Triplet-Triplet Energy Transfer between Like Molecules

Akinori INOUE, Hiroshi CHUMAN, and Nozomu EBARA

Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received February 5, 1977)

The previously proposed method of studying T-T energy trasfer between like molecules using isotopic mixtures was further improved and applied to an investigation of naphthalene and phenanthrene molecules. Critical transfer distances of 15 and 13 Å were determined for naphthalene and phenanthrene, respectively. The present method has the advantage that it is free from the effect of S-S energy transfer.

Triplet-triplet energy transfer between organic molecules in rigid media has been investigated extensively. Most of the previous works were concerned with energy transfer between unlike molecules. The phosphorescence intensities of donor molecules have been measured as a function of acceptor concentration[1,2] and their time dependences have been analyzed.[3-5] However, not much of the most fundamental information about T-T energy transfer between like molecules is available, possibly due to experimental difficulties. The above methods, which use donor-acceptor systems, are not applicable to this case. The previous studies employed the methods of concentration depolarization[7,8] or magneto-photoselection of phosphorescence.[9] These methods, however, have the fatal drawback that the results are masked by the effect of singlet-singlet energy transfer, whenever it occurs. Studies have been made with several molecules like naphthalene and phenanthrene using these methods;[7,9] in these studies the authors assumed that the singlet-singlet transfer was not efficient. However, as is shown in a later section, the critical transfer distances of these molecules for S-S transfer, estimated from Förster's theory,[10] are comparable to those in the T_1 state. The effect of S-S transfer seems to be large enough in these cases to preclude determination of reliable critical transfer distances in the triplet states, so that the earlier methods should be used only with reservation.

In a previous paper (I),[11] we have developed a new method of studying T-T transfer between like molecules, using isotopic mixtures, and have made an investigation of naphthalene molecules. Phosphorescence decay curves for equal amounts of protonated and perdeuterated naphthalene in poly(methylmethacrylate) were measured as a function of concentration. The new method utilized the fact that the phosphorescence lifetime of a protonated compound (H) and that of a deuterated compound (D) usually differ greatly, while their electronic properties are quite similar.

In (I), however, a somewhat oversimplified model was introduced, which might lead to a rather large value for the critical transfer distance R_0. In the present paper, measurements of phosphorescence decay curves were made again for naphthalene molecules in order to get more accurate data than in (I). The results were analyzed beased on an improved model. The present method was also successfully applied to the investigation of phenanthrene molecules.

Experimental

The methods used for the purification of naphthalene isotopic isomers and for the phosphoresence measurements are the same as in (I). Commercial phenanthrene-d_0 and -d_{10} were sublimed *in vacuo* and then used for the measurements. Plastic specimens including phenanthrene molecules were also prepared by the same method as in (I), *i.e.*, by polymerizing methyl methacrylate solutions at about 80 °C, with no inhibitor being used. Specimens were annealed at about 100 °C for a few hours. The concentration change due to polimerization were taken into account by the use of the specific gravities of methyl methacrylate and its polymer (PMMA). The specific gravity of 1 M naphthalene in PMMA was approximately 1.18, almost identical to that of pure PMMA (1.19). Thus, the change of density for PMMA because of the presence of solute molecules can be ignored.

All the measurements were made at 77 K. The volume contraction of PMMA by cooling from room temperature to 77 K was estimated to be only a few percent. Hence, this effect was also ignored. The fluorescence and absorption spectra were measured for EPA solutions of naphthalene and phenanthrene and their deuterated compounds at 77 K with a hand-made spectrofluorimeter.

Results and Discussion

The previous experiments[11] on naphthalene isotopic mixtures can be summarized as follows:

a) The phosphorescence decay curves could be expressed in terms of two exponential functions in the concentration region studied;

$$f(t) = D_1 \exp(-k_1 t) + D_2 \exp(-k_2 t). \tag{1}$$

b) The decay rate of each component varied little with concentration.

c) The decay rate of the long-lived component (k_2) was similar to that of the phosphorescence of the solution of pure D (β), whereas the short-lived component had a slightly smaller decay rate (k_1) than that of the H molecule (α).

d) The ratio of the pre-exponential factors, the short-lived over the long-lived components, r ($=D_1/D_2$), increased with increasing concentration. The change was drastic at higher concentrations.

e) The phosphorescence spectrum of the isotopic mixture was simply a susperposition of those for H and D, indicating that impurity molecules or triplet excimers or exciplexes are not responsible for the concentration dependence of the phosphorescence decay curves.

