

References and Notes

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The Effect of Micellar Phase on the State and Dynamics of Some Excited State Charge Transfer Complexes

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Abstract: The effect of micellar phase on kinetic processes of electron transfer reactions of exciplexes formed by pyrene (P) and *N,N*-dimethylaniline (DMA) has been studied. Transitory species are produced by a 10-ns pulse of 347.1-nm light from a Q-switched ruby laser and detected by rapid spectrophotometric or conduction techniques. Singlet excited pyrene (P*) readily accepts an electron from DMA to form an ion pair (P⁻ and DMA⁺), and the fate of the ion pairs depends critically on the micellar environment. In the case of cationic micelles, DMA⁺ is quickly expelled from the micellar surface while P⁻ is retained, leading to a long anion lifetime (~500 μs). On the other hand, an anionic micellar surface traps DMA⁺ ions and enhances the geminate ion recombination process with P⁻. Several pyrene derivatives such as pyrenebutyric acid, pyrenesulfonic acid, pyrenetetrasulfonic acid, pyrenedodecanoic acid, and pyrenecarboxaldehyde which are solubilized at different sites in micelles are also selected as e⁻ acceptors to investigate the effect of separation between P* and DMA on the forward and back e⁻ transfer processes. Similar studies were carried out with the molecule P-(CH₂)₃-DMA which forms intramolecular exciplexes. Here neither ion can escape from the exciplex owing to the restraint of the propyl chain. The physical and chemical properties of excited states of this molecule-micellar system are dramatically different from those of intermolecular complexes. Micellar systems suggest the constituent ions of exciplexes. This has implications for conversion of light energy into ionic fragments which can be subsequently utilized.

Introduction

Since Weller^{2a} first identified exciplexes or excited charge transfer complexes, these systems have received detailed attention and are now comparatively well characterized. The formation of a charge transfer complex between any two molecules depends on the overall energetics of the processes leading to the transfer of an electron from one molecule of the pair to the other. Excitation of the partners often provides sufficient incentive for this process to take place. The polarity of the surrounding medium also sharply affects the nature of and extent of formation of the exciplex. The formation of an exciplex results in a diminution of the natural spectroscopic properties of the excited but separated partners of the pairs, and in the formation of new properties which are specific to the exciplex. In polar media such as alcohols or acetonitrile the exciplex dissociates into ions of the molecular pair. The dynamics of these varied processes have been extensively studied in simple solvents.^{2b,3-7}

An intriguing extension of exciplex studies is provided by molecules of configuration A-(CH₂)_n-D where the electron acceptor A and donor D are linked by a number of methylene groups. Intra- rather than intermolecular exciplexes are then found on excitation. Diffusion of A and D is no longer a parameter of the system, and the ability of the electron to jump

from D to A under different geometrical orientations of D and A is now of prime importance.

The present paper describes the effect of the micellar phase on formation and subsequent reactions of exciplexes. Micelles possess a lipid or hydrocarbon-like core bounded by a polar water-lipid interface, which, consisting of the head group of the surfactant, may be anionic, cationic, or neutral in nature. Molecules may be absorbed in the surface of the micelle or be incorporated into the lipid structure. Such events lead to quite dramatic modifications of radiation induced reactions of these solubilized species.⁸ The solvent-dependent nature of exciplexes and their highly polar nature suggest that charged micellar surfaces should have some influence on these species.

Laser photolysis and time-resolved fluorescent techniques were used to investigate various pathways of the exciplex in micellar systems. Photoconduction experiments where the currents are observed subsequent to the excitation of the exciplex by the laser light were carried out to elucidate directly the formation of the dissociated ion radicals. Both the intermolecular exciplex (pyrene and *N,N*-dimethylaniline) and intramolecular exciplex pyrene-(CH₂)₃-*N,N*-dimethylaniline were investigated in cationic, anionic, as well as nonionic micelles. A comparison of the fates of exciplexes in micelles and simple solvents is documented and discussed. Several pyrene derivatives such as pyrenesulfonic acid (PSA), pyrenebutyric acid (PBA), pyrenetetrasulfonic acid (PTSA), pyrenedodecanoic acid (PDA), and pyrenecarboxaldehyde (PCHO)

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which are solubilized at different sites in micelles are also selected as e^- acceptors to study effect of distance and separation between the A^* (excited singlet states) and D on the forward and back electron transfer processes.

The data and conclusions that follow construct and suggest models for electron transfer processes in model biological systems. The effect of micelles on effectively prolonging the separation of the dissociated ions of the exciplex provides information of use to the storage of light energy as chemical energy.

Experimental Section

Fluorescence spectra were measured on an Aminco-Bowman spectrofluorimeter. Laser photolysis studies were carried out on a q-switched frequency double ($\lambda = 347.1$ nm) ruby laser with an output of some 100 mJ in pulses of less than 20 ns duration. The laser pulse intensity was varied by interposing transparent Pyrex microscope slides into the beam path. Most laser photolysis experiments were deliberately carried out at low laser intensity in order to avoid other high-intensity radiation induced processes such as biphotonic photoionization.

The photoconductivity changes in simple solvents and nonionic micelles were followed by a dc voltage divider method which has been described earlier.⁹ With solutions of high conductance, viz., ionic micelles, the large dc voltage generated by this method was backed off by a comparative method utilizing a third electrode and a differential oscilloscope amplifier. The dc voltage was applied only momentarily before the laser pulse. All solutions were degassed with N_2 for 30 min prior to utilization.

The prolonged period of bubbling is necessary in order to achieve long (ms) lifetimes for the P^- ions.

Materials. Sodium dodecyl sulfate (NaLS) (Matheson Coleman and Bell, USP grade), cetyltrimethylammonium bromide (CTAB, Fluka, purum), cetylpyridinium chloride (Eastman), sodium cetyl sulfate (NaCS, Schwarzmann), sodium laurate (Eastman), cetylammmonium chloride (CACl, Eastman), dodecyltrimethylammonium chloride (DTAC, Eastman), and cetyltrimethylammonium chloride (CTAC, Eastman) were repeatedly recrystallized from MeOH. Cetyltributylammonium bromide (CTBAB) was prepared by refluxing (30 h) hexadecyl bromide with tributylamine in absolute alcohol. The compound was repeatedly recrystallized from absolute ether, ~60%, mp 80 °C. A critical micellar concentration (cmc) for CTBAB of $3.6\text{--}4.2 \times 10^{-4}$ M was determined by using relative intensity ratio of pyrene vibrational bands. Pyrene (P, Kodak) was passed through silica gel in cyclohexane solution and then recovered. Nonylphenoxy poly(ethyleneoxy) ethanol (Igepal CO-630, GAF Corp.) and *N,N*-dimethylaniline (DMA, Fisher reagent grade) were used directly without further purification. 1-Pyrenebutyric acid (PBA) and 1-pyrenecarboxaldehyde (PCHO) (Pfaltz & Bauer, both) were repeatedly recrystallized from benzene. 1-Pyrenesulfonic acid (PSA, Frinton Laboratories) was recrystallized from an ethanol-water mixture, and 1,3,6,8-pyrenetetrasulfonic acid (PTSA, Eastman) was recrystallized from water. 11-(1-Pyrenyl)dodecanoic acid (PDA) was prepared in this laboratory and details will be published separately. The preparation of *N,N*-dimethyl-4-[3-(1-pyrenyl)propyl]aniline³⁵ (P_3) is as follows.

