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STUDY ON TRIPLET-TRIPLET ENERGY TRANSFER BETWEEN LIKE MOLECULES USING ISOTOPIC MIXTURE

Akinori INOUE and Nozomu EBARA
Department of Chemistry, College of General Education, The University
of Tokyo, 3-8 Komaba, Meguro-ku, Tokyo 153

A novel method is presented to elucidate triplet-triplet energy transfer between like molecules, in which phosphorescence decay is observed for rigid solutions containing both hydrogenated and deuterated organic molecules. It is shown that a critical transfer distance is obtained from the concentration dependence of the phosphorescence decay curves.

Energy transfer between like molecules has been the subject of general interest in connection with the nature of molecular interactions in solution or in solid phase. Most of the investigations reported so far consisted in the measurements of the concentration depolarization of emission.1) Unfortunately, one can not investigate triplet-triplet energy transfer by this method when energy transfer in the singlet state is efficient.

In the present report, we propose a new method for investigating T-T transfer between like molecules in rigid solutions. The method consists in analyzing the phosphorescence decay of the solution containing both hydrogenated compound (H) and its deuterated anlogue (D), in which the energy transfer between H and D alters the decay profile from mere superposition of the decay curves of both components.

In the case of donor-acceptor systems, several theoretical treatments such as Inokuchi-Hirayama's formula2) are available for the decay of donor phosphorescence. In the present system, however, an exact analysis is much more complex since the energy transfer is reversible. Although the full analysis is under progress and will be reported elsewhere, we present here an alternative method adopting Perrin model3) to avoid the complexity. This model applies well to aromatic hydrocarbons, of which T-T energy transfer is adequately described in terms of exchange mechanism.4)

We assume that energy transfer takes place only when molecules happen to fall within a critical transfer distance, R_0, and that at distances $\leq R_0$, the rate of energy transfer is much larger than those of intramolecular deactivation processes. In this way, equilibrium of excitation exchange is established among molecules in the neighborhood.

Based on this model, three types of sites exist in the rigid solution which give luminescence of different decay characteristics; (a) H molecules isolated from D molecules, (b) D molecules isolated from H molecules, and (c) H and D molecules which are situated within the distance of R_0. Here, the critical transfer distances of H⟶D and D⟶H are assumed to be equal, because they are insensitive function of transfer rate in exchange mechanism.

The phosphorescence decay was measured by cutting off the excitation radiation by a mechanical shutter after a stationary state of excitation was established. The phosphorescence decay curve, f(t), is then expressed as

$$f(t) = A[C_1\exp(-\alpha t) + C_2\exp(-\beta t) + C_3\exp(-\gamma t)] \quad \text{--- (1)}$$

where, α, β, and γ are the decay constants of sites (a), (b), and (c), and A is a constant. The radiative rate constants and quantum yields of intersystem crossing are assumed to be equal for H and D. Preexponential factors, C_1, C_2, and C_3 are determined by the probabilities that molecules belong to sites (a), (b), and (c), multiplied by photoequilibrium concentrations of excited molecules in the respective sites, so that,

$$C_1 = (1/\alpha)\exp(-Nvc),\ C_2 = (1/\beta)\exp(-Nvc),\ \text{and}\ C_3 = (2/\gamma)[1 - \exp(-Nvc)] \quad \text{--- (2)}$$

with $N=6.02 \times 10^{20}$, $v=(4/3)\pi R_0^3\ \mathrm{cm}^3$, and c, the concentration by mol/ℓ.[5] The concentration of H and D are chosen to be equal. Equations (1) and (2) show that the preexponential factors are strongly dependent upon the concentration. Thus, by measuring the relative magnitudes of preexponential factors of the three components as functions of concentration, the critical transfer distance can be obtained.

Specimens of poly (methylmethacrylate) containing equal amounts of naphthalene-h_8 and -d_8 were used. Commercial methylmethacrylate was treated with aqueous solution of sodium hydroxide, dried over magnesium sulfate and distilled under reduced pressure. Naphthalene-h_8 and -d_8 were purified by zone melting. All the phosphorescence measurements were made at 77 K. The radiation at 315 nm of Xe arc was selected by a monochromator and was used as an excitation source. Phosphorescence was passed through a monochromator and viewed by an HTV R374 photomultiplier tube. Appropriate filters were used to eliminate scattered incident radiation. Phosphorescence decay curves were recorded by a Riken Denshi SP-J-5V recorder of response time of less than 0.2 sec. High-resolution phosphorescence spectra were measured by using a high pressure mercury lamp and a Spex 1700-II monochromator. The analysis of decay curves were made by computer simulation based on the least-squares method.

