>+</sup>, 96897-09-5; Me<sub>2</sub>-2DQ, 96913-24-5; Me<sub>2</sub>-3DQ<sup>2+</sup>, 96897-10-8; Me<sub>2</sub>-3DQ<sup>+</sup>, 96897-11-9; Me<sub>2</sub>-3DQ, 96897-12-0; 1,2-dibromoethane, 106-93-4; 1,3-dibromopropane, 109-64-8.

## Fluorescence Study of Pyrene and Naphthalene in Cyclodextrin-Amphiphile Complex Systems

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**Abstract:** Amphiphilic molecules are shown to interact with pyrene- $\beta$ -cyclodextrin (Py- $\beta$ -CD) complexes leading to an extremely hydrophobic environment for pyrene (Py) in aqueous solution. The three-component systems give rise to a 1:1:1 complex of Py,  $\beta$ -CD, and the surfactant. The binding constant of Py and  $\beta$ -CD increases significantly in the presence of the surfactants, which suggests an improvement in the solubility of Py in aqueous  $\beta$ -CD systems. Larger binding constants of Py and  $\beta$ -CD were obtained in the presence of shorter chain amphiphiles between C<sub>4</sub> and C<sub>16</sub> surfactants. Fluorescence quenching of Py in Py- $\beta$ -CD-pyridinium surfactants (C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup>) systems obeyed first-order kinetics, which were independent of the concentration of C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup> above a certain concentration, while the quenching rate constant was markedly affected by the chain length of the pyridinium surfactants. Smaller rate constants are obtained for longer chain surfactants. The observed kinetics are explained in terms of a 1:1:1 complex formation of Py,  $\beta$ -CD, and C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup>, and the chain-length-dependent rate constants are interpreted by assuming a "diffusion-controlled reaction within limited space". On the other hand, Stern-Volmer kinetics were observed for Py fluorescence quenching in the Py- $\beta$ -CD-C<sub>16</sub>C<sub>2</sub>V<sup>2+</sup> (1-ethyl-1'-hexadecyl-4,4'-bipyridinium ion) system. This is ascribed to the long-range nature of the reaction in Py(S<sub>1</sub>)-viologen group systems compared with that in Py(S<sub>1</sub>)-pyridinium group systems. In the naphthalene- $\beta$ -CD (N- $\beta$ -CD) system, reduced association constants were observed in the presence of surfactants, which is markedly different from that observed in the Py- $\beta$ -CD system. A determination of the dynamic parameters of the equilibrium showed that the entry rate constant of naphthalene into  $\beta$ -CD was reduced in the presence of surfactants, while the exit rate constant was unchanged. The exit rate was appreciably reduced in the Py- $\beta$ -CD system on addition of surfactants. Quenchers such as oxygen, nitromethane, copper(II) ion, thallium(I) ion, etc., which reside in the aqueous phase also quench excited Py in  $\beta$ -CD. The influence of CD with and without surfactant on the rate depends on the nature of the quenching reaction, and on the degree of screening by the host system on the guest molecule. It is demonstrated in the present study that the introduction of amphiphilic molecules into the Py- $\beta$ -CD complex system improves the organization of the system and simplifies the reaction mechanism. The unique types of reaction kinetics observed are due to the selective organization of reactants in the CD system.

The past decade has witnessed an ever-increasing interest in the effects of organized assemblies on photochemical reactions.<sup>1</sup> Reactants accommodated in molecular assemblies, i.e., micelles, microemulsions, vesicles, etc., often achieve a greater degree of organization compared to homogeneous solution, a feature which may promote unique reaction features, features which may mimic reactions in biosystems and also may have an application for energy storage. Photophysical and photochemical properties of

organic molecules included in the cavity of cyclodextrins (CD's) have also been studied from a similar standpoint.<sup>2</sup> The cavity of CD's can provide a hydrophobic environment for a guest molecule while still in aqueous solution. Earlier studies indicate substantial binding constants for many organic molecules with CD's.<sup>3</sup> However, complicated behavior of formation of the in-

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clusion complex, viz., 2:1 and 2:2 complexes, etc., as well as 1:1 complex, has been observed;<sup>2b,4</sup> the solubility of hydrophobic molecules in CD solutions is poor compared with other systems such as aqueous micelles, and these factors are considered to be serious disadvantages of CD's systems. Functionalization of CD's has been directed toward improving their properties.<sup>1a,5</sup>

Another approach to improve the system is by the addition of a third component to the host-guest systems. Edwards and Thomas<sup>6</sup> noticed that a more hydrophobic environment can be achieved in a Py- $\beta$ -CD system on addition of surfactants, e.g., sodium lauryl sulfate (NaLS) or cetyltrimethylammonium bromide (CTAB). Turro et al.<sup>7</sup> have reported that addition of acetonitrile increased both the phosphorescence intensity and lifetime of 1-bromonaphthalene and 1-chloronaphthalene in the  $\beta$ -CD system, indicating a significant effect of additives on the photophysical properties of guest molecules included in the CD cavity. Nakajima has demonstrated an increased binding constant of Py and  $\beta$ -CD in the presence of ethanol. In  $\gamma$ -CD systems, Kano et al.<sup>4b</sup> have observed the breakup of the ground-state dimer of Py, in other words, a transition from a 2:1 to 1:1 complex, in the presence of butanol. Therefore, it is expected that the third molecule which contains a hydrophobic moiety can interact with CD to increase the hydrophobicity of the CD cavity by excluding water molecules from the cavity. This may lead to the different organization of the host-guest systems, i.e., the increased binding constant or the transition between different types of host-guest interactions, namely, from a 2:1 to 1:1 complex. The unique organization of reactants peculiar to CD systems in the presence of a third component can be monitored in terms of fast reaction kinetics, viz., via quenching kinetics which has been successful in micellar systems, where a statistical distribution of molecules in the micelles gives rise to totally different kinetics<sup>9</sup> from that observed in homogeneous systems. However, a systematic study of the effect of a third component on the host-guest systems is lacking.

In the present paper, preliminary results are given on fluorescence studies of Py- $\beta$ -CD naphthalene- $\beta$ -CD systems in the presence of amphiphilic molecules, where surfactants with various chain lengths and head groups were employed. Steady-state fluorescence spectra were utilized to monitor the interaction of surfactants with the guest-CD complex. Fluorescence decay kinetics and quenching and triplet quenching studies were used to determine the type of complexes formed, the binding constants and the dynamic parameters of association. Also, an unusual type of reaction kinetics observed in the three component complex system will be described.

## Experimental Section

**Materials.** Pyrene, Py (Eastman), was purified by silica gel chromatography. Naphthalene, N (Eastman), was recrystallized.  $\beta$ -Cyclodextrin,  $\beta$ -CD (Aldrich), was recrystallized from water. Sodium *n*-alkyl sulfates,  $C_nSO_4^-Na^+$  ( $n = 4, 6, 8, 10, 12$ ), obtained from Eastman, were recrystallized from an ethanol-acetone mixture. *n*-Alkylammonium chlorides,  $C_nNH_3^+Cl^-$  ( $n = 2, 4, 6, 8$ ), purchased from Pfaltz and Bauer or Eastman, were recrystallized from an ethanol-ether mixture. *n*-Alkyltrimethylammonium bromides,  $C_nN(CH_3)_3^+Br^-$  ( $n = 10, 12, 16$ ), were recrystallized from an ethanol-ether mixture. *n*-Alkylpyridinium bromides,  $C_nPd^+Br^-$  ( $n = 2, 5, 6, 7, 8, 10$ ), were prepared by refluxing *n*-alkyl bromides (Aldrich) and pyridine (Fisher) under a  $N_2$  atmosphere for 24 h. *n*-Alkyl bromides and pyridine were passed through a silica gel column before use. Dodecylpyridinium chloride (Matheson Coleman & Bell) and cetylpyridinium chloride (Sigma) were recrystallized from ethanol. 1-Ethyl-1'-hexadecyl-4,4'-bipyridinium ( $C_{16}C_2V^{2+}$ ) dibromide was prepared according to the literature,<sup>10</sup> while 1,1'-diheptyl-4,4'-bi-

pyridinium ( $C_7C_7V^{2+}$ ) dibromide (Aldrich) was used as received. Methviologen ( $MV^{2+}$ ) chloride (Aldrich) was recrystallized from water. Copper(II) sulfate (J. T. Baker), thallium(I) sulfate (Fisher), sodium nitrite (J. T. Baker), and Fremy's salt (Alfa) were used without further purification.

