Phosphorimetric Investigation of Triplet-Triplet Energy Transfer in Fluid Solution

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The mechanism of triplet-triplet (T-T) energy transfer in fluid solution has been studied by means of phosphorimetry in the temperature range 0—60 °C with acetophenone as energy donor, 1,4-dibromonaphthalene as acceptor and isooctane, isopentane or carbon tetrachloride as solvent. From the temperature dependence of the energy transfer, α and k_{dif} could be evaluated separately, k_{dif} denoting the diffusion-controlled rate constant for the encounter of donor and acceptor molecules and αk_{dif} corresponds to the rate constant for the overall energy transfer reaction. The α values are 0.28 at 25 °C in isopentane and 0.43 at 21 °C in isooctane, indicating that the T-T energy transfer process is not strictly diffusion-controlled. The k_{dif} values are nearly equal to those predicted by a modified Debye equation.

In a previous paper,[1)] it was suggested by means of laser pulse photolysis that the triplet-triplet (T–T) energy transfer process is not strictly diffusion controlled in fluid solution. The overall T-T energy transfer rate constant k_t can be expressed as $k_t=\alpha k_{\text{dif}}$, where k_{dif} is the diffusion-controlled rate constant. We calculated k_{dif} from the standard Debye equation,

$$k_{\text{dif}} = 8RT/3000\eta \tag{1}$$

and obtained an α value smaller than unity.

Since the study by Porter and Wilkinson,[2)] considerable attention has been given to whether the T-T energy transfer is diffusion controlled or not.[1–9)] In most cases, the question was discussed through a comparison of k_t with k_{dif} which was predicted either by Eq. (1) or by a slightly modified Debye equation, *i. e.*,

$$k_{\text{dif}} = 8RT/2000\eta \tag{2}$$

However, we cannot place much reliance on the results because of the assumptions involved in the evaluation of k_{dif}.

We have examined the mechanism of T-T energy transfer in a fluid solution without resort to theoretical prediction. The experiment was carried out with the aid of the donor and acceptor phosphorescence emissions observed in fluid solution. Since it is generally difficult to detect phosphorescence in a fluid solution, most studies on T-T energy transfer have been made by means of T-T absorption or analysis of photochemical products. However, in the former method the first order rate constant for triplet decay is difficult to determine, because an exciting flash of very high intensity is used; the latter method is not suitable for obtaining direct information on the energy transfer process.

Acetophenone was chosen as the energy donor and 1,4-dibromonaphthalene as acceptor, isooctane, isopentane and carbon tetrachloride being used as solvents. We utilized the fact that both acetophenone and 1,4-dibromonaphthalene show phosphorescence with an appreciable intensity even in a fluid solvent provided that the solvent is fully degassed.[1,10–12)]

Experimental

Reagents of Wako Pure Chemical Industries, Osaka were used. Acetophenone was purified by high-vacuum distillation, and 1,4-dibromonaphthalene (DBN) by vacuum sublimation. Spectro-grade isooctane and carbon tetrachloride were used without further purification. Isopentane was passed through a silica gel column.

The sample solutions consisted of acetophenone of a constant concentration (1.0×10^{-2} M) and DBN of varying concentrations (10^{-5}—10^{-4} M), with isooctane, isopentane or carbon tetrachloride as solvent. Each of these solutions was degassed repeatedly (7 or 8 times) by freeze-thaw cycles until the phosphorescence intensity of acetophenone reached a maximum. A representative example of the effect of degassing on the phosphorescence intensity is shown in Fig. 1, in which the phosphorescence intensity of DBN in isooctane is plotted against the number of freeze-thaw cycles.

