

for a geometrical statistical distribution of quenchers among the water pools.

The following are the two additional assumptions used in this model. (1) Both of the reacting species, the fluorescent probes and the quenchers are solubilized exclusively in the water pools. (2) There is an absence of exchange of the reactants between water pools within the time of the excited state reaction. The total concentration of excited probes at time t is given by

$$([P^*]_T)_t = \sum_{n=0}^{\infty} ([P^*]_n)_{t=0} e^{-(k_1+nk_q)t} \quad (A1)$$

where $[P^*]$ is the concentration of an excited probe located in a water pool containing \bar{n} quencher molecules, k_1 is the sum of all first-order processes leading to the deactivation of P^* in the absence of quencher, and k_q is the first-order quenching rate constant that competes with k_1 in the deactivation of P^* in a water pool that contains only one quencher.

For a geometric distribution (G_n) of quenchers among the water pools eq A1 becomes

$$([P^*]_T)_t = \sum_{n=0}^{\infty} G_n ([P^*]_T)_{t=0} e^{-(k_1+nk_q)t} \quad (A2)$$

where $G_n = \bar{n}^n / (1 + \bar{n})^{n+1}$ and \bar{n} is the average occupancy of a water pool, i.e., $\bar{n} = [Q]_T / [WP]_T$. Upon expansion and rearrangement of eq A2 one obtains

$$([P^*]_T)_t = ([P^*]_T)_{t=0} \left(\frac{e^{-k_1 t}}{1 + \bar{n}} \right) \times \left[1 + \left(\frac{\bar{n}}{1 + \bar{n}} \right) e^{-k_q t} + \left(\frac{\bar{n}}{1 + \bar{n}} \right)^2 e^{-2k_q t} + \dots \right] \quad (A3)$$

Recognizing that the infinite series in eq A3 is equivalent to $1/(1 - X)$ where

$$X = [\bar{n}/(1 + \bar{n})] e^{-k_q t}$$

leads to

$$([P^*]_T)_t = ([P^*]_T)_{t=0} e^{-k_1 t} / (1 + \bar{n})(1 - X) \quad (A4)$$

which can be further simplified to give

$$([P^*]_T)_t = ([P^*]_T)_{t=0} e^{-k_1 t} / [1 + \bar{n}(1 - e^{-k_q t})] \quad (A5)$$

which can be rewritten in the natural log form

$$\ln \left(\frac{([P^*]_T)_t}{([P^*]_T)_{t=0}} \right) = -k_1 t - \ln [1 + \bar{n}(1 - e^{-k_q t})] \quad (A6)$$

Note that in cases where $k_q \gg k_1$ and at sufficiently long times such that $k_q t \gtrsim 3$, eq A6 reduces to

$$\ln \left(\frac{([P^*]_T)_t}{([P^*]_T)_{t=0}} \right) = \ln \left(\frac{1}{1 + \bar{n}} \right) - k_1 t \quad (A7)$$

Equation A7 predicts that in the limit of large t a plot of $\ln [(P^*]_T)_t / ([P^*]_T)_{t=0}]$ vs. t should be linear with a slope which is equal to the reciprocal of the excited P^* life time in the absence of Q , which, when extrapolated to $t = 0$, should give a Y intercept given by $1/(1 + \bar{n})$. On the other hand, according to the Poisson statistical distribution model this intercept would be given simply by \bar{n} .

From the estimated value of \bar{n} the total water pool concentration can be calculated which can further be used to determine the "spherical" size of the water pool. It is therefore very important to note that, depending on which statistical distribution is adopted, one could calculate very different values on \bar{n} and therefore $[WP]_T$. Thus, establishing the type of distribution applicable to the system under investigation is essential if this simple and convenient method is to be used to determine a meaningful concentration of such multimolecular aggregates.

Photoinduced Electron Transfer in Organized Assemblies

S. S. Atik and J. K. Thomas*¹

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received November 20, 1980

Abstract: Photoexcitation of the charge-transfer systems pyrene-dimethylaniline and pyrene-dibutylaniline has been studied in several organized assemblies, micelles, microemulsions, and vesicles. Both steady state measurements and pulse laser photolysis data show that the quenching of excited pyrene on the surface by the anilines is rapid but can be described by diffusional-type processes. Detailed mechanisms of the processes are discussed. The main products of the quenching are pyrene anions and dialkylaniline cations. Increasing the size of the assemblies, i.e., micelle to microemulsion, or increasing the rigidity of the reactants' environment, i.e., micelle to vesicle, led to decreased yields of ions. The yields of ions in these latter systems can be restored if polar derivatives of pyrene are used in place of pyrene, thus locating the pyrene chromophore in the region of the assembly surface. Several reactions of the photoproduct pyrene anion were studied, as the lifetime of the anion is sufficiently long (> 1 ms) to promote electron transfer between cationic ions such as Eu^{3+} and methyl viologen, in spite of the fact that these ions are strongly repelled by the cationic surfaces of the assemblies. It is concluded that efficient electron transfer and subsequent ion separation only occur when the reactants are located on strongly charged surfaces, where the reactants may move relatively freely, while still remaining bound to the surface. A photodiode effect is suggested to explain the efficient ion separation observed.

