BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2732—2739 (1970)

Studies on Triplet Energy Transfer by Means of an Emission-Absorption Flash Technique. I. Reversible Energy Transfer between Xanthene Dyes and Anthracenes

Koichi Kikuchi, Hiroshi Kokubun and Masao Koizumi

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

(Received March 24, 1970)

Choosing eosin and erythrosin as donor and anthracene and 9-methylanthracene as acceptor, we have kinetically investigated the triplet energy transfer process by flash technique involving emission measurement. In these systems the differences of T-levels of donor and acceptor are of the order of kT at most, and it was anticipated that a reversible energy transfer would occur. It has been established that it actually occurs in eosin-anthracene and erythrosin-anthracene, and very likely occurs in erythrosin-9-methylanthracene. Furthermore, it has been found that in the first two systems the energy transfer rate for the process, donor→acceptor is about half that for the process, acceptor→donor. This means that the rate in the present systems is determined by some other factor than the triplet level. Discussions have been given on the model for energy transfer.

According to Parker *et al.*,[1] triplet energy transfer between some dyes and aromatic hydrocarbons gives rise to various types of delayed fluorescence. Their observations, however, were qualitative in nature. By a flash apparatus modified so as to measure the emission as well as absorption,[2] the present authors made a quantitative study on the reversible energy transfer between eosin and anthracene.[3] We could demonstrate that an equilibrium, $D^T+A \rightleftarrows D+A^T$ practically holds between donor and acceptor.

The result of our studies will contribute to our knowledge concerning the efficiency of the triplet energy transfer. It is often assumed that when the transfer is highly exothermic its rate is diffusion-controlled.[4,5] But when the triplet levels of donor and acceptor are close to each other the rate becomes slower; Bäckström and Sandros proposed that in endothermic transfer the rate is governed by an exponential factor $\exp(-\Delta E)$, where ΔE is an endothermic energy.[5] Recent work has raised some criticism on the condition for diffusion controlled energy transfer.[6] It has been suggested that the energy transfer in less viscous solvents competes with the diffusion apart of donor and acceptor, which makes the energy transfer rate appreciably slower than the diffusion rate.[7] Such a suggestion has been made chiefly on the basis of the viscosity dependence of the bimolecular rate constant between quencher and triplet molecule. It may be expected that clearer understanding will be obtained by comparing the forward and backward energy transfer rates of a reversible system, for which the encounter rate is practically the same for forward and backward processes. Furthermore, such studies will enable us to examine experimentally whether and how the transfer efficiency is influenced by other factors than the triplet levels of donor and acceptor.

The object of the present paper is to describe the details on the reversible energy transfer be-

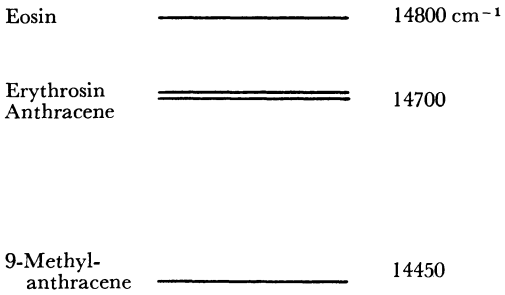


Fig. 1. Triplet energy levels.

---

[1] C. A. Parker, C. G. Hatchard and T. A. Joyce, *Nature*, **205**, 1285 (1965).

[2] K. Kikuchi, H. Kokubun and M. Koizumi, *Photochem. Photobiol.*, **7**, 499 (1968); This Bulletin, **41**, 1545 (1968).

[3] K. Kikuchi, H. Kokubun and M. Koizumi, *Z. Physik. Chem. N. F.*, **62**, 75 (1968).

[4] A. D. Osborne and G. Porter, *Proc. Roy. Soc.* (London), **A284**, 9 (1965). W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

[5] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **16**, 958 (1962).

[6] S. Nordin and R. L. Strong, *Chem. Phys. Lett.*, **2**, 429 (1968).

[7] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

tween eosin and anthracene which has already been communicated briefly,[3] and to extend a similar study to the systems, erythrosin-anthracene eosin-9-methylanthracene and erythrosin-9-methylanthracene, all in ethanol.