The phosphorescence spectra were measured at various temperatures between 0° and 60 °C with a Hitachi MPF-2A fluorescence spectrophotometer equipped with a temperature-controlled water bath. The donor phosphorescence spectra were corrected for spectral sensitivity of a monochromator-photomultiplier system using quinine sulfate and β-naphthol as standards. The donor phosphorescence quantum yields were determined by comparing the corrected phosphorescence spectra with a corrected fluorescence spectrum of quinine sulfate in 0.5 M sulfuric acid, which has a fluorescence quantum yield of 0.51. The acceptor phosphorescence spectra were uncorrected because of large correction errors involved over the insensitive spectral region of the photomultiplier. Thus, the relative intensities of the peak were used in the acceptor phosphorescence analysis.

The phosphorescence decay was measured by means of the second harmonic of a giant pulse ruby laser[1)] or a xenon flash for excitation.

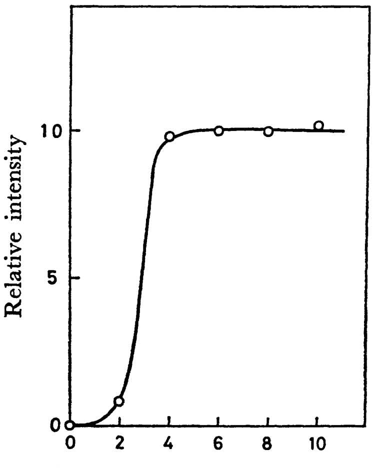

Fig. 1. Effect of degassing on the phosphorescence intensity of DBN in isooctane at room temperature.

Results

Changes in the phosphorescence spectrum of the acetophenone-1,4-dibromonaphthalene (DBN) system in isooctane at 25 °C caused by the increase of the concentration of DBN are shown in Fig. 2. In the absence of acetophenone no phosphorescence emission was observed from DBN upon excitation at 340 nm, which was adopted as the excitation wavelength throughout the T-T energy transfer experiments. The spectral changes are therefore regarded as due to the T-T energy transfer from acetophenone to DBN. Similar spectral changes were observed in isopentane and carbon tetrachloride at various temperatures (0—60 °C).

The Stern-Volmer plots for the quenching of the phosphorescence of acetophenone by DBN in isooctane at different temperatures are shown in Fig. 3, where ϕ_D^0 and ϕ_D are the quantum yields of the donor phosphorescence in the absence and presence of the acceptor, respectively, $[^1A]_0$ being the initial concentration of the acceptor in its ground state. The plot is linear for any temperature, the slope increasing with decreasing temperature. Stern-Volmer plots of essentially the same nature are obtained on changing the solvent from isooctane to isopentane or carbon tetrachloride (Figs. 4 and 5).

Under our experimental conditions of a weak excitation intensity and a low acceptor concentration, the reaction scheme involving the T-T energy transfer may be expressed as

$$^1D \longrightarrow {}^3D^* \tag{3a}$$

$$^3D^* \longrightarrow {}^1D \qquad k_1 \tag{3b}$$

$$^3D^* + {}^1A \longrightarrow ({}^3D^*\ldots{}^1A) \qquad k_{\mathrm{dif}} \tag{3c}$$

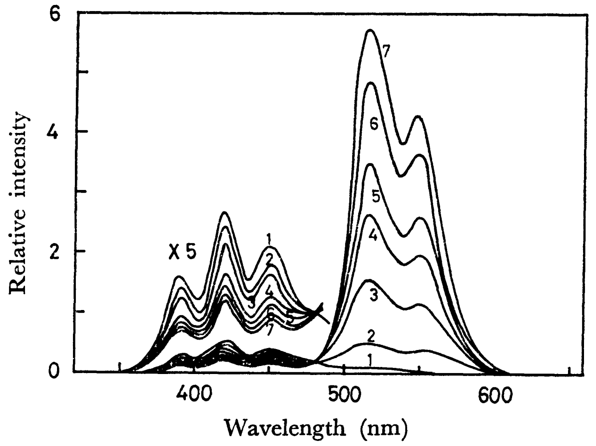

Fig. 2. Phosphorescence spectra (uncorrected for instrument response) of acetophenone-DBN system obtained by excitation at 340 nm in isooctane at 25 °C. The concentrations of DBN: (1) 0; (2) 0.12×10^{-4} M; (3) 0.25×10^{-4} M; (4) 0.74×10^{-4} M; (5) 0.98×10^{-4} M; (6) 1.23×10^{-4} M; (7) 1.47×10^{-4} M.