**Apparatus.** Fluorescence lifetimes were determined with a laser system consisting of a PRA LN-1000 nitrogen laser (337.1 nm, 0.5 ns, up to 1.5 mJ per pulse) for excitation, a  $\beta$  & L visible monochromator, and a Hamamatsu R928 photomultiplier for luminescence monitoring. The response time of this system is less than one 1 ns when the signal is captured by a Tektronix 7192AD digitizer with a 7A29 amplifier and a 7B10 time base, via 50-ohm cables and terminators. All the data were analyzed by using a Tektronix 4052A computer, which was interfaced to the digitizer.

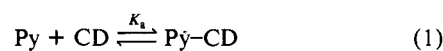
A Perkin-Elmer 552 spectrophotometer and a Perkin-Elmer MPF 44B spectrofluorimeter were used for stationary measurement.

**Procedure.** Py and N were dissolved in water or in  $\beta$ -CD solutions by stirring at an elevated temperature overnight, followed by centrifugation of the solutions at 8000 rpm for 30 min to remove microcrystals. Ultrapure nitrogen gas was used to deoxygenate the sample solutions. Most of the measurements were carried out at room temperature ( $21 \pm 1$  °C). Concentrations of  $\beta$ -CD were calculated on the basis of a dodecahydrated form.

## Results and Discussion

### (1) Fluorescence Decay of Pyrene in Aqueous $\beta$ -CD Solutions.

The time dependence of Py fluorescence in aqueous solution is well described in terms of a single exponential function with a lifetime of  $225 \pm 10$  ns. However, a nonexponential decay of fluorescence was observed in the presence of  $\beta$ -CD as depicted in Figure 1A. Previous studies<sup>8</sup> showed that Py forms a 1:1 inclusion complex with  $\beta$ -CD:



Nakajima<sup>8a</sup> has determined an association constant,  $K_a = 190 M^{-1}$ , by means of a steady-state fluorescence yield measurement at various concentrations of  $\beta$ -CD. It can be assumed that two types of emitting species, Py and Py-CD, are present in  $\beta$ -CD solution, which cause the nonexponential decay of Py fluorescence. Therefore, the time-dependent decay of Py fluorescence can be described by

$$F(t) = F(0)\{\alpha \exp(-k_1t) + (1 - \alpha) \exp(-k_2t)\} \quad (2)$$

where  $\alpha$  is a proportion of Py-CD,  $k_1$  is a decay constant of emission from Py-CD, and  $k_2$  is a decay constant of Py emission in water. The determination of  $\alpha$  at various concentrations of  $\beta$ -CD leads to the determination of  $K_a$ , since eq 1 gives:

$$[Py-CD]/[Py] = K_a[CD] \quad (3)$$

and also

$$\frac{\alpha}{1 - \alpha} = \frac{[Py-CE]}{[Py]} \left( \frac{\epsilon^{Py-CD}}{\epsilon^{Py}} \right)_{\lambda_{ex}} \frac{\Phi(Py-CD)}{\Phi(Py)} \quad (4)$$

where the ratio of the absorption coefficients at an excitation wavelength of 337 nm is assigned to be unity according to Nakajima,<sup>8a</sup> and a quantum yield ratio of 1.7 was used: Nakajima used  $\Phi(Py-CD)/\Phi(Py) = 1.5$ .<sup>8a</sup> In the present study, the following approximate relation was employed for the estimation of the quantum yield ratio:

$$\frac{\Phi(Py-CD)}{\Phi(Py)} = \frac{\tau(Py)}{\tau(Py-CD)} \quad (5)$$

where  $\tau(Py)$  and  $\tau(Py-CD)$  are the fluorescence lifetime of Py in water and that of Py-CD, respectively. Direct application of eq 2 for the Py fluorescence decay in  $\beta$ -CD solution may give an inaccurate value of  $\alpha$  because of the similar magnitudes of  $k_1$  and  $k_2$ . Therefore, a quenching method, which enhances the difference between  $k_1$  and  $k_2$ , was utilized for the determination of  $\alpha$ . Copper(II) and thallium(I) ions, which do not affect the equilibrium, eq 1, quench by fluorescence independently in water and

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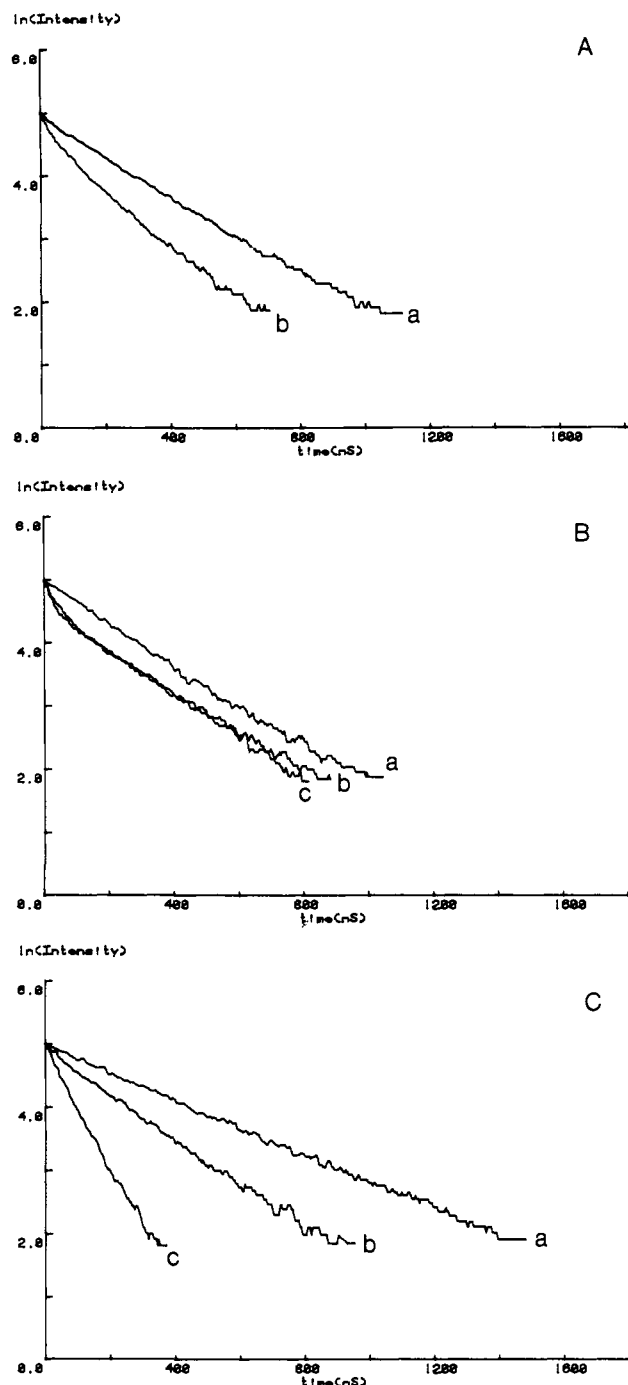
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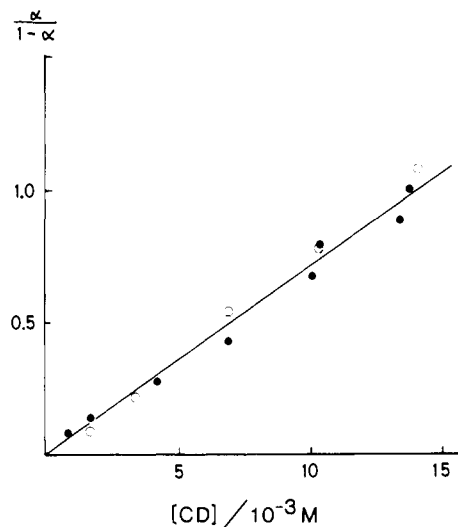


