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Multi-channel Possibility of Electron Transfer Reaction in the Excited State

Noboru MATAGA

Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

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Recently, we have studied the quenching of pyrene fluorescence by several electron acceptors and donors in polar solvents.[1] We have observed extraordinary strong quenching in the case of pyrene-TCNE-acetonitrile system, where the value of δ in the equation of relative fluorescence yield, $\eta'/\eta=\delta/(1+k_q\tau[\mathrm{B}])$, is remarkably smaller than unity. We have further confirmed that k_q is not simply proportional to the diffusion coefficient, D, at low temperatures, *i. e.*, $k_q \propto D^m$ $(m<1)$ in contrast to other systems where $k_q \propto D$. These facts for pyrene-TCNE system have been given a tentative interpretation that somewhat long range electron transfer process in a quite loose encounter pair is involved in the reaction.[1]

As we have pointed out previously,[2] the mechanism of fluorescence quenching reaction due to the electron transfer process in a polar solvent may be discussed on the basis of Marcus' theory of electron transfer.[3] According to Marcus,[3a] the reaction scheme may be written as,

$$\underset{\swarrow 1/\tau}{\mathrm{A}^*} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{A}^*\cdots\mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{A}^{\pm}\cdots\mathrm{B}^{\mp} \xrightarrow{k_3} \qquad (1)$$

Then, we have,

$$\begin{aligned} k_q &= k_1/[1+(k_{-1}/k_2)+(k_{-1}k_{-2}/k_2k_3)] \\ &= k_1/[1+(k_{-1}/k_2{}^0)\exp(\Delta F^*/\boldsymbol{R}T) \\ &\quad +(k_{-1}/k_3)\exp(\Delta F^0/\boldsymbol{R}T)] \end{aligned} \qquad (2)$$

where $k_2=k_2{}^0\exp(-\Delta F^*/RT)$, $k_2/k_{-2}=\exp(-\Delta F^0/RT)$, ΔF^* and ΔF^0 are respectively the free energy of activation and the standard free energy for the electron transfer process. Rehm and Weller[4] have shown by measuring k_q for many systems that k_q is nearly constant and equal to $1.6\times10^{10}\mathrm{M}^{-1}\mathrm{sec}^{-1}$ for $\Delta F^0 \lesssim -10$ kcal/mol while it becomes much smaller for $\Delta F^0 > -10$ kcal/mol. They have derived also numerical values for rate constants of Eq. (2) and equations for ΔF^* in terms of ΔF^0, which reproduce satisfactorily the observed k_q values. ΔF^0 value can be estimated by Eq. (3),

$$\Delta F^0 = E^{(+)}(\mathrm{B}) - E^{(-)}(\mathrm{A}) - C - \Delta E(\mathrm{A}^*)$$

or (3)

$$\Delta F^0 = E^{(+)}(\mathrm{A}) - E^{(-)}(\mathrm{B}) - C - \Delta E(\mathrm{A}^*)$$

where $E^{(+)}$ and $E^{(-)}$ are oxidation and reduction potentials of electron donor and acceptor, respectively, ΔE is the excitation energy of A to the luminescent state and C is the coulomb interaction energy in $\mathrm{A}^{\pm}\cdots\mathrm{B}^{\mp}$. C is approximately given by $C \approx e^2/\varepsilon R_{ab}$, where R_{ab} is the inter-ionic distance and ε is the dielectric constant of solvent.

For several pyrene-quencher systems in acetonitrile, we have evaluated ΔF^0 as follows. $E^{(+)}$ and $E^{(-)}$ values in acetonitrile solution were taken from literature.[5] R_{ab} was assumed to be 7 Å. (Even if we take somewhat smaller or larger value for R_{ab}, our conclusion in this report remains unchanged.) Then, ΔF^0 values are -2.5 eV, -1.5 eV, -0.45 eV and -0.55 eV for the quenchers TCNE, TCNB (tetracyanobenzene), *p*-DCNB (*p*-dicyanobenzene) and DMA (*N*,*N*-dimethylaniline), respectively. TCNE, TCNB and *p*-DCNB work as electron acceptors while DMA works as a donor.

If the $|\Delta F^0|$ value is very large just as in the case of pyrene-TCNE system, it might be possible that the electron transfer reaction occurs not only to the ground state of $\mathrm{A}^{\pm}\cdots\mathrm{B}^{\mp}$ but also to its various excited states when the ion radicals have low energy excited levels. The pyrene cation and anion radicals have presumably three excited levels in the range of excitation energies of 1.5—2.0 eV and 1.3—2.0 eV, respectively.[6] Accordingly, the standard free energies of the electron transfer processes leading to the

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[1] T. Okada, H. Oohari and N. Mataga, This Bulletin, **43**, 2750 (1970).

[2] N. Mataga, T. Okada and N. Yamamoto, *Chem. Phys. Lett.*, **1**, 119 (1967).

[3] R. A. Marcus, a) *J. Chem. Phys.*, **24**, 966 (1956); b) *Ibid.*, **26**, 867 (1957); c) *Ibid.*, **26**, 872 (1957); d) *Ibid.*, **43**, 679 (1965); e) *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

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[5] M. E. Peover, *Trans. Faraday Soc.*, **58**, 2370 (1962); E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963); H. Beens and A. Weller, *Acta Phys. Polon.*, **34**, 593 (1968). The $E^{(+)}$ value of DMA in acetonitrile has been measured kindly by T. Kubota and H. Miyazaki at Shionogi Research Laboratory, to whom the author expresses his sincere gratitude.

[6] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 4372 (1966); R. Zahradnik and P. Cársky, *J. Phys. Chem.*, **74**, 1240 (1970).

excited states of $A^{\pm}\cdots B^{\mp}$, are all lower than -0.5 eV, in the case of pyrene-TCNE system. Thus, there are presumably four reaction paths of electron transfer, all of which have the rate constant of 10^{10}M^{-1} sec.$^{-1}$. On the other hand, only the electron transfer process to the ground state of $A^{\pm}\cdots B^{\mp}$ is possible when TCNB, p-DCNB and DMA are used as the quenchers. In these cases, the rate constant of the reaction to the excited states of $A^{\pm}\cdots B^{\mp}$ is much smaller than 10^{10}M^{-1} sec^{-1} according to the treatment of Marcus.[3)]

From the reasoning described above, the reaction in the case of pyrene-TCNE system may be a multichannel process, the rate constant of which is the sum of four rate constants, $k_q=\sum_i k_{qi}$. Accordingly, it may be possible for the electron transfer process from the excited pyrene to TCNE to occur at much larger intermolecular distance compared to the case of the other single channel systems.