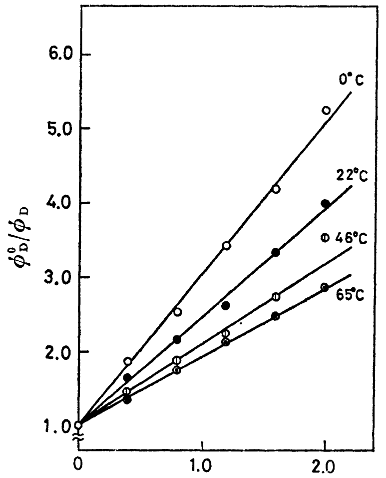

Fig. 3. Stern-Volmer plots for the quenching of the phosphorescence of acetophenone by DBN in isooctane at different temperatures between 0 and 65 °C.

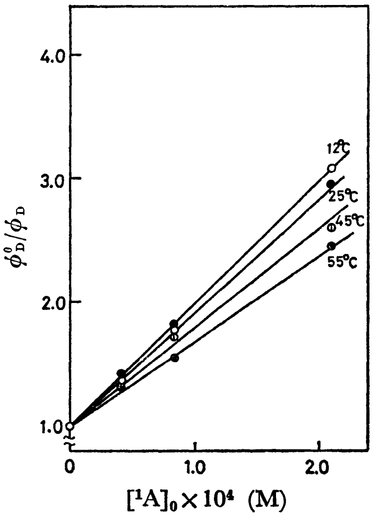

Fig. 4. Stern-Volmer plots for the quenching of the phosphorescence of acetophenone by DBN in isopentane at different temperatures between 12 and 55 °C.

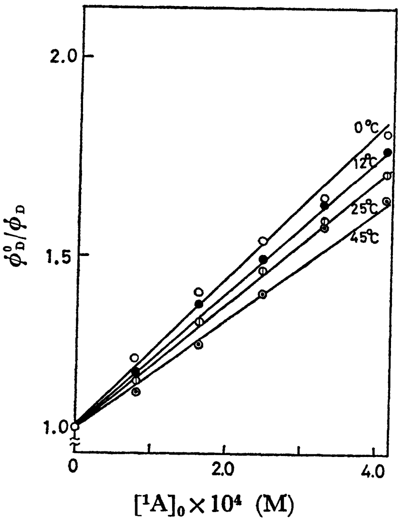

Fig. 5. Stern-Volmer plots for the quenching of the phosphorescence of acetophenone by DBN in carbon tetrachloride at different temperatures between 0 and 45 °C.

$$(^3D^*...^1A) \longrightarrow {}^3D^* + {}^1A \quad k_{-dif} \tag{3d}$$

$$(^3D^*...^1A) \longrightarrow (^1D...^1A) \quad k_1' \tag{3e}$$

$$(^3D^*...^1A) \longrightarrow (^1D...^3A^*) \quad k_{et} \tag{3f}$$

$$(^1D...^3A^*) \longrightarrow {}^1D + {}^3A^* \tag{3g}$$

$$^3A^* \longrightarrow {}^1A \tag{3h}$$

where $^3D^*$, ^1D and $^3A^*$, ^1A represent the excited triplet and ground singlet states of donor (D) and acceptor (A), respectively and k_1 and k_1' denote the sums of all unimolecular decay processes including both radiative and nonradiative transitions. The process expressed by (3c) corresponds to the encounter of a donor molecule in the triplet state and an acceptor molecule in the ground state; process (3d) represents the dissociation of the encounter complex, and (3f) the energy transfer from the donor to the acceptor.

