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Kinetic Study of Triplet-Triplet Energy Transfer in Fluid Solution by Means of Laser Pulse Photolysis[1]

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The kinetics of triplet-triplet (T-T) energy transfer in fluid solution has been studied by means of laser pulse photolysis with acetophenone as the energy donor and naphthalene as the acceptor. Decay curves of phosphorescence of the donor and rise-and-decay curves of sensitized T-T absorption of the acceptor were obtained. These were analyzed to determine the unimolecular and bimolecular rate constants (denoted by k_1 and k_2 respectively) for the deactivation processes of the triplet state of donor or acceptor and the rate constant (k_t) for the T-T energy transfer. In isooctane at room temperature these rate constants were found to be: $k_1=0.67\times10^6$ sec^{-1} and $k_2=2.0\times10^{10}$ M^{-1} sec^{-1} for acetophenone, $k_2'=1.6\times10^{10}$ M^{-1} sec^{-1} for naphthalene, and $k_t=1.0\times10^{10}$ M^{-1} sec^{-1}. The k_t value obtained from the donor phosphorescence is in good agreement with that from the acceptor T-T absorption. The experimental results suggest that T-T transfer and T-T annihilation processes are not strictly diffusion-controlled.

Triplet-triplet (T-T) energy transfer between molecules in fluid solution has been extensively investigated since the work of Bäckström and Sandros.[2–9] It is generally believed that, when the transfer is exothermic by at least 3 kcal/mol, the transfer rate is nearly equal to the encounter frequency predicted by the Debye equation for diffusion-controlled kinetics, provided that the solvent viscosities are greater than 3 cP.[5]

On the other hand, Nordin and Strong pointed out on the basis of computational analysis that an energy difference greater than 3 kcal/mol between donor and acceptor triplet states does not necessarily lead to diffusion-controlled quenching.[6] Wagner and Kochevar also indicated that the triplet energy transfer is not totally diffusion-controlled in solvents of low viscosity.[7]

T–T energy transfer has so far been studied through spectroscopic and photochemical experiments performed by either steady excitation or the usual flash photolysis method in which the flash duration is of the order of microseconds.[10,11] Such a duration is too long for direct observation of the T–T transfer process in fluid solution.

In an attempt to obtain detailed information on energy transfer and other rate processes associated with the donor and acceptor triplet states, we re-examined T–T energy transfer in solution by using a frequency-doubled ruby laser with a pulse duration of 25 nsec. Acetophenone was chosen as the energy donor and naphthalene as the acceptor, and isooctane was used as a solvent of low viscosity. We utilized the fact that acetophenone shows a phosphorescence emission of appreciable intensity even in a fluid solution, provided that the solvent is fully degassed. In this way we were able to measure both the phosphorescence of the donor and the sensitized T–T absorption of the acceptor, and hence it was possible to investigate the dynamic behavior of the donor and acceptor triplet species simultaneously.

Experimental

Reagents were obtained from Wako Pure Chemical Industries, Osaka. Acetophenone was purified by high-vacuum distillation. Spectro-grade isooctane was used without further purification. Sample solutions consisted of acetophenone of a constant concentration (1.0×10^{-2} M) and naphthalene of varying concentrations ($\sim10^{-4}$ M), with isooctane as the solvent. Each solutions was degassed repeatedly by freeze-thaw cycles until the phosphorescence intensity of acetophe-

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[1] Presented at the Symposium on Molecular Structure held by the Chemical Society of Japan at the Kyoto Hall, Kyoto, Oct. 16, 1971.

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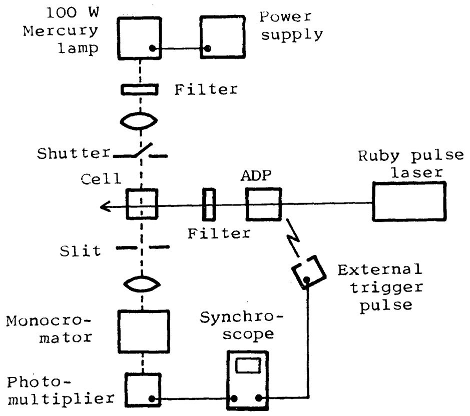

Fig. 1. Diagrammatic representation of the apparatus for laser pulse photolysis.

none reached a maximum.