Photoinduced electron-transfer processes are of considerable interest in biology and chemistry, and several different systems have been studied from simple aqueous solutions of ions to complex molecules such as chlorophyll. The urgency of alternative sources of energy has given some impetus to studies in this field, as the photoproduction of ions has intriguing possibilities for energy storage. An essential feature for efficient storage of energy is that

the photogenerated ions should be prevented from subsequent rapid recombination, a prevalent event in homogeneous media. To this end, simple micellar systems have been used successfully to separate the ions for long periods of time.^{2,3} These early data showed

(1) The authors would like to thank the NSF for support of this work under Grant No. CHE 78-24867.

a considerable effect of micellar type on the effectiveness of the efficiency photoproducted ions. Hence, the present work describes the use of systems other than micelles to facilitate the photo-processes.

A simple, but well-understood, electron-transfer system was chosen, i.e., pyrene-dimethylaniline. Photoexcitation of this system leads to the formation of excited complexes, or exciplexes in nonpolar media, and ions in polar media.⁴⁻⁹ Detailed attention has been paid to these systems in homogeneous solvents via spectroscopic and fast laser techniques. It is generally agreed that photoexcitation of the arene/amine system leads to the formation of a charge-transfer complex which requires a precise orientation of the reactants. In polar media an electron is donated from the amine to the excited arene, forming an arene anion and amine cation. The choice of pyrene and dimethylaniline is opportune, as the pyrene anion has a strong absorption at $\lambda = 4930 \text{ \AA}$, while the amine cation absorbs at $\lambda = 4580 \text{ \AA}$. Thus, the extent of the electron transfer can be measured directly and conveniently.

In the earlier micellar system, it was found that excitation of the pyrene-dimethylaniline system rapidly produced large yields of ions. This is partly due to solubilization of the reactants in close proximity on the micelle surface. In noncharged micelles the kinetic behavior of the ions was reminiscent of that observed in homogeneous media, i.e., rapid (μs) recombination. In anionic micelles, an initial extremely fast decay of the ions was observed and attributed to the close proximity of the pyrene anion and amine cations on the micelle surface. The negative charge of the micelle restricts the escape of the cation from the vicinity of the anion, thus leading to a very rapid reverse e^- transfer giving pyrene and DMA. This process would have to occur while the species P^- and DMA^+ were still in close proximity, that is, within a time short compared to the time required for the loose ion pair to diffuse apart. In cationic micelles, long-lived ions ($>\text{ms}$) were observed, and attributed to the expulsion of the amine cation by the positively charged micelle surface and retention of the pyrene anion.

The work described here seeks to elaborate more thoroughly on the above observations by: (1) determining the actual rate of e^- transfer on the micelle surface, for both forward and back reactions; (2) investigate the nature of the e^- transfer (viz., is e^- tunneling and important feature?); (3) vary the escape capability of the photoproducted products by using amines with different N-alkyl substituents; and (4) vary the nature of the assembly used to compartmentalize the reactants in order to investigate the nature of the approach of the excited reactants, and to determine the optimum features for maximum ion production. The data are used to speculate on the design of systems for efficient photo-production leading to long-lived ions.

Experimental Section

Fluorescence spectra were measured on a Perkin-Elmer MPF 44 spectrofluorometer; absorption spectra were run on a Perkin-Elmer spectrophotometer. Laser flash photolysis experiments were carried out with a Korad KI frequency doubled ruby laser, utilizing a 20 ns, 0.1 J pulse of 3471 \AA light.¹⁰ The output of the photomultiplier monitoring either absorption, or emission, of light by, or from, the sample was captured on a Tektronix 7912 AD transient capture unit. The data were subsequently transferred to a Tektronix 4051 computer for data handling. This instrument was capable of accurately monitoring signals during the 20-ns laser pulse, thus enabling events of about 2 ns to be observed.

(2) Waka, Y.; Hamamoto, K.; Mataga, N. *Chem. Phys. Lett.* **1978**, *53*, 242.

(3) Katusin-Razem, B.; Wong, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1679.

(4) Leonhardt, H.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 791.

(5) Mataga, N. "Molecular Association"; Forster, R., Ed.; Academic Press: London, 1979; Vol. 2, p 2.

(6) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393, 397.

(7) Ottolenghi, M. *Acc. Chem. Res.* **1973**, *6*, 153.

(8) Hui, M. H.; Ware, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 4718.

Nemzek, T. L.; Ware, W. R. *J. Chem. Phys.* **1975**, *62*, 477.

(9) Chuang, T. J.; Hoffman, G. W.; Eisenthal, K. B. *Chem. Phys. Lett.* **1974**, *25*, 201.

(10) Richards, J. T.; West, G.; Thomas, J. K. *J. Phys. Chem.* **1970**, *74*, 413.

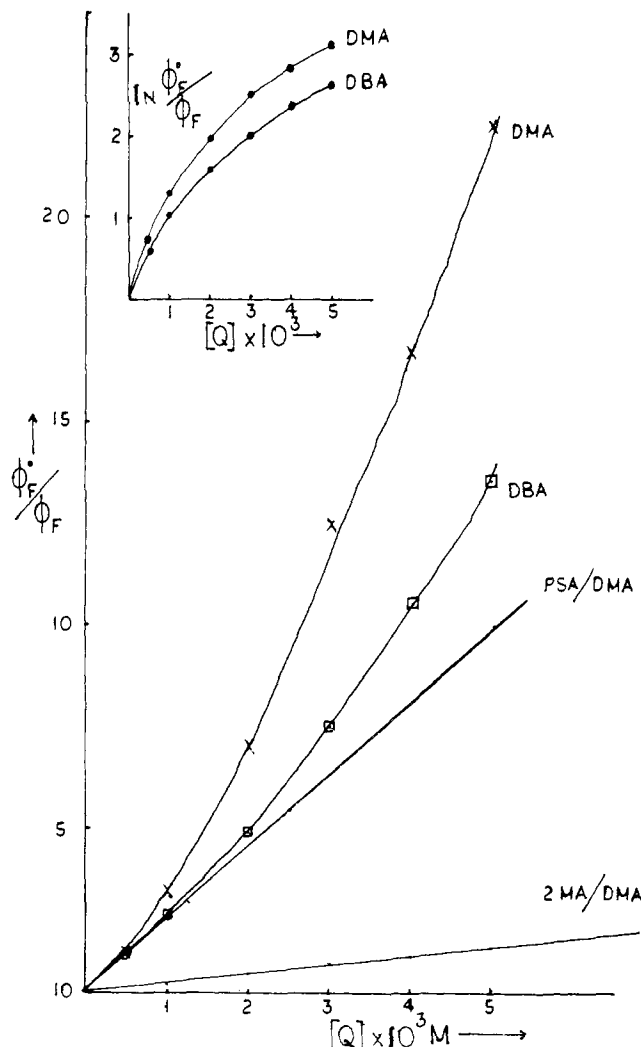
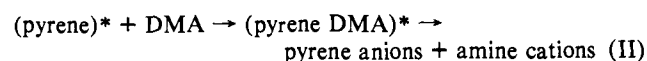