The triplet levels of these substances are very close to each other[8] as shown in Fig. 1; in particular, the levels of erythrosin and anthracene are almost the same.

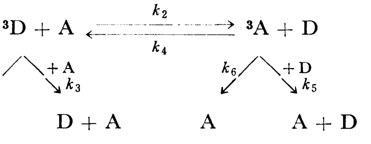
Experimental

Materials. 9-Methylanthracene of K & K Lab., Inc. was subjected to zone-melting and recrystallized from ethanol. G. R. grade ethanol of Wakojunyaku was used without further purification. Other substances were purified by standard methods.

Apparatus and Procedures. Essentially the same as has been described.[2]

Results

The elementary processes related with the energy transfer are those involved in the scheme



in which D is a xanthene dye and A, anthracene. The differential equations to be solved are

$$-\frac{d[^3D]}{dt} = \{k_1+(k_2+k_3)[A]\}[^3D] - k_4[D][^3A] \quad (1)$$

$$-\frac{d[^3A]}{dt} = \{k_6+(k_4+k_5)[D]\}[^3A] - k_2[A][^3D] \quad (2)$$

When the dyes as donor are excited exclusively by means of a suitable filter, the initial condition is put as

$$[^3D] = [^3D]_0 \qquad [^3A] = 0$$

In the early stage of the decay, the above equations are written as follows with a good approximation, since most donor molecules are in the triplet state and the concentration of triplet acceptor is small.

$$-\frac{d[^3D]}{dt} = \{k_1 + (k_2 + k_3)[A]\}[^3D] \quad (3)$$

$$\frac{d[^3A]}{dt} = k_2[A][^3D]$$

Thus the rate constant of ^3D-decay is given by $k_1+(k_2+k_3)$ [A]. In order to keep such a situation for a long time, the concentrations of donor and acceptor should be made as low as possible. Of course the later stage under such a condition is not observable on account of very low concentrations of ^3D.

In order to study the later stage, higher concentrations of donor and acceptor must be used. In the later stage where the concentrations of donor and acceptor are approximately constant, the solution of (1) and (2) are expressed as the sum of two exponential terms in which the exponents of the two terms are given correctly as follows.

$$\beta_{\substack{1\\2}} = \frac{1}{2}\{k_1 + (k_2 + k_3)[A] + k_6 + (k_4 + k_5)[D]\}$$
$$\pm \frac{1}{2}[\{k_1 + (k_2 + k_3)[A] - k_6 - (k_4 + k_5)[D]\}^2$$
$$+ 4k_2k_4[A][D]]^{1/2} \quad (4)$$

But one terms with an exponent β_1 can safely be neglected and the exponent β_2 $(=\beta)$ for the remaining term is approximated as

$$\beta = \frac{k_2[A]\{k_6 + k_5[D]\} + k_4[D]\{k_1 + k_3[A]\}}{k_2[A] + k_4[D]} \quad (5)$$

if

$$k_2[A] > k_3[A] + k_1 \qquad k_4[D] > k_5[D] + k_6 \quad (6)$$

Furthermore the relation

$$[^3A]/[^3D] \simeq k_2[A]/k_4[D] \quad (7)$$

holds which shows the existence of equilibrium, $^3D + A \rightleftarrows D + {}^3A$. Although an attempt to give exact criterion for the above two extremes was not made, the two extremes could be distinguished by the linear relations in the log$[^3D]$ *vs.* t plot and with quite different slopes.

It will be seen that relations (5) and (7) really hold in the case of eosin-anthracene and erythrosin-anthracene, and approximately in erythrosin-9-methylanthracene but not in eosin-9-methylanthracene.