**Figure 1.** Fluorescence decay curves of Py in  $\beta$ -CD systems: (A)  $5 \times 10^{-7}$  M Py in  $N_2$ -saturated (a) and  $O_2$ -saturated (b)  $\beta$ -CD solution ( $[\beta\text{-CD}] = 13.7$  mM); (B)  $5 \times 10^{-7}$  M Py in 13.7 mM  $\beta$ -CD solution containing 0 (a), 5 (b), and 10 mM (c) of  $Ti^+$ ; (C)  $5 \times 10^{-7}$  M Py in 13.7 mM  $\beta$ -CD solution in the presence of 20 mM of  $C_{10}N(CH_3)_3^+Br^-$  (a),  $C_{10}Pd^+Br^-$  (b), and  $C_8Pd^+Br^-$  (c).

in the Py- $\beta$ -CD associated systems, obeying the Stern-Volmer relation:

$$k_1 = k_1^0 + k_{1q}[Q] \quad k_2 = k_2^0 + k_{2q}[Q] \quad (6)$$

The values of  $\alpha$ ,  $K_1^0$ ,  $k_{1q}$ ,  $k_2^0$ , and  $k_{2q}$  were determined by a computer fitting of the experimental decay curves, typically shown in Figure 1B, in terms of eq 2 at different concentrations of quencher,  $[Q]$ . A constant value of  $\alpha$  was obtained at a fixed concentration of  $\beta$ -CD irrespective of the various concentration of quenchers. Value of  $k_1^0 = 2.6 \times 10^6$  s $^{-1}$  and  $k_2^0 = 4.8 \times 10^6$  s $^{-1}$  were obtained in the absence of quencher. The  $k_2^0$  value agrees well with the reciprocal of the Py fluorescence lifetime obtained independently in water ( $4.4 \times 10^6$  s $^{-1}$ ). Figure 2 shows a plot of



**Figure 2.**  $\alpha/(1-\alpha)$  vs. concentration of  $\beta$ -CD.  $\alpha$  values were determined from  $Cu^{2+}$  quenching (O) and  $Ti^+$  quenching (●) of Py fluorescence.

**Table I.** Bimolecular Quenching Rate Constants ( $M^{-1} s^{-1}$ ) in  $\beta$ -CD Systems

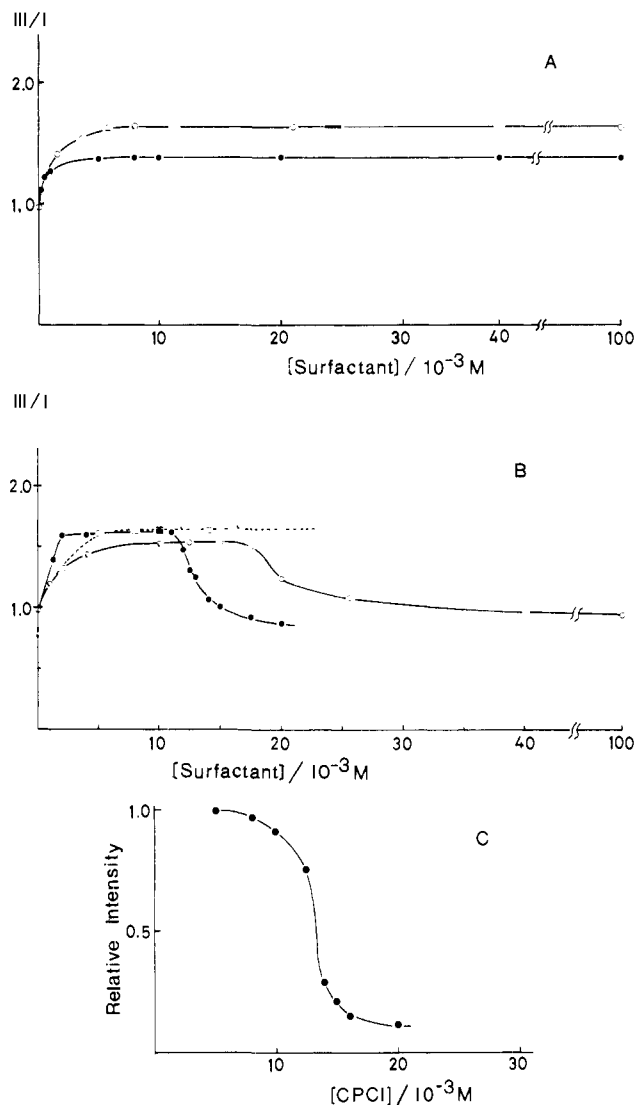
quencher	medium			
	$H_2O$	$\beta$ -CD	$\beta$ -CD + NaLS <sup>a</sup>	$\beta$ -CD + CTAB <sup>b</sup>
$O_2$	$1.1 \times 10^{10}$	$1.2 \times 10^9$	$6 \times 10^8$	$6 \times 10^8$
$CH_3NO_2$	$8.1 \times 10^9$	$5.6 \times 10^8$	$2.5 \times 10^7$	$1.7 \times 10^7$
$Ti^+$	$6.3 \times 10^9$	$2 \times 10^7$	$<10^7$	$<10^7$
$C_2Pd^+Br^-$	$7.9 \times 10^9$	$7 \times 10^7$	$5 \times 10^7$	$3.5 \times 10^7$
$Cu^{2+}$	$4.5 \times 10^9$	$1.7 \times 10^8$	$6.5 \times 10^8$	$2.2 \times 10^8$
$MV^{2+}$	$7.8 \times 10^9$	$5 \times 10^9$	$4.0 \times 10^9$	$6.8 \times 10^8$
$C_{16}C_2V^{2+}$	$7.6 \times 10^9$			
$C_{16}Pd^+$	$3.6 \times 10^9$			

<sup>a</sup> $[\beta\text{-CD}] = 13.7$  mM;  $[\text{NaLS}] = 15$  mM. <sup>b</sup> $[\beta\text{-CD}] = 13.7$  mM;  $[\text{CTAB}] = 10$  mM.

$\alpha/(1-\alpha)$  vs.  $[\text{CD}]$ . The association constant,  $K_a = (44 \pm 6) M^{-1}$ , was determined from the slope of the plot using eq 3 and 4. The concentration of Py did not affect the value of  $K_a$  in the range between  $5 \times 10^{-7}$  and  $4 \times 10^{-6}$  M. The  $K_a$  value determined in the present study was one-fourth that determined by Nakajima.<sup>8a</sup> The discrepancy may result from the different method used.

A marked protective effect of  $\beta$ -CD was observed for the Py quenching of fluorescence by oxygen, nitromethane,  $Ti^+$ , and  $Cu^{2+}$  as shown in Table I. The quenching in Table I may be divided into two groups, those that require contact of excited Py and quencher and those that do not. The latter category includes  $Cu^{2+}$  and  $MV^{2+}$ . Quenching by  $MV^{2+}$  is electron transfer and is only slightly affected by  $\beta$ -CD, as the electron may be transferred over the distance larger than the collisional distance of Py and  $MV^{2+}$ . A similar mechanism applies to  $Cu^{2+}$  although the  $\beta$ -CD does reduce the efficiency of reaction to a larger extent than  $MV^{2+}$ . Reaction of  $CH_3NO_2$  and  $C_2Pd^+Br^-$  with Py are also electron transfer in nature but are markedly affected by  $\beta$ -CD. This indicates that a close approach of the reactants is required for reaction. Thallium(I) ions cause intersystem crossing of excited Py and require close contact of the two reactants. This mechanism is clearly reflected in the dramatic reduction in reaction efficiency by  $\beta$ -CD. Oxygen also causes intersystem crossing of excited Py, but the relatively small effects of the host molecule on the reaction efficiency indicate that close contact is not required for this reaction.

