Micellar Control of Intramolecular Excimer Formation of Bound Substrates

By JACK EMERT,* PATRICE PHALON, ROBERT CATENA and DHARMARAO KODALI
(*Department of Chemistry, Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York* 11201)

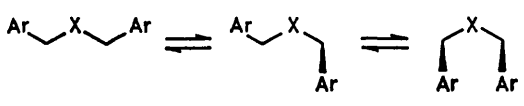
Summary Excimer formation of bis(arylmethyl)ammonium chlorides can be facilitated or inhibited in aqueous micelles, depending on their binding geometry.

THE partition in favour of reactants in organized assemblies with the resultant changes in the course, rate, and selectivity of reactions has been well documented.[1] However, the effect of aggregated systems on the conformations of bound substrates has received almost no attention.[2] We describe herein evidence for a novel micelle-induced conformational transition in molecules of type (**1a**) in aqueous solution.

$$ArCH_2XCH_2Ar$$
(**1**)

a; X = $NH_2^+Cl^-$
b; X = CH_2
c; X = O
d; X = NHR^+Cl^-(R=Me, Et, C_5H_{11}, C_8H_{17}, $C_{12}H_{25}$)
Ar = Aryl

Interactions between aryl groups in the ground states of compounds (**1a**—**c**) are normally repulsive, causing them to adopt predominantly *trans–trans* (*tt*) and *trans–gauche* (*tg*) conformations (Scheme). Exciting one of the aryl groups causes the interactions between the rings to become attractive so that formation of the eclipsed conformer (e) (Scheme) can be observed by the appearance of a broad, structureless, red-shifted excimer band in the fluorescence spectrum. The relative intensities of the excimer and monomer bands (I_d/I_m) have previously been related to the nature of Ar, the temperature, and the viscosity of the medium.[3]



SCHEME

However, though excimer formation with probes (**1b**) and (**1c**) has been shown to be substantially inhibited by the relatively viscous environment in the interior of micelles,[4] the presence of micelles facilitated excimer formation in the ionic series (**1a**). Thus, dibenzyl, bis-(*p*-methylbenzyl), bis-(4-biphenylmethyl), bis-(α-naphthylmethyl), and *NN*-dimethyl-2-benzyl-3-phenylpropyl-

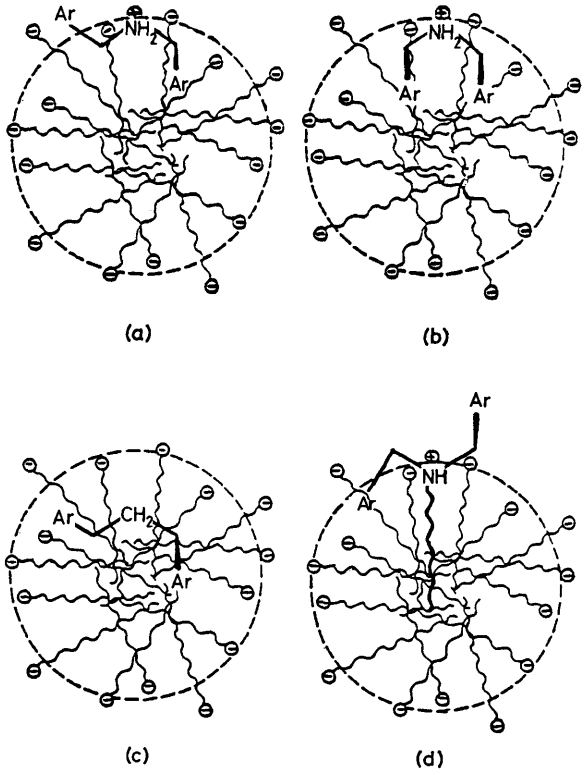


FIGURE 1. Comparison of the hydrophobic interactions of SDS micelles with (a) (**1a**) in the *tg* conformation, (b) (**1a**) in the eclipsed conformation, (c) (**1b**) in the *tg* conformation, and (d) (**1d**) (R=$C_{12}H_{25}$) in the *tg* conformation.

ammonium chloride (10^{-4} M) all exhibited substantially enhanced excimer yields (87%, 37%, 77%, 64%, and 67% higher I_d/I_m values, respectively) when made completely soluble in sodium dodecylsulphate micelles (SDS) at 20 °C. Similarly, anionic probes such as dibenzylacetate made soluble in cationic micellar systems such as cetyltrimethylammonium chloride (CTAC) displayed the same kind of behaviour (9% higher I_d/I_m).†

These enhanced excimer yields are attributed to micellar stabilization of the eclipsed conformations of the probes in solution relative to their extended conformations. In both the *tt* and *tg* states, only one of the aromatic moieties of (**1a**) can be directed towards the hydrophobic micellar interior [Figure 1(a)]. When the aromatic nuclei are eclipsed, however, both rings are able to interact with the micellar core [Figure 1(b)] and excimer formation is facilitated. Neutral probes are not subject to this effect because they are not anchored to the micellar surface and both aromatic rings can interact with the hydrophobic core even in the extended conformations merely by penetrating deeper into the micelle [Figure 1(c)].

