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Transfer of Electronic Excitation Energy from 2,2-Diphenylethanol to 2,6-Diphenylpyridine in Solvents of Different Viscosity

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Measurement of emission spectra indicates that in diluted solution of 2,2-diphenylethanol (DPE) - 2,6-diphenylpyridine (DPP) system in solvents of different viscosity, the rate parameters k_{xy} associated with nonradiative energy transfer from donor X (DPE) to acceptor Y (DPP) decrease with increasing viscosity of the medium. Further k_{xy} values are higher than diffusion controlled rates k_d. The Förster critical transfer distance R_0 is much greater than the sum of the radii of the donor and acceptor, r_x+r_y. The observations seemingly indicate that energy-transfer from donor DPE to acceptor DPP mainly occurs by coulombic interaction over the dipole–dipole interaction distance which exceeds the molecular dimensions. In the DPE–DPP system, there is no evidence of external quenching.

For a donor–acceptor system X–Y, nonradiative energy transfer may occur due to diffusion and interaction between the molecules or electronic excitation energy transfer from X to Y. Several theories related to Förster mechanism have been published before[1–6] and several models of energy transfer mechanism have been proposed.[6] Dependence of energy transfer efficiency on viscosity of media has been discussed for some donor–acceptor systems.[6–15] This paper concerns emission from very dilute solutions of 2,2-diphenylethanol (DPE) and 2,6-diphenylpyridine (DPP) in different solvents. The objectives are to investigate whether long-range dipole-dipole or short-range electron-exchange mechanism controls the energy transfer from DPE to DPP, to examine the dependence of energy-transfer processes on viscosity of the medium and to ascertain the role of intermolecular association, if any. Rate parameters associated with the nonradiative decay processes have been evaluated.

Experimental

Pure (99%) 2,2-diphenylethanol obtained from Aldrich Chemical Ltd., was used after sublimation under reduced pressure. 2,6-Diphenylpyridine and the solvent 2-methyl-1-propanol (isobutyl alcohol) (*i*-BuOH) supplied by Aldrich, and the other solvents hexane, methanol (MeOH), 1-butanol (*n*-BuOH) (E. Merck), 2-propanol (*i*-PrOH) (J.T. Baker) were used without further purification. The solvents were of spectroscopic grade and were tested before use for absence of any emission in the region of wavelengths studied.

The concentration of 2,2-diphenylethanol was fixed at 7.04×10^{-4} mol dm^{-3} approximately throughout the experiment. The concentration of DPP was varied between 10^{-6} and 10^{-5} mol dm^{-3}. The excitation wavelengths were selected at 260 nm for DPE and 300 nm for DPP.

Experimental details of measuring the absorption spectra, emission spectra, and the fluorescence lifetime of DPE in different solvents are as described elsewhere.[16,17]

Results and Discussion

Fluorescence emission of DPE and DPP in hexane, when excited by (1) the DPE absorption (λ_{ex}=260 nm) and (2) by the DPP absorption (λ_{ex}=300 nm) shows the following characteristics. In the first case the DPE fluorescence intensity falls off appreciably when a small amount of DPP (concentration 10^{-6} mol dm^{-3}) is added keeping the concentration of DPE in hexane fixed. The S_1 state of DPE lies higher than the S_1 state of DPP and the fluorescence spectrum of DPE (X) and the absorption spectrum of DPP (Y) overlap with each other. Therefore the condition for transfer of excitation energy from DPE to DPP, one of the probable causes for fluorescence quenching, is satisfied. It is to be noted here that the absorption spectrum of DPE in different solvents does not change with addition of DPP (concentration 10^{-6} to 10^{-5} mol dm^{-3}), which means there is no ground state complexation between the two. In the second case (λ_{ex}=300 nm), there is no change in the DPP fluorescence intensity when DPE is added to a solution in which DPP concentration in hexane is fixed. This may indicate that the possible route for fluorescence quenching of the donor DPE in presence of acceptor DPP is through singlet singlet excitational energy transfer. For, if other pathway like complex formation were responsible for quenching, one should expect DPP fluorescence quenching in the second case.