**(2) Fluorescence Decay of Pyrene in  $\beta$ -CD Solution in the Presence of Amphiphilic Molecules.** A marked change was observed both for the absorption and the emission spectra of Py in  $\beta$ -CD solution on addition of surfactant molecules to the system. In particular, an intensity enhancement of the Py emission spectrum was clearly observed in the presence of a series of  $C_nSO_4^-Na^+$  and  $C_nNH_3^+Cl^-$  (or  $C_nN(CH_3)_3^+Br^-$ ). No change



**Figure 3.** (A) III/I ratio of Py fluorescence as a function of concentrations of C<sub>4</sub>SO<sub>4</sub><sup>-</sup>Na<sup>+</sup> (●) and C<sub>6</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> (○). [β-CD] = 13.7 mM; [Py] = 5 × 10<sup>-7</sup> M. (B) III/I ratio as a function of concentrations of NaLS (○), CTAB (●), and CPCI (□). [β-CD] = 13.7 mM; [Py] = 5 × 10<sup>-7</sup> M. (C) Relative yield of Py fluorescence against the concentration of CPCI. [β-CD] = 13.7 mM; [Py] = 5 × 10<sup>-7</sup> M.

in the spectroscopic properties of Py can be observed when surfactant systems without β-CD are examined. This intensity enhancement phenomenon is due to the change in microenvironment experienced by Py,<sup>11</sup> and a convenient parameter, III/I ratio (which stands for the ratio of first and third vibronic bands of Py fluorescence), has been established as a measure of the polarity of the medium.<sup>11b</sup> Figures 3A and 3B depict the III/I ratio of Py as a function of concentration of surfactants in several systems in 13.7 mM β-CD solution containing 5 × 10<sup>-7</sup> M Py. In general, an increase was observed in the III/I ratio for the increasing concentrations of β-CD, indicating that Py experiences a more hydrophobic environment, and finally a plateau was reached above a concentration of 2–8 mM, the exact value more or less depending on the surfactant. The plateau values, 1.4–1.7 in the presence of surfactants, is almost identical with the III/I ratio observed in hydrocarbon solution. For surfactants with relatively small cmc, a sharp decrease in III/I ratio was observed at higher concentrations. For example, the III/I ratio abruptly decreased at 17–20 mM C<sub>12</sub>SO<sub>4</sub><sup>-</sup>Na<sup>+</sup>, or NaLS (cmc = 8 × 10<sup>-3</sup> M), and also at 12–14 mM C<sub>16</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>Br<sup>-</sup> or CTAB (cmc = 9 × 10<sup>-4</sup> M). This

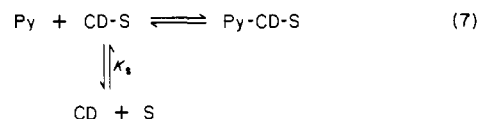
**Table II.** Association Constants and Reciprocal Lifetimes of Py in Py-CD-Surfactant Systems

surfactant (concn, mM)	$K_a, M^{-1}^a$	$1/\tau_0, s^{-1}$
no	44	$4.4 \times 10^6$
C <sub>4</sub> SO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> (20)	3000	$2.2 \times 10^6$
C <sub>6</sub> SO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> (20)	1400	$2.1 \times 10^6$
C <sub>8</sub> SO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> (20)	660	$2.1 \times 10^6$
C <sub>10</sub> SO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> (15)	280	$2.1 \times 10^6$
C <sub>12</sub> SO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> (15)	130	$2.2 \times 10^6$
C <sub>4</sub> NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup> (40)	86	$2.5 \times 10^6$
C <sub>6</sub> NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup> (20)	1300	$2.1 \times 10^6$
C <sub>8</sub> NH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup> (20)	790	$2.2 \times 10^6$
C <sub>10</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup> (20)	440	$2.2 \times 10^6$
C <sub>12</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup> (15)	170	$2.2 \times 10^6$
C <sub>16</sub> N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> Br <sup>-</sup> (10)	330	$2.2 \times 10^6$

<sup>a</sup>Errors: ±15%.

phenomenon was ascribed to the formation of micelles which remove Py from the β-CD because of their larger affinity of the micelles for hydrophobic molecules. In the presence of C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup>, a similar increase and leveling off in III/I ratio were also observed as typically shown for C<sub>16</sub>Pd<sup>+</sup>Cl<sup>-</sup> or CPCl in Figure 3B; however, a relative fluorescence yield was significantly reduced at 12–14 mM CPCl (cmc = 9 × 10<sup>-4</sup> M) as seen in Figure 3C. This is also an indication of micellar formation since it was observed that Py fluorescence was statically quenched in micellar CPCl solutions, and, therefore, fluorescence is considered to originate only from Py complexed with β-CD in the present system containing CPCl. Both the decrease in the III/I ratio of β-CD solutions in the presence of increasing amount of NaLS or CTAB and the decrease in Py fluorescence yield at higher concentrations of CPCl are indicative of a saturation of interaction between β-CD and surfactant molecules. The saturation took place at a surfactant concentration of 10–13 mM (taking the cmc into account) which is a little below the concentration of β-CD used (13.7 mM). This surfactant-CD interaction has previously been recognized by Okubo et al.<sup>12</sup> as an increased "apparent cmc" in micellar solutions of NaLS and CTAB by the addition of CD molecules, which was studied using conductivity measurements. They assumed intuitively that a 1:1 surfactant-CD complex is formed.

More strikingly, in the presence of surfactant molecules (ca. above 3–10 mM), a single exponential decay of Py fluorescence ( $\alpha > 0.96$  in eq 2) with a decay constant of 2.1–2.2 × 10<sup>6</sup> s<sup>-1</sup> was observed.<sup>13</sup> A typical example is shown in Figure 1C for the system containing 20 mM C<sub>10</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>Br<sup>-</sup>. This was rationalized by the increased association of Py and β-CD in the presence of excess surfactant molecules, S, as shown in the following scheme:



The value of the association constant of surfactant and CD,  $K_s$  in eq 7 is not known except in a few systems; Okubo et al.<sup>12</sup> have determined  $K_s(\beta\text{-CD-NaLS}) = 356 M^{-1}$  and  $K_s(\beta\text{-CD-CTAB}) = 2240 M^{-1}$ , for example. However, the saturation of the III/I ratio may indicate that most Py is in the form of Py-CD-S at a sufficient high concentration of surfactant. Therefore, the association constant,  $K_a$ , in the presence of excess surfactant as also determined by means of the analysis of Py fluorescence decay curves described in section 1 (see Table II for the values of  $K_a$ ). It is apparent from Table II that a larger value of  $K_a$  is obtained in the presence of surfactants which have a shorter hydrocarbon chain. However, no interaction was observed between β-CD and C<sub>2</sub> surfactants (C<sub>2</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> and C<sub>2</sub>Pd<sup>+</sup>Br<sup>-</sup>), which may not be sufficiently hydrophobic.<sup>14</sup> The effect of surfactant in the present system can be understood by its complexation with β-CD, thus excluding water molecules originally occupying the cavity of β-CD

(11) (a) Nakajima, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3272–3277. (b) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039–2044.

(12) Okubo, T.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1976**, *80*, 2661–2664.

(13) Complete single exponential decay of Py fluorescence was not achieved in the presence of NaLS or CTAB.

(14) Only a slight interaction was observed for C<sub>4</sub>NH<sub>3</sub><sup>+</sup>Cl<sup>-</sup> with β-CD.

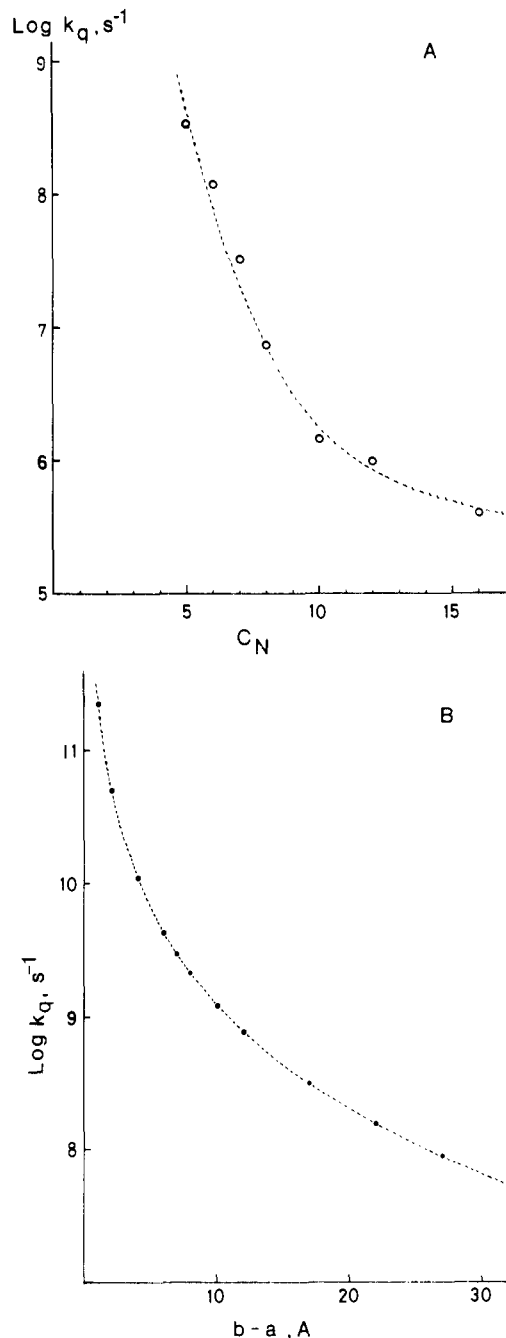


Figure 4. (A)  $\text{Log } k_q$  vs. the number of carbon chain of pyridinium surfactants.  $[\beta\text{-CD}] = 13.7 \text{ mM}$ ;  $[\text{Py}] = 5 \times 10^{-7} \text{ M}$ ;  $[\text{C}_n\text{Pd}^+\text{X}] = 20 \text{ mM}$ . (B) Relation between calculated  $k_q$  and  $(b - a)$ .

leading to a more hydrophobic environment. Accordingly, Py interacts more strongly with the cavity in the presence of surfactants. Shorter surfactant chains may provide more room for Py to interact in the cavity of CD-S complexes.