***N,N*-Dimethyl-4-acetylaniline** was prepared by reductive methylation of 4-acetylaniline according to Pearson and Bruton:¹⁰ mp 101–104 °C (lit.¹⁰ mp 102–104 °C); NMR ($CDCl_3$) δ 7.90 (d, 2 H_A benz, $J_{AB} = 9$ Hz), 6.67 (d, 2 H_B benz, $J_{AB} = 0$ Hz), 3.02 (s, 6 H, $N(CH_3)_2$), 2.50 ppm (s, 3 H, $COCH_3$).

***N,N*-Dimethyl-4-[3-(1-pyrenyl)-1-oxo-2-propenyl]aniline.** A suspension of 2-pyrenecarboxaldehyde (2.82 g, 12.2 mM) in 0.1 M alcoholic NaOH (50 mL) was added to the solution of *N,N*-dimethyl-4-acetylaniline (2 g, 12.2 mM) in 0.1 M alcoholic NaOH (50 mL). After overnight stirring at room temperature under a N_2 atmosphere and product was separated from the cooled mixture by filtration. An orange-colored solid was obtained in a pure state (TLC) by washing with boiling methanol, yield 3 g or 66.5%. For the elemental analysis the compound was recrystallized from dichloromethane-hexanes and acetone, mp 245–247 °C. Anal. Calcd for $C_{27}H_{21}ON$: C, 86.37; H, 5.64; N, 3.73. Found: C, 86.15; H, 5.54; N, 3.72. IR (KBr) 1660 (m) ($-CO-$), 1610 (s), 1580 cm^{-1} sh (m) (aromatic, $-CH=CH-$, strong conjugation).

***N,N*-Dimethyl-4-[3-(1-pyrenyl)-1-oxopropyl]aniline.** A solution of *N,N*-dimethyl-4-[3-(1-pyrenyl)-1-oxo-2-propenyl]aniline (1.3 g, 3.46 mM) in THF (250 mL) was hydrogenated in a Parr apparatus using 10% palladium on carbon as a catalyst. The crude product obtained after evaporation of THF was recrystallized from dimethoxyethane giving a pale yellow solid. 820 m (63%), mp 145–147 °C. Anal. Calcd for $C_{27}H_{23}ON$: C, 85.91; H, 6.14; N, 3.71. Found: C, 86.20; H, 6.23; N, 3.59. IR (KBr) 1660 (s) ($-CO-$), 1610 cm^{-1} (s) (aromatic). NMR ($CDCl_3$) 7.78–8.43 (m, 11 H, 2 H_A benz, 9 H pyrene), 6.56 (d, 2 H_B benz, $J_{AB} = 9$ Hz), 3.2–3.93 (m, 4 H, $(-CH_2-)_2$), 2.93 ppm (s, 6 H, $N(CH_3)_2$).

***N,N*-Dimethyl-4-[3-(1-pyrenyl)propyl]aniline.** The saturated ketone obtained above (600 mg, 1.59 mM) was reduced in diethylene glycol (8 mL) with hydrazine hydrate (95%, 0.25 mL) and sodium hydroxide (0.25 g). After refluxing for 2.5 h H_2O was added followed by extraction with benzene. The crude product was recrystallized from hexane and further purified on a silica gel column with benzene, 260 mg (45%), mp 96–97 °C. Anal. Calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85. Found: C, 88.91; H, 7.06; N, 3.63. IR (KBr) 1610 cm^{-1} (w) (aromatic); NMR ($CDCl_3$) 7.62–8.2 (m, 9 H, pyrene), 7.06 (d, 2 H_A benz, $J_{AB} = 9$ Hz), 6.62 (d, 2 H_B benz, $J_{AB} = 9$ Hz), 3.23 (br t, 2 H, pyrene $-CH_2-$, $J = 7.5$ Hz) [2.77 (s, $N(CH_3)_2$), 2.64 (br t, $-CH_2Ph-$, $J = 7.5$ Hz) 8 H], 1.88–2.34 ppm (m, 2 H, $-CH_2CH_2CH_2-$).

Results and Discussion

Location of Arene Probes in Micellar Solutions. The dynamic sites of solubilization of pyrene (P) and several pyrene derivatives have been determined by NMR and fluorescence techniques.^{12,13} It is concluded that pyrene is solubilized in the interior micelles while the pyrene chromophore of pyrenesulfonic acid (PSA) and pyrenecarboxaldehyde (PCHO) are located in the micellar surface region. NMR data indicate that the pyrene chromophore of pyrenebutyric acid (PBA) is located in the micellar outer core region. The absorption spectrum of dimethylaniline (DMA) in micellar solution resembled that in water rather than the spectrum in nonpolar solvents. NMR studies also suggest that DMA is located at the micellar water interface in CTAB.¹⁴

Quenching of Pyrene Fluorescence by DMA in Micellar Solution. Pyrene fluorescence is efficiently quenched by DMA in micelles. Figure 1 shows the Stern-Volmer plot of pyrene monomer fluorescence intensity ratio I_0/I_F vs. [DMA] in NaLS and CTAB micelles. The fluorescence intensity in the absence and presence of DMA are represented by I_0 and I_F , respectively. Unlike the linear dependence of I_0/I_F vs. [DMA] as reported by Mataga¹⁵ for the quenching of pyrene fluorescence by DMA in acetonitrile, the data in micelles showed curvature, Figure 1. A low quenching efficiency is noted at low quencher concentrations followed by a much higher efficiency at higher quencher concentration. This is indicative of two types of quenching kinetics in micelles.

Figure 2 shows the effect of DMA on typical fluorescence decay curves together with the corresponding semilogarithmic plot of the data. In the absence of DMA (Figure 2a), a smooth exponential decay is observed in NaLS micelles. Addition of DMA to the system causes an initial fast decay to appear and the kinetic plot exhibits a shape corresponding to the sum of two exponential functions (Figure 2b). However, in the case of homogeneous solvents (Figure 2c) addition of a similar concentration of DMA to the pyrene system gives rise to a single exponential fluorescence decay.