Emission of DPE in solvents of different viscosity ranging from 0.29×10^{-3} to 4.30×10^{-3} kg m^{-1} s^{-1} in the presence of DPP has been measured. As the DPP concentration is increased in the binary solution of DPE in each of the solvents, the DPE fluorescence intensity decreases and the DPP fluorescence intensity increases (Fig. 1). This is indicative of increase in S_1 state population of DPP at the expense of the S_1 state of DPE which is depleted through energy transfer. The energy transfer quantum efficiency f_{xy}, which is a measure of

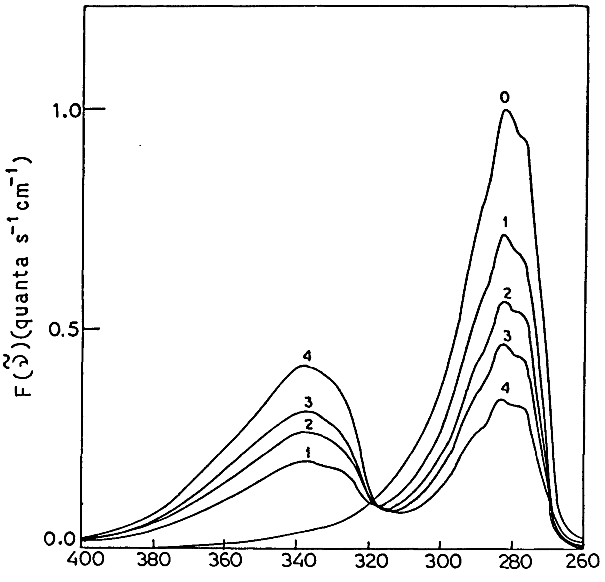

Fig. 1. Fluorescence spectra of DPE in isobutyl alcohol (7.4×10^{-4} mol dm^{-3}) at 303 K (excitation wavelength: 260 nm). Concentration (mol dm^{-3}) of DPP in (0) 0; (1) 8.67×10^{-6}; (2) 1.30×10^{-5}; (3) 1.73×10^{-5} (4) 2.17×10^{-5}.

fraction of excited donor molecules X (DPE) which transfer their energy to the acceptor molecules Y (DPP) has been determined by the relation(1):

$$\frac{I_2}{I_1}=\frac{n_2}{n_1}\left[\frac{1-e^{-{}^{2}\varepsilon_a c_a l}}{1-e^{-{}^{1}\varepsilon_a c_a l}}+\frac{1-e^{-{}^{2}\varepsilon_d c_d l}}{1-e^{-{}^{1}\varepsilon_a c_a l}}f_{xy}\right], \tag{1}$$

which is valid as discussed in our previous paper[6] for very low concentration of donor and acceptor molecules. The expression (1) is obtained from the following relations

$$I_1=An_1(1-e^{-{}^{1}\varepsilon_a c_a l})\phi_a \tag{1a}$$

and

$$I_2=An_2[(1-e^{-{}^{2}\varepsilon_a c_a l})\phi_a+(1-e^{-{}^{2}\varepsilon_d c_d l})f_{xy}\phi_a]. \tag{1b}$$

The subscripts "a" and "d" stand for energy acceptor and donor respectively. ϕ stands for quantum yield. I_1 is the intensity of the acceptor when it is excited directly whereas I_2 is the fluorescence intensity of the same acceptor due to the excitation of the donor. n_1 and n_2 denote the concentrations of these acceptors, respectively. We formulated[6] the expression (1) for very diluted systems of donor and acceptor and this relation is nothing but the modified version of the expression

$$I_2/I_1=n_2/n_1 f_{xy}. \tag{1c}$$

The simplified Eq. 1c was used by earlier authors[14] for solutions in which donor and acceptor concentrations were large (in neat form or in the mixture with diluent where donor or acceptor concentration were high with respect to the diluent). In deriving Eq. 1 used in the present investigation for high dilution of donor (ca. 10^{-4} mol dm^{-3}) and acceptor (ca. 10^{-5} mol dm^{-3}), allowance has been given for possible absorption of some energy by the acceptor which has S_1 state lower relative to the S_1 of donor when the donor molecule is excited by its S_1 band. The quantity n_2/n_1 in Eq. 1 has been measured

Table 1. Values of the Energy-Transfer Efficiency f_{xy}, and Its Radiative, ${}^{R}f_{xy}$ and Nonradiative ${}^{NR}f_{xy}$ Parts, and the Energy Transfer Nonradiative Rate Constant, k_{xy}, for DPE(X)–DPP(Y) System in Solvents of Different Viscosity (η) at 303 K. (Concentration of DPE is ca. 7.4×10^{-4} mol dm^{-3})