The measured phosphorescence spectra and lifetimes at lower concentrations for both molecules were close to those in the literature,[6] indicating that the effect of impurity could be ignored.

The concentration dependence of the phosphorescence lifetimes of H and D were measured and are shown in Fig.1. Up to the concentration of 0.66 M, the

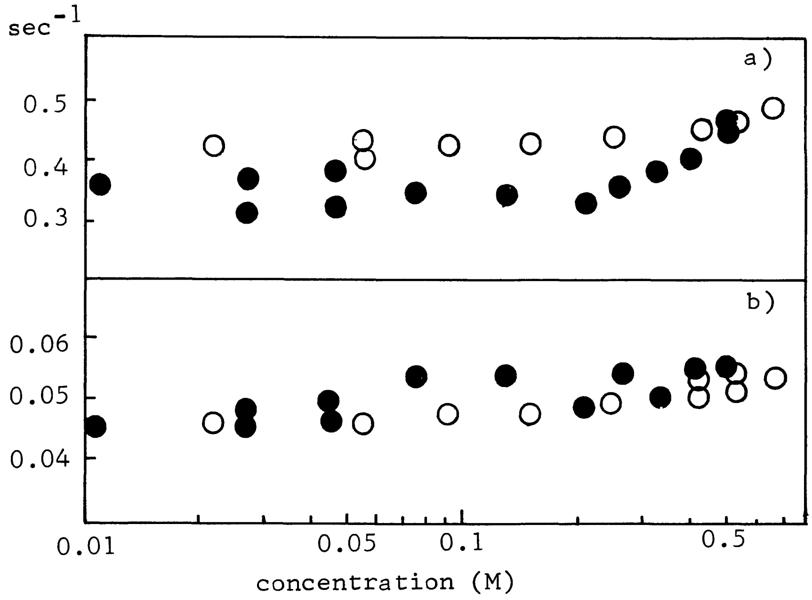

Fig.1. Concentration dependence of the phosphorescence decay rate;
a) ○, α; ●, k_1
b) ○, β; ●, k_2

decay curves of the specimens containing either H or D were expressed by single exponential functions, from which the values of α and β were obtained. Deviation from exponential decay, possibly due to triplet-triplet annihilation, were observed for both compounds at higher concentrations. Hence, only the data obtained at lower concentrations were used.

With regard to the phosphorescence of the mixed solutions of H and D, in the concentration range from 0.01 to 0.33 M, the decay curves were, contrary to the expectation, well expressed in terms of two exponential functions, rather than three,

$$D_1\exp(-k_1t) + D_2\exp(-k_2t). \qquad ---(3)$$

This, however, is justified because the value of γ is very close to that of α, as is shown below, and the accuracy of experiment did not allow resolution of first and the third terms of Eq.(1). The concentration dependence of the decay rates, k_1 and k_2 are also shown in Fig.1.

The value of γ can be calculated by assuming that an equilibrium is established in the excitation exchange among molecules constituting site (c). If n H molecules and m D molecules are involved in this site, we get

$$\gamma = (n\alpha + m\beta K)/(n + mK) = [(n/m)\alpha + \beta K]/[(n/m) + K] \qquad ---(4)$$