Figure 1. Variation in the fluorescence efficiency ϕ_F^0/ϕ_F where ϕ_F^0 and ϕ_F are the fluorescence efficiencies in the absence and presence of scavenger, respectively, vs. the scavenger concentration. The luminescence probes used are pyrene, pyrenesulfonic acid, and 2-methylantracene, and the quenchers are dimethylaniline, DMA, and dibutylaniline, DBA. Insert: Plot of $\ln \phi_F^0/\phi_F$ vs. [DMA] and [DBA].

Benzylcetyldimethylammonium bromide, BHDC, sodium lauryl sulfate, NaLS, and cetyltrimethylammonium bromide, CTAB, were purchased as Biochemical grade from BDH; pyrene was purchased from Aldrich and recrystallized from ethanol; pyrene butyric acid, PBA, pyrenetetrasulfonic acid, PTSA, pyrenesulfonic acid, PSA, dimethylaniline, DMA, dibutylaniline, DBA, didodecyltrimethylammonium bromide, DDAB, and hexanol were purchased from Eastman Chemicals. Water was doubly distilled, and solutions were degassed by prolonged bubbling with nitrogen.

Results and Discussion

Quenching of the Fluorescence of Pyrene. The lifetime of pyrene fluorescence in CTAB micelles ($5 \times 10^{-2} \text{ M}$) was measured as 165 ns and in CTAC micelles as 350 ns ($5 \times 10^{-2} \text{ M}$). The yield of the fluorescence decreased on addition of DMA or DBA due to reaction II. The quenching process is very efficient and in the



case of pyrene occurs efficiently with one of each reactant on the micelle.

Typical data are shown in Figure 1 for the quenching of excited probes of pyrene, PSA, and 2-methylantracene by DMA and/or DBA. The insert shows the logarithm of quenching ($\ln \phi_F^0/\phi_F$) vs. [quencher] for DMA and DBA. The data in Figure I are non linear indicating that a simple competition of reactions I and II

does not suffice to explain the data. The insert also shows the absence of significant static quenching, i.e., a micelle containing P* and one or more DMA or DBA still fluoresces, but with lower yield than those containing P* alone. The decay of the pyrene fluorescence is also nonexponential, Figure 2, both on CTAB and CTAC, with DMA and DBA. An initial rapid decay followed by a slower decay is clearly observed for CTAC systems. This effect becomes less pronounced in CTAB where k_q and $1/\tau_0$ are comparable because of the much shorter lifetime of P*.

These data are explained as being due to a Poisson distribution of the amine among the micelles, which at low concentrations leads to micelles with both excited pyrene and amine, resulting in rapid intramicellar quenching, and also to micelles containing only excited pyrene. Figure 2 also shows that the latter decay is more rapid with DMA than with DBA. This is due to the fact that DMA partitions between the micelles and the aqueous phase, while DBA tends to associate almost completely with the micelles. A small amount aqueous DMA causes the slow decay to become faster via homogenous quenching.

Figures 1 and 2 clearly demonstrate the nonexponential nature of the pyrene fluorescence decay in the presence of DMA or DBA. The solid lines drawn through the data points were calculated by using the expression below:¹¹

$$I_f(t) = I_f(t=0) \exp[-k_1 t - \bar{n}(1 - e^{-k_q t})] \quad (1)$$

Where $I_f(t)$ and $I_f(t=0)$ are the pyrene fluorescence intensities at t and $t=0$, respectively, \bar{n} is $[\text{DMA}]_M/[\text{micelle}]$, while k_q is the first order intramicellar quenching rate constant for a micelle containing only one quencher and k_1 is defined by

$$k_1 = \tau_0^{-1} + k_Q[\text{DMA}]_{\text{aq}} \quad (2)$$

In the latter expression τ_0^{-1} is the inverse of the pyrene fluorescence lifetime in the absence of quencher and k_Q is the bimolecular rate constant for quenching due to DMA in the aqueous phase whose concentration is given by

$$[\text{DMA}]_{\text{aq}} = [\text{DMA}]_T / 1 + K[\text{micelle}] \quad (3)$$

where $[\text{DMA}]_T$ is the total $[\text{DMA}]$ and K is the association constant. In the DMA system, good agreement between experiment and theory could not be obtained by simply varying the two parameters \bar{n} and k_q and taking $k_1 = 1/\tau_0$. However, good agreement was obtained (shown in Figure 2) by varying the parameter k_1 also. The fact that optimal fitting could only be obtained with values of $k_1 > 1/\tau_0$ suggests that DMA partitions between the micellar and aqueous phases, as indicated by the equation given above. Furthermore, the fact that the value of \bar{n} that gave the best agreement between data and theory is smaller than that estimated based on an aggregation number of 75 for CTAB¹² also suggests a partition of DMA between water and micelle.