We are here concerned with photostationary conditions. Since the concentrations of the encounter complexes ($^3D^*\cdots{}^1A$) and ($^1D\cdots{}^3A^*$) are considered to be very small as compared with those of the "free" triplet species $^3D^*$ and $^3A^*$, respectively, we can regard the donor and acceptor phosphorescence emissions as due exclusively to the free species. Furthermore, we may safely assume that $k_1' \ll k_{et}$. Thus it follows from the above reaction scheme that

$$\phi_D{}^0/\phi_D = 1 + \alpha k_{dif}\tau_0[^1A]_0 \tag{4}$$

with

$$\alpha = \frac{k_{et}}{k_{-dif}+k_{et}} \tag{4'}$$

where $\tau_0(=1/k_1)$ is the phosphorescence lifetime of the donor in the absence of acceptor. α represents the probability that energy transfer occurs during the lifetime of the encounter complex. Equation (4) is compatible with the linear relations between ϕ_D^0/ϕ_D and $[^1A]_0$ (Figs. 3—5). Thus, from the slopes of the straight lines in these figures, the values of $\alpha k_{dif}\tau_0$ can be obtained for each temperature. The results given in Table 1 show that the quantity $\alpha k_{dif}\tau_0$ depends on the temperature.

Table 1. Values of $\alpha k_{dif}\tau_0$ at various temperatures in different solvents

Solvent	$\alpha k_{dif}\tau_0 \times 10^{-4}$, M^{-1}				
Isopentane		1.0 (12 °C)	0.9 (25 °C)	0.8 (40 °C)	0.7 (55 °C)
Isooctane	2.0 (0 °C)	1.5 (21 °C)	1.3[a)] (25 °C)	1.2 (46 °C)	0.9 (65 °C)
Carbon tetrachloride	0.20 (0 °C)	0.18 (12 °C)	0.17 (25 °C)	0.16[a)] (25 °C)	0.15 (45 °C)

a) Obtained from the sensitized acceptor phosphorescence.

Let us examine the spectral data concerning the sensitized acceptor phosphorescence. It can be shown that the following equation is derived from the reaction scheme:

$$\frac{1}{\phi_A} = \frac{1}{\theta}\left(1+\frac{1}{\alpha k_{dif}\tau_0[^1A]_0}\right) \tag{5}$$

where ϕ_A is the quantum yield of the sensitized acceptor phosphorescence and θ the fraction of triplet acceptor molecules which phosphoresce. Plots of $1/\phi_A$ against $1/[^1A]_0$ in isooctane and carbon tetrachloride at 25 °C give straight lines (Fig. 6). From the intercepts and slopes of these lines, we can obtain the values of $\alpha k_{dif}\tau_0$. The values were found to be in good agreement with those obtained from the quenching of the donor phosphorescence (*cf.* Table 1). This indicates

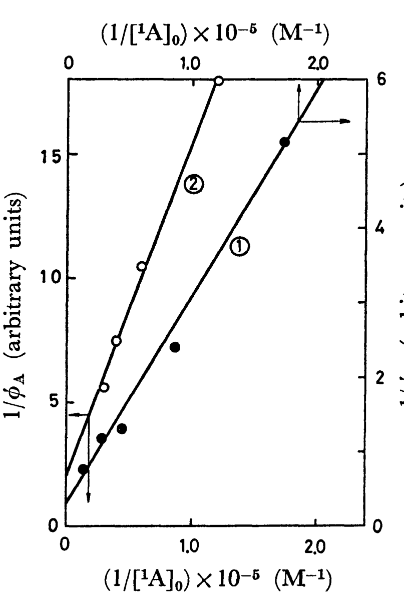

Fig. 6. Plots of $1/\phi_A$ *vs.* $1/[^1A]_0$ for acetophenone-DBN system in isooctane (1) and in carbon tetrachloride (2) at 25 °C.

