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EXCIPLEX QUENCHING BY QUATERNARY AMMONIUM SALTS IN CHLOROFORM

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Exciplex emission from pyrene-N,N-dimethylaniline and pyrene-1,4-dicyanobenzene was quenched by various quaternary ammonium salts in chloroform. The quenching rate constants depended on the structure of the quaternary ammonium salts. Electrostatic interaction between the dipolar exciplex state and the quaternary ammonium salt may be responsible for the present exciplex quenching.

The Coulombic repulsion or attraction between photochemically produced ions and charged groups at the micelle-water and polyelectrolyte-water interface influences the efficiencies of backward electron transfer reactions.[1)] However, such electrostatic interaction is not confined to molecular aggregated systems. We have demonstrated that the quantum efficiency is very much improved by the use of a sensitizer having tetraalkylammonium substituent or by the addition of some electrolytes such as tetraethylammonium chloride for the photooxidation of leuco dye[2)] and/or the photoreduction of methylviologen in a non-aggregated homogeneous solution. In these studies, we have proposed that the electrostatic field brings about an enhanced charge separation efficiency of the photochemically produced ion radical pair even in a homogeneous solution. In this communication, we report that the excited charge transfer state (i.e., exciplex) is quenched by various quaternary ammonium salts in chloroform. We consider that the present results are direct evidence for the participation of electrostatic interactions between electrolytes and a photochemically produced dipole in charge transfer reactions.

Pyrene(Py) and 1,4-dicyanobenzene(DCB) were recrystallized from ethanol. N,N-Dimethylaniline(DMA) was purified by vacuum distillation over KOH under nitrogen atmosphere. Spectrograde chloroform was used as supplied. Cetyltrimethylammonium chloride(CTAC), dodecyltrimethylammonium chloride(DTAC), cetylpyridinium chloride

(CPCl), tetraethylammonium chloride(Et_4NCl), tetra-n-butylammonium chloride(Bu_4NCl) and perchlorate(Bu_4NClO_4) were purified by repeated recrystallizations from appropriate solvent systems. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluorometer. All the sample solutions were deaerated by argon gas purging.

The examples of exciplex quenching by Et_4NCl are shown in Fig.1. It is noteworthy that the Py monomer fluorescence is scarcely quenched. Furthermore, in the Py-DMA system, the exciplex fluorescence maximum slightly shifted to red with increasing the concentration of the salt. Various quaternary ammonium salts also quenched the Py-DMA and Py-DCB exciplex fluorescence, and linear Stern-Volmer plots were obtained(Fig.2). In the case of the quencher CPCl, both Py monomer and exciplex fluorescence was quenched. The acceptor property of pyridinium salt$^{4)}$ may be responsible for this. For CPCl, the modified Stern-Volmer equation(1)$^{5)}$ is applicable, where I_E° (I_M°) and I_E (I_M) are exciplex(monomer) fluorescence intensities in the absence and presence of the quencher, respectively. Knowing the exciplex lifetimes(τ_e) of Py-DMA exciplex(25.2ns) and Py-DCB exciplex(30.5ns)$^{6)}$ in chloroform, the exciplex quenching rate constants(kq) can be determined as presented in Table 1. The quenching rate constants were in the order of 10^9 - $10^{10} M^{-1} s^{-1}$, and the kq values in the Py-DCB system were slightly greater than those in the Py-DMA system and depended on the structures of the ammonium groups but not on the nature of the counter ions.