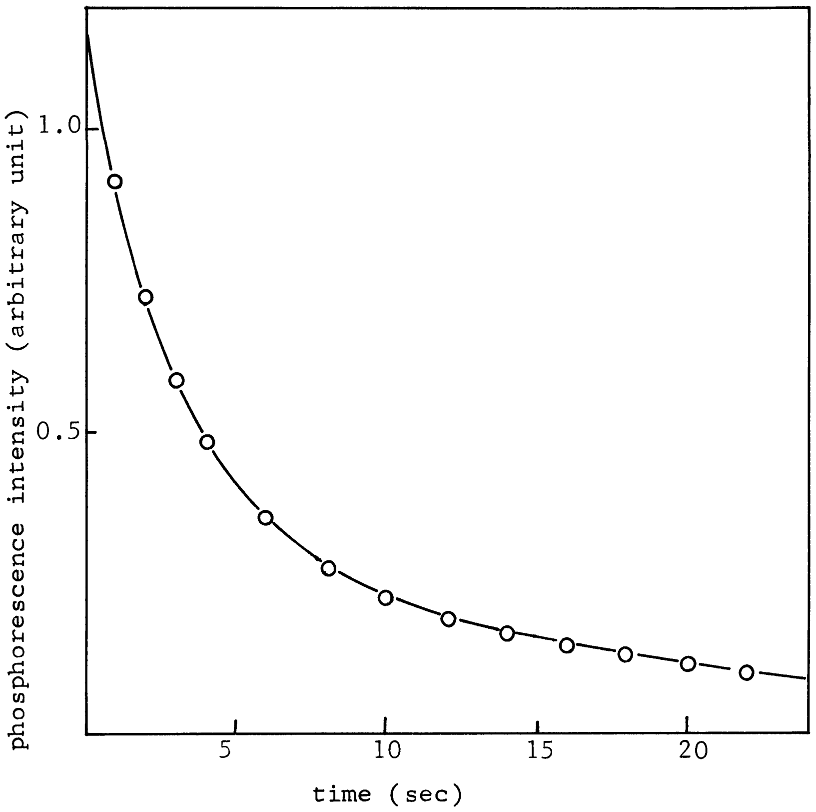

Fig.2. Phosphorescence decay curve of the mixture of H and D (each 0.13 M);
o, experimental data;
–, decay curve obtained by simulation

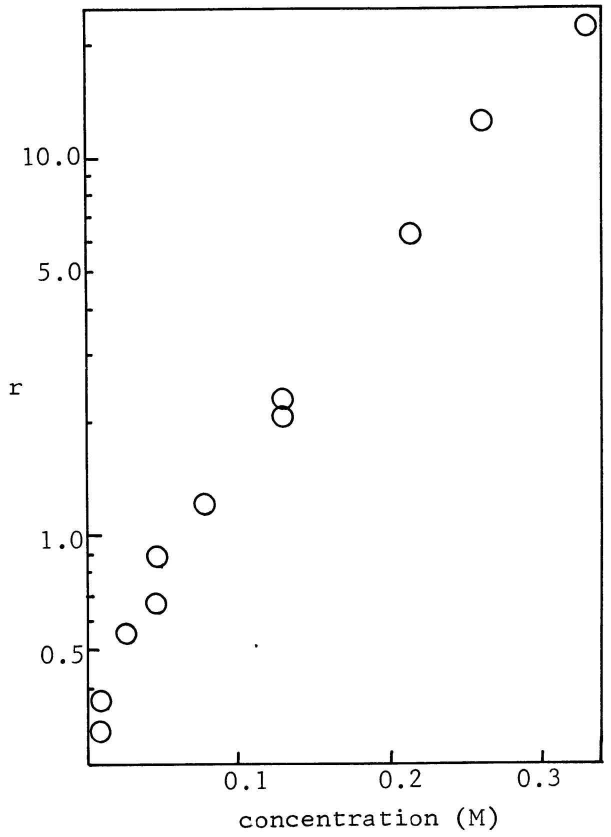

Fig.3. Concentration dependence of r

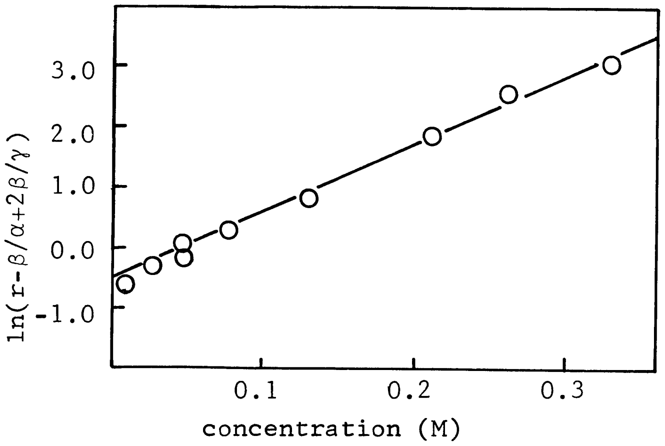

Fig.4. A logarithmic plot of $(r-\beta/\alpha+2\beta/\gamma)$ versus c.