Eosin-anthracene. The dependence of the decay curves of eosin at low concentrations (1.0×10^{-6}, 5×10^{-7} M) upon the concentration of anthracene was studied. The observed first order rate constants are plotted against the anthracene

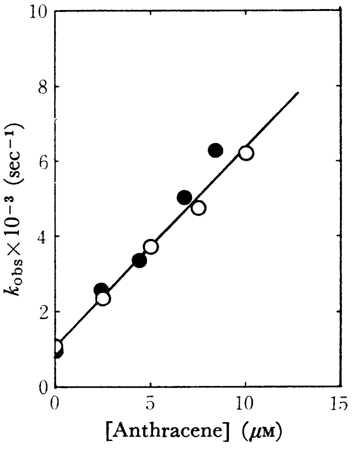


Fig. 2. Effect of anthracene concentration on the first-order rate constant of triplet eosin.
○ [Eosin]$=1\times10^{-6}$ M ● [Eosin]$=5\times10^{-7}$ M

---

[8] K. Gollnick, "Advances in Photochemistry," Vol. VI, ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Wiley (Interscience), New York (1968), p. 40.

concentration in Fig. 2. From the plot one obtains

$$k_2+k_3=(5.1\pm 0.5)\times 10^8\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1} \qquad (8)$$

In a similar way the dependence of the decay constant of triplet anthracene on [eosin] was studied. The result is shown in Fig. 3. As is expected, the slopes in the initial stage are linear but decrease remarkably in the later stage. The dependence of the observed first order rate constant on [eosin] is given in Fig. 4. From the slope we get

$$k_4+k_5=(1.2\pm 0.2)\times 10^9\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

Figure 5 gives the decay curves of triplet eosin[*1] for 10^{-5} M eosin at various concentrations of anthracene. It is seen that the slopes are almost independent of the anthracene concentrations.

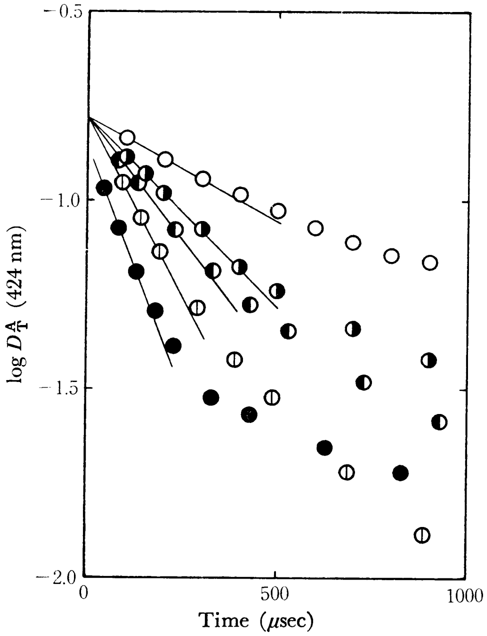


Fig. 3. Effect of eosin concentration on the decay curve of triplet anthracene.
[Anthracene] $=2\times10^{-6}$ M
[Eosin]: ○ 0 M ⦶ 2.7×10^{-7} M
◑ 5×10^{-7} M ● 5.8×10^{-6} M
◐ 1.2×10^{-6} M

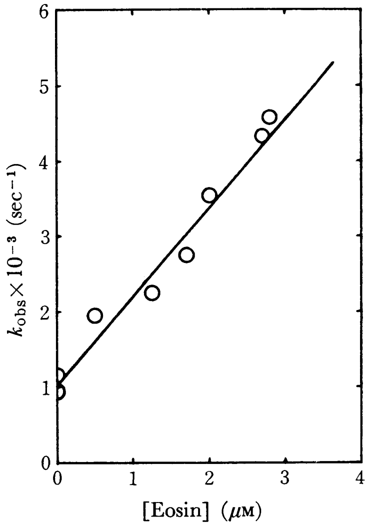


Fig. 4. Effect of eosin concentration on the first-order rate constant of triplet anthracene.
[Anthracene] $=2\times10^{-6}$ M.