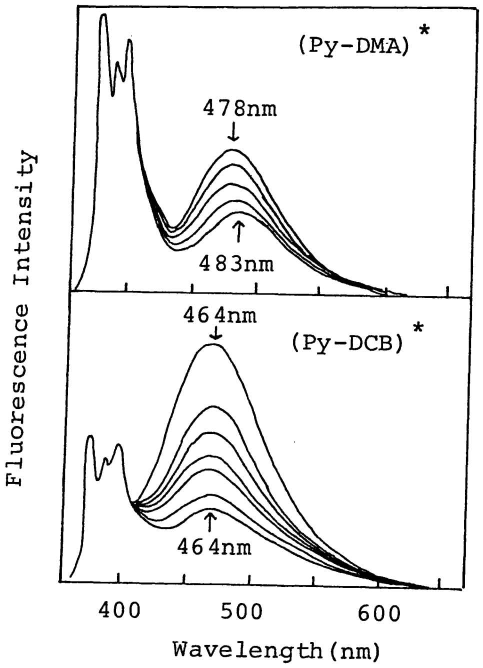


Fig.1 Exciplex quenching by Et_4NCl in chloroform. $[Py]=1X10^{-5}M$, $[DMA]=[DCB]=1X10^{-2}M$.

$$I_E^{\circ} I_M / I_E I_M^{\circ} = 1 + kq\tau_e[Q] \qquad (1)$$

The quaternary ammonium salts used in this study, except for CPCl, do not possess electron donating or accepting ability, so that the present exciplex quenching cannot be explained by the charge transfer interaction between the exciplex states and the quaternary ammonium salts. A possible increase of water content by the addition of the salts which are sometimes hygroscopic cannot account for the quenching, since the exciplex emission maxima and the intensity in water saturated chloroform

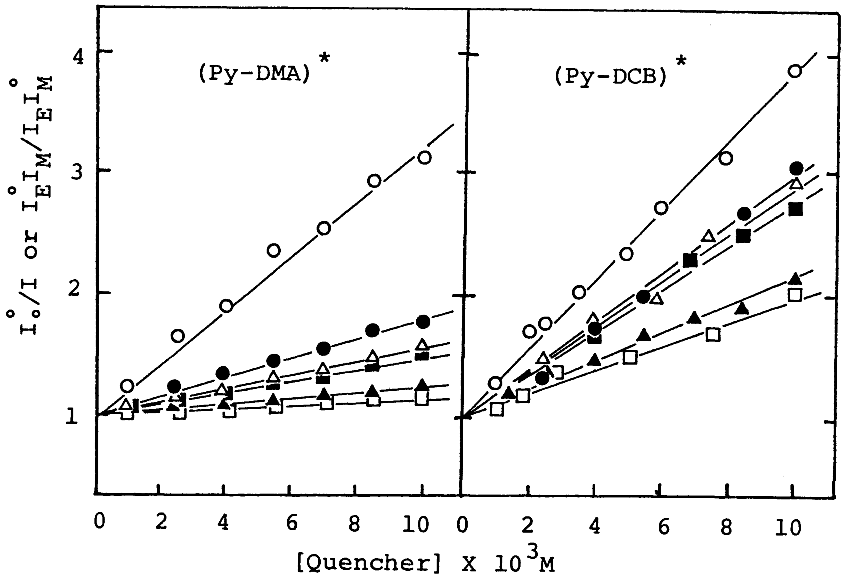


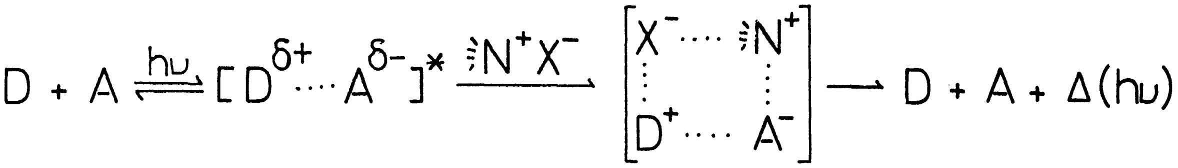
Fig.2 Stern-Volmer exciplex quenching plots in $CHCl_3$. CPCl(○), Et_4NCl(●), Bu_4NClO_4(△), Bu_4NCl(■), DTAC (▲), CTAC(□). [Py]=$1X10^{-5}$M, [DMA]=[DCB]=$1X10^{-2}$M

are almost identical with those in dry chloroform. Furthermore, Py excimer fluorescence([Py]=$1X10^{-2}$M in chloroform) was not quenched at all by these quaternary ammonium salts, except for CPCl, indicating the polar nature of exciplex to be related to the quenching. From these results, we tentatively propose the following quenching mechanism.