from a simple kinetic equation. Here, K is the equilibrium constant for the energy transfer process $H \rightleftharpoons D$. The energy of the lowest triplet state of naphthalene-h_8 is lower than that of naphthalene-d_8 by about 110 cm^{-1}.[6a] Assuming that the equilibrium is established by Boltzmann distribution, we get K=0.13. The values of γ are then 0.38,0.39,and 0.34 sec^{-1} for n/m =1, 2, and 0.5, respectively, which are close to the value of α ($\sim$0.4 sec^{-1}).

Figure 2 shows a typical phosphorescence decay curve, together with a simulation curve determined by the least-squares method.

The concentration dependence of the ratio of the preexponential factors, $r=D_1/D_2$, was very large (Fig.3), which would be constant if energy transfer does not take place. The ratio is now expressed as

$$r = (C_1+C_3)/C_2 = [(1/\alpha)\exp(-Nvc)+(2/\gamma)(1-\exp(-Nvc))]/[(1/\beta)\exp(-Nvc)]$$

$$= (\beta/\alpha-2\beta/\gamma) + (2\beta/\gamma)\exp(Nvc) \qquad ---(5)$$

where C_1, C_2, and C_3 are defined in Eq.(2). Plot of $\ln[r-(\beta/\alpha-2\beta/\gamma)]$ against c gave a straight line as was expected (Fig.4), from the slope of which we get R_0=17 A. The value seems somewhat large as compared with the usual donor-acceptor systems.[4] In the present analysis, we disregarded stepwise energy transfer process within a molecular train containing same isotopic isomers. A preliminary calculation including this effect indicates that the value of R_0 becomes somewhat smaller but not much.

The results are not due to a complex or exciplex formation between H and D molecules since no spectral change was observed with the increasing concentration. They are not attributed to singlet-singlet transfer between H and D molecules. Unlike the method using phosphorescence depolarization, the present method suffers little from effect of S-S transfer since it depends only upon the difference between the S-S transfer yields of H→D and that of the reversed process. This difference, using Förster's equation7), with parameters from a literature,8) proved to be within an experimental error.

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References

1) For singlet-singlet transfer, for example, E.Gaviola and P.Pringsheim, Z. Phys., 24, 24 (1924). For triplet-triplet transfer;
   (a) N.K.Chaudhuri and M.A.El-Sayed, J.Chem. Phys., 42, 1947 (1965);
   (b) S.Siegel and L.Goldstein, ibid., 44, 2780 (1966), 45, 1860 (1966);
   (c) H.S.Judeikis and S.Siegel, ibid., 53, 3500 (1970);
   (d) Y.Gondo, M.Hirai, T.Iwao, T.Kakibaya, T.Kuroi, H.Nagatomo, and Y.Kanda, Chem. Lett., 463 (1975).
2) M.Inokuchi and F.Hirayama, J. Chem. Phys., 43, 1978 (1965).
3) F.Perrin, Compt. rend., 178, 1978 (1924).
4) (a) V.L.Ermolaev, Dokl. Akad. Nauk SSSR, 139, 348 (1961); Engl. Transl. Soviet Phys.-Doklady, 6, 600 (1962);
   (b) V.L.Ermolaev, Uspekhi Fiz. Nauk, 80, 3 (1963); Engl. Transl. Soviet Phys.-Uspekhi, 6, 333 (1963).
5) S.Chandrasekhar, Rev. Mod. Phys., 43, 86 (1943).
6) (a) F.R.Lipsett and G.Macpherson, Can. J. Phys., 44, 1485 (1966);
   (b) S.P.McGlynn, J.Daigre, and F.J.Smith, J. Chem. Phys., 39, 675 (1963)
7) Th.Förster, Discussions Faraday Soc., 27, 7 (1959).
8) I.B.Berlman, "Energy Transfer Parameters of Aromatic Compounds", Academic Press, New York (1973).

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