The unusual quenching behavior in micellar solutions is best explained by the extent of association of DMA with micelles. At low DMA concentrations the majority of the DMA remains in the water phase. In order to quench pyrene fluorescence, DMA has to penetrate the micelle and the quenching efficiency is low.^{8,16} At higher DMA concentrations, some DMA will associate with micelles. The fluorescence can now be quenched either by DMA which is solubilized on the micelle-water interface or by DMA which resides in water. The quenching efficiency of the former process is much higher than that of the

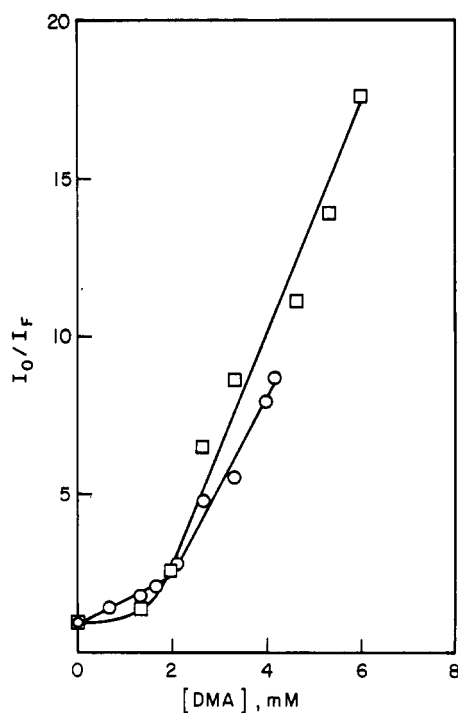


Figure 1. The Stern-Volmer plot of pyrene monomer fluorescence intensity ratio I_0/I_F vs. [DMA] in NaLS (O) and CTAB (□) micelles.

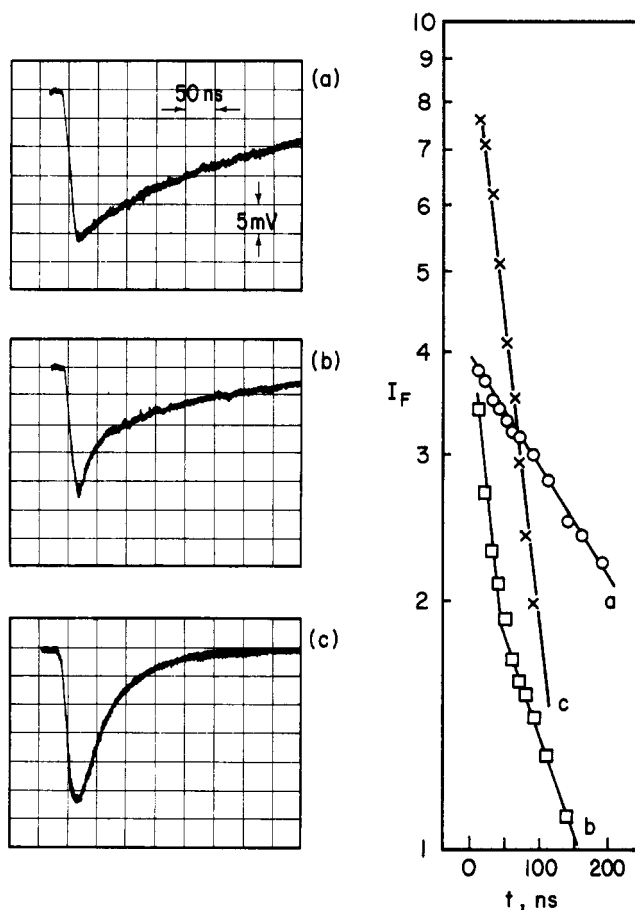


Figure 2. The effect of DMA on the fluorescence decay of pyrene monomer in micelles and MeOH: (a) [NaLS] = 0.05 M; (b) [NaLS] = 0.05 M, [DMA] = 2 mM; (c) MeOH, [DMA] = 2 mM.

latter.^{8,16} The initial rapid decay followed by a subsequent slower decay as shown in the semilogarithmic plot of Figure 2b corresponds to quenching by DMA which resides in the

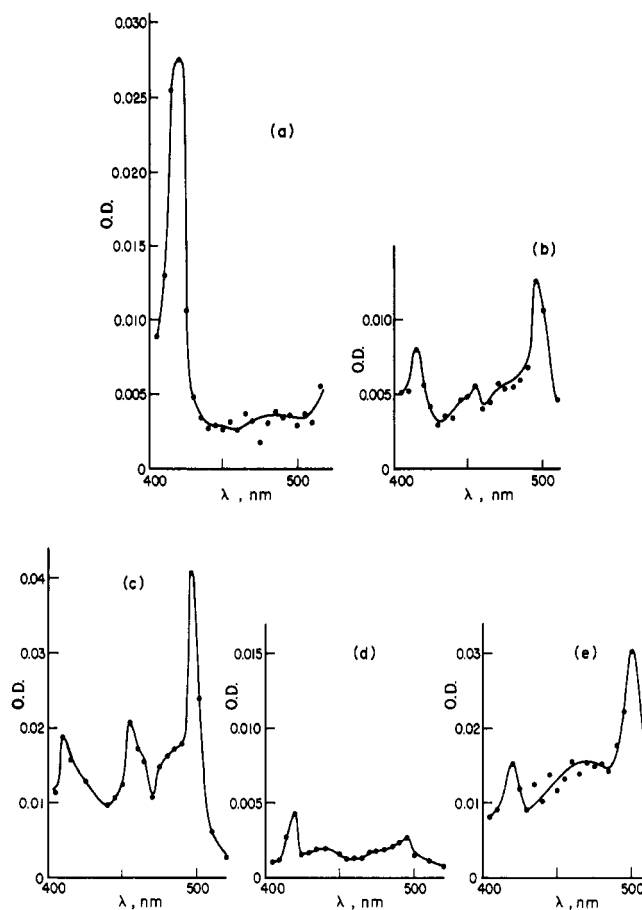


Figure 3. Transient absorption spectra of 50 μM pyrene and 10^{-2} M DMA following laser photolysis in (a) cyclohexane, (b) MeOH, (c) 0.02 M CTAB, (d) 0.01 M Igepal, and (e) 0.05 M NaLS.

micelle-water interface, and by DMA in the water phase, respectively. Increasing DMA concentration increases the contribution of the initial fast decay (as the amount of DMA associated with each micelle increases); therefore the quenching efficiency is higher at higher DMA concentration. Similar effects have been observed with CH_2I_2 as a quencher of pyrene fluorescence in micelles.¹⁶

Figure 2c shows the fluorescence decay and the corresponding semilogarithmic plot in methanol in the presence of DMA. Simple pseudo-first-order decay was obtained over the whole DMA concentration range. This clearly demonstrates that the distribution of DMA between two phases, micellar and water, sharply alters the quenching kinetics.