Table 1 Exciplex quenching by quaternary ammonium salts in $CHCl_3$

Q	kq, $X10^{-9}M^{-1}s^{-1}$	
	(Py-DMA)*	(Py-DCB)*
CTAC	0.72	3.3
DTAC	1.0	3.8
Bu_4NCl	1.9	5.8
Bu_4NClO_4	2.0	6.1
Et_4NCl	3.1	6.4
CPCl	9.0	9.7

The linear Stern-Volmer plots in Fig.2 indicate bimolecular quenching mechanisms. Furthermore, we consider that the electrostatic interaction between ammonium salts and dipolar exciplex state may be responsible for the present quenching. In nonpolar solvents such as chloroform or dichloroethane, ammonium salts do not dissociate to free ions but favor to form ion pairs,7) so that the ion pairing between the ammonium salt and the dipolar exciplex state will be the main deactivation path of the exciplex state as schematized below. The sequence of kq in Table 1 agrees with the decreasing order of the size of ammonium group. Since an ion pairing favors for smaller size of ion,7) the present results support the above mechanism. Furthermore, the exciplex fluorescence maximum of the



$$D + A \overset{h\nu}{\rightleftharpoons} [D^{\delta+}\cdots A^{\delta-}]^{*} \xrightarrow{\vdots N^{+}X^{-}} \begin{bmatrix} X^{-}\cdots \vdots N^{+} \\ \vdots \qquad \vdots \\ D^{+}\cdots A^{-} \end{bmatrix} \longrightarrow D + A + \Delta(h\nu)$$

Py-DMA system shows a red shift with increasing the salt concentration(Fig.1). This red shift may be direct evidence of the formation of the intermediate association complex between ammonium salt and the exciplex.

In conclusion, the present results indicate that the electrostatic field of the electrolytes such as surfactants or polyions play an important role in charge transfer or electron transfer processes. The use of these electrostatic effects will be an effective approach to improve the quantum efficiency of electron transfer reaction and hence the solar energy conversion efficiency relevant to electron transfer processes. The present results warn that the use of exciplex emission as an environmental probe in micelles, vesicles, and/or bilayer membranes should be deliberately reconsidered.

References

1) B.Katusin-Rozem, M.Wong, and J.K.Thomas, J.Am.Chem.Soc., 100, 1679(1978); S.S.Atik and J.K.Thomas, ibid., 103, 3550(1981); Y.Waka, K.Hamamoto, and N.Mataga, Chem. Phys.Lett., 53, 242(1978).

2) S.Tazuke, Y.Kawasaki, N.Kitamura, and T.Inoue, Chem.Lett., 1980, 251.

3) Y.Kawanishi, N.Kitamura, and S.Tazuke, "Symposium on Photochemistry,Japan", Preprint IIIA-117, (1981) Sapporo.

4) E.M.Kosower, "An Introduction to Physical Organic Chemistry", p-179, John Wiley (1968).

5) R.A.Caldwell, D.Creed, D.C.DeMarco, L.A.Melton, H.Ohta, and P.H.Wine, J.Am.Chem. Soc., 102, 2369(1980).

6) Determined by a single photon counting method. The authors are greatly indebted to Mr.Y.Yamaguchi and Mr.T.Matsumaru of Dai-ni SEICO Co.LTD. for their permission and instruction for conducting the lifetime measurements with their single photon counting system.

7) E.Hirsch and R.M.Fuoss, J.Am.Chem.Soc., 82, 1018(1960).

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