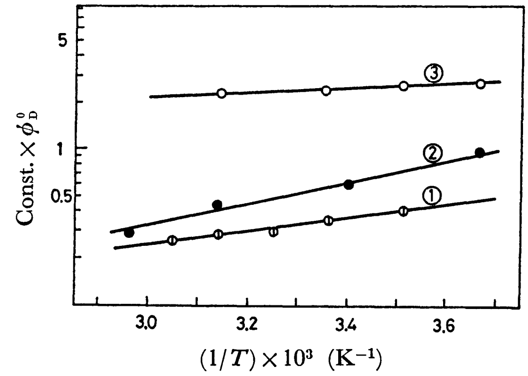

Fig. 7. Temperature dependence of ϕ_D^0 in various solvents: (1) isopentane, (2) isooctane; (3) carbon tetrachloride.

Table 2. Data for the donor phosphorescence in the absence of the acceptor in various solvents, and the values of ΔE_{flow} and η of the solvents

Solvent	$\phi_D{}^0\times 10^4$,[a)]	$\tau_0\times 10^6$,[a)] s	ΔE kcal/mol	ΔE_{flow} kcal/mol	η[b)] cP
Isopentane	0.95	0.63	1.8	1.5	0.225
Isooctane	2.7	1.6	2.8	2.1	0.504
Carbon tetrachloride	5.1		0.9	2.6	0.969

a) At 25 °C. b) At 20 °C, taken from Ref. 21.

that the reaction scheme involving processes (3a)—(3h) describes satisfactorily the T-T energy transfer phenomenon in fluid solution.

Figure 7 shows the temperature dependence of ϕ_D^0. In each of the solvents a linear relation is found between log ϕ_D^0 and $1/T$.

Lifetimes of the donor phosphorescence at 25 °C in the absence of the acceptor are given in Table 2. The phosphorescence decay was found to be exponential in all the solvents.

Discussion

Evaluation of α and k_{dif}. Although we have obtained the values of $\alpha k_{dif}\tau_0$ at various temperatures from the slopes of the Stern-Volmer plots (Table 1), it is necessary to evaluate α and k_{dif} separately in order to establish whether the T-T energy transfer process is diffusion-controlled or not in a fluid solution.

On reference to Eq. (4′) the changes in slope of the Stern-Volmer plots caused by temperature change are expressed as

$$y(T) = \frac{k_{et}}{k_{et}+k_{-dif}} k_{dif}\tau_0 \tag{6}$$

which is rewritten as

$$\frac{k_{dif}\tau_0 - y(T)}{y(T)} = \frac{k_{-dif}}{k_{et}} \tag{7}$$

We examine here the temperature dependence of the quantum yield of the donor phosphorescence in the absence of the acceptor, ϕ_D^0. From the fact that the phosphoressence decay is exponential, the donor lifetime τ_0 as defined in Eq. (4) is expressed in the form

$$\tau_0 = 1/(k_r + k_q),$$

where k_r denotes the rate constant for the radiative transition in the donor molecule, and k_q the sum of the rate constants for unimolecular and pseudo-unimolecular quenching processes of the donor; the latter quenching process might be caused by solvent molecules and by some quenching impurities. The quantum yield ϕ_D^0 is expressed in the form

$$\phi_D^0 = \phi_{ISC} k_r \tau_0 = \text{Const.} \times \tau_0,$$

where ϕ_{ISC} is the intersystem crossing quantum yield of the donor.

In a fluid solution, it can safely be assumed that $k_r \ll k_q$, so that $\tau_0 = 1/k_q$. In addition, it is recognized that the quenching constant k_q has a diffusion-controlled character.[13] Therefore k_q can be written as

$$k_q = \text{Const.} \times \exp(-\Delta E/RT) \tag{8}$$

where ΔE is an activation energy. Thus, ϕ_D^0 has the form

$$\phi_D^0 = \text{Const.} \times \exp(\Delta E/RT)$$

The foregoing considerations are supported by the fact that a linear relation exists between log ϕ_D^0 and $1/T$ in each of the solvents (Fig. 7). From the slopes of the straight lines, ΔE values are calculated to be 1.8, 2.8, and 0.9 kcal/mol, respectively, in isopentane, isooctane, and carbon tetrachloride as solvents. These values are approximately equal to the activation energies of flow, ΔE_{flow}, for the solvents except for the value in carbon tetrachloride. The data for ΔE and ΔE_{flow} are given in Table 2.