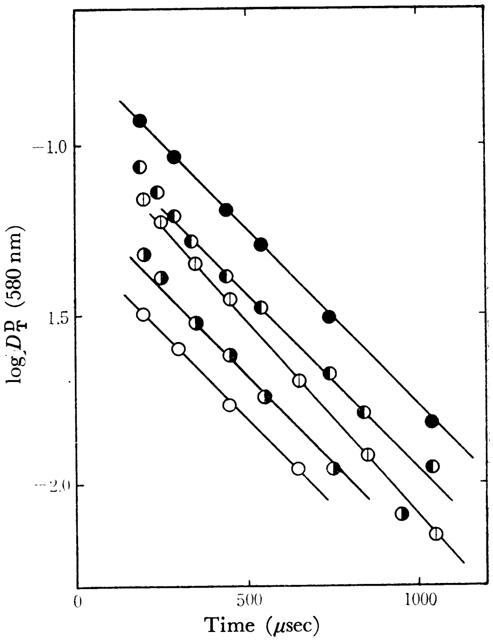


Fig. 5. Effect of anthracene concentration on the decay curve of triplet eosin.
[Eosin] $=1\times10^{-5}$ M
[Anthracene]: ● 0 M ◑ 2×10^{-5} M
◐ 5×10^{-6} M ○ 4×10^{-5} M
⦶ 1×10^{-5} M

The decay of triplet anthracene in this case can be studied either by its triplet-triplet absorption or by the intensity of the delayed fluorescence. The latter is related to the former by the relation, $I_{\mathrm{DF}}^{\mathrm{A}}=\alpha\phi_{\mathrm{F}}pk_{\mathrm{TT}}^{\mathrm{A}}[D_{\mathrm{T}}^{\mathrm{A}}/\varepsilon]^2$ ($I_{\mathrm{DF}}^{\mathrm{A}}$, intensity of the anthracene delayed fluorescence; α, experimental parameter; ϕ_{F}, fluorescence quantum yield; p, efficiency for the formation of singlet excited state. Other constants are the usual ones). In the present case, the latter method is more suitable because the anthracene T-T absorption is superposed by the absorption of eosin semiquinone[9] which is produced by a reaction between triplet eosin and alcohol. The relations between coexisting triplet eosin and triplet anthracene are

---

[*1] Decay curves are shown by the log $D_{\mathrm{T}}^{\mathrm{D}}$ *vs. t* plots, where D is the optical density and, suffixes D, T mean donor and triplet.

9) A. Kira and S. Kato, *Sci. Rep. of Tohoku Univ., Ser.* 1, **48**, 142 (1965).

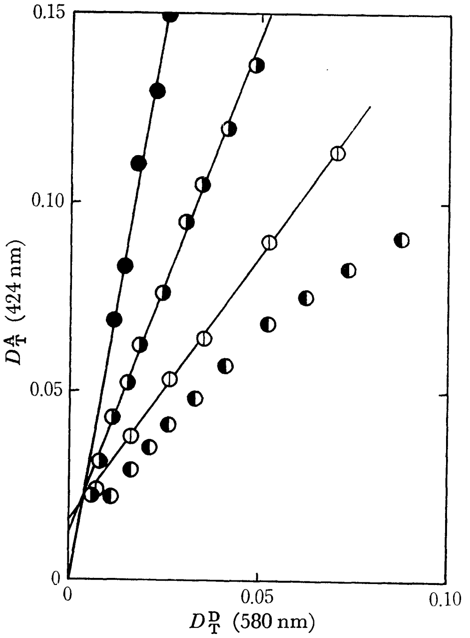


Fig. 6a. Relationship between triplet-triplet absorption of eosin and of anthracene.
[Eosin] = 1×10^{-5} M
[Anthracene]: ◐ 5×10^{-6} M ◑ 2×10^{-5} M
○ 1×10^{-5} M ● 4×10^{-5} M

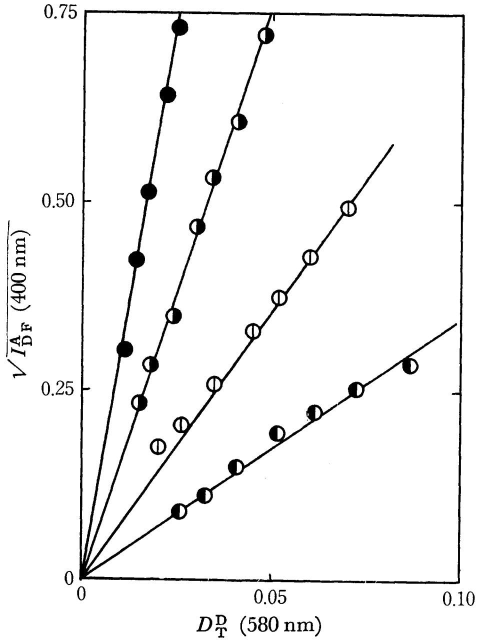


Fig. 6b. Relationship between triplet-triplet absorption of eosin and delayed fluorescence of anthracene.
[Eosin] = 1×10^{-5} M
[Anthracene]: ◐ 5×10^{-6} M ◑ 2×10^{-5} M
⦶ 1×10^{-5} M ● 4×10^{-5} M