Our new results have features similar to the above. The concentration dependences of k_1, α, β, and r are

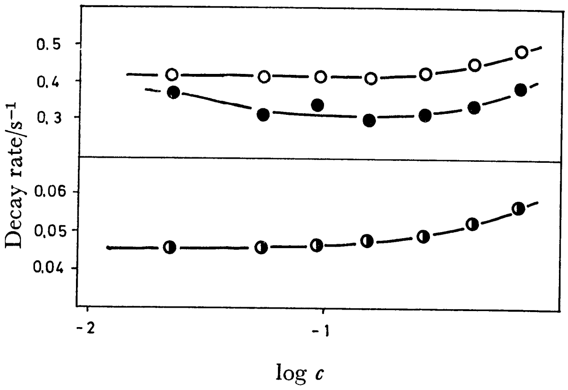

Fig. 1. Concentration dependences of α(○), β(◑), and γ(●) for naphthalene.

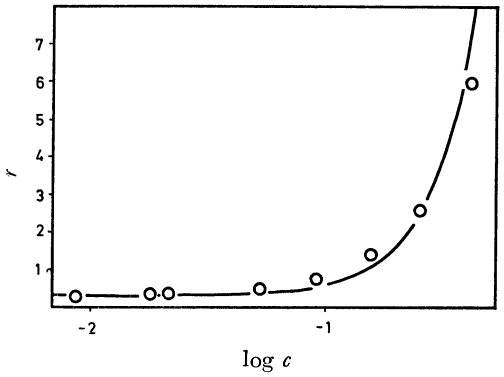

Fig. 2. Concentration dependence of r for naphthalene; -○- experiments; —calculated using Eq. 8.

shown in Figs. 1 and 2.

The previous data were interpreted in terms of triplet-triplet energy transfer between H and D molecules. It was assumed that energy transfer took place only between H-D pairs whose intermolecular separations were smaller than the critical transfer distance R_0. This gave the value of $R_0=17$ Å for naphthalene molecules. This value is relatively large compared with those reported for the energy transfer between unlike molecules.[1–6] The difference of the values may not be due to any intrinsic difference in the transfer mechanism, but may instead be ascribed to the assumptions included in (I). In (I), energy transfer was assumed to take place only between pairs and transfer among more than three molecules was ignored. This assumption may not be valid at higher concentrations.

In the present analysis, we have developed an improved model. The following emitting species were assumed to be present in the rigid solutions: A) isolated H molecules and clusters composed only of H molecules, B) isolated D molecules and clusters composed only of D molecules, and C) clusters containing both H and D molecules. Here, the word "cluster" is used to represent a group of molecules in which no molecules are isolated by distances larger than R_0 from all other members of the group, but they are separated by distances larger than R_0 from all molecules which do not belong to this group. Thus the rate of energy transfer between molecules within a cluster is much faster than the intramolecular decay process, whereas the energy transfer between two clusters can be assumed to be forbidden. The molecules in a cluster can be assumed to retain their individualities.

Phosphorescence decay rates of A and B clusters are identical to those of the isolated molecules, α for H and β for D, respectively, while the phosphorescence from C clusters has various lifetimes, depending on their compositions.

The decay rate of a cluster composed of n_{H} H molecules and n_{D} D molecules is

$$\gamma_s = (s\alpha+K\beta)/(s+K), \tag{2}$$

with

$$s = n_{\mathrm{H}}/n_{\mathrm{D}},$$

where K is the ratio of the rate constants of the T-T transfer processes H→D and D→H.

In a cluster with the same total number of molecules, n, the ratio s shows a binomial distribution. For a C cluster with two molecules, which is certainly the most numerous one when the concentration is not so high, s is exactly unity. Hence, among all C clusters the most numerous clusters are those with the ratio s not much different from unity. Moreover, γ_s is a relatively slowly varying function of s, as can be verified easily ($\gamma_{1/2}=0.25$, $\gamma_1=0.30$, and $\gamma_2=0.34$ when $\alpha=0.40$, $\beta=0.047$ s^{-1}, and $K=0.37$). It can then be shown that the decay rates of C clusters extend from α to β with a very sharp peak at γ_1, so that they can be safely approximated by a single rate constant $\gamma=\gamma_1$.