Phosphorescence spectra were measured at room temperature with a Hitachi MPF-2A fluorescence spectrophotometer.

The apparatus for laser pulse photolysis is schematically shown in Fig. 1. A Japan Electron Optics Laboratory JLS-R3A giant pulse ruby laser with a peak output of 150 MW and pulse width of 25 nsec was used. The sample in a 10-mm square quartz cell was excited by the second harmonic (347 mμ) of the ruby laser generated by an ADP crystal. It should be noted that only the donor molecule of acetophenone absorbs at 347 mμ. To observe the rise and decay of T–T absorption, light from a 100-W extra-high pressure mercury lamp was passed through the cell at right angles to the laser beam, dispersed by a grating monochromator, and was then detected by an RCA 1P28 photomultiplier and an Iwasaki 100 MHz oscilloscope. In order to measure the phosphorescence decay, the emission from the solution excited by the frequency-doubled laser pulse was detected instead of the light from the mercury lamp (Fig. 1).

The exciting pulse of the second harmonic had an energy of 4×10^{-7} einstein/pulse, which was reproducible within an error of $\pm10\ \%$. Since the principal source of error is the variation in energy of the pulse, the overall experimental error may safely be assumed to be $\pm20\ \%$.

Most of the measurements were made with the above-mentioned exciting pulse (hereafter called normal- or high-intensity pulse). For certain purposes, we used an exciting pulse whose energy was reduced to 1 % of the energy of the normal-intensity pulse by means of a suitable system of glass filters (hereafter called low-intensity pulse).

The donor phosphorescence was observed at 420 mμ, and the acceptor T–T absorption at 410 mμ, unless otherwise stated. All the emission and absorption measurements were made at room temperature (about 20 °C).

Results and Discussion

Kinetic Scheme. Creation and degradation of triplet states in fluid solution involving intermolecular triplet-triplet energy transfer may be expressed by the following mechanisms:

$$^1\mathrm{D} \longrightarrow {}^3\mathrm{D}^* \qquad \text{(1a)}$$

$$^3\mathrm{D}^* \longrightarrow {}^1\mathrm{D} \qquad k_1 \qquad \text{(1b)}$$

$$^3\mathrm{D}^* + {}^3\mathrm{D}^* \longrightarrow {}^1\mathrm{D}^* + {}^1\mathrm{D} \qquad k_2 \qquad \text{(1c)}$$

$$^3\mathrm{D}^* + {}^1\mathrm{A} \longrightarrow {}^1\mathrm{D} + {}^3\mathrm{A}^* \qquad k_t \qquad \text{(1d)}$$

$$^3\mathrm{A}^* \longrightarrow {}^1\mathrm{A} \qquad k_1' \qquad \text{(1e)}$$

$$^3\mathrm{A}^* + {}^3\mathrm{A}^* \longrightarrow {}^1\mathrm{A}^* + {}^1\mathrm{A} \qquad k_2' \qquad \text{(1f)}$$

where ^{1}D, ^{3}D* and ^{1}A, ^{3}A* represent the ground and triplet states of donor (D) and acceptor (A), respectively; k_1 or k_1' is the sum of the rate constants for all unimolecular decay processes including both radiative and nonradiative transitions; k_2 or k_2' is the bimolecular rate constant for T–T annihilation, and k_t is that for T–T energy transfer. The formation of the triplet excited dimer can be neglected, since it has only a small rate constant[12] and does not appreciably contribute to the triplet decay.