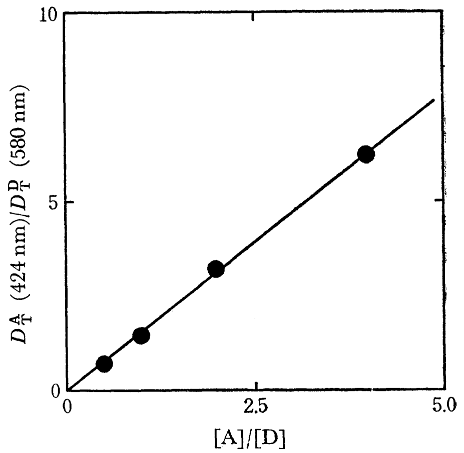


Fig. 7. Proof of the existence of equilibrium.
^{3}D + A $\rightleftarrows$ D + ^{3}A, [D] = 1×10^{-5} M

given in Figs. 6a, b and 7. It is clearly seen that a linear relation holds more satisfactorily between $\sqrt{I^{\rm A}_{\rm DF}}$ and $D^{\rm D}_{\rm T}$ than between $D^{\rm A}_{\rm T}$ and $D^{\rm D}_{\rm T}$. This, as stated above, is due to the superposition of the absorption from eosin semiquinone over the triplet anthracene absorption. Such situations are frequently encountered in the study of the behavior of the triplet state. Mixed T-T annihilation is another point to be noted. Although a mixed T-T annihilation ^{3}D+^{3}A→A*+D does not occur in the present system, another type, ^{3}D+^{3}A→D*+A does occur; this however does not prohibit the usage of delayed fluorescence intensity of anthracene as a measure of its triplet concentration. If the former were to occur, $I^{\rm A}_{\rm DF}$ would not simply represent the concentration of triplet anthracene. The linear relation between $D^{\rm A}_{\rm T}/D^{\rm D}_{\rm T}$ and [A]/[D] shown in Fig. 7 is nothing but the one expected from the existence of equilibrium, ^{3}D+A$\rightleftarrows$D+^{3}A. Using the values of molecular extinction coefficient of ^{3}D and ^{3}A, the value of k_2/k_4 is evaluated to be 0.40*2+0.05.

The above result, however, is not enough to verify the existence of the equilibrium in question; it must be shown that the relation $k_2[{\rm A}]$, $k_4[{\rm D}] \gg k_1+k_3[{\rm A}]$, $k_6+k_5[{\rm D}]$ really holds. The values of k_3 and k_5 can be estimated as follows. Putting

$$k_2[{\rm A}]/(k_2[{\rm A}]+k_4[{\rm D}]) = f \tag{9}$$

one can transform eq. (5) as follows.

$$\beta = f(k_6+k_5[{\rm D}]) + (1-f)(k_1+k_3[{\rm A}]) \tag{10}$$

Hence

$$\beta - k_1 = f\{k_6 - k_1 + (k_5 + k_4k_3/k_2)[{\rm D}]\} \tag{11}$$

It was experimentally found that β is practically equal to k_1, independent of [A]. One can use this result to estimate the values of k_3 and k_5 as follows. The right side of eq. (11) should be less

---

[*2] The value reported in Ref. 2 should be corrected.

than $0.1\times k_1$, if one assumes the experimental error for the decay constant as *ca.* 10%. Thus

$$-2\times10^2 < f\{(k_6-k_1) + (k_5+k_3k_4/k_2)[\mathrm{D}]\} < 2\times10^2 \qquad (12)$$

Inserting the value of $k_2/k_4=0.40$ and the values of [A] and [D] into Eq. (9), f is found to change from zero to 0.54 and further from Eq. (12) one obtains the following relation.

$$1.2\times10^8 < k_5 + 2.5\,k_3 < 1.9\times10^8$$

From this, we get

$$k_5 < 1.9\times10^8 \qquad k_3 < 7.6\times10^7$$

In the case that $k_3=k_5$, we have $3.5\times10^7<k_3=k_5<5.5\times10^7$ Thus the values of k_3 and k_5 are estimated to be at most less than 10% of k_2 and k_4 respectively. The values of (k_2+k_3) and (k_4+k_5) then give $k_2/k_4\approx0.4$ which agrees satisfactorily with the one already described.