In view of these results we may assume that in a hydrocarbon solvent ΔE agrees with ΔE_{flow}. Thus it follows from Eq. (8) that $k_{dif}\tau_0$ is independent of temperature, since $k_q = 1/\tau_0$ and k_{dif} can be expressed as Const. $\times \exp(-\Delta E_{flow}/RT)$. The difference between the values of ΔE and ΔE_{flow} for carbon tetrachloride as a solvent cannot be explained from the present experimental data alone. It might be due to such a specific effect as an external heavy-atom effect of the solvent on the donor phosphorescence.

Let us now return to Eq. (7). k_{-dif} should show the same temperature dependence as k_{dif}. On the other hand, for the donor-acceptor pair under study, k_{et} would not appreciably vary with temperature. The right-hand side of Eq. (7) can then be written as

$$\frac{k_{-dif}}{k_{et}} = C\exp\left(-\frac{B}{RT}\right) \tag{9}$$

where C and B are constants. Even if k_{et} depends on temperature, Eq. (9) holds provided that k_{et} is assumed to be expressed by an Arrhenius type equation. Substitution of Eq. (9) into Eq. (7) gives

$$\frac{A - y(T)}{y(T)} = C\exp\left(-\frac{B}{RT}\right) \tag{10}$$

where A stands for $k_{dif}\tau_0$. If an appropriate value is inserted into A, a polt of $\log\{[A-y(T)]/y(T)\}$ against $1/T$ should yield a straight line.

Figure 8 shows the plots in question for different A values. It is seen that, when A equals 3.5×10^4 M^{-1} (the solid line), the plot gives a striaght line for acetophenone–DBN system in isooctane; from the slope of the line B is found to be 3.5 kcal/mol. A similar treatment of the same system in isopentane leads to $A = 3.2 \times 10^4$ M^{-1} and $B = 2.2$ kcal/mol.

By the use of $A(\equiv k_{dif}\tau_0)$ thus determined the values of α are immediately obtained (*cf.* Table 1), with the results shown in Table 3. It is seen that α is definitely smaller than unity. This shows that the T-T energy transfer is not diffusion-controlled under the present experimental conditions. Furthermore, α is found to decrease with increasing temperature. The lowering of the solvent viscosity accompanied by temperature

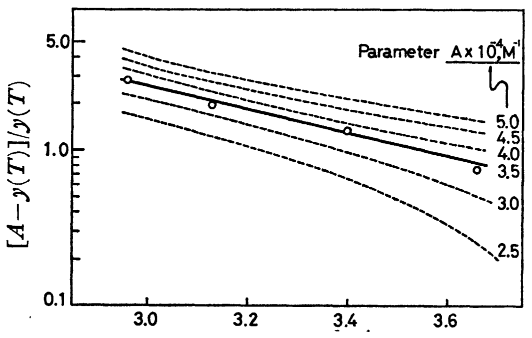

Fig. 8. Plots of $\log[A-y(T)]/y(T)$ *vs.* $1/T$ in isooctane solvent for different values of parameter A.

Table 3. Values of α at various temperatures in isopentane and isooctane

Solvent	α			
Isopentane	0.31 (12 °C)	0.28 (25 °C)	0.25 (40 °C)	0.21 (55 °C)
Isooctane	0.57 (0 °C)	0.43 (21 °C)	0.34 (46 °C)	0.26 (65 °C)

rise will increase the value of $k_{-\mathrm{dif}}$, leaving k_{et} essentially unchanged. This causes a decrease in magnitude of α, since α is expressed as $1/(1+k_{-\mathrm{dif}}/k_{\mathrm{et}})$. In contrast, as temperature decreases, or the solvent viscosity increases, α becomes larger and tends to approach unity, so that the T-T transfer is reduced to a diffusion-controlled process. These statements are in agreement with the previous observations that T-T energy transfer is diffusion-controlled in solvents of relatively high viscosity,[3] but in less viscous solvents it is not strictly diffusion-controlled.[1,4]