The rate equations for the donor-acceptor system after pulse excitation are given by

$$-\frac{d[^3\mathrm{D}^*]}{dt} = (k_1 + k_2[^3\mathrm{D}^*] + k_t[^1\mathrm{A}])[^3\mathrm{D}^*] \qquad (2)$$

$$\frac{d[^3\mathrm{A}^*]}{dt} = k_t[^1\mathrm{A}][^3\mathrm{D}^*] - (k_1' + k_2'[^3\mathrm{A}^*])[^3\mathrm{A}^*] \qquad (3)$$

Although these equations cannot be solved exactly, we can determine the rate parameters if we choose appropriate experimental conditions.

Rate Constants Derived from the Donor Phosphorescence. The phosphorescence spectrum of acetophenone in isooctane at room temperature is similar in location and shape to the spectrum of that in a rigid-glass solution at low temperature (Fig. 2).[13]

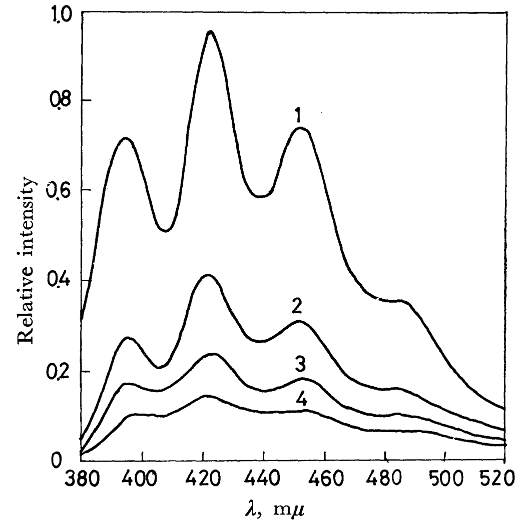

Fig. 2. Phosphorescence spectra of acetophenone–naphthalene system obtained by steady excitation at 340 mμ in isooctane. The concentrations of naphthalene: (1) 0; (2) 0.8×10^{-4}; (3) 2.0×10^{-4}; (4) 4.0×10^{-4} M.

When the acetophenone–naphthalene system was excited at 347 mμ by the normal-intensity pulse, the phosphorescence of the donor generally showed non-exponential decay. On the other hand, excitation by the low-intensity pulse led to a phosphorescence decay curve which was exponential within the limit of experimental errors. These observations indicate that the importance of the term involving k_2 on the right hand side of Eq. (2) largely depends upon the intensity of the exciting light.

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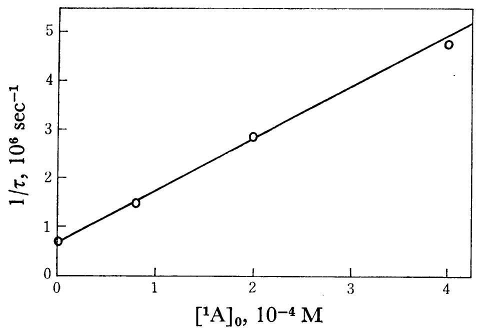

Fig. 3. Plot of $1/\tau$ *vs.* $[^1A]_0$ for acetophenone–naphthalene system in isooctane.

The phosphorescence lifetime τ as obtained from the decay curve corresponding to the low-intensity pulse decreases with increase in the amount of naphthalene added as an acceptor. The plot of $1/\tau$ against the initial acceptor concentration $[^1A]_0$ is found to be linear within the limit of experimental errors (Fig. 3). With the low-intensity pulse, the term involving k_2 can be neglected in Eq. (2), and $[^1A]=[^1A]_0-[^3A^*]$ can be replaced by $[^1A]_0$, so that $1/\tau$ is expressed as

$$1/\tau = k_1 + k_t[^1A]_0$$

The linear relation in Fig. 3 can thus be understood. From the intercept and slope of the straight line, we at once obtain

$$k_1 = 0.67\times10^6\ \mathrm{sec}^{-1}$$
$$k_t = 1.1\times10^{10}\ \mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$$