Solvents	η	τ_x	[Y]	f_{xy}	${}^{R}f_{xy}$	${}^{NR}f_{xy}$	k_{xy}	k_d
	$10^{-3}\times$ kg m^{-1} s^{-1}	ns	mol dm^{-3}				10^{11} dm^3 mol^{-1} s^{-1}	10^{10} dm^3 mol^{-1} s^{-1}
Hexane	0.29	11.8	8.67×10^{-6}	0.34	0.14	0.20	15.13	7.62
			1.30×10^{-5}	0.43	0.22	0.21		
			1.73×10^{-5}	0.51	0.29	0.22		
			2.17×10^{-5}	0.62	0.38	0.24		
MeOH	0.51	21.4	8.67×10^{-6}	0.43	0.14	0.29	12.98	3.51
			1.30×10^{-5}	0.52	0.22	0.30		
			1.73×10^{-5}	0.60	0.30	0.30		
			2.17×10^{-5}	0.70	0.37	0.33		
i-PrOH	1.77	20.0	8.67×10^{-6}	0.36	0.14	0.22	11.63	1.18
			1.30×10^{-5}	0.48	0.22	0.26		
			1.73×10^{-5}	0.58	0.30	0.28		
			2.17×10^{-5}	0.69	0.37	0.32		
n-BuOH	2.30	30.0	8.53×10^{-6}	0.34	0.15	0.19	8.33	0.99
			1.28×10^{-5}	0.51	0.23	0.28		
			1.71×10^{-5}	0.58	0.30	0.28		
			2.13×10^{-5}	0.70	0.39	0.31		
i-BuOH	4.30	35.9	8.67×10^{-6}	0.33	0.14	0.19	5.93	0.54
			1.30×10^{-5}	0.45	0.22	0.23		
			1.73×10^{-5}	0.56	0.30	0.26		
			2.17×10^{-5}	0.63	0.37	0.26		

using a diffusion plate in the path of the incident radiation at both the excitation wavelengths to minimize the stray radiations.[6].

In case of very dilute solutions where concentrations of X and Y are low, radiative apart from nonradiative energy transfer processes will also make significant contribution and f_{xy} should be expressed as,

$$f_{xy} = {}^{R}f_{xy} + {}^{NR}f_{xy}. \tag{2}$$

The radiative transfer efficiency ${}^{R}f_{xy}$ is determined from the relation of the overlap integral[18] as

$${}^{R}f_{xy} \approx 2.303\,[\mathrm{Y}]\,l\int_0^{\infty} F_x(\bar{\nu})\,\varepsilon_y(\bar{\nu})\,\mathrm{d}\bar{\nu}. \tag{3}$$

In the expression F_x $(\bar{\nu})$ is defined as the relative fluorescence quantum intensity at frequency normalized by the relation $\int_0^{\infty} F_x(\bar{\nu})\,\mathrm{d}\bar{\nu}$. The nonradiative transfer efficiency ${}^{NR}f_{xy}$ is calculated from the relation (2). The values of f_{xy}, ${}^{R}f_{xy}$ and ${}^{NR}f_{xy}$ are given in Table 1. It is observed from Fig. 1 that as the concentration of the acceptor DPP i.e. [Y] is increased the intensity of DPP fluorescence emission increases accompanied by the decrease of the fluorescence intensity of the energy donor DPE. This might be due to the fact that the fraction of the excited donors (X) transferring energy to the acceptor molecules (Y) would increase with increase of the concentration of the acceptors [Y]. The observed increase in f_{xy} values with increase of acceptor concentration (Table 1) is in accord with the idea. Moreover from Table 1 it is seen that with increase of [Y] both the components of f_{xy}, radiative (${}^{R}f_{xy}$) and nonradiative (${}^{NR}f_{xy}$) parts increase regularly (Table 1), the increment in the values of the radiative part ${}^{R}f_{xy}$ being larger. It might be proposed that the dominance of the radiative part is due to high dilution of donor (ca. 10^{-4} mol dm^{-3}) and acceptor (ca. 10^{-6} to 10^{-5} mol dm^{-3}) in the system used in the present investigation. It is well-known that in highly dilute solution of donor and acceptor radiative energy-transfer process has a significant role unlike in the situations in which donor and acceptor concentrations are high. In the latter case non-radiative process dominates over the radiative one in energy-transfer mechanism. However, the changes in the values of ${}^{R}f_{xy}$ or ${}^{NR}f_{xy}$ with [Y] are found to be independent of the viscosity of the solvent and are consistent with the view that S_1 state of DPP is populated from S_1 of DPE by energy-transfer process.