Support for this explanation was obtained by examining probes (**1d**). Successive substitution of the nitrogen of dibenzylammonium chloride with larger and larger R groups should at least partially invert the orientation of the probes in the micelle since a long straight-chain alkyl residue would be expected to compete with the benzyl groups for space in the micellar core [Figure 1(d)]. In this inverted geometry, excimer formation should be *retarded* relative to free solution because it would require the extension of both benzyl groups into the bulk medium.

Figure 2, in which are plotted the I_d/I_m values of the probes (**1d**) (5×10^{-4} M) in 0·05 M SDS $(I_d/I_m)_{SDS}$ relative to their values in free solution $(I_d/I_m)_w$ as a function of the length of R, demonstrates that this is indeed the case.† As the R group is varied from H to dodecyl, excimer formation becomes inhibited in the micelle and $(I_d/I_m)_{SDS}/(I_d/I_m)_w$ decreases dramatically. These data indicate that micelles are capable of controlling the conformations of bound probes and suggest the possibility that the reactivity of solubilized substrates can also be altered by aggregated systems in this manner.

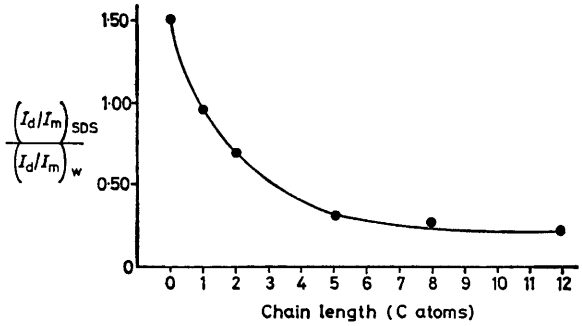


FIGURE 2. $(I_d/I_m)_{SDS}/(I_d/I_m)_w$ for probes (**1d**) as a function of chain length.

It should be noted, however, that, as observed with the cyclodextrin complexes of these compounds,[5] their absorption spectra are largely unperturbed by the presence of the micelles. Thus, this effect is only observed in the excited state.

We thank the National Institutes of Health for support of this work.

(*Received, 22nd April* 1981; *Com.* 474.)

† I_d/I_m values in the micelles are compared with those in water except for the insoluble bis-(4-biphenylmethyl)ammonium chloride and the *N*-dodecyl-*NN*-dibenzylammonium chloride which aggregates in aqueous solution. In these cases the values are compared with those in ethanol.

[1] J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems,' Academic Press, N.Y., 1975.
[2] H. Takahashi, Y. Nakayama, H. Hori, K. Kihara, H. Okabayashi, and M. Okuyama, *J. Colloid Interface Sci.*, 1976, **54**, 102; F. H. Menger and J. M. Jerkunica, *Tetrahedron Lett.*, 1977, 4569.
[3] J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley–Interscience, N.Y., 1964; W. Klöpffer, *Ber. Bunsenges Phys. Chem.*, 1970, **74**, 693; P. Avouris, J. Kordas, and M. A. El-Bayoumi, *Chem. Phys. Lett.*, 1974, **26**, 373; E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, 1970, **92**, 3586; Y. C. Wang and H. Morawetz, *ibid.*, 1976, **98**, 3611; M. Goldenberg, J. Emert, and H. Morawetz, *ibid.*, p. 7171.
[4] J. Emert, C. Behrens, and M. Goldenberg, *J. Am. Chem. Soc.*, 1979, **101**, 771; K. A. Zachariasse, *Chem. Phys. Lett.*, 1978, **57**, 429; N. J. Turro, M. A. Kawa, and A. Yekta, *J. Am. Chem. Soc.*, 1979, **101**, 772.
[5] J. Emert, D. Kodali, and R. Catena, *J. Chem. Soc., Chem. Commun.*, 1981, preceding Communication.