In the case of the normal-intensity pulse, the term neglected before should be included, but Eq. (2) should be simplified at the instant of pulse excitation, that is, at $t=0$. Thus, if the phosphorescence intensity of the donor is denoted by I, Eq. (2) can be written in the form:

$$-\left[\frac{1}{I}\frac{\mathrm{d}I}{\mathrm{d}t}\right]_{t=0} = k_1 + k_2[^3D^*]_0 + k_t[^1A]_0 \qquad (4)$$

where $[^3D^*]_0$ is the concentration of the initially produced triplet state of the donor, *i.e.* $[^3D^*]$ at $t=0$.

Figure 4 shows a plot of $-[(1/I)(\mathrm{d}I/\mathrm{d}t)]_{t=0}$ against $[^1A]_0$, which gives a straight line as expected from Eq. (4). From the intercept of the line, we obtain $k_1+k_2[^3D^*]_0=2.5\times10^6\ \mathrm{sec}^{-1}$. It will be shown later that $[^3D^*]_0=0.90\times10^{-4}$ M. Thus, recalling that $k_1=0.67\times10^6\ \mathrm{sec}^{-1}$, we obtain

$$k_2 = 2.0\times10^{10}\ \mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$$

Further, from the slope of the straight line, we obtain

$$k_t = 0.90\times10^{10}\ \mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$$

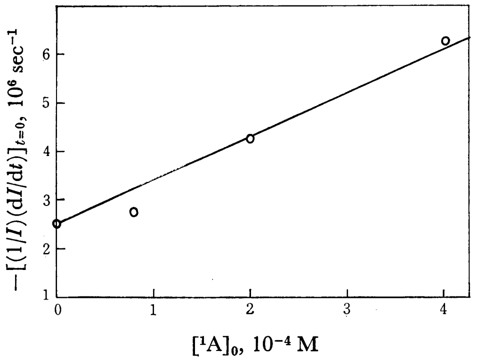

Fig. 4. Plot of $-[(1/I)(\mathrm{d}I/\mathrm{d}t)]_{t=0}$ *vs.* $[^1A]_0$ for acetophenone–naphthalene system in isooctane.

We here refer to spectral data resulting from the steady excitation on the usual spectrophotometer. The intensity of the phosphorescence spectrum of acetophenone, obtained by steady excitation at 340 mμ, decreases with the increasing amount of naphthalene (Fig. 2). The phosphorescence quenching is interpreted to be due to the T–T energy transfer from acetophenone to naphthalene.

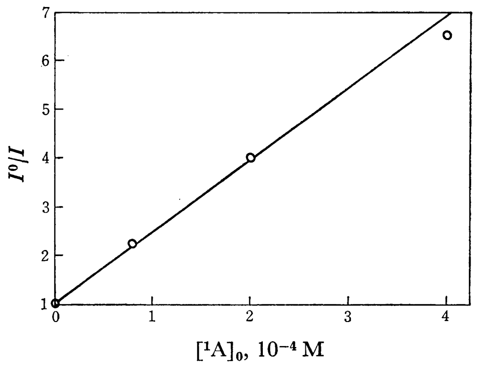

Fig. 5. Stern-Volmer plot for the quenching of phosphorescence of acetophenone by naphthalene in isooctane.

A Stern-Volmer plot for the quenching of acetophenone phosphorescence is given in Fig. 5. The plot is linear as expected. In the case of steady excitation, T–T annihilation can be disregarded on account of the low intensity of exciting light. Consequently, the following equation of Stern-Volmer type is obtained by reference to Eq. (2):

$$I^0/I = 1 + k_t[^1A]_0/k_1 \qquad (5)$$

where I^0 and I are the steady intensities of the donor phosphorescence in the absence and presence of the acceptor, respectively. From the slope of the straight line in Fig. 5, $k_t/k_1=1.5\times10^4\ \mathrm{M}^{-1}$ is obtained; hence, by use of the known value of k_1, it follows that

$$k_t = 1.0\times10^{10}\ \mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$$