Erythrosin-anthracene. This system is particularly interesting because the triplet levels of donor and acceptor are almost the same. Similar experiments as in eosin-anthracene system were performed. Figure 8 shows the dependence of the decay constant of triplet erythrosin, k_{obs} upon [anthracene] at [erythrosin] = 1.0×10^{-6} M. From the slope we get,

$$k_2 + k_3 = (7.3\pm1.0)\times10^8\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

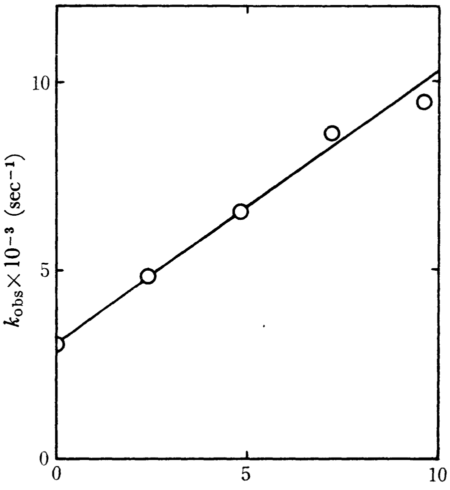


Fig. 8. Effect of anthracene concentration on the first-order rate constant of triplet erythrosin. [Erythrosin] = 1×10^{-6} M

From the dependence of ^{3}A decay on [erythrosin] at low anthracene and erythrosin concentrations, we obtain $k_4+k_5=(1.7+0.2)\times10^9\,\mathrm{M}^{-1}\mathrm{sec}^{-1}$. Putting $k_2/k_4=0.45$ (see below) and $|\beta-k_1|=0.1\,k_1$ we obtain the following relation by similar reasoning as performed for eosin

$$-5\times10^2 < 0.6\{-4.7\times10^3 + (k_5+5.5k_3)10^{-5}\} < 5\times10^2$$

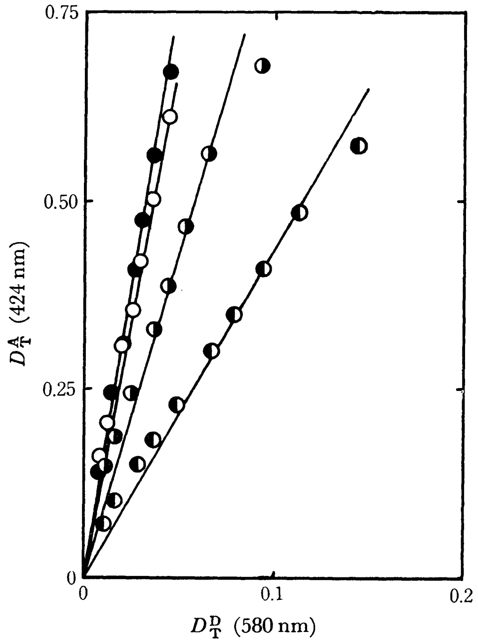


Fig. 9a. Relationship between triplet-triplet absorption of erythrosin and of anthracene.
[Erythrosin] = 1×10^{-5} M
[Anthracene]: ◐ 3×10^{-6} M ○ 9×10^{-6} M
◑ 6×10^{-6} M ● 1.2×10^{-5}