Each decay curve is thus expected to be composed of three exponential functions:

$$f(t) = A[(k^{\mathrm{r}}_{\mathrm{H}}\rho_{\mathrm{H}}/\alpha)\exp(-\alpha t) + (k^{\mathrm{r}}_{\mathrm{D}}\rho_{\mathrm{D}}/\beta)\exp(-\beta t) + (k^{\mathrm{r}}_{\mathrm{HD}}\rho_{\mathrm{HD}}/\gamma)\exp(-\gamma t)], \tag{3}$$

where $k^{\mathrm{r}}_{\mathrm{H}}$ and $k^{\mathrm{r}}_{\mathrm{D}}$ are the radiative rate constants for the phosphorescence of A and B clusters, and ρ_{H}, ρ_{D}, and ρ_{HD} are the probabilities that molecules belong to the respective clusters, when they are excited. $k^{\mathrm{r}}_{\mathrm{HD}}$ is an effective radiative rate constant for C clusters:

$$k^{\mathrm{r}}_{\mathrm{HD}} = (k^{\mathrm{r}}_{\mathrm{H}}+Kk^{\mathrm{r}}_{\mathrm{D}})/(1+K). \tag{4}$$

The singlet absorption cross section and the rate for intersystem crossing are assumed to be the same for H and D molecules. Equation 4 applies to a phosphorescence decay of the mixture after the steady state condition for excitation is established.

The observed phosphorescence decay curves for isotopic mixtures consisted of two exponential functions instead of three over a wide concentration range, as mentioned before. This was because γ is close to α and, in the distribution of decay rates, the peak at α is too low compared with that at γ. That such a distribution of rate constants can be represented by a single rate constant can be shown by a model calculation, so that

$$k_1 = \gamma,$$

and

$$D_1 = A[(k^{\mathrm{r}}_{\mathrm{H}}\rho_{\mathrm{H}}/\alpha)+(k^{\mathrm{r}}_{\mathrm{HD}}\rho_{\mathrm{HD}}/\gamma)]. \tag{5}$$

The value of K is equal to the ratio of overlap of the phosphorescence and S-T adsorption spectra in the framework of Dexter's theory.[12] Due to the lack of spectroscopic data, the constant was equated in (I) to the Boltzman factor, 0.13, as is often employed. In this approximation, however, several factors such as the correction for spectral line width cannot be taken into account. Hence, we discard this value. K was estimated to be 0.37 using Eq. 2 and the values of α, β, and γ.

This valus was found to be constant for 0.1 to 0.4 M solutions.

The ratio, r, of the pre-exponential factors of the short-lived to long-lived components is then

$$r = [(k_{\mathrm{H}}^{\mathrm{r}}\rho_{\mathrm{H}}/\alpha)+(k_{\mathrm{HD}}^{\mathrm{r}}\rho_{\mathrm{HD}}/\gamma)]/(k_{\mathrm{D}}^{\mathrm{r}}\rho_{\mathrm{D}}/\beta). \tag{6}$$

Since we are dealing with solutions containing equal amounts of H and D molecules, it is evident that

$$\rho_{\mathrm{H}} = \rho_{\mathrm{D}},$$

and

$$\rho_{\mathrm{HD}} = 1 - (\rho_{\mathrm{H}}+\rho_{\mathrm{D}}) = 1 - 2\rho_{\mathrm{D}},$$

so that

$$r = p\beta/\alpha - 2(\beta/\gamma)(p+K)/(1+K) + (\beta/\gamma\rho_{\mathrm{D}})(p+K)/(1+K), \tag{7}$$

where p is the ratio $k_{\mathrm{H}}^{\mathrm{r}}/k_{\mathrm{D}}^{\mathrm{r}}$. Denoting as w_n the fraction of clusters composed of n molecules altogether, regardless of H or D molecules,

$$\rho_{\mathrm{D}} = \sum_n 2^{-n}w_n.$$

If the concentration is not too high, the terms with large n are expected to be small, since each w_n is small and is accompanied by a factor 2^{-n}. Thus, we can retain only w_1 and w_2 and neglect higher terms. By this approximation only clusters composed of not more than two molecules are considered for A and B clusters. On the other hand, since the factor 2^{-n} is not present for C clusters, all possibilities are taken into account by using $\rho_{\mathrm{HD}}=1-2\rho_{\mathrm{D}}$. The present approximation is valid in the concentration range where $w_1>w_2$; otherwise, higher terms must be taken into account for ρ_{H} and ρ_{D}. The validity of this condition will be examined below. Equation 7 then leads to

$$r = p\beta/\alpha - 2(\beta/\gamma)(p+K)/(1+K) + (\beta/\gamma)(p+K)/(1+K)[(w_1/2)+(w_2/4)]. \tag{8}$$

w_1 is the probability of a molecule having no neighbors within the active sphere, $v=4\pi R_0^3/3$ (cm^3), so that

$$w_1 = \exp(-Nvc). \tag{9}$$

Here, $N=6.02\times10^{20}$ mol^{-1} and c is the total concentration of H and D together (M). w_2 is given by[13)]

$$w_2 = 4\pi Nc\exp(-4\pi R_0^3Nc/3) \times\int_0^{R_0}R^2\exp[-\pi Nc(R_0^2R-R^3/12)]\mathrm{d}R. \tag{10}$$

Figure 2 depicts the comparison of the concentration dependence of the experimental value of r to that calculated using Eq. 8, with experimentally determined parameters α, β, and γ. The value of p was taken from the paper by Kanamaru.[14)] The best fit was obtained with R_0=15 Å. This value is smaller than the previous value of 17 Å.