The equilibrium constant,  $K_a$ , of Py and  $\beta\text{-CD}$  decreases with temperature both in the absence and in the presence of surfactant. A linear relation was observed for the plot of  $\ln K_a$  vs.  $1/T$  in the absence and in the presence of  $20 \text{ mM } \text{C}_6\text{SO}_4^-\text{Na}^+$ . From the plot, we obtained  $\Delta H = -6.8 \text{ kcal/mol}$  and  $\Delta S = -15.5 \text{ cal/mol}\cdot\text{K}$  in the absence of surfactant, and  $\Delta H = -12.0 \text{ kcal/mol}$  and  $\Delta S = -26.5 \text{ cal/mol}\cdot\text{K}$  in the presence of  $\text{C}_6\text{SO}_4^-\text{Na}^+$ , respectively.

Py fluorescence quenching by hydrophilic quenchers was observed in the presence of surfactants in  $\beta\text{-CD}$  system. In Table I, the observed Stern-Volmer quenching rate constants in the presence of  $15 \text{ mM NaLS}$  and  $10 \text{ mM CTAB}$  were listed. Although larger rate constants are obtained in the NaLS-CD system for positively charged quenchers, the magnitudes of constants are

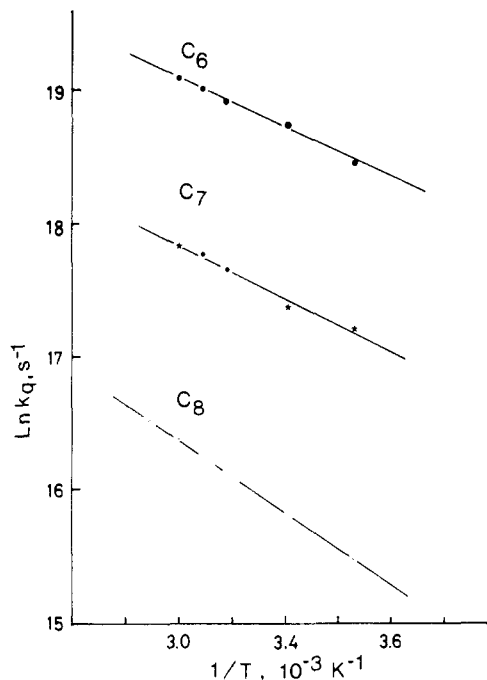


Figure 5. Arrhenius plots of first-order quenching constants of  $\text{C}_6$ ,  $\text{C}_7$ ,  $\text{C}_8$  pyridinium surfactants.  $[\beta\text{-CD}] = 13.7 \text{ mM}$ ;  $[\text{Py}] = 5 \times 10^{-7} \text{ M}$ ;  $[\text{C}_n\text{Pd}^+\text{Br}^-] = 30 \text{ mM}$ .

Table III. Thermodynamic Parameters of Py Fluorescence Quenching in Py-CD- $\text{C}_n\text{PdBr}$  Systems ( $21^\circ\text{C}$ )

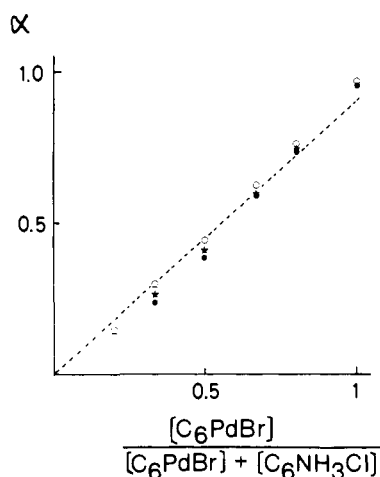
	$\text{C}_6$	$\text{C}_7$	$\text{C}_8$
$E_a$ , kcal/mol	1.8	1.9	2.7
$\Delta G^\ddagger$ , kcal/mol	6.3	7.1	8.0
$\Delta S^\ddagger$ , cal/(mol·K)	-17	-19	-20

not so different from those in surfactant-free  $\beta\text{-CD}$  system. It was also noticed that the quenching constant was significantly reduced for the system where complex formation is necessary for the quenching mechanism, namely,  $\text{Tl}^+$  quenching; however, this was not the case for the  $\text{Cu}^{2+}$  and  $\text{MV}^{2+}$  quenching systems which undergo electron transfer.

**(3) Pyrene Fluorescence Decay in the Presence of Pyridinium Surfactants.** A single exponential decay was also observed for Py fluorescence in the presence of  $\text{C}_n\text{Pd}^+\text{Br}^-$  or  $\text{C}_n\text{Pd}^+\text{Cl}^-$  ( $n > 5$ ). Representative decay curves are shown in Figure 1C. However, a reduced lifetime, which is constant above certain concentration of surfactants, was observed. This suggests that a three-component complex,  $\text{Py-CD-S}$ , is exclusively formed at excess concentration of pyridinium surfactants, and that an "intramolecular-like" quenching of Py fluorescence takes place within this complex. The length of the hydrocarbon chain of pyridinium surfactants as found to significantly affect the rate constant of this quenching reaction. The first-order quenching rate constants of pyridinium surfactants were plotted against the number of carbons in the chain of the surfactant in Figure 4A. A temperature study was carried out for the quenching by  $\text{C}_6$ ,  $\text{C}_7$ , and  $\text{C}_8$  pyridinium bromides over the range from  $0$  to  $75^\circ\text{C}$ . Arrhenius plots of the quenching constants are given in Figure 5. The thermodynamic parameters obtained are listed in Table III, and it can be seen that one of the characteristics of these systems is the large negative values of  $\Delta S^\ddagger$ .

The "diffusion-controlled reaction model in a limited space" proposed by Tachiya<sup>15</sup> was used to explain the chain-length dependent quenching constant of pyridinium surfactants. In this model, reactants A and B are confined in a sphere of radius  $b$ . The first-order quenching constant  $k_q$  is given by:

$$k_q = D\alpha^2 \quad (8)$$



**Figure 6.**  $\alpha$  vs. the mole fraction of  $C_6Pd^+Br^-$ .  $[\beta\text{-CD}] = 13.7 \text{ mM}$ ,  $[\text{Py}] = 5 \times 10^{-7} \text{ M}$ ;  $[C_6Pd^+Br^-] + [C_6NH_3^+Cl^-] = 10 \text{ mM}$  (O),  $14 \text{ mM}$  (★), and  $20 \text{ mM}$  (●).

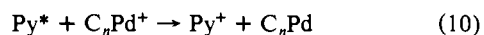
where  $D$  is the diffusion coefficient of  $B$  and  $\alpha_1$  is the smallest positive root of eq 9:

$$\tan\{(b-a)\alpha\} = b\alpha \quad (9)$$

in which  $a$  is the reaction radius. Figure 4B depicts  $k_q$ 's computed in terms of eq 8, where the values of  $D$  and  $a$  are assumed to be  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $8 \text{ \AA}$ , respectively, as a function of  $(b-a)$ . Assuming that the chain length of the pyridinium surfactants is proportional to  $b$ , the present chain-length-dependent quenching constant can be qualitatively understood by the Tachiya's model as seen in Figure 4B. The calculated  $k_q$  values were, however, ca. two orders of magnitude larger than those obtained experimentally. This is connected with the chosen value of  $D$  ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), which is that of free molecules in water. Because of the restricted mobility arising from complexation of  $\beta\text{-CD}$ , a smaller value of  $D$  ( $\sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) would give agreement between theory and experiment.