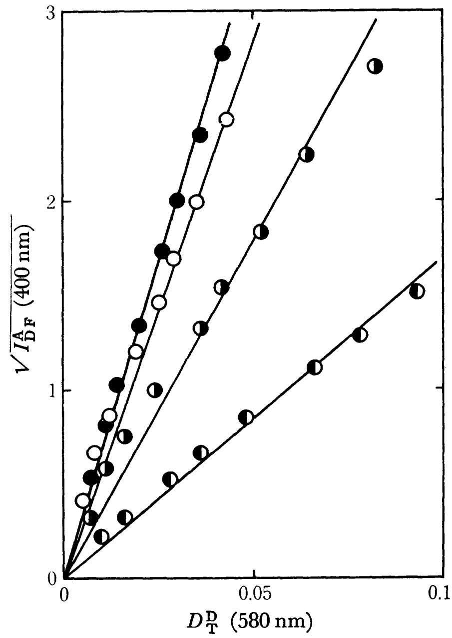


Fig. 9b. Relationship between triplet-triplet absorption of erythrosin and delayed fluresecence of anthracene.
[Erythrosin] = 1×10^{-5} M
[Anthracene]: ◐ 3×10^{-6} M ○ 9×10^{-6} M
◑ 6×10^{-6} M ● 1.2×10^{-5} M

The results obtained are summarized as follows.

$$k_5 < 5.3 \times 10^8 \qquad k_3 < 2.5 \times 10^8$$

In the case $k_5 = k_3$, we have

$$1.2 \times 10^8 < k_5 = k_3 < 1.8 \times 10^8$$

In the system the values of k_3 and k_4 are 30% of the values of k_2 and k_4, respectively at most.

At 1.0×10^{-5} M of erythrosin, the $\log D_T^D$ *vs.* t plots in the later stage give almost the same slope from [anthracene]=0 to 12.0×10^{-5} M. The relation between the coexisting ^{3}D and ^{3}A in the later stage are given in Figs. 9 and 10.

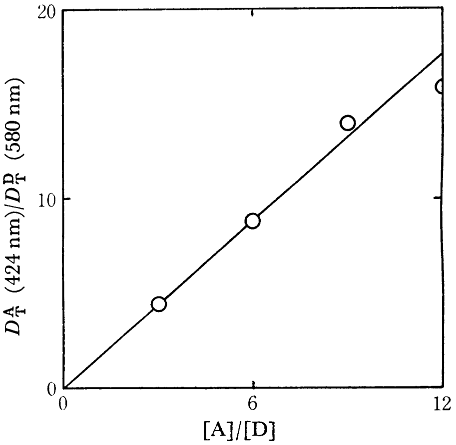


Fig. 10. Proof of the existence of equilibrium. $^3\text{D} + \text{A} \rightleftarrows \text{D} + {}^3\text{A}$, [D]$=2.6 \times 10^{-5}$ M

It is seen that quite a similar relation to that in the case of eosin (Figs. 6 and 7) holds. It is to be noted that a good linear relation in Fig. 9a suggests that there is scarcely any absorption of intermediate such as semiquinone in the region of T-T absorption of anthracene. The value of k_2/k_3 was evaluated to be 0.45+0.05.

Erythrosin-9-methylanthracene. It is expected that the quasi-equilibrium $^3\text{D}+\text{A} \rightleftarrows \text{D}+{}^3\text{A}$ is more difficult to hold in this case than in the former two cases, because the difference of triplet levels of donor and acceptor is more than twice as large as that of eosin and anthracene and the decay constant of triplet erythrosin is also about two times larger than that of eosin. Figure 11 gives the plot of decay constant of triplet erythrosin, k_{obs} against [9-methylanthracene] at low [erythrosin]. From the slope, we get

$$k_2 + k_3 = 2.2 \pm 0.4 \times 10^9 \text{M}^{-1}\text{sec}^{-1} \tag{12}$$

From a similar experiment for the triplet 9-methylanthracene, we have

$$k_4 + k_5 = (3.3 \pm 0.3) \times 10^8 \text{M}^{-1}\text{sec}^{-1} \tag{13}$$

At higher concentrations of erythrosin (2.6×10^{-5} M), the plots of $\log D_T^D$ *vs.* t at various acceptor concentrations, give about the same slopes as in the previous two cases. Figure 12 gives the relation between the triplet absorbance of erythrosin