Using the value of τ_0 shown in Table 2, we obtain $k_{\mathrm{dif}}=5.1\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in isopentane and $2.2\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in isooctane at 25 °C. These values differ from the k_{dif} values derived from the standard Debye equation (1), but agree well with the corresponding values predicted by the modified Debye equation (2). This is consistent with the results obtained by Osborne and Porter for T-T energy transfer in viscous solution.[3]

Estimation of k_{et}. From Smoluchowski's theory of the diffusion-controlled process,[14] the rate constant for the encounter of donor and acceptor molecules is given by[15-17]

$$k_{\mathrm{dif}} = \frac{4\pi R_0 DN}{1000} \tag{11}$$

where R_0 is the sum of the radii of the donor and acceptor molecules in the encounter complex, D the sum of their respective diffusion coefficients D_{d} and D_{a}, and N is Avogadro's number. In this equation the transient term is neglected, since it is very small under present conditions of phosphorescence measurement.

The value $D=D_{\mathrm{d}}+D_{\mathrm{a}}$ was determined with the aid of the following relations:

$$\begin{aligned} D_{\mathrm{d}} &= TC_{\mathrm{d}}/\eta \\ D_{\mathrm{a}} &= TC_{\mathrm{a}}/\eta \end{aligned} \tag{12}$$

where C_{d} and C_{a} each are assumed to be a constant common to hydrocarbon solvents.[17] The C values, found in the literature,[18,19] for benzoic acid in toluene and for 1-bromonaphthalene in benzene were used, respectively, as C_{d} for acetophenone in isooctane and C_{a} for DBN in the same solvent.

By inserting the values of D determined in this way and k_{dif} obtained before into Eq. (11), R_0 in isooctane is calculated to be about 9 Å. The mean of the donor and acceptor radii ($R_0/2$) is somewhat greater than the mean of the radii estimated from the molar volumes of the donor and acceptor (3 Å).

On the basis of random-walk theory,[15,16] Wagner and Kochea gave the following relation:[4]

$$\frac{1-\alpha}{\alpha} = \frac{k_{-\mathrm{dif}}}{k_{\mathrm{et}}} = \frac{\xi}{k_{\mathrm{et}}}\cdot k_{\mathrm{dif}} \tag{13}$$

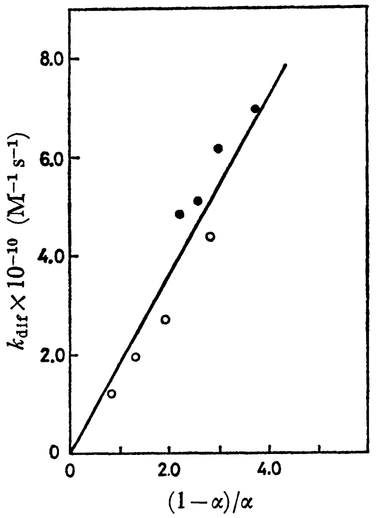

Fig. 9. Plots of k_{dif} *vs.* $(1-\alpha)/\alpha$: ○, in isooctane; ●, in isopentane.

with

$$\xi = \frac{3000}{2\pi NR_0{}^3} \tag{14}$$

The plot of k_{dif} against $(1-\alpha)/\alpha$ was found to give a straight line (Fig. 9). The value of k_{et}/ξ is determined to be $1.8\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ from the slope of the line. By inserting the R_0 value into Eq. (14) ξ is found to be 1.1 M. We thus immediately obtain $k_{\mathrm{et}}=2.0\times10^{10}\ \mathrm{s}^{-1}$. This k_{et} value, which corresponds to $R_0=9$ Å, is smaller by a factor of 10 than the value obtained in a mixed crystal.[20] This discrepancy may be understood by noting that the rate of T-T energy transfer should vary with the distance between donor and acceptor molecules,[22] and that the distance concerned is greater in the solution than in the mixed crystal.

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