Rate Constants Derived from the Acceptor T–T Absorption. Figure 6 represents typical examples showing the time behavior of the transient absorption at 410 mμ obtained for a mixture of acetophenone and naphthalene in isooctane by excitation with a normal-intensity laser pulse. The intensity of absorption first rises rapidly, reaches a maximum or a peak, and then decays rather slowly. The maximum intensity value increases with the amount of naphthalene, provided that the concentration of acetophenone is kept constant.

We made a series of measurements, changing the wavelength at which the transient absorption was monitored, and plotted the absorption intensity at a definite time after the pulse excitation as a function of the monitoring wavelength. The resulting spectrum agreed well with the T–T absorption spectrum of naphthalene in literature. No transient absorption could be detected from a solution of acetophenone

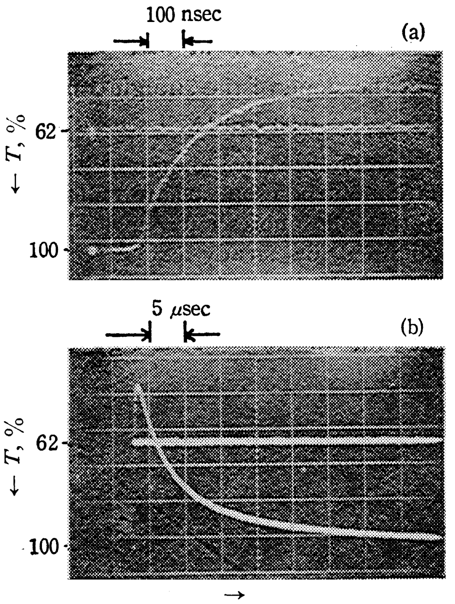

Fig. 6. Rise and decay of the sensitized T–T absorption of naphthalene. (a) rise curve; (b) rise-and-decay curve. $[^1A]_0=2.0\times10^{-4}$ M.

alone or of naphthalene alone in isooctane under the present experimental conditions.

The foregoing observations clearly indicate that the transient absorption as given in Fig. 6 is due to the T–T transition in triplet naphthalene molecules produced by T–T energy transfer in which acetophenone acts as a donor and naphthalene as an acceptor. We note that the wavelength of 410 mμ corresponds to a peak in the T–T absorption spectrum of naphthalene.

The absorbance for the transient T–T absorption at a particular wavelength, *i.e.* 410 mμ in the present experiment, will be denoted by A_b, or by $A_b(t)$ when it is desirable to show explicitly that the absorbance is a function of time. There is, of course, the following relation between A_b and $[^3A^*]$:

$$[^3A^*] = A_b/\varepsilon l \tag{6}$$

where ε and l are the molar extinction coefficient for the T–T absorption of acceptor and the effective absorbing path length, respectively.

Let us denote the time at which the peak occurs in the $A_b(t)$ curve by t_p. Then, at any time t later than t_p by at least three microseconds, the decay curve of $A_b(t)$ is represented by the following relation between $[^3A^*]$ and t:

$$1/[^3A^*] = k_2't + C \tag{7}$$

where C is a constant. At the time under consideration $[^3D^*]$ is so small that the first term on the right-hand side of Eq. (3) can be neglected; k_1' also is negligible because of its relatively small magnitude.[12] Equation (3) is thus simplified to give Eq. (7).