It is pertinent to note that Ware¹⁷ found it necessary to invoke time-dependent rate constants in order to quantitatively explain the quenching of anthracene fluorescence by DMA. Such processes would also lead to nonlinearity of the Stern-Volmer plots, and may contribute to the present data. However, the exact parallel of the present data with that obtained previously¹⁶ with CH_2I_2 strongly supports the former quenching mechanism.

Formation of Intermolecular Exciplexes. The laser-induced transient absorption spectra of 5×10^{-5} M P and 10^{-2} M DMA in cyclohexane, methanol, and CTAB, NaLS, and Igepal micelles are shown in Figure 3. In nonpolar solvent such as cyclohexane (Figure 3a), a single strong peak, $\lambda_{\text{max}} \sim 420$ nm, is predominant in the spectrum (400–500 nm). This is the characteristic pyrene triplet-triplet absorption.^{18,19} In polar solvents, e.g., methanol (Figure 3b), in addition to the T-T absorption, a stronger absorption appears at 494 nm which resembles the spectrum of P^- . The smaller peak around 460 nm is attributed to the absorption of the dimethylaniline cation,

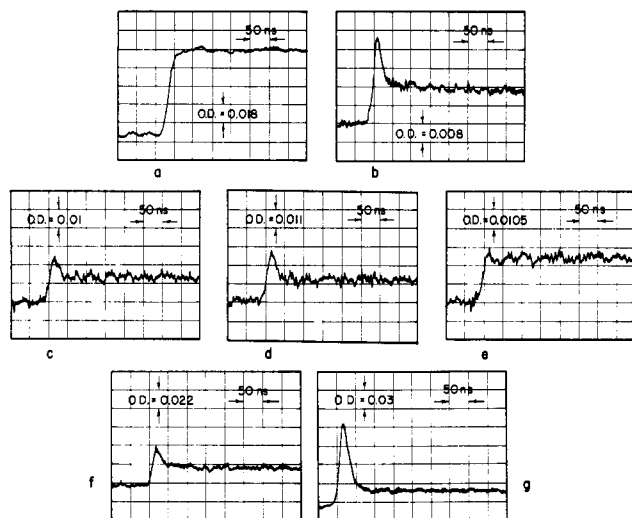
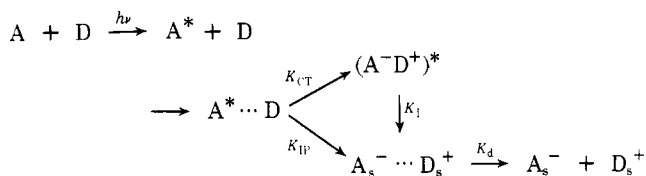


Figure 4. The oscilloscope trace of P^- (monitored at 493 nm) dissociated from P/DMA exciplexes following laser photolysis in micellar solutions: (a) 0.02 M CTAB; (b) 0.02 M NaLS; (c) 0.02 M NaLS, 10 °C; (d) 0.02 M NaLS, 20 °C; (e) 0.02 M NaLS, 40 °C; (f) 0.02 M NaLS, 50 μ M PBA; (g) 0.02 M NaLS, 50 μ M PDA.

DMA⁺. The mechanisms suggested in simple solvents for the electron transferred reaction is as follows:¹⁸



where the rate constants K_{IP} and K_I increase with increasing solvent polarity, $(A^-D^+)^*$ is the fluorescent exciplex, and $A_s^- \cdots D_s^+$ is the nonfluorescent solvated ion pair which subsequently dissociates into ions.

The transient absorption spectra of P and DMA in cationic (CTAB), anionic (NaLS), and nonionic (Igepal) micelles are shown in Figures 3c–e, respectively. The intensities of various absorption bands depend dramatically on the type of micellar surface charge. The intensity of the pyrene anion (λ 494 nm) decreases significantly from cationic micelle CTAB to neutral micelle Igepal with a further decrease in anionic micelle NaLS.

Low laser intensities ($<10^{-2}$ J/pulse) were used in the present work in order to minimize two-photon photoionization processes. At these intensities, the photoionization of pyrene resulted in a yield of cation which was unobservable, i.e., $<10^{-7}$ M/pulse.

It has already been established that the polarity of the environment of pyrene in these systems varies from micelle to micelle.²⁰ For example, pyrene experiences a less polar environment in NaLS compared to CTAB and Igepal owing to the different extent of H₂O penetration into micelles and/or the position of pyrene in the micelle. This would account for some of the differences in the absorption intensities of the pyrene anion P^- in various micelles. However, the intensity of the P^- absorption in NaLS is comparable to that in cyclohexane even though the polarity of pyrene is drastically different in these two systems.²⁰ Furthermore, the P^- intensity differs significantly in CTAB, Igepal, and MeOH in spite of the similar environmental polarity for pyrene in these systems. Therefore the formation of P^- ions from P/DMA exciplexes in micellar systems is controlled by factors other than polarity of the micellar interior.

It is particularly instructive to look into the decay of P^- radicals in micelles. Figures 4a and 4b show the decay of P^-

in CTAB and NaLS, respectively. In cationic micelles CTAB, P^- decays very slowly and uniformly while in anionic micelles, NaLS, P^- decays via two distinct processes, an initial fast decay with a lifetime of a few nanoseconds followed by a subsequent slow decay.

The fast initial decay of P^- radical in NaLS is best explained by the back electron transfer reaction from P^- to its gegenion DMA⁺. Such geminate recombination processes arising from nonhomogeneous initial distribution of primary irradiation products known as "spur" or "cage" effect in radiation chemistry²¹ have been reported by Thomas et al.²² and treated theoretically by Mozumder et al.²³ However, direct observation of geminate recombination of ion pairs in the more selective photochemical excitation could only be observed by picosecond spectroscopy,^{16,24} or in highly viscous systems at low temperature.²⁵ Therefore, the detection of ion recombination of P^- and DMA⁺ in NaLS micelles by nanosecond laser photolysis is intriguing in that the strong interaction between the environment and ions can change the physicochemistry of energy dissipation of the exciplex.

Excitation of P within the micelle leads to electron transfer from DMA located at the micelle–H₂O interface. Strong Coulombic interaction forces between the large negatively charged surface head group and the newly formed DMA⁺ could "trap" the DMA⁺ and prevent diffusion away from the micelle. This encourages geminate ion recombination of P^- and DMA⁺ as illustrated by the fast initial decay of P^- in NaLS micelles. In the case of cationic micelles CTAB, following transfer of an electron from DMA to P*, the resulting DMA⁺ is rapidly displaced from the cationic micelles owing to strong Coulombic repulsive forces. The separation between P^- and DMA⁺ becomes too large for electrons to transfer back from P^- to DMA⁺. Therefore, most P^- can escape from their gegenions DMA⁺, and ion decay is slow. Similar fast initial ion recombination processes are also found in other anionic micelles such as sodium cetyl sulfate (NaCS) or sodium laurate, while in all cationic micelles such as cetyltrimethylammonium chloride (CTAC) and dodecyltrimethylammonium bromide (DTAB), no initial fast ion recombination could be detected. The charged surface of micelles can either catalyze or retard the ion recombination process depending on the attractive or repulsive force between DMA⁺ radicals and the micellar surface. Owing to the ultrafast nature of the geminate ion recombination process it is critical that DMA sits close to the micellar surface so that after transfer of an electron to P*, DMA⁺ can quickly diffuse away from the micellar surface. The DMA⁺ then escapes the Coulombic electric field of its counteranion in cationic micelles.