Figures 1 and 2 clearly demonstrate the nonexponential nature of the fluorescence decay in the presence of DMA or DBA. The solid lines drawn through the points were calculated by using the theoretical expression given in eq 1.

From the experimentally obtained \bar{n} and the aggregation number of CTAB it is possible to determine $[\text{DMA}]_{\text{aq}}$ which then is used to calculate k_Q ($1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) from eq 2. Based on this treatment the association constant obtained for DMA with CTAB is found to be $4.8 \times 10^3 \text{ M}^{-1}$.

On the other hand, the more hydrophobic DBA appears to be completely associated with the CTAB micelle as indicated by the best-fit values of \bar{n} and k_1 .

The difference in the partitioning behavior of DMA and DBA is more clearly exhibited in the cetyltrimethylammonium chloride, CTAC, micellar system (Figure 2). In the case of the CTAC micelle, the much longer lifetime of unquenched excited P* (350 ns) separates the intramicellar (k_q) and aqueous-micellar (k_1)

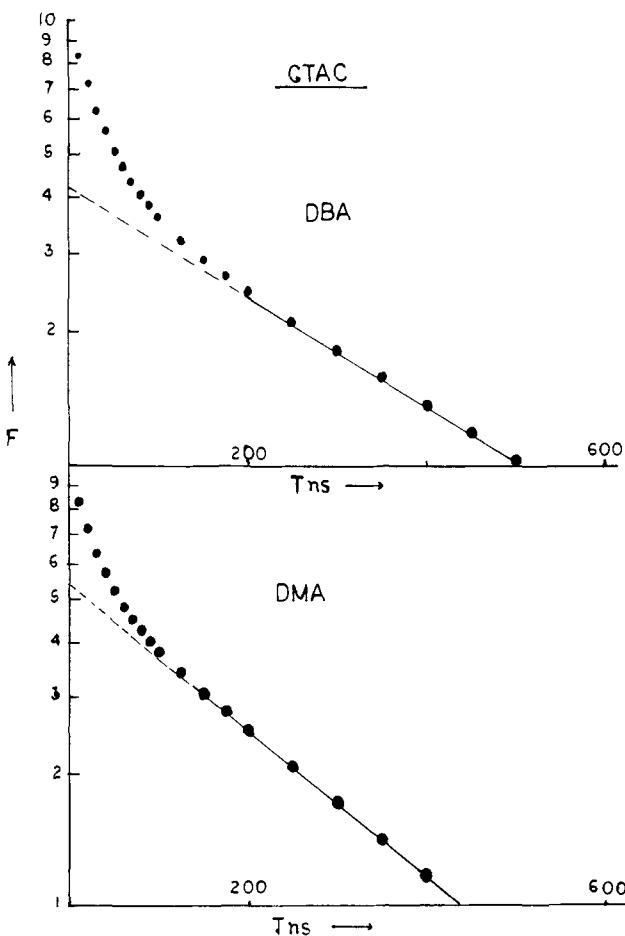
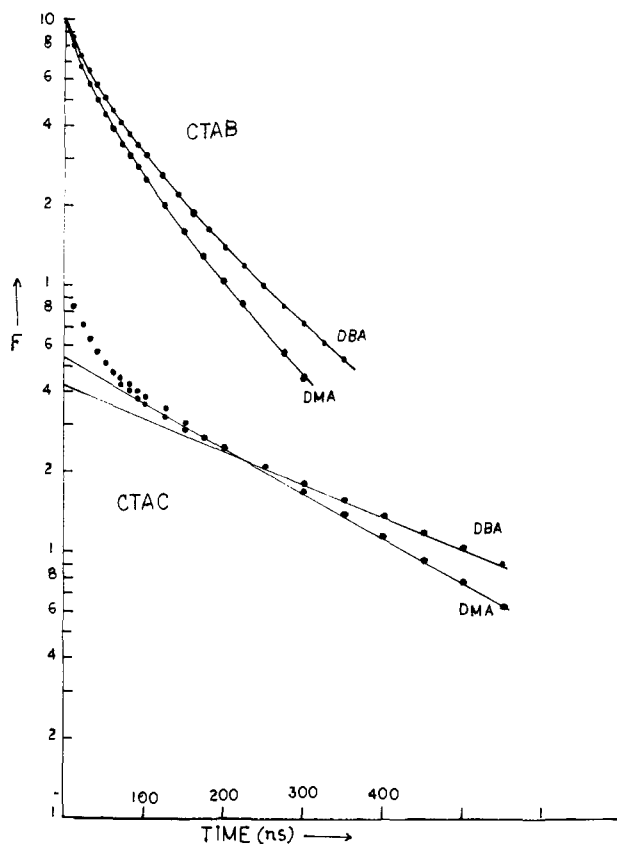


Figure 2. Rate of decay of pyrene fluorescence plotted as $\log F$ vs. time for CTAB and CTAC micelles and for the systems pyrene-DBA and pyrene-DMA.

(11) Atik, S. S.; Singer, L. A. *Chem. Phys. Lett.* 1978, 59, 519.

(12) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Micromolecular System"; Academic Press: New York, 1975.