A plot of $1/[^3A^*]$ against t is shown in Fig. 7. The values of $[^3A^*]$ were derived on the basis of Eq. (6) from experimental data for A_b; the ε value at 410 mμ was taken to be 1.4×10^4,[14] and l was estimated to be 0.7 cm. We see that the relation of $1/[^3A^*]$ to t can be satisfactorily expressed in the form of Eq. (7) for $t>3$ μsec. From the slope of the straight line we obtain

$$k_2' = 1.6\times10^{10}\ \mathrm{M^{-1}\cdot sec^{-1}}.$$

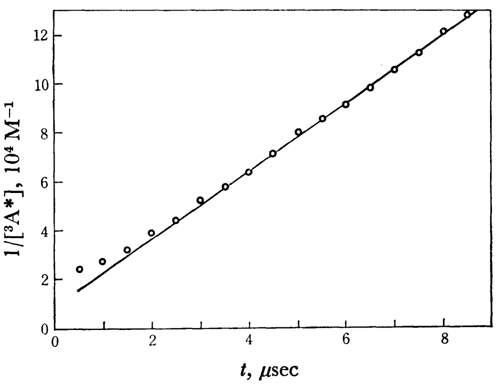

Fig. 7. Plot of $1/[^3A^*]$ *vs.* t for acetophenone–naphthalene system in isooctane. $[^1A]_0=2.0\times10^{-4}$ M.

Let us consider the rate of rise of absorbance at the instant of excitation (*cf.* Fig. 6a). At $t=0$, Eq. (3) becomes

$$\left[\frac{d[^3A^*]}{dt}\right]_{t=0} = k_t[^1A]_0[^3D^*]_0 \tag{8}$$

Therefore, a plot of the initial slope of the $[^3A^*]-t$ curve, $(d[^3A^*]/dt)_{t=0}$, against the initial acceptor concentration, $[^1A]_0$, should yield a straight line with a slope of $k_t[^3D^*]_0$. This is valid as may be seen in Fig. 8. As will be shown later, $[^3D]_0$ is evaluated as 0.90×10^{-4} M. Hence, from the slope of the straight line, we obtain

$$k_t = 1.0\times10^{10}\ \mathrm{M^{-1}\cdot sec^{-1}}$$

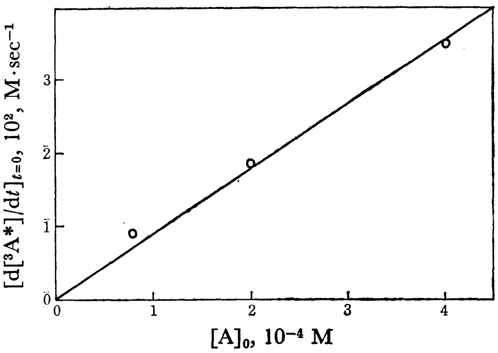

Fig. 8. Plot of $[d[^3A^*]/dt]_{t=0}$ *vs.* $[^1A]_0$ for acetophenone–naphthalene system in isooctane.

This is in good agreement with the k_t values derived from the data on donor phosphorescence.

Evaluation of $[^3D^*]_0$. The initial concentration of the donor triplet $[^3D^*]_0$ immediately after the excitation with the normal- or high-intensity laser pulse is important in determining rate parameters.

The experiments related to Figs. 4 and 8 were carried out under the same conditions with respect to the intensity of exciting pulse. According to the definition of t_p, we have $d[^3A^*]/dt=0$ at $t=t_p$. Thus by neglecting the term of k_1' it follows from Eq. (3) that

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Table 1. Rate constants of various processes of triplet energy deactivation and transfer for acetophenone–naphthalene pair in isooctane at room temperature

Observation	$k_1 \times 10^{-6}$ sec^{-1}	$k_2 \times 10^{-10}$ M$^{-1}\cdot$sec^{-1}	$k'_2 \times 10^{-10}$ M$^{-1}\cdot$sec^{-1}	$k_t \times 10^{-10}$ M$^{-1}\cdot$sec^{-1}	α
Donor phosphorescence (steady excitation)				1.0	0.76
Donor phosphorescence (laser pulse excitation)	0.67	2.0		1.1 0.9	0.83 0.61
T–T absorption of A (laser pulse excitation)			1.6	1.0	0.76