Since the ion recombination processes involve dynamic movement of cations as well as anions, changing the viscosity of environment around the ions may affect the diffusion kinetics of both ions. Figures 4c–e shows the oscilloscope trace of P^- in NaLS in the presence of DMA at three different temperatures. Increasing the temperature decreases the ion recombination process (Figures 4c–e). At higher temperatures the viscosity of the system decreases, P^- can diffuse more readily, and the probability of ion recombination decreases since more P^- can escape from the electric field of the gegenions DMA⁺. No ion recombination process could be observed in CTAB even at low temperature (10 °C). The encounter probability between DMA⁺ and P^- is still low even though the viscosity of the system increases. Further decrease in temperature is impossible because of precipitation of micelles at low temperature.

Addition of inert electrolyte to micellar systems has little effect on the ion recombination process. Even though electrolytes are known to neutralize part of micellar surface charges, the extent of neutralization is small.²⁶ Therefore, the cationic and anionic micellar surface could still effectively trap

Table I. The Effect of Micellar Phase and Additives on the Decay (First Half-Life, $\tau_{1/2}$) of Pyrene Anion Radicals P^- Dissociated from Exciplex P/DMA System^a

	$\tau_{1/2}$, μ s
MeOH	6
20 mM CTAB	500
20 mM NaLS	66.6
10^{-2} M Igepal	13.1
20 mM CTAB + 0.2 mM NaOH	71.4
20 mM CTAB + 0.1 M NaCl	230
20 mM CTAB + 0.02 M Na_2SO_4	190

^a [P] = 50 μ M; [DMA] = 10^{-2} M.

or repel the DMA^+ and affect the ion recombination process.

Several pyrene derivatives such as pyrenebutyric acid (PBA) and pyrenedodecanoic acid (PDA) were used as acceptors to study the ion-recombination processes in micelles. With a hydrophilic carboxylic head group attached to pyrene chromophore, the solutes PBA and PDA are expected to bind more strongly to the micellar surface. Figures 4f and 4g show that the ion recombination process in NaLS micelles is similar for both pyrene (P) and PBA while the recombination probability for PDA^- and DMA^+ is much higher. This is somewhat surprising since PDA is expected to bury the pyrene chromophore further inside the micelle, and the back transfer of e^- should be less favored. However, the packing of PDA in micelles may be unfavorable as the large P chromophore is attached to the end of a long hydrocarbon chain. In other words, PDA may be wrapped around the micellar surface with the pyrene chromophore on the surface, rather than toward the micellar core. In this case the probability of forward and back electron transfer between PDA^* and DMA would be higher than in systems where P is within the micelles.

In conclusion, the presence of a micellar phase has a dramatic effect on the dynamics of the electron transfer processes and the fate of dissociated ion radicals in exciplex systems. The back electron transfer reaction from P^- to DMA^+ is catalyzed in the case of anionic micelles where DMA^+ is trapped tightly by the micellar surface. In the case of cationic micelles, separation of ion pairs is greatly enhanced by the repulsive Coulombic force between DMA^+ and the micellar surface. The decay of the subsequent anion, which is left and protected in the micelle, is very slow as discussed in the next section.

Decay of Dissociated Ions in Micellar Systems. Table I shows the half-life of P^- ions measured in the laser photolysis of P and DMA in MeOH and micelles. The first half-life of P^- increases from 6 μ s in MeOH to 500 μ s in CTAB micelles. This readily demonstrates that micelles play a unique role in separating and stabilizing ion pairs formed from exciplexes. Recombination of ion pairs is prevented in the micellar systems, and the stability of individual ion radicals is enhanced by a factor of 100. In the case of CTAB micelles, DMA^+ can be quickly expelled from the micellar surface immediately after electron transfer from DMA to P^* . On the other hand, P^- is retained by the positive charge of the micellar environment and accordingly may be a rather stable species. The reentry of DMA^+ into the micelle for neutralization with P^- is unfavorable owing to repulsion of the large micellar positive surface potential. The ionic processes of exciplexes in micelles are just the opposite of photoionization events in micelles, where photoelectrons are ejected into the aqueous phase and parent cations are stabilized by the micelles.

It is noteworthy that the half-life of P^- , which has escaped geminate recombination from the parent cation, is considerably longer in ionic micelles (both NaLS and CTAB) compared to nonionic micelles. This indicates the importance of surface

Table II. The Decay of Anion Radicals (First Half-Life, $\tau_{1/2}$) of Exciplexes in Micellar Systems

Micelles	A^-	D^+	$\tau_{1/2}$, μ s
0.02 M CTAB	50 μ M P	10^{-2} M DMA	500
0.02 M CTAB	50 μ M PBA	10^{-2} M DMA	466
0.02 M CTAB	50 μ M PDA	10^{-2} M DMA	22
0.02 M CTAB	50 μ M PSA	10^{-2} M DMA	960
0.02 M CTAB	50 μ M PCHO	10^{-2} M DMA	1030
0.02 M CTAB	50 μ M PTSA	10^{-2} M DMA	906
0.02 M CTAB	50 μ M PSA	10^{-2} M DMA	960
0.02 M CTBAB	50 μ M PSA	10^{-2} M DMA	935
0.02 M DTAC	50 μ M PSA	10^{-2} M DMA	400
0.02 M CTAC	50 μ M PSA	10^{-2} M DMA	392
0.02 M CACl	50 μ M PSA	10^{-2} M DMA	200 ns

Table III. The Half-Life ($\tau_{1/2}$) of Locally Excited (LE) and Charge Transfer (CT) States of $P(CH_2)_3DMA$ in Micelles and Simple Solvents

Micelle	$\tau_{1/2}$, ns	
	LE	CT
Igepal	127	24
CTAB	15.4	20.6
NaLS	140	26
MeOH	104	20
Hexane	124	69.4

charges for micelles which functions as a permeability barrier to charged species.

As indicated in Table I, additives such as NaOH, NaCl, and Na_2SO_4 all increase the decay rate of P^- in CTAB micelles. This may be a consequence of an increased rate of exit of P^- from micelles on addition of these inert solutes.