The non-radiative energy transfer efficiency ${}^{NR}f_{xy}$ can be expressed as[19]

$$[\mathrm{Y}]/{}^{NR}f_{xy} = (1 + k_e/k_{xy})[\mathrm{Y}] + (k_i + k_f)/k_{xy}, \tag{4}$$

where k_e, k_{xy}, k_i, and k_f are the rate parameters in s^{-1} of external quenching, nonradiative transfer, internal and fluorescence quenching respectively. By definition $k_f + k_i = k_x = 1/\tau_x$, τ_x being the fluorescence lifetime. [Y] is the concentration of acceptor (DPP). A plot of [Y]/${}^{NR}f_{xy}$ versus [Y] shows straight lines for different solvents. Intercepts of the straight lines obtained, yield k_x/k_{xy} and k_{xy} is calculated using $\tau_x = 1/k_x$. From Table 1, where k_{xy} values are given, it is seen that the k_{xy} decreases regularly with increase of viscosity of solvents. The straight lines have unit slope which means that in each case $k_e = 0$ and the external quenching does not play any role in the fluorescence quenching of the donor with addition of acceptor.

The radii r_x and r_y (X=DPE and Y=DPP) are calculated from the relation $r = 1/2\,(V_1/N)^{1/3}$ where V_1 is the Le Bas molar volume[20] and N is the Avogadro number. The calculated radii r_x and r_y are 3.7 and 3.8 Å respectively and $r = r_x + r_y$ is 7.5 Å. The diffusion coefficient D is given by[21]

$$D = RT/4\pi\eta r f N, \tag{5}$$

where the terms have their usual meanings. The micro-friction coefficient, f in Eq. 5 was evaluated[21] from the relation (6) introduced by Gierer and Wirtz[22] taking into account the molecular structure of the environment of the diffusing molecule,

$$f = 0.16 + 0.4(r_{\mathrm{solute}}/r_{\mathrm{solvent}}). \tag{6}$$

Here, r_{solute} and r_{solvent} may be obtained separately by assuming the Le Bas molar volumes containing spherical molecules packed in an orderly cubic array. As shown above, the radii are expressed by $r_m = 1/2(V_1/N)^{1/3}$, where V_1 is the Le Bas molar volumes[20] and N is the Avogadro number.

The sum of the diffusion coefficients for donor and acceptor ($D_x + D_y$) (Table 2) is large in solvents of low viscosity which allows for close approach of donor and acceptor molecules to each other and hence energy-transfer efficiency is large. The converse is true for highly viscous media.

The Förster critical transfer distance R_0 has been calculated from the well-known formula.[14] R_0 slightly depends on viscosity and is greater than r $(= r_x + r_y)$, the collisional separation distance (Table 2). In the present investigation the two experimental findings (Tables 1 and 2) that 1) k_{xy} values are larger than the diffusion controlled rate k_d and 2) the magnitude of R_0 values exceeds the collisional separation distance $(r = r_x + r_y)$, suggest that the energy-transfer from DPE to DPP

Table 2. Values of Förster Critical Transfer Distance, R_0, Sum of Molecular Radii, $r_x + r_y$, Value of $D_x + D_y$, for the System of DPE–DPP in Solvents of Different Viscosity at 303 K