$$[^3D^*]_{t_p} = k_2'[^3A^*]^2_{t_p}/k_t[^1A]_{t_p} \tag{9}$$

The values for rate constants k_2' and k_t have already been obtained without the knowledge of $[^3D^*]_0$, $[^1A]_{t_p}$ being equal to $[^1A]_0-[^3A^*]_{t_p}$. For $[^1A]_0=2.0\times10^{-4}$ M, $[^3A^*]_{t_p}$ is found to be 0.39×10^{-4} M from the A_b value at t_p. Hence $[^3D^*]_{t_p}$ is determined to be 0.15×10^{-4} M from Eq. (9). On the other hand, the ratio between $[^3D^*]_{t_p}$ and $[^3D^*]_0$ can be obtained by use of the decay curve of the donor phosphorescence. Thus, for $[^1A]_0=2.0\times10^{-4}$ M, we find that $[^3D^*]_{t_p}/[^3D^*]_0=0.17\pm0.02$. This along with the value of $[^3D^*]_{t_p}$ leads to

$$[^3D^*]_0 = 0.90\times10^{-4}\ \text{M}$$

Considerations on the Values of Rate Constants. The rate constants determined by various procedures are summarized in Table 1. It is obvious that the values of k_t obtained from the donor phosphorescence caused by steady or laser-pulse excitation and from the sensitized acceptor T–T absorption caused by laser-pulse excitation are in good agreement within the limit of experimental errors. This indicates that the behavior of triplet states in less viscous solvents can be satisfactorily described by the reaction scheme given in Eq. (1).

The triplet-triplet energy transfer process given in Eq. (1d) can be represented by a more detailed mechanism involving an encounter complex:

$$^3D^* + {}^1A \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftarrows}} [^3D^*\cdots{}^1A] \xrightarrow{k_{et}} {}^1D + {}^3A^*$$
$$\text{(I)} \qquad\qquad \text{(II)}$$

Process (I) corresponds to the encounter of a donor molecule in the excited triplet state and an acceptor molecule in the ground state. Process (II) represents the energy transfer from the donor to the acceptor in the encounter complex. It can then be shown that k_t in Eq. (1d) is expressed as

$$k_t = \alpha\overrightarrow{k} \tag{10}$$

with

$$\alpha = k_{et}/(\overleftarrow{k}+k_{et})$$

The encounter between donor and acceptor molecules can be regarded as a diffusion-controlled process. Thus, if the Debye equation is applicable to such a process, the rate constant $\overrightarrow{k}$ is given by

$$\overrightarrow{k} \equiv k_{dif} = \frac{8RT}{3000\eta} \tag{11}$$

Using the $\overrightarrow{k}$ value obtained from this equation and the observed k_t values, α is calculated to be less than unity from Eq. (10), as is shown in Table 1.

The fact that the parameter α is less than unity leads to the view that the overall energy-transfer process as given by Eq. (1d) is not diffusion-controlled in a strict sense. Because of the assumptions involved in the evaluation of k_{dif}, too much reliance cannot be placed on the value of α. However, in our recent experiments on the temperature dependence of T–T energy transfer for acetophenone–1,4-dibromonaphthalene pair in isooctane, it was found that the value of α decreases with the decreasing solvent viscosity caused by the rise in temperature; for example, $\alpha(0\ ^\circ\text{C})=0.57$ and $\alpha(65\ ^\circ\text{C})=0.26$. This shows the value of k_{et} to be comparable to that of $\overleftarrow{k}$ and thus gives evidence in favor of the above-mentioned view.

A similar result is also obtained for the T–T bimolecular annihilation process: when the values of k_2 and k_2' described before are compared with twice the diffusion-controlled rate constant k_{dif} evaluated from Eq. (11), it can be seen that k_2 and k_2' are about seven-tenths as large as $2k_{dif}$. This factor 0.7 corresponds to the parameter α given in Eq. (10), and is comparable to the values of α shown in Table 1.