Several pyrene derivatives which are located at different sites in CTAB micelles were used to accept e^- from DMA after excitation. The subsequent decay of these anion radicals is shown in Table II. The half-lives of these anions are longer for surface probes such as PSA^- , $PTSA^-$, and $PCHO^-$ compared to core probes such as P^- and PBA^- . Strong association between these surface probes and micellar head groups must have decreased the exit rate of these anions, leading to a long-lived anion radical. The anion PDA^- decays surprisingly rapidly in CTAB micelles; the loose packing of PDA in micelles may enhance its exit rate from micelles.

The stability of P^- radicals in cationic micelles is independent of surfactant chain length, head group, and counterions. The shorter lifetimes of PSA^- anions in DTAC and CTAC micelles may be attributed to the presence of trace amounts of impurities which cannot be removed by recrystallization. (The lifetime is still longer by an order of 10 compared to other types of micelles.) The abnormally short lifetime of PSA^- in CACl micelles is due to the reaction between the acidic surface head group NH_3^+ and PSA^- radicals. In the case of cetylpyridinium chloride micelles, no anion radical can be observed. The fluorescence of pyrene in these micelles is rapidly quenched by the surrounding pyridinium head group before interaction with DMA is possible. Therefore, no exciplex fluorescence or ion radicals could be detected.

Micellar Effect on the Fluorescence Spectra of the Intramolecular Exciplex $P(CH_2)_3DMA$ (P_3). Fluorescence spectra of P_3 in MeOH, hexane, CTAB, NaLS, and Igepal are shown in Figure 5. The fluorescence spectra in each system consist of two regions, a locally excited (LE) or pyrene region below 400 nm and a CT exciplex fluorescence region which shows a red shift in polar solvents. The relative fluorescence intensity ratio of CT state to LE state decreases according to the order of hexane, Igepal, MeOH, CTAB, and NaLS. In the latter two systems the fluorescence intensity of the exciplex CT states is negligibly weak.

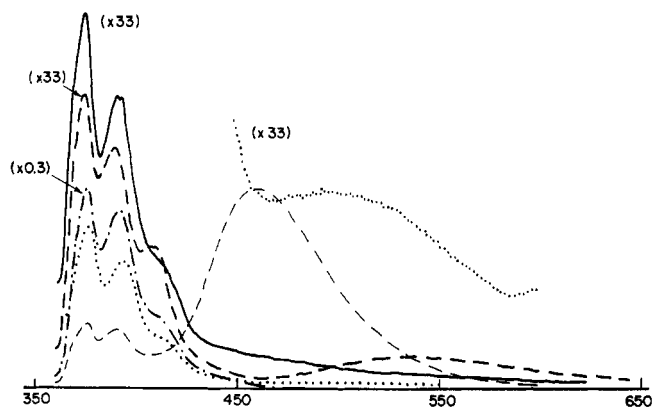


Figure 5. Fluorescence spectra of 50 μM P-(CH₂)₃-DMA in hexane (---), MeOH (-.-), Igepal (...), NaLS (-.-.-), and CTAB (—).

The fluorescence intramolecular exciplex (aromatic-(CH₂)_n-NR₂) in simple solvents has received detailed study in order to determine the role of excited state geometry on the dynamics of electron transfer process in the exciplex.²⁸⁻³⁰ For propyl derivatives ($n = 3$) in nonpolar solvents it is suggested that some overlapping sandwich configuration between the D and A* moieties is required for efficient electron transfer. In the case of polar solvents, this geometrical requirement may be less rigid if strong interaction shifts the energy surfaces of A*-(CH₂)₃-D and A⁻-(CH₂)₃-D⁺. The decreased radiative transition probability of CT state in polar solvents may arise either from this solvent induced electronic change of CT state or from some additional quenching processes such as solvation of CT exciplex state to give nonfluorescent ion pairs. In the case of anthracene-(CH₂)₃-DMA the initial electron transfer processes in both polar and nonpolar solvents are all completed within 50 ps after the excitation pulse.

The presence of exciplex fluorescence in Igepal but not in CTAB or NaLS micelles could be best explained by the sandwich geometrical requirements discussed previously. It has been established that the packing of polyoxyethylene units in Igepal is quite loose, that water can readily penetrate up to the phenoxyl group, and that the segmental mobility of the ethylene oxide is very high in the palisade layer. With a more hydrophilic group DMA linked to pyrene, it is reasonable to suggest that the probe is located in the more disordered palisade layer rather than in the rigid micellar inner core. The probability of forming a sandwichlike molecule is large under such conditions. This could account for the high (exciplex) fluorescence intensity of P₃ in Igepal. In ionic micelles such as NaLS and CTAB, the micellar core is more compacted and ordered. The orientation of the propyl (CH₂CH₂CH₂) chain into a favorable configuration for electron transfer to occur between P and DMA moieties is more difficult. Therefore, the quantum yield of exciplex fluorescence is extremely low in ionic micelles.

Table III indicates the half-life of both fluorescent states in each system. The lifetime measurements were obtained from laser photolysis. The half-life of the LE state of the pyrene moiety of P₃ is shorter than the half-life of fluorescence of pyrene itself in simple solvents and micelles. Some rapid quenching of the pyrene moiety fluorescence by the DMA moiety must take place. A much lower quantum yield of the LE state of P₃ compared to that of pyrene fluorescence supports this point. The fluorescence lifetime of an exciplex is known to decrease with increasing solvent polarity. As shown in Table III, the fluorescence lifetime of the CT state decreases in the order hexane, NaLS, Igepal, CTAB, MeOH.

Micellar Effect on Transient Absorption Spectra of P₃. Figure 6 shows transient absorption spectra of P-(CH₂)₃-DMA in hexane, methanol, Igepal, CTAB, and NaLS, re-

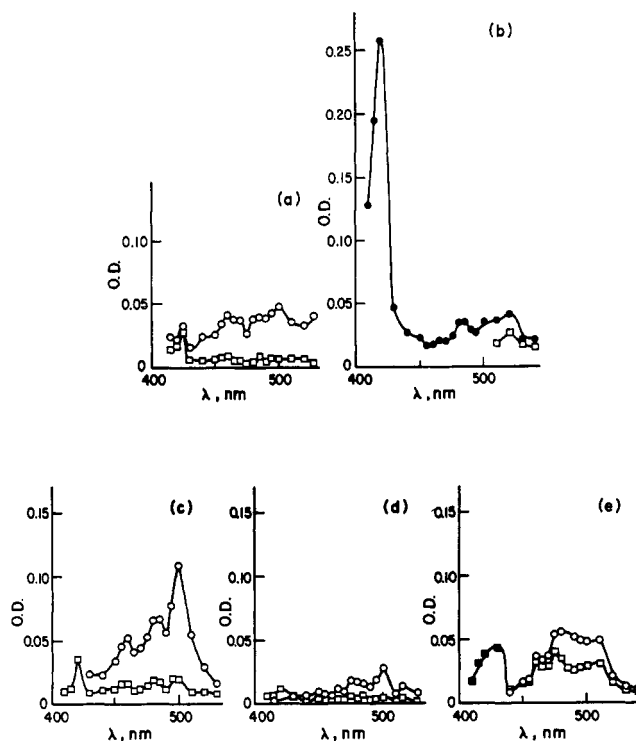


Figure 6. Transient absorption spectra of 50 μM P-(CH₂)₃-DMA following laser photolysis in (a) MeOH, (b) hexane, (c) 10 mM Igepal, (d) 20 mM CTAB, and (e) 50 mM NaLS, respectively: O, at the end of laser pulse; □, 150 ns after the laser pulse; ○, (OD)_{max}; ■, 900 ns after the laser pulse.