We applied the same method to phenanthrene systems. In this case, decay curves were also found to be consistent with two exponential functions. No anomalous emission which might be ascribed to an impurity or excimer (exciplex) was observed in the phosphorescence spectra. The value of each decay rate, whose concentration dependence is shown in Fig. 3, does not change much with concentration. The ratio r changes greatly with concentration (Fig. 4). The calculated curve based on Eq. 8 with R_0=13 Å fitted well with the experiments.

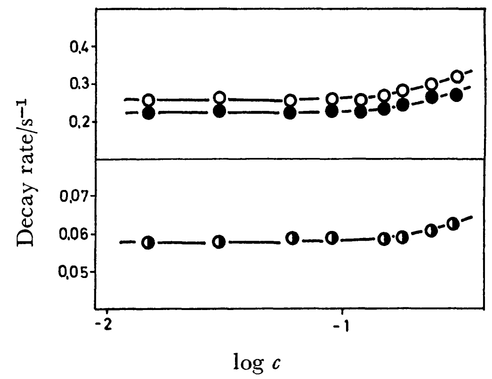

Fig. 3. Concentration dependences of α(○), β(◑), and γ(●) for phenanthrene.

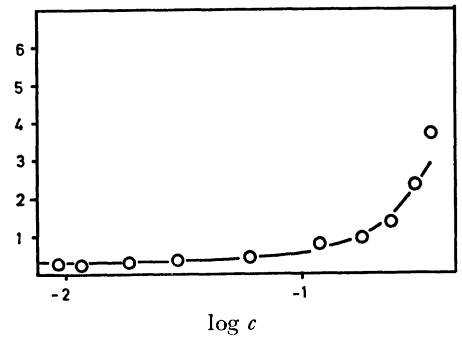

Fig. 4. Concentration dependence of r for phenanthrene;
-○- experiments; — calculated using Eq. 8.

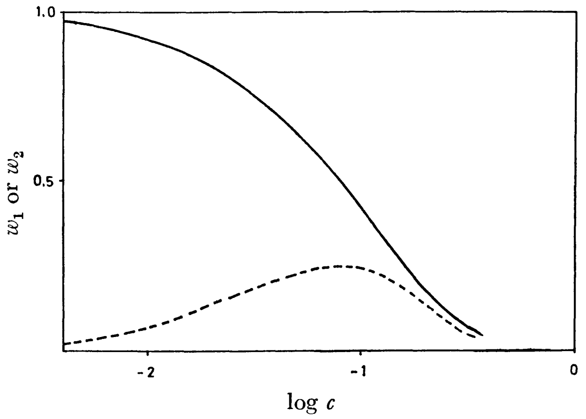

Fig. 5. Calculated w_1 (—) and w_2 (---) with R_0=15 Å as a function of concentration.

The concentration dependences of w_1 and w_2 with R_0=15 Å are depicted in Fig. 5. The condition $w_1>w_2$ is shown to be obeyed in the concentration range studied, and it is evident that this inequality holds for smaller values of R_0. Thus, neglecting higher terms in w_n is justified in the present case.

In the above approximation, the initial steady state triplet population in each kind of cluster is assumed to be proportional to its lifetime. This requires that the redistribution of excitation among different kinds of clusters should be forbidden also in the singlet state, or that the initial equilibrium populations in the excited singlet state are the same for all kinds of clusters. We have measured the absorption and fluorescence spectra of H and D molecules at 77 K for naphthalene and phenanthrene, from which the critical concentrations c_{HD} for singlet-singlet energy transfer H→D and c_{DH} for D→H were calculated by the standard method.10) These were 0.17 and 0.15 M for naphthalene and 0.31 and 0.31 M for phenanthrene. The critical distances for S-S transfer are then 14 Å for naphthalene and 11 Å for phenanthrene. These are close to, but do not exceed the critical distances for T-T transfer, and assure that the transfer between clusters in the singlet state is forbidden.