The peculiar Py fluorescence quenching behavior of pyridinium surfactants in  $\beta\text{-CD}$  system can be utilized to obtain some idea of the association behavior of the surfactants with  $\beta\text{-CD}$ . In the presence of  $C_6NH_3^+Cl^-$  and  $C_6Pd^+Br^-$ , the observed Py fluorescence decay can be fitted by eq 2. The observed  $k_1 = 1.2 \times 10^8 \text{ s}^{-1}$  and  $k_2 = 2.1 \times 10^6 \text{ s}^{-1}$  are the decay constants of Py fluorescence in each single surfactant system,  $C_6Pd^+Br^-$ -CD and  $C_6NH_3^+$ -CD, respectively. The values of  $k_1$  and  $k_2$  were constant at any ratio of  $C_6Pd^+Br^-$  and  $C_6NH_3^+Cl^-$  in the mixed surfactant system. The observed  $\alpha$  values were plotted against the molar fraction of  $C_6Pd^+Br^-$  in  $13.7 \text{ mM}$   $\beta\text{-CD}$  solution. Regardless of the total surfactant concentration employed, an almost linear dependence of  $\alpha$  vs. the molar fraction of  $C_6Pd^+Br^-$  was observed as depicted in Figure 6. This was also confirmed in  $C_8NH_3^+Cl^-$ - $C_6Pd^+Br^-$  and  $C_{12}NH_3^+Cl^-$ - $C_{12}Pd^+Cl^-$  mixed surfactant systems in  $\beta\text{-CD}$  solution. These data, along with the "saturation phenomenon" observed for low CMC surfactants, e.g., NaLS, CTAB, and CPCl, strongly support the 1:1 complex formation of surfactants and  $\beta\text{-CD}$ .

The mechanism of Py fluorescence quenching by pyridinium surfactants can be ascribed to electron transfer given by:

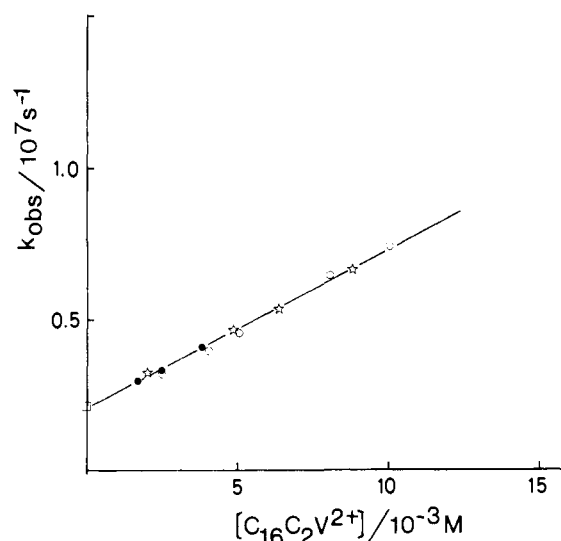


Reaction 10 is exothermic ( $\Delta G = -1 \text{ eV}$ ), while energy transfer is unrealistic from energetic considerations. Transient absorption studies using a nanosecond laser flash photolysis apparatus<sup>16</sup> failed to detect any transient species such as  $\text{Py}^+$  in the spectrum range between 350 and 700 nm. On the other hand, efficient  $\text{Py}^+$  formation was observed in Py fluorescence quenching reactions

**Table IV.** Yields of  $\text{Py}^+$  Fluorescence Quenching with CPCl in Different Media

medium	$\Phi(\text{Py}^+)^a$	medium	$\Phi(\text{Py}^+)^a$
$\text{CH}_3\text{CN}$	0.63	0.1 M NaLS	<0.005
EtOH	0.50	0.5 M NaLS	0.03
50% EtOH/ $\text{H}_2\text{O}$	0.03	0.05 M CTAB	<0.005
EG <sup>b</sup>	<0.005	$\beta\text{-CD}$	<0.005

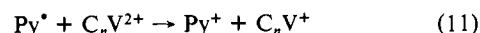
<sup>a</sup> Yields were determined by the same method as described by Nakamura et al. (*J. Phys. Chem.* **1984**, *88*, 3435, based on  $\epsilon(\text{Py}^+ \text{ at } 450 \text{ nm}) = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .)  $[\text{CPCl}] = 10 \text{ mM}$  was used. <sup>b</sup> Ethylene glycol.



**Figure 7.** Stern-Volmer plot of Py fluorescence quenching by  $C_{16}C_2V^{2+}$ .  $[\beta\text{-CD}] = 13.7 \text{ mM}$ ;  $[\text{Py}] = 5 \times 10^{-7} \text{ M}$ ; no CTAB (O);  $[\text{CTAB}] + [C_{16}C_2V^{2+}] = 5 \text{ mM}$  (●);  $[\text{CTAB}] = [C_{16}C_2V^{2+}] = 10 \text{ mM}$  (★).

with  $C_2$ ,  $C_6$ ,  $C_8$ ,  $C_{16}$  pyridinium salts both in ethanol and in acetonitrile, though the  $\text{Py}^+$  formation was low in a 50% ethanol-water mixture or in aqueous NaLS micelles. The yields of  $\text{Py}^+$  on quenching with  $C_{16}$  pyridinium chloride in several different media are summarized in Table IV. The lack of observation of  $\text{Py}^+$  in aqueous media can be attributed to the rapid back electron transfer.

For the sake of comparison with pyridinium surfactants, bipyridinium (or viologen) surfactants,  $C_{16}C_2V^{2+}$  and  $C_7C_7V^{2+}$ , were also studied in Py-CD systems. A constant III/I ratio of 1.6–1.7 was observed above  $1 \text{ mM}$   $C_{16}C_2V^{2+}$ , indicating a similar interaction of this surfactant with  $\beta\text{-CD}$  compared to other surfactants. However, Stern-Volmer-type kinetics with a second-order rate constant,  $k_q = 5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , as observed for Py fluorescence quenching in the presence of  $>2 \text{ mM}$   $C_{16}C_2V^{2+}$ . Identical Stern-Volmer plots were obtained in the absence or presence of CTAB as shown in Figure 7. The second-order kinetics is in contrast to the quenching in the relevant Py-CD- $C_{16}Pd^+Cl^-$  system where only first-order kinetics with a rate constant  $k_q = 4.0 \times 10^5 \text{ s}^{-1}$  was observed. Therefore,  $C_{16}C_2V^{2+}$  molecules, whether complexed with  $\beta\text{-CD}$  or not, can randomly quench the fluorescence of Py through diffusional encounters.  $C_{16}C_2V^{2+}$  molecules other than those complexed with a particular Py molecule in a CD cavity could participate in the quenching reaction leading to a second-order process, since the first-order quenching process is expected to be slow by analogy with the Py-CD- $C_{16}Pd^+Cl^-$  system. As mentioned above, second-order quenching kinetics was absent in Py-CD- $C_nPd^+$  systems. The stronger electron-accepting ability of the bipyridinium group can account for this difference in quenching type and efficiency. The free-energy change of the electron-transfer reaction:



is estimated to be  $-1.5 \text{ V}$ . The products of reaction 11,  $\text{Py}^+$  ( $\lambda_{\text{max}} 450 \text{ nm}$ ) and  $C_nV^+$  ( $\lambda_{\text{max}} 395 \text{ nm}$ ), were actually confirmed via

(16) For instance: Hashimoto, S.; Thomas, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 5230–5237.