Table I. Kinetic Parameters from Fluorescence Decay Analysis

micellar system	quencher	\bar{n}	$k_1 \times 10^{-7}, s^{-1}$	$k_q \times 10^{-7}, s^{-1}$	steady-state data	
					$(\phi_F/\phi_F^0)_{\text{exptl}}$	$(\phi_F/\phi_F^0)_{\text{theory}}$
0.05 M CTAB	0.0005 M DMA	0.60	0.833	2.5	0.47 ± 2	0.49
	0.0005 M DBA	0.80	0.625	1.5	0.57 ± 2	0.59
0.05 M CTAC	0.0005 M DMA	0.62	0.385	3.0		
	0.0005 M DBA	0.85	0.286	2.0		

Table II. Wavelength of Maximum Fluorescence of DMA and DBA in Various Media

medium	$\lambda_{\text{max}}, \text{nm}$	
	DMA	DBA
cyclohexane	332	337
hexadecane		338
ethanol	345	345
water	361	341
0.05 M CTAB	353	345
0.01 M DDAB	354	346

fluorescence quenching rate processes which now occur over widely separated time regions as indicated by the distinct two-component (fast and slow) nature of the observed fluorescence decay (Figure 2). In this particular case the values of \bar{n} and k_1 are directly obtained from the extrapolated intercept and slope of the linear portion of the natural log of the fluorescence decay. Thus, the optimal fit (solid line) is obtained by varying only the parameter k_q . Quite different values of k_1 and \bar{n} are derived for DMA and DBA (Figure 2). These values clearly indicate the partial and complete incorporation of DMA and DBA into the CTAC micelle, respectively.

A steady-state Stern-Volmer type expression that takes into account the statistical distribution of totally bound quenchers among the micelles has been derived.¹³ A modified expression that also considers the partitioning of quenchers between the micelles and aqueous bulk phase can be readily shown to be given by

$$\frac{\phi_f}{\phi_f^0} = \sum_{n=0}^{\infty} \frac{P_n}{1 + nk_q\tau_0 + k_Q\tau_0[\text{DMA}]_{\text{aq}}}$$

$$P_n = \bar{n}^n / e^{-\bar{n}} / n! \quad \bar{n} = [\text{DMA}]_{\text{M}} / [\text{micelle}]$$

$$[\text{DMA}]_{\text{T}} = [\text{DMA}]_{\text{aq}} + [\text{DMA}]_{\text{M}}$$

As a test for the reliability of the results obtained from the fluorescence decay analysis, the extent of total fluorescence quenching ϕ_f/ϕ_f^0 effected in the presence of 5.0×10^{-4} M DMA or DBA in the CTAB micellar system was measured under steady-state continuous excitation of deaerated solutions. A very good agreement was obtained between the experimentally obtained values and the calculated ones based on the theoretical expression given above employing the kinetic parameters ascertained from the time-dependent fluorescence intensity analysis (Table I).

Table I also gives k_q , the specific rate constant of pyrene quenching in micelles containing one quencher molecule in (CTAB) or (CTAC). It is apparent that the micellar quenching rate for DMA is more rapid than that for DBA. This is attributed to a decreased mobility of DBA, compared to DMA, on the micelle. It is interesting to note that cetylpyridinium ions also quench pyrene in CTAB micelles with $k_q = 1.4 \times 10^7 s^{-1}$. This larger molecule also has a lower mobility than DMA in the micelle, but is similar to that of DBA.

Table II provides evidence to support the above suggestions regarding the relative mobilities of DMA and DBA. This table shows the λ_{max} for DMA and DBA fluorescence in various solvents, in CTAB, and in DDAB. It is quite apparent that the fluorescence

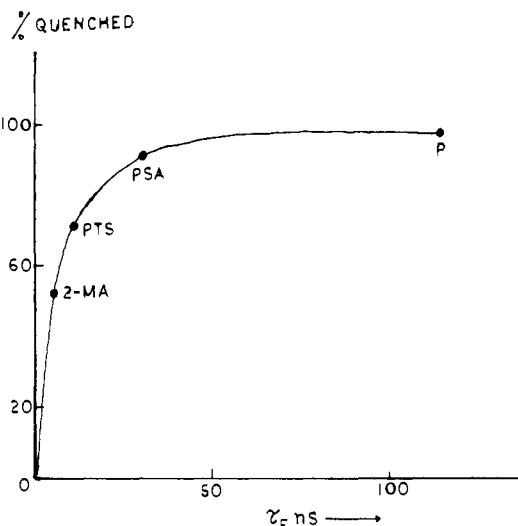


Figure 3. Variation in the percentage of fluorescence quenched by 5×10^{-3} M DMA in CTAB (0.05 M) with 5×10^{-5} M of the following arenes: 1, 2-methylanthracene; 2, pyrenetetrasulfonic acid; 3, pyrenesulfonic acid.

