

ELECTRON TRANSFER DISTANCES OBTAINED BY PICOSECOND STUDY OF FLUORESCENCE
DYNAMIC QUENCHING

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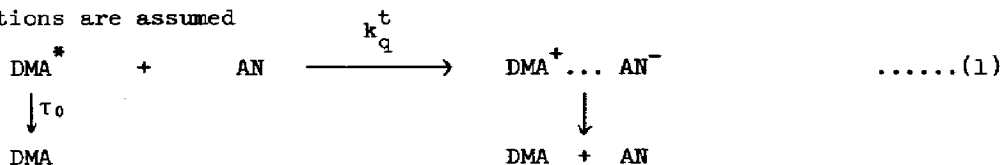
Abstract: Electron transfer distances have been obtained by analyzing the transient effect in the diffusion-controlled fluorescence quenching reaction of N,N-dimethylaniline (DMA) by acrylonitrile (AN). We obtained 6.0 ± 0.8 Å in cyclohexane and 8.9 ± 0.9 Å in acetonitrile. This indicates that a longer range electron transfer occurs in a polar solvent than in a non-polar solvent.

Introduction: It is known that the electron transfer reaction occurs more easily as increasing the solvent polarity. A very large distance of 50 Å has been obtained in pyrene-tetracyanoethylene-acetonitrile.¹⁾ On the other hand, the radius obtained in anthracene-N,N-diethylaniline became the sum of van der Waals radii in hexane as well as in acetonitrile.²⁾ In order to confirm whether electron transfer distance are dependent on the solvent polarity, the reaction radii were determined by using a picosecond laser and a streak camera. This technique is very useful for such a purpose, since the transient effect is recognized until ~ 100 ps after the excitation pulse in usual solvents of low viscosity.

Experimental: The apparatus were the same as described elsewhere³⁾ with a small improvement. The 4th harmonic (266 nm, 20 ps) of a Nd³⁺ YAG laser was used as an exciting light source. The relay lens was an UV transmitting optics. The distortion of the time base and vertical intensity of the camera were fully corrected. Fluorescence lifetimes in a few ns region were also measured by a channel plate photomultiplier and a corrected transient digitizer.

Solutions of purified DMA and AN were thoroughly degassed in separate amples and mixed in vacuum just before measurements. Broadening of absorption spectra in cyclohexane by adding AN greater than 0.5 M was recognized, but fluorescence spectra did not change. This suggests that even though complex is formed and is excited, the fluorescence of complex is quenched instantaneously. This "complex" seems not to affect the dynamic quenching processes, and the influence of the complex formation on K_{sv} could be included in an error.

Results and Discussions: The following quenching mechanism and decay functions are assumed



$$I(t) = I_0 \exp\left[-\frac{1}{\tau_0} - k_q^{\circ} \left(1 + \frac{2R'}{\sqrt{\pi D t}}\right) [\text{AN}]\right] t \quad \dots\dots(2)$$

$$\lim_{[\text{AN}] \rightarrow 0} K_{sv}^{\circ} = K_{sv}^{\circ} = k_q^{\circ} \tau_0 \left(1 + \frac{R'}{\sqrt{\tau_0 D}}\right) \quad \dots\dots(3)$$

$$k_q^{\circ} = 4\pi N' R' D, \quad R' = R / (1 + D/\kappa R). \quad \dots\dots(4)$$

Notations are followed by ref.4. Observed fluorescence decay curves are shown in Fig.1. Small, but definite, deviations from a single exponential decay could be observed.

The Stern-Volmer constants K_{sv}° were determined from steady state fluorescence measurements, where the concentrations of AN were below $2.2 \times 10^{-2} \text{M}$ in cyclohexane and $0.75 \times 10^{-2} \text{M}$ in acetonitrile. The fluorescence quenching constants $k_q^s (= K_{sv}^{\circ} / \tau_0)$ indicate the reaction proceeds by the diffusion controlled process. Apparent transient quenching rate constants can be estimated from the average lifetimes τ_{av} . These values are almost same as k_q^t in Table 2. and 33% and 63% greater than k_q^s in cyclohexane and acetonitrile, respectively. Intuitively this suggests that the second term $R'/\sqrt{\pi D t}$ is large and contributes to k_q^t more effectively in acetonitrile than in cyclohexane. Fitting the observed decay curves by convolution with Eq.2 under the condition of Eq.3, obtained R' , D , and other parameters are tabulated in Tables 1, 2.