spectively. In polar solvents such as methanol (Figure 6a) the absorption band of P⁻ around 495 nm is observed, while in nonpolar solvents such as hexane (Figure 6b), only the triplet-triplet absorption spectrum around λ 420 nm is observed. No absorption could be detected in the 500-nm region immediately after the excitation pulse owing to strong overlap in the exciplex fluorescence. Similar absorption spectra of P₃ in acetonitrile and diethyl ether have been reported by Mataga.²⁹ The transient absorption spectra of intermolecular and intramolecular complexes are quite similar in simple solvents. However, in the case of micelles, significant differences in the kinetics of the forward and backward electron transfer processes are found for both intramolecular and intermolecular exciplexes.

Figures 6c-e shows the transient absorption spectra of P₃ in Igepal, CTAB, and NaLS, respectively, the spectrum of P⁻ being the strongest band in nonionic Igepal micelles. This band is much broader in NaLS micelles, and much weaker in CTAB micelles. As indicated earlier the packing of the head group of the (OCH₂CH₂) unit in Igepal is loose, and more water may penetrate into nonionic micelles. It has been suggested that two or three water molecules might associate with each OCH₂CH₂ unit.³¹ Therefore, the absorption of the exciplex may resemble that of a strongly solvated ion pair.

Figures 7a-c shows the decay of P⁻ in NaLS, CTAB, and Igepal, respectively. In NaLS, P⁻ decays slowly, while in CTAB the majority of P⁻ decays in the first few nanoseconds, while the remainder decays slowly. Unlike the case of the intermolecular complex P and dma are now linked together by the (CH₂)₃ chain. This restricts both rotational and translational motion of DMA and P. It is unlikely that the exciplex will escape the micelle during the lifetime of the excited state. The extent of the interaction between these types of exciplexes and other molecules depends on the stabilization which DMA⁺ attains.^{28,32} It is reasonable to assume that DMA⁺ would be more stable in anionic micelles NaLS than in cationic micelles

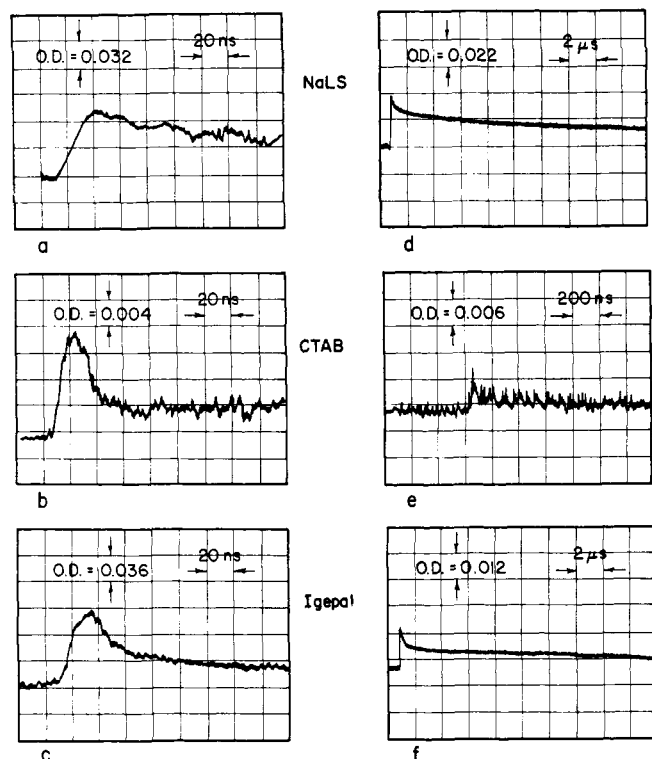


Figure 7. Oscilloscope trace of $P(CH_2)_3DMA$ after laser photolysis in micellar solutions monitored at 493 (a, b, c) and 460 nm (c, d, e), respectively.

CTAB owing to the strong Coulombic interaction between the DMA^+ and head group. In CTAB electrons may efficiently transfer from the P^- moiety to the DMA^+ moiety to relieve the strain, leading to the fast initial decay of P^- . In a similar fashion to the intermolecular exciplex, increasing the micellar viscosity by lowering the temperature decreases the rate of ion recombination. Addition of DMA to the micellar system has little effect on the yield and decay of P^- transients. The separation between DMA and P moieties of P_3 is about 4 Å. Therefore, external DMA cannot compete efficiently with DMA which is already linked to the P moiety in P_3 .

Figures 7d–f shows the transient decay of DMA^+ in oxygen-saturated solutions of NaLS, CTAB, and Igepal, respectively. Reactive species such as anions, triplet states, and radicals should all be removed shortly after the laser pulse by O_2 . The decay of the cations, which is unaffected by O_2 , can be clearly observed under such circumstances. The lifetime of DMA^+ is longest in NaLS, decreases in Igepal, and decreases significantly in CTAB micelles. The decay of both cation and anion moieties of P_3 clearly demonstrates that anionic micelles such as NaLS interact and stabilize the positive charge of the cationic group of P_3 thus decreasing the rate of recombination of the ion pairs. In the case of cationic micelles, the accommodation of a cation into the cationic micellar surface is unfavorable; this leads to the fast recombination of ion pairs.