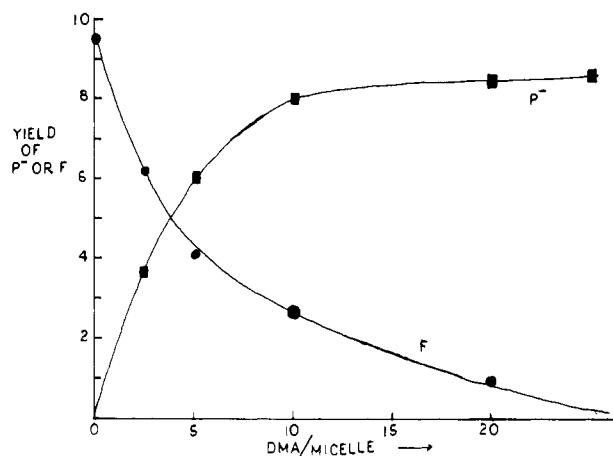


Figure 4. Variation in the yields of pyrene anion and pyrene fluorescence with [DMA] in the excitation of 5×10^{-5} M pyrene in 5×10^{-2} M CTAB.

exhibits a pronounced red shift with increasing medium polarity. By comparison with these data the environments of DMA and DBA in CTAB and DDAB can be ascertained. In both systems the DMA environment is more polar than that of DBA. This suggests that the butyl groups of DBA draw the molecule further into the micelle compared to DMA, thus leading to decreased environment polarity and more restriction to movement. The yield of exciplex emission is very small in the above studies in keeping with the polar nature of the reaction environment. However, the exciplex emission with DBA/pyrene is $5 \times$ that of DMA/pyrene, again indicating a more hydrophobic environment for DBA compared to DMA.

Figure 3 shows the effectiveness of 5 mM DMA in quenching the fluorescence of pyrene, PSA, PTSA, and 2-methylanthracene, plotted as percent quenching vs. fluorescence lifetime. It is seen

(13) (a) Attk, S. S.; Singer, L. A. *Chem. Phys. Lett.* **1979**, *66*, 234. Attk, S. S.; Nam, M.; Singer, L. A. *Chem. Phys. Lett.* **1979**, *67*, 75. (b) Yekta, A.; Alkawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543.

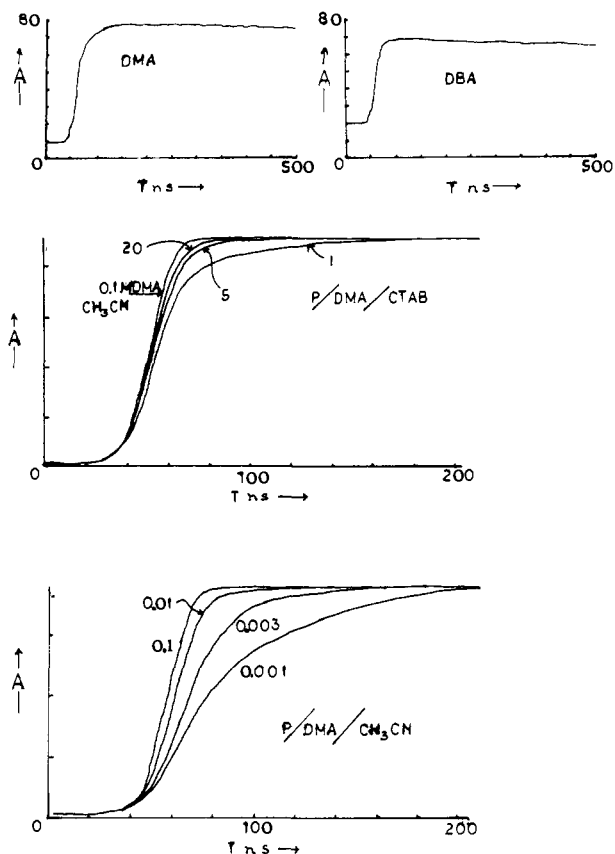


Figure 5. Rate of formation of pyrene anion P^- , monitored at $\lambda = 4930 \text{ \AA}$, in acetonitrile solutions and in CTAB solutions with various concentrations of DMA in acetonitrile: $-0.1, 0.01, 0.003,$ and 0.001 M DMA. In CTAB: 1, 2, and 5 DMA/micelle. Insert: Formation of P^- in CTAB with DMA and DBA.

that the quenching is inversely proportional to the fluorescence lifetime. This implies that the quenching process is dynamic and has no appreciable static contribution. This supports the completely dynamic picture put forward to analyze the data in Figures 1 and 2.

Yield of Pyrene Anion. Figure 4 shows the relative yield of P^- anion measured on a laser flash photolysis experiment at $\lambda = 4930 \text{ \AA}$ vs. the average number of DMA or DBA/micelle. This figure also shows the decrease in the fluorescence yield measured under continuous irradiation on the Perkin-Elmer MPf 44. The concomitant decrease in fluorescence and buildup of ions alternate pathways for quenching, i.e., quenching leads to the production of ions. Exciplex emission, triplet formation, etc., are small and will not be considered in the discussion.

Rate of Formation of Ionic Products. The locally high concentration of reactants on the micelle surface even with one P^* and one DMA leads to rapid photoproduction of ions. The insert for Figure 5 shows typical data for pyrene ion formation in CTAB/DMA and CTAB/DBA.

More rapid rates of production of P^- were followed by a comparison method as follows: Several acetonitrile solutions of DMA or DBA at different concentrations containing pyrene were pulsed irradiated with the laser, and the rise of P^- with time during and following the pulse was noted. These data are shown in Figure 5. The rate of rise of P^- increases with increasing $[\text{DMA}]$ and the lifetime of the process, calculated as k for reaction II, is 2.0×10^{10} in acetonitrile. Figure 5 also shows similar experiments with pyrene and DMA or DBA in CTAB micelles. Comparison of the two sets of data shows that the ionic products are formed very rapidly in micelles, but not instantaneously. Estimates of rates of P^- formation in micelles can be made by comparing the data with corresponding experiments in acetonitriles.