The free energy change ΔG by electron transfer in acetonitrile can be estimated to be $\Delta G \sim -1.0 \text{eV}$. If one assumes electron transfer occurs from DMA^* to AN in cyclohexane and form a non-fluorescent exciplex, which may be more stable than solvated ion pair, the value is estimated as $\Delta G \sim -0.8 \text{eV}$. Thus one can assume that the fluorescence quenching due to electron transferring.

Reaction radius in cyclohexane is 6Å and is nearly equal to the encounter distance. But in acetonitrile the distance 9Å is larger than the sum of the van der Waals radii. The difference can not be explained by a simple cage effect which might be different in each solvent.

References: 1) T. Okada, H.Oohari, and N.Mataga, Bull.Chem.Soc.Jap., 43, 2750(1970). 2) T.J.Chuang and K.B.Eisenthal, J.Chem.Phys., 62, 2213(1975).

3) M.Sumitani, N.Nakashima, K.Yoshihara, and S.Nagakura, Chem.Phys.Lettl, 51, 183(1977). 4) T.L.Nemzek and W.R.Ware, J.Chem.Phys., 62, 477(1975).

Table 1. Fluorescence Quenching Constants I

Solvent	ϵ	τ_0	K_{sv}^0 M^{-1}	k_q^s $10^{10} M^{-1} s^{-1}$	τ_{av} ps
Cyclohexane	2.023	2.69±0.03	44.8±0.2	1.69	91±2
Acetonitrile	37.5	4.46±0.03	85.3±0.2	1.91	69±2

ϵ : dielectric constant at 20 °C, τ_0 : fluorescence lifetime of DMA, K_{sv}^0 : Stern-Volmer constant for low concentration limit of AN, τ_{av} : obtained by fitting with a single exponential function, $k_q^s = K_{sv}^0 / \tau_0$, errors: standard deviations.

Table 2. Fluorescence Quenching Constants II

Solvent	R' A	D $10^{-5} cm^2 s^{-1}$	k_q^0 $10^{10} M^{-1} s^{-1}$	$k_q^t (t=100ps)$ $10^{10} M^{-1} s^{-1}$
Cyclohexane	6.0±0.8	3.0±0.4	1.37	2.23
Acetonitrile	8.9±0.9	2.2±0.3	1.49	3.09

R' : reaction radii, D: diffusion constant, $k_q^0 = 4\pi R' D N'$, $k_q^t = k_q^0 (1 + \frac{R'}{\sqrt{\pi D t}})$, errors: estimated by fitting decay curves.

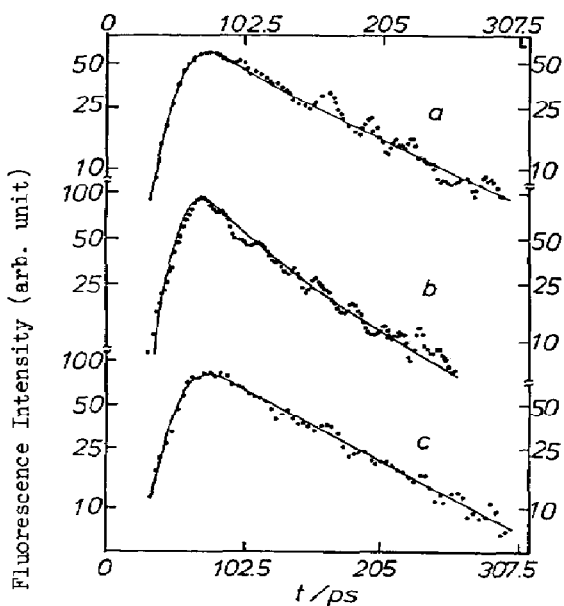


Fig.1. Observed (...) and convoluted (—) typical decay curves. N,N-dimethylaniline ($8 \times 10^{-5} M$), acrylonitrile ($0.456 M$), a: in cyclohexane, b: in acetonitrile. c: erythrosin (reference) ($10^{-6} M$ in water) shows exponential decay with the lifetime of 90ps.