In quite a few cases the S-S critical transfer distances between like molecules never exceed the T-T transfer distances,15) so that the present method can very often be used without any correction. In cases where the S-S critical distances $R_{0\mathrm{S}}$ is larger than R_0, the following small correction may suffice:

The fractions of A and B clusters which are not isolated in an S-S transfer but are isolated in a T-T transfer are

$$\Delta\rho_{\mathrm{H}} = \Delta\rho_{\mathrm{D}} = \rho_{\mathrm{D}}(R_0) - \rho_{\mathrm{D}}(R_{0\mathrm{s}}),$$

in which the probability ρ is considered to be a function of isolation distance. The populations of singlet excitation in these portions are to be modified by $2/(1+q)$ for A clusters and $2q/(1+q)$ for B clusters. Here q is an equilibrium constant and can be derived from Förster's theory:16)

$$q = (\eta_{\mathrm{HD}}/\eta_{\mathrm{H}})(1-\eta_{\mathrm{DH}}/\eta_{\mathrm{D}})/(\eta_{\mathrm{DH}}/\eta_{\mathrm{D}})(1-\eta_{\mathrm{HD}}/\eta_{\mathrm{H}}). \qquad (11)$$

η_{H} and η_{D} are the fluorescence quantum yields of H and D molecules, respectively, in the absence of S-S transfer to their isotopic isomers and η_{HD} and η_{HD} are those in the presence of the latter. The probabilities ρ_{H} and ρ_{D} in Eq. 6 are then to be replaced by $\rho_{\mathrm{H}}+\Delta\rho_{\mathrm{H}}(1-q)/(1+q)$ and $\rho_{\mathrm{D}}-\Delta\rho_{\mathrm{D}}(1-q)/(1+q)$, respectively.

In the present case, no such correction was required, as mentioned above, and the calculation of this value by using Förster's formulae10)

$$\eta_{\mathrm{HD}}/\eta_{\mathrm{H}} = 1 - \sqrt{\pi}x \exp(x^2)[1-2\Phi(\sqrt{2}x)],$$

$$\Phi(y) = (1/\sqrt{2\pi})\int_0^y \exp(-t^2/2)\mathrm{d}t,$$

$$x = \sqrt{\pi}c/2c_{\mathrm{HD}},$$

shows that q is almost unity within the concentration range studied.

In this way, the present method seems to have wide applicability for investigations of T-T energy transfers, because the effect of S-S transfer is usually ignorable, or, if not, correction for it can be made easily. On the contrary, the conventional methods such as photoselection of phosphorescence cannot be used when even a small amount of S-S transfer manifests itself.

The critical transfer distance for the triplet energy transfer between identical molecules obtained in the present work is of the same order of magnitude as those reported previously for unlike molecules.1–6) The difference of the values for naphthalene and phenanthrene may not be important when we consider the experimental errors and the precision of approximation employed in the analysis.

References

1) V. L. Ermolaev, *Uspekhi Fiz. Nauk.*, **80**, 3 (1963); Engl. Transl., *Soviet Physics-Uspekhi*, **6**, 333 (1963).

2) J. T. Dubois and F. Wilkinson, *J. Chem. Phys.*, **38**, 2541 (1963).

3) M. Inokuchi and F. Hirayama, *J. Chem. Phys.*, **43**, 1978 (1965).

4) H. Kobashi, T. Morita, and N. Mataga, *Chem. Phys. Lett.*, **20**, 376 (1973).

5) G. B. Strambini and W. C. Galley, *J. Chem. Phys.*, **63**, 3467 (1975).

6) G. B. Strambini and W. C. Galley, *Chem. Phys., Lett.*, **39**, 257 (1976).

7) N. K. Chaudhuri and M. A. El-Sayed, *J. Chem. Phys.*, **42**, 1947 (1965).

8) Y. Gondo, M. Hirai, T. Iwao, T. Kakibaya, T. Kuroi, H. Nagamoto, and T. Kanda, *Chem. Lett.*, **1975**, 463.

9) S. Siegel and L. Goldstein, *J. Chem. Phys.*, **44**, 2780 (1966).

10) Th. Förster, *Ann. Phys.*, **2**, 55 (1948).

11) A. Inoue and N. Ebara, *Chem. Lett.*, **1975**, 1137.

12) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

13) R. S. Knox, *Physica*, **39**, 361 (1968).

14) N. Kanamaru, H. R. Bhattachariee, and E. C. Lim, *Chem. Phys. Lett.*, **26**, 174 (1974)

15) I. B. Berlman, "Energy Transfer Parameters of Aromatic Compounds," Academic Press, New York and London (1973).

16) Th. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959).