Effect of Structure on the Yield of Photoelectron Transfer. Table III shows the yield of P^- , measured at $\lambda = 4930 \text{ \AA}$, in the

Table III. Relative Yield of P^- (493 nm)^a

	CTAB	A	B	C
P	1.0 (0.40)	0.50 (0.32)	0.24 (0.12)	0.85 (0.67)
PBA	1.0	0.90	0.77	0.80
PSA	1.0	0.87	0.66	0.96
PTS	1.0	0.95	0.90	

^a $5.0 \times 10^{-5} \text{ M}$ P(PBA, PSA, PTS)/($5-10$) $\times 10^{-3} \text{ M}$ DMA. Better than 95% of the fluorescence is quenched: A, 0.05 M CTAB + 0.1 M hexanol; B, 0.05 M CTAB + 0.25 M hexanol + 0.3 M dodecane (1.83% (w/w) CTAB, 2.5% hexanol, 5.0% dodecane); C, 0.01 M DDAB. Values in parentheses are obtained for DBA (0.005 M).

photoassisted electron transfer from DMA, or DBA to pyrene, pyrenebutyric acid, pyrenesulfonic acid, or PTSA, in various organized assemblies which were constructed as follows: 1, spherical micelle, CTAB in water ($5 \times 10^{-2} \text{ M}$); 2, rod micelle, 0.1 M CTAB in water (0.25 M KBr); 3, vesicle, didodecyltrimethylammonium bromide in water following sonication; and 4, microemulsion (oil in water), CTAB, hexanol, and dodecane in water.

The following additional observations on ion yield in the P/DMA system are helpful in interpreting the data in Table I: (a) The yield of ions from the exciplex increases with increasing dielectric constant or medium polarity. (b) The yield of ions tends to decrease with increasing viscosity; for example, the yield of ions in ethylene glycol is $<10\%$ of that in acetonitrile. The dielectric constants of both media are similar, but the viscosity of ethylene glycol is $30\times$ that of acetonitrile. The lower yield in glycol is probably due to a decreased probability of escape of ions from the solvent cage in more viscous media.

The introduction of the P/DMA into more viscous media by changing the system, spherical micelle, rod-micelle, vesicle, leads to a lower ion yield. Viscosity, or rigidity, plays a similar role when DBA is used in place of DMA. The larger butyl group leads to a slower diffusion of DBA compared to DMA which, in turn, leads to a smaller ion yield. In the case of a polar form of pyrene, such as PSA, etc., which resides at the icelle surface, the restriction of movement, or viscosity experienced by the ions on the P/DMA or PSA/DMA systems, is similar, and similar ion yields are observed.

In microemulsions the medium of pyrene is less rigid than that in a micelle, but lower yields of ions are observed. This is due to a polarity effect as pyrene is located primarily in the oil center of the microemulsion and photoexcitation leads to excited pyrene which encounters DMA in the vicinity of the microemulsion surface.^{14,15} However, the environment of the excited encounter complex is not that of the surface and ion formation is reduced. However, polar derivatives of pyrene are located at the microemulsion surface and the encounter complex experiences a polar environment as in a micelle.

Addition of a co-surfactant to the system leads to a decrease in the ion yield. Previous studies^{11,12} show that the micellar environment of pyrene becomes less viscous on addition of a co-surfactant, but also less polar. The decreased ion yield in these systems suggests that the overall effect is due to the decreased polarity of the encounter complex.

Other e^- transfer systems¹⁶ show similar effects, i.e., the yield of ion products on excitation is highest in micellar systems and decreases in larger systems such as vesicles, etc.

In reversed micellar systems¹⁷ and water in oil microemulsions,¹⁸ it is found that the exciplex of pyrene and dimethylaniline is quenched by the water pool and that no ions are formed. This contrasts with derivatives associated with the water pools such as PSA, which do give ions on excitation in the presence of amines.

(14) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.

(15) Gregoritch, S. J.; Thomas, J. K. *J. Phys. Chem.* **1980**, *84*, 1491.

(16) Matsuo, T.; Nagamura, T.; Itoh, K.; Nishijima, T. *Mem. Fac. Eng., Kyushu Univ.* **1980**, *40*, 25.

(17) McNeill, R.; Thomas, J. K. *J. Colloid Interface Sci.*, in press.

(18) Atik, S. S.; Thomas, J. K., unpublished data.

Table IV. Reaction Rate Constants for Pyrene Anions, P⁻, with Acceptors

solute	homogeneous soln, M ⁻¹ s ⁻¹	cationic micelle, M ⁻¹ s ⁻¹
O ₂	2.0 × 10 ¹⁰	5.0 × 10 ⁹
Eu ³⁺	2.7 × 10 ⁹	1.3 × 10 ⁷ (10 ⁻² M CTAB)
MV ²⁺	2.6 × 10 ¹⁰	3.3 × 10 ⁷ (6 × 10 ⁻² M CTAB) 1.8 × 10 ⁷ (10 ⁻² M CTAB)
cetylpyridinium chloride	2.6 × 10 ¹⁰	10 ⁷ (s ⁻¹) [1st order decay]
CO ₂	~10 ⁷	~10 ⁷

The data suggest that the initial electron transfer to pyrene takes place without restriction with regard to orientation of pyrene and amine. The back electron transfer however appears to be inefficient unless a significant overlap of pyrene anion and amine cation occurs, such as in an exciplex where a sandwich structure is formed. Delocalization of e⁻ over the pyrene ring structure hinders the back e⁻ transfer in other more random arrangements of the ions, such as occur in micelles, etc. Similar photo-"diode" effects are seen in systems where the donor and acceptor are joined by short methylene chains.¹⁹

Reactions of P⁻ in Micelles. Table IV shows the rate constants for reaction of P⁻ in CTAB micelles with CO₂, O₂, Eu³⁺, methyl viologen, MV²⁺, and cetylpyridinium chloride; the rate constants in homogeneous solutions of acetonitrile are also shown for comparison. In all cases the rates in homogeneous solution approach diffusion control and are ~10¹⁰ M⁻¹ s⁻¹. The rate constant for reaction of P⁻ with O₂ is significantly decreased in CTAB micelles and is similar to the decreased rate of quenching of pyrene fluorescence by O₂ which is diffusion controlled in methanol but 5 × 10⁹ M⁻¹ s⁻¹ in CTAB micelles.²⁰ This is interpreted as a decreased motion of O₂ due to the rigidity of the micellar environment.