Solvents	η	R_0	R_{eff}[a]	$r_x + r_y$	$D_x + D_y$
	$10^{-3} \times$ kg m^{-1} s^{-1}	Å	Å	Å	10^{-9} m^2 s^{-1}
Hexane	0.29	21.4	10.7	7.5	9.45
MeOH	0.51	24.6	12.3	7.5	3.75
i-PrOH	1.77	23.1	11.55	7.5	1.35
n-BuOH	2.30	23.7	11.85	7.5	1.11
i-BuOH	4.30	24.5	12.25	7.5	0.59

a) $R_{\mathrm{eff}} = R_0/2$, considering Voltz model.[6]

occurs mainly through Förster dipole–dipole interaction. Energy-transfer process has two parts: One is diffusion controlled part and the other is migration controlled part. Here, we can safely neglect the migration controlled part as the calculated values for energy migration efficiency parameter f_M obtained from the relation

$$f_M = 1/[1+(R/R_0)^6] \quad (7)$$

for very low concentration of both the donor and acceptor molecules are found to be of the order of 10^{-5}. It should be pointed out here that at low and also at high concentration of DPE no detectable excimer emission is observed. So the possibility of excimer formation as an intermediate transfer step could be ruled out. Further, from Table 1 it is observed that k_{xy} decreases with the increase of the viscosity of the medium of donor and acceptor. In solvent of low viscosity (high D_x+D_y value as shown in Table 2) large diffusion allows greater mobility of the donor and acceptor molecules so that they might come closer. This results in more efficient transfer of excitational energy from donor to acceptor and larger value of k_{xy}, relative to that observed in solvents of high viscosity (Table 1). However the magnitude of k_{xy} should normally exceeds that of k_d $(=8RT/3000\eta)$, the collisional diffusion controlled rate (Table 1) since the energy transfer by coulombic interaction over the dipole–dipole interaction distance R_0 exceeds the molecular dimension $(=r_x+r_y)$ as indicated in Table 2.

References

1) M. Yokota and O. Tanimoto, *J. Phys. Soc. Jpn.*, **22**, 779 (1966).

2) U. Goselle, M. Hauser, U. K. A. Klein, and R. Frey, *Chem. Phys. Lett.*, **34**, 519 (1975).

3) M. D. Galanin, *Sov. Phys. JETP*, (*Engl. Transl.*), **1**, 317 (1955).

4) M. J. Pilling and P. R. Butter, *Chem. Phys. Lett.*, **41**, 239 (1979).

5) K. Allinger and A. Blumen, *J. Chem. Phys.*, **72**, 4608 (1980).

6) G. K. Mallik, T. K. Pal, P. K. Mallik, T. Ganguly, and S. B. Banerjee, *Spectrochim. Acta, Part A*, **45**, 1273 (1989).

7) A. Weinreb, *J. Chem. Phys.*, **35**, 91 (1961).

8) J. B. Birks, M. Salete, and S. C. P. Leite, *J. Phys. B*, **3**, 417 (1970).

9) J. B. Birks, M. Salete, and S. C. P. Leite, *J. Phys. B*, **3**, 513 (1970).

10) J. B. Birks, "Organic Molecular Photophysics," ed by J. B. Birks, Wiley-Interscience, London (1975), Vol. 1, p. 557.

11) M. D. Lumb, "Luminescence Spectroscopy," ed by M. D. Lumb, Academic Press, London, New York, and San Francisco (1978), p. 144.

12) L. F. Vieira Ferreira, *J. Lumin.*, **34**, 235 (1986).

13) L. F. Vieira Ferreira, *J. Lumin.*, **35**, 301 (1986).

14) R. D. Mathad, G. C. Chikkur, and N. Umakantha, *J. Chem. Phys.*, **84**, 2187 (1986).

15) L. F. Vieira Ferreira, *J. Photochem. Photobiol.*, **42A**, 111 (1988).

16) K. Chatterjee, S. Laha, S. Chakravorti, T. Ganguly, and S. B. Banerjee, *Can. J. Chem.*, **62**, 1369 (1984).

17) G. K. Mallik, T. K. Pal, S. Laha, T. Ganguly, and S. B. Banerjee, *J. Lumin.*, **33**, 377 (1985).

18) J. B. Birks, "Photophysics of Aromatic Molecules," ed by J. B. Birks, Wiley-Interscience, London, New York, Sydney, and Toronto (1970), p. 522.

19) J. B. Birks, *Proc. Phys. Soc.*, **77**, 1096 (1961).

20) S. Glasstone, "Text Book of Physical Chemistry," 2nd ed, Van Nostrand (1946), p. 524.

21) J. H. Gorrell, Jr. and J. T. Dubois, *Trans. Faraday Soc.*, **63**, 347 (1967).

22) A. Gierer and K. Wirtz, *Z. Naturforsch., A*, **8**, 532 (1953).