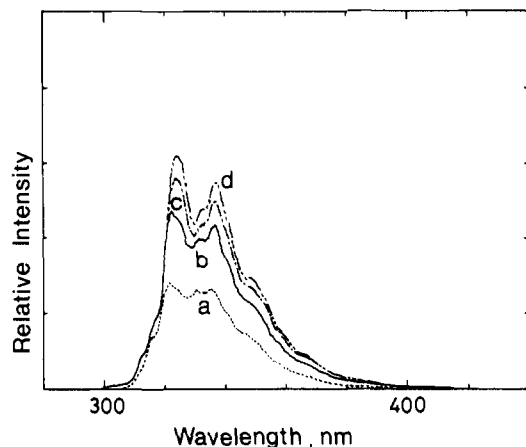


Figure 8. Fluorescence spectra of naphthalene in: (a) water, (b) 13.7 mM  $\beta$ -CD solution, (c) 13.7 mM  $\beta$ -CD solution containing 20 mM  $C_4SO_4^-Na^+$ , (d) 13.7 mM  $\beta$ -CD solution containing 20 mM  $C_8SO_4^-Na^+$ .  $[N] = 6.0 \times 10^{-6}$  M;  $\lambda_{ex} = 278$  nm (isobestic point).

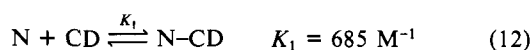
Table V. Equilibrium and Kinetic Constants for the Association of Naphthalene with  $\beta$ -CD

surfactant (concn, mM)	$K_1, M^{-1}$	$k_{-}, s^{-1}$	$k_{+}, M^{-1} s^{-1}$	$\tau_T, ms$
no	$850 \pm 80$ (685 <sup>b</sup> )	$1 \times 10^5$	$8.5 \times 10^7$	0.6
$C_4SO_4^-Na^+$ (20)	$320 \pm 30^c$			
$C_6SO_4^-Na^+$ (20)	$68 \pm 10^c$			
$C_8SO_4^-Na^+$ (20)	$31 \pm 4^c$	$1 \times 10^5$	$3.1 \times 10^6$	3.8
BNK-1 <sup>a</sup>	700	$5 \times 10^4$	$3.5 \times 10^7$	

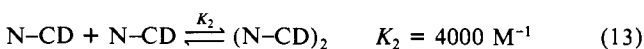
<sup>a</sup> [1-(4-bromo-1-naphthoyl)methyl]trimethylammonium bromide: ref 18c. <sup>b</sup> Reference 4a. <sup>c</sup>  $6.0 \times 10^{-6} M \leq [N] \leq 1.0 \times 10^{-4} M$ .

their transient spectra. Stern-Volmer quenching kinetics were also observed for Py fluorescence quenching by  $C_7C_9V^{2+}$  in 13.7 mM  $\beta$ -CD solutions containing 80 mM  $C_4SO_4^-Na^+$  ( $k_q = 1.4 \times 10^9 M^{-1} s^{-1}$ ).

(4) Interaction of Naphthalene and  $\beta$ -CD in the Presence of Amphiphiles. Hamai<sup>4a</sup> has previously shown the formation of a 1:1 complex between naphthalene (N) and  $\beta$ -CD:



followed by further 2:2 complex formation:



The enhancement of N fluorescence intensity in the presence of  $\beta$ -CD was utilized for the determination of  $K_1$ . In addition, the observation of excimer emission at higher concentrations of N and  $\beta$ -CD confirmed that the equilibrium in eq 13 took place.

In the present study, the effect of amphiphiles was investigated in naphthalene- $\beta$ -CD systems for comparison with the behavior observed in Py- $\beta$ -CD systems. Figure 8 depicts the fluorescence spectra (uncorrected) of  $6.0 \times 10^{-6}$  M naphthalene in water, in  $\beta$ -CD solution, in  $\beta$ -CD solution containing  $C_4SO_4^-Na^+$ , and in  $\beta$ -CD solution containing  $C_8SO_4^-Na^+$ . Spectra identical with that in water were observed in surfactant solutions in the absence of  $\beta$ -CD. In the presence of excess amphiphiles, a further intensity enhancement of the N fluorescence compared with the  $\beta$ -CD system was observed. This is reminiscent of Py- $\beta$ -CD-surfactants systems. Therefore, a three-component complex formation in N- $\beta$ -CD-surfactants system is also suggested. The Benesi-Hildebrand treatment of the fluorescence data used by Hamai<sup>4a</sup> was applied to obtain the association constants in the presence of amphiphiles. Table V lists the values of  $K_1$  in the absence and in the presence of  $C_4$ -,  $C_6$ -, and  $C_8SO_4^-Na^+$ . The smaller values of  $K_1$  obtained in the presence of amphiphiles are markedly different from the binding constants in the corresponding Py systems. It is noteworthy that smaller values of  $K_1$  were observed in the presence of amphiphiles with longer methylene chains. The

Table VI. Equilibrium and Kinetic Constants of Pyrene with  $\beta$ -CD

surfactant (concn, mM)	$K_1, M^{-1}$	$k_{-}, s^{-1}$	$k_{+}, M^{-1} s^{-1}$	$\tau_T, ms$
no	44	$5 \times 10^4$ (a)	$2.2 \times 10^6$ (a)	7
$C_4SO_4^-Na^+$ (20)	3000	$4 \times 10^3$	$1.2 \times 10^7$	77
$C_{12}SO_4^-Na^+$ (15)	130	$6 \times 10^3$	$7.8 \times 10^5$	26

<sup>a</sup> Because of the poor solubility of Py, the determination of exact value was not possible; instead, only the lowest limiting value was estimated.

dynamic parameters for the association of N and  $\beta$ -CD (the entry rate constant,  $k_{+}$ , of N to  $\beta$ -CD and the exit rate constant,  $k_{-}$ , of N from  $\beta$ -CD, where  $K_1 = k_{+}/k_{-}$ ) were determined by a triplet quenching study, a method which has been employed by Almgren et al.<sup>17a</sup> for the determination of kinetic parameters for the association of phosphorescence probes with micelles. The usefulness of the method in the CD system has been demonstrated by Turro et al.<sup>7,17b</sup> The details of the method have been given in the literature.<sup>17</sup>

The time course of the triplet-triplet absorption (T-T absorption) of naphthalene ( $\lambda_{max} = 415$  nm) produced by excitation with laser light ( $\lambda = 308$  nm) was monitored in the presence of various concentrations of the quencher,  $NaNO_2$ . In water single exponential decay of T-T absorption of N was observed with a reduced lifetime at higher concentrations of  $NaNO_2$ ; Stern-Volmer kinetics were observed with a quenching rate constant of  $k_q = (9 \pm 1) \times 10^8 M^{-1} s^{-1}$ . The single exponential decay of T-T absorption was also observed for N in  $\beta$ -CD systems both in the absence and in the presence of  $C_8SO_4^-Na^+$ . However, Stern-Volmer behavior was not observed; instead, the lifetime of T-T absorption leveled off at higher concentrations of quencher. From the quenching behavior,<sup>17</sup> the values of  $k_{-}$  were determined both in the presence and in the absence of  $C_8SO_4^-Na^+$ . The values of  $k_{+}$  were evaluated from the measured  $K_1$  and  $k_{-}$ . All the parameters are listed in Table V.

Dynamic parameters for the association equilibrium of Py- $\beta$ -CD are also determined utilizing the quenching of Py T-T absorption ( $\lambda_{max} = 415$  nm) decay in the presence of Frem's salt, whose quenching rate constant for Py triplet was  $(6.3 \pm 0.5) \times 10^7 M^{-1} s^{-1}$  in 50% ethanol-water mixture. Table VI shows the dynamic parameters in Py- $\beta$ -CD system. Quite different effects of surfactant were observed for N- $\beta$ -CD compared with Py- $\beta$ -CD systems. A reduction in the  $k_{+}$  value leaving  $k_{-}$  unchanged is responsible for the diminished value of the association constant in the N- $\beta$ -CD system in the presence of the surfactant; however, a significant reduction was observed for the values of  $k_{-}$  in the Py- $\beta$ -CD system containing surfactant. In the Py- $\beta$ -CD systems, longer chain surfactants appeared to reduce the  $k_{+}$  value, which explains the reduction of the association constants in the presence of longer chain surfactants. The dimension of naphthalene is smaller than the size of  $\beta$ -CD cavity. Therefore, in the case of N- $\beta$ -CD complex, complete inclusion of N inside the cavity of  $\beta$ -CD can be expected. It is pertinent to note that naphthalene derivatives do not form a complex with  $\alpha$ -CD which has a smaller cavity size than  $\beta$ -CD.<sup>3c</sup> Accordingly, it is expected that the complexation of amphiphiles with  $\beta$ -CD renders an unfavorable situation for N inclusion with the  $\beta$ -CD. This may account for the decreased binding constants in the presence of surfactants, where the space-filling effect of surfactant molecule inhibits the entry of N into the  $\beta$ -CD, leading to the reduced value of  $k_{+}$ . However, in the Py- $\beta$ -CD systems, increased association constants were obtained in the presence of amphiphiles. Py has larger dimensions than N and is not completely included inside the cavity of  $\beta$ -CD. A considerably smaller association constant of Py with  $\beta$ -CD compared to N with  $\beta$ -CD indicates the very weak nature of the interaction of Py with  $\beta$ -CD in the absence of surfactants. The increased hydrophobicity by the complexation with surfactants must be responsible for the larger binding constant of Py with

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$\beta$ -CD, or the diminished value of  $k_-$  from  $\beta$ -CD in the presence of surfactants. For Py, the stabilization by hydrophobic interaction with the  $\beta$ -CD-surfactant complex can be considerably larger than that of the  $\beta$ -CD-surfactant complex with N which is less hydrophobic than Py. Therefore, the degree of "fitting" of the cavity of CD with N is more important in order to form a complex.