Both Eu³⁺ and MV²⁺ show significantly decreased rates of reaction with P⁻ in CTAB micelles. This is not unexpected as these cations should be repelled by the positive potential of the micelle. The rates of reaction increased linearly with [cation] and are independent of [micelle] which indicates that these ions ap-

(19) Eisenthal, K. *Acc. Chem. Res.* 1975, 8, 118.(20) Thomas, J. K. *Acc. Chem. Res.* 1977, 10, 133.

proach the micelle surface to react with P⁻, rather than P⁻ exiting into the aqueous phase followed by an encounter with the cation.

Cetylpyridinium chloride, CP⁺, is located in the micelle and the kinetic motion leading to a decreased yield of P⁻ is that of P⁻ and CP⁺ on the micelle surface. The rate constant *k_q* is similar to that found for CP⁺ quenching of excited pyrene on CTAB micelles (*k_q* = 1.4 × 10⁷ s⁻¹)¹¹ and for pyrene excimer formation (*k* = 5.0 × 10⁶ s⁻¹). These data suggest that P⁻ and CP⁺ have to diffuse together on the micelle surface in order for the reverse e⁻ transfer process to occur. This process takes ~10⁻⁷ s for P⁻ and a cation, which indicates that the DMA⁺ exit rate from the CTAB micelles is much faster than 10⁻⁷ s. However, the rate of back reaction is not as rapid as that observed for P⁻ and DMA⁺ in anionic NaLS micelles which occurs within 20 ns. This may be due to the higher mobility of DMA⁺ on the micelle surface compared to CP⁺, or to a tunneling of e⁻ from P⁻ back to DMA⁺, a process which does not occur with CP⁺ and P⁻. There is some evidence to this effect for a rapid <1 ns back reaction of P⁻ and DMA⁺ when linked together by a propyl chain.¹⁹

It is suggested that the above reactions are e⁻ transfer in nature. This was substantiated in the case of MV²⁺, where the enhanced decay of P⁻ was matched by a concomitant rise of the reduced MV²⁺ observed at 6000 Å.

It is instructive to note that MV²⁺ quenches excited pyrene P* with *k_q* = 10¹⁰ M⁻¹ s⁻¹ in methanol and 5.0 × 10⁷ M⁻¹ s⁻¹ in CTAB micelles. The decreased rate constant observed in CTAB compared to acetonitrile, 1/200, is close to that observed in similar experiments for the reaction of P⁻ and MV²⁺. This also suggests that for reaction to occur, MV²⁺ approaches either P⁻ or P* in the micelle surface. There is no evidence of e⁻ tunneling to MV²⁺.

Conclusion

The present data show that photoinduced electron transfer occurs more efficiently in micellar systems where the more water soluble product is repelled from the micellar surface due to electrostatic repulsion of product and micelle. Location of the reactants away from the water-colloid interface leads to lower ion yields; lower yields also result from a decreased mobility of the ion fragments in the medium. Time-resolved studies indicate that the e⁻ transfer process with the original photoexcited pair and with subsequent ionic reactions is diffusion controlled. No evidence of transfer of e⁻ over large distances (>5 Å) is observed.

These data are helpful in constructing assemblies that may be used for efficient photoinduced e⁻ transfer reactions and photo-"diode" effects, leading to ionic products.

Hydrolysis of 3-(*m*-Nitrophenyl)-3-methoxyphthalide

Daniel P. Weeks* and Donald B. Whitney

Contribution from the Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079. Received January 5, 1981

Abstract: The hydrolysis of 3-(*m*-nitrophenyl)-3-methoxyphthalide to *o*-(*m*-nitrobenzoyl)benzoic acid is general-base catalyzed in acetate buffers at pH 4-6. The rate expression is: *k*_{obsd} = 1.60 × 10⁻⁶ + 6.38 × 10⁻⁴[H⁺] + 2.08 × 10⁻⁵[OAc⁻] + 49[OH⁻]. Entropies of activation are -26.6, -39.0, and -6.59 eu at pH 1.26, 5.08, and 7.70, respectively. The solvent isotope effect on the catalytic rate constant is 2.65. In acidic solution the reaction proceeds by an A1 mechanism, in basic solution, a B_{AC}2. The buffer catalysis is interpreted as general-base catalysis of nucleophilic attack by water on the carbonyl carbon.

Reactions of acyl compounds in aqueous solution provide many examples of how the reaction mechanism can change with subtle changes in structure or reaction conditions. In partial acylals, 1, an "ester" carbonyl is combined with an "acetal" carbon atom. These compounds provide the interesting union of two functional groups each of which reacts readily in aqueous solution.

Salomaa¹ has shown that simple partial acylals react in aqueous acid as acetals do. That is, the mechanism is an acid-catalyzed unimolecular (A1) process. If the ester carbonyl is used as a point of reference this is an A_{AL}1 mechanism. Newman and Hishida²

(1) Salomaa, P. *Acta Chem. Scand.* 1957, 11, 132, 141, 235.