Transient Photocurrent Measurement of Inter- and Intramolecular Complexes in Micelles. Figures 8a and 8b show the transient photocurrents in solution of pyrene and MDA in MeOH, and Igepal excited by laser pulses of 347.1-nm light. Ions are formed immediately on excitation and decay with a half-life of 4 μs in MeOH. In the case of Igepal solutions the conduction signal grows to a maximum and then decays with a half-life of 36 μs (Figure 8c). The detection of photocurrents following excitation of P and DMA in polar solvents is direct proof of formation of dissociated ions from exciplexes in these polar solvents. Similar measurements have been carried out by Mataga for several exciplex systems in simple polar sol-

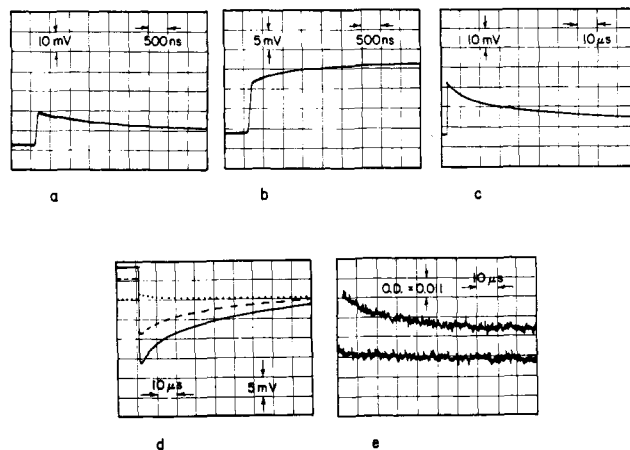


Figure 8. Oscilloscope traces showing the changes in conduction (a, b, c, d) and absorption (e) (at 465 nm) following laser photolysis of inter- and intramolecular exciplex in micellar solutions: (a) $[P] = 50 \text{ mM}$, $[DMA] = 10^{-2} \text{ M}$, MeOH; (b) and (c) $[P] = 50 \text{ mM}$, $[DMA] = 10^{-2} \text{ M}$, $[Igepal] = 10^{-2} \text{ M}$; (d) $[P] = 50 \text{ mM}$, $[DMA] = 10^{-2} \text{ M}$, $[CTAB] = 10^{-2} \text{ M}$, $[PSA] = 50 \text{ μM}$, $[DMA] = 10^{-2} \text{ M}$, $[CTAB] = 10^{-2} \text{ M}$, ... $[P(CH_2)_3DMA] = 50 \text{ μM}$, $[CTAB] = 10^{-2} \text{ M}$; (e) $[P] = 50 \text{ μM}$, $[DMA] = 10^{-2} \text{ M}$, $[CTAB] = 20 \text{ mM}$.

vents.³³ According to their studies, the photocurrent rises with the laser pulse in the solutions of P/DMA in acetonitrile, while in the case of solutions of P/*p*-dicyanobenzene in dichloromethane the peak conduction is achieved at about 200–300 ns after the excitation pulse. It is suggested that ionic dissociation occurs from nonrelaxed states and relaxed ion pair states in the former and latter systems, respectively. The 4-μs rise time of the photocurrent in solutions of P and DMA in Igepal micelles is obviously too long to be attributed to the relaxation time of ion pairs. Factors other than relaxation may play a role in the slow buildup of current. The signal height is directly proportional to both mobility and concentration of charge carriers, and the movements of ions toward electrodes in the system will be affected by the micelles. The mobility of an ion which is associated with a micelle will be smaller than that of a free ion. Therefore, it seems reasonable to suggest that the slow rise time of the photocurrents may be attributed to the time for ions to dissociate and exit completely from micelles into water.

The intensity of the photocurrents increases linearly with laser intensity indicating a monophotonic process, as distinct from a biphotonic process which takes place in photoionization processes.³⁴ Increasing laser intensity increases the decay rate of the photocurrents curve, as expected for a bimolecular decay of ions.

The photoconduction experiments in ionic micelles are complicated by the high conductance of the system. A differential system using a third electrode was used to neutralize the effects arising from this effect. The photoconduction curve of ($5 \times 10^{-5} \text{ M}$) P and 10^{-2} M DMA in 10^{-2} M CTAB is shown in Figure 8d. The photocurrent curves decay with a first half-life around 50 μs, which is much shorter than the half-life of pyrene anion radicals as observed optically. A similar decay curve is obtained in PSA/DMA/CTAB as shown in Figure 8d. As indicated earlier, if P^- ion radicals remain in micelles, then the contribution to the photocurrents from P^- would be small owing to its greatly reduced mobility. Therefore, the different lifetimes of P^- and PSA^- which were obtained optically would not be detected in the photocurrent measurements (Figure 8d), since the photocurrent corresponds to the movement of the more mobile DMA^+ . This statement is substantiated by the similarity between the optical decay curves of DMA^+ (Figure 8e) and photocurrent decay curves of P (or PSA)/DMA in CTAB micelles.

Even though formation of ion pairs is also a main pathway

of energy dissipation of intramolecular exciplexes in polar solvents, the photoconductivity of such systems is small, for unlike the intermolecular complex the ion pairs cannot completely dissociate. Figure 8d shows the photocurrent curves resulting from the excitation of 50 μM $\text{P}(\text{CH}_2)_3\text{DMA}$ in CTAB micelles. The intensity of photocurrent is much smaller than that observed with P/DMA intermolecular exciplex, owing to the smaller mobility of the associated ion pairs of the intramolecular exciplex. Addition of DMA to $\text{P}(\text{CH}_2)_3\text{DMA}$ in TCAB has little effect on the intensity of photocurrents, in agreement with the earlier optical measurements.

Conclusion

These studies show that micellar environments have a significant effect on the state and dynamics of electron transfer processes of exciplexes. In the case of intermolecular exciplexes radical ions which are dissociated from the exciplex can be protected from neutralization and escape geminate ion recombination. The success of this process depends on whether one of the ions can be expelled from micelles immediately following the initial electron transfer process. This micellar catalyzed ion-pair separation process leads to the formation of very stable and long-lived ion radicals which could be detected both by transient absorption and photoconduction techniques. On the other hand, if the micellar surface "traps" the ion pair owing to strong Coulombic interaction, then rapid ion recombination processes result. Such processes, which usually are only detected in highly viscous systems, nevertheless are readily observed in micelles.

If the donor and acceptor are linked together by methylene groups, then their translational and rotational freedom is restricted. Since neither ion can rapidly escape from the micelles, the resulting physical and chemical properties are dramatically different from those of intermolecular complexes.

Preliminary data indicate that the micellar phase, which functions as a barrier against neutralization of separated ion pairs, can significantly stabilize the ionic products. The present study may act as a model for biological systems since charge transfer complexes play important roles in many photobiological processes. Micelles serve as simple systems for studying the effect of surface charge on these systems as encountered in membranes. The stabilization of ions by the correct choice of a micellar system suggests possibilities for the use of such systems in the conversion of light energy into chemical energy. Future studies are underway to further stabilize ions resulting from energy transfer in micellar and bilayer systems following excitation with visible light.

References and Notes

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 - (34) J. T. Richards, G. West, and J. K. Thomas, *J. Phys. Chem.*, **74**, 413 (1970).
 - (35) In the course of this work we learned that Misumi et al.¹¹ prepared *N,N*-dimethyl-4-[3-(1-pyrenyl)propyl]aniline in a different way starting with acetylpyrene and *N,N*-dimethyl-4-aminobenzaldehyde. We acknowledge the opportunity to read the manuscript.