Surfactant in the N- $\beta$ -CD system caused a disruption of excimer formation. For instance, Hamai<sup>4a</sup> observed excimer emission in the system containing  $5.8 \times 10^{-5}$  M N and  $1 \times 10^{-3}$  M  $[\beta\text{-CD}] < 1 \times 10^{-2}$  M. However, the excimer emission was undetected with the condition:  $[\text{N}] = 1-2 \times 10^{-4}$  M and  $6 \times 10^{-4}$  M  $[\beta\text{-CH}] \leq 1.37 \times 10^{-2}$  M in the presence of 20 mM of  $\text{C}_4^-$ ,

$\text{C}_6^-$ , and  $\text{C}_8\text{SO}_4^- \text{Na}^+$ . This can also be attributed to the space-filling effect of surfactants in the CD cavity, preventing the further aggregation of N-CD complexes.

Consequently, different features were observed for the effects of surfactants with guest-CD systems depending on the size and hydrophobicity of the guest molecules.

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Registry No. Py, 129-00-0; N, 91-20-3;  $\beta$ -CD, 7585-39-9.

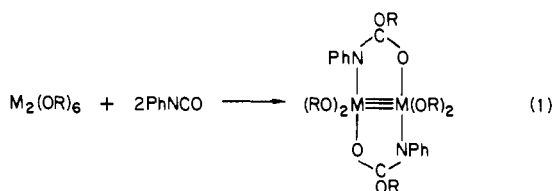
## Mechanistic Insight into the Reaction of Phenyl Isocyanate with Ditungsten Hexa-*tert*-butoxide: Isolation and Characterization of Early Intermediates

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**Abstract:** By working at low temperature ( $-80$  to  $-45$  °C) the purple crystalline compound  $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-PhNCO})$  (**1**), which is known to be a precursor in the preparation of  $\text{W}_2(\text{OCMe}_3)_4[\mu\text{-PhNC}(\text{OCMe}_3)\text{O}]_2$  (**2**) from  $\text{W}_2(\text{OCMe}_3)_6$  and PhNCO, has been isolated and its structure determined. The molecule consists of a  $(\text{RO})_3\text{W}=\text{W}(\text{OR})_3$  ( $\text{R} = \textit{tert}$ -butyl) moiety ( $\text{W}-\text{W} = 2.488$  (1) Å) bridged by the PhNCO molecule and the structure is quite similar to that of  $\text{W}_2(\text{OR})_6(\mu\text{-tolylNCNtoly})$  recently reported by us. Compound **1** will react with additional PhNCO at temperatures above  $-15$  °C to give **2**. It has also been found that **1** reacts with  $\text{PMe}_3$  to give  $\text{W}_2(\text{OR})_5(\text{PMe}_3)[\mu\text{-PhNC}(\text{OR})\text{O}]$  (**3**), which has also been structurally characterized. The molecule contains a  $(\text{RO})_3\text{W}=\text{W}(\text{OR})_2\text{PMe}_3$  moiety bridged by the bidentate  $\text{PhNC}(\text{OR})\text{O}^-$  ligand. Crystallographic data for the two compounds are as follows. **1**:  $P2_1/c$ ;  $a = 11.054$  (6) Å,  $b = 17.821$  (7) Å,  $c = 19.401$  (8) Å,  $\beta = 100.52$  (2)°;  $V = 3758$  (2) Å<sup>3</sup>,  $Z = 4$ . **3**:  $P1$ ;  $a = 10.2916$  (6) Å,  $b = 21.1376$  (7) Å,  $c = 22.0929$  (6) Å,  $\alpha = 117.04$  (1)°,  $\beta = 90.33$  (4)°,  $\gamma = 93.73$  (4)°;  $V = 4268.2$  (3) Å<sup>3</sup>,  $Z = 4$ . Mechanistic pathways for the formation of **2** are discussed critically in the light of the new structural information.

Dimolybdenum and ditungsten hexaalkoxides are known to react readily with phenyl isocyanate. Chisholm and co-workers found that  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$  reacts in the presence of pyridine to give  $\text{cis-Mo}_2(\text{O-}i\text{-Pr})_4[\mu\text{-PhNC}(\text{O-}i\text{-Pr})\text{O}]_2$  and in our laboratory we found that  $\text{W}_2(\text{OCMe}_3)_6$  reacts to give  $\textit{trans-W}_2(\text{OCMe}_3)_4[\mu\text{-PhNC}(\text{OCMe}_3)\text{O}]_2$ . Both of these reactions as well as the full characterization of both products by spectroscopic data and X-ray crystallography have recently been reported in a joint publication.<sup>1</sup> Although the stereochemistry of the two products differs, the type of reaction is otherwise the same in each case, as shown schematically in eq 1. The key transformation, which takes place



twice, is the migratory insertion of PhNCO into an M-OR bond to form the anion of a carbamate ester which takes up a bidentate bridging posture with respect to the triply bonded  $\text{M}_2$  core.

In the case of the  $\text{W}_2(\text{OCMe}_3)_6$  reaction the observation that at least one intermediate was stable in solution at low temperature

encouraged us to attempt to determine, at least in part, how the overall transformation represented by eq 1 takes place. We have been able to gain direct insight into at least one and perhaps two of the first steps and we report those results here.

### Experimental Section

Ditungsten hexa-*tert*-butoxide,  $\text{W}_2(\text{OCMe}_3)_6$ , was prepared<sup>2</sup> by Na/Hg reduction of  $\text{WCl}_6$  in THF at  $-10$  °C in the presence of  $\text{LiOCMe}_3$ , followed by recrystallization from hexane at  $-10$  °C. All reactions were done under an argon atmosphere.

**Preparation of  $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-C}_6\text{H}_5\text{NCO})$ .** A weighed amount of  $\text{W}_2(\text{OCMe}_3)_6$  (400 mg, 0.5 mmol) was dissolved in a 20 mL of toluene. The solution was cooled to  $-79$  °C. At this temperature 0.2 mL (1.6 mmol) of phenyl isocyanate was added to the solution by using a syringe. The solution began to turn from red to purple. After 1 h, the reaction mixture (totally purple) was allowed to warm up to  $-45$  °C where it was stirred for 2 h. The solution was then filtered into a precooled ( $-45$  °C) storage tube. Crystals of **1** were obtained by removing the solvent slowly under vacuum ( $5 \times 10^{-3}$  torr;  $-45$  °C for 8 h) in 80-90% yield based on tungsten.

**Preparation of  $\text{W}_2(\text{OCMe}_3)_5(\text{PMe}_3)[\mu\text{-(C}_6\text{H}_5\text{)NC(O)OCMe}_3]$  (**3**).** A weighed amount (ca. 100 mg, 0.11 mmol) of  $\text{W}_2(\text{OCMe}_3)_6(\mu\text{-C}_6\text{H}_5\text{NCO})$  (**1**) was dissolved in 10 mL of toluene at  $-79$  °C. Trimethylphosphine, 0.1 mL (1.6 mmol), was added at this temperature. No color change was observed. After 2 h of stirring at  $-79$  °C there was still no color change, and the solution was allowed to warm up over a period of 2 h to room temperature where it was then stirred for 2 h. The color

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