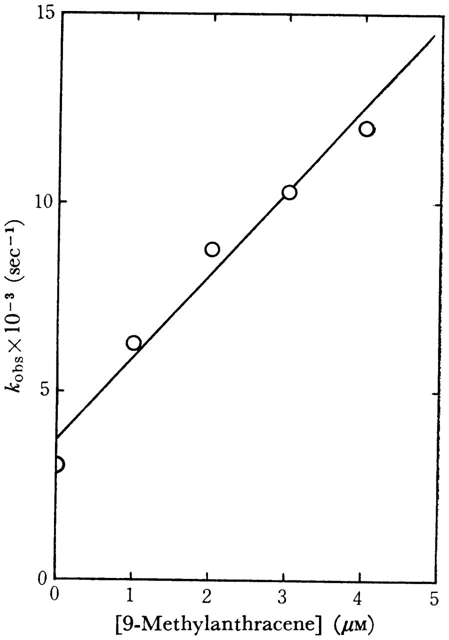


Fig. 11. Effect of 9-methylanthracene concentration on the first-order rate constant of triplet erythrosin.
[Erythrosin]$=1 \times 10^{-6}$ M

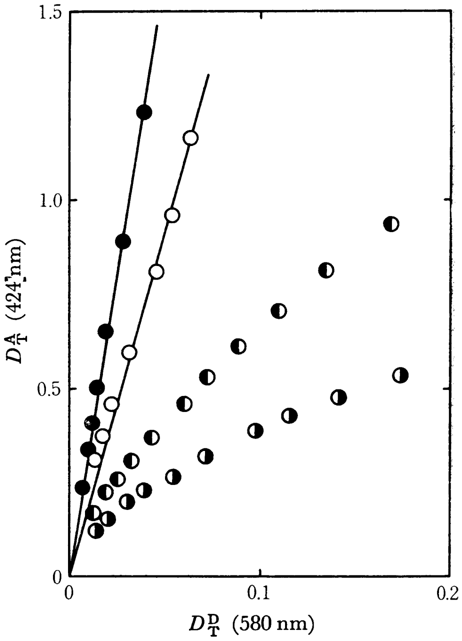


Fig. 12. Relationship between triplet-triplet absorption of erythrosin and of 9-methylanthracene.
[Erythrosin]$=2.6 \times 10^{-5}$ M
[9-Methylanthracene]: ◑ 4.7×10^{-6} M
◐ 9.5×10^{-6} M
○ 1.9×10^{-5} M
● 3.8×10^{-5} M

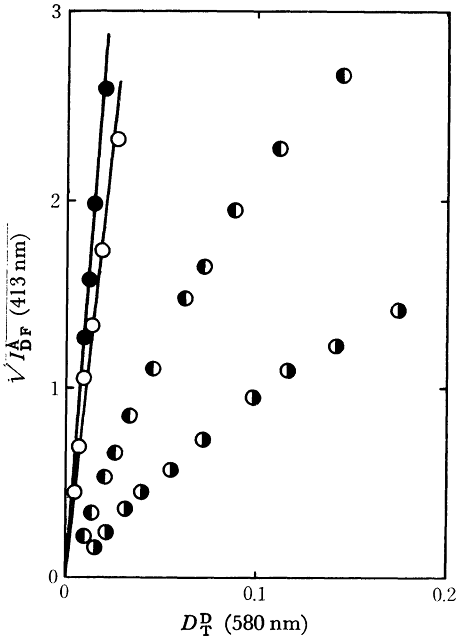


Fig. 13. Relationship between triplet-triplet absorption of erythrosin and delayed fluorescence of 9-methylanthracene.
[Erythrosin] = 2.6×10^{-5} M
[9-Methylanthracene]: ◑ 4.7×10^{-6} M
◐ 9.5×10^{-6} M
○ 1.9×10^{-5} M
● 3.8×10^{-5} M

and 9-methylanthracene and Fig. 13, the relation between the delayed fluorescence of 9-methylanthracene and triplet erythrosin. It is seen that the linear relation holds approximately in both cases, suggesting the existence of quasi-equilibrium. However, the upper limits estimated for k_3 and k_5 are, respectively, 2.1×10^9 and 3.3×10^8 which are comparable with the values of (k_2+k_3) and (k_4+k_5). Hence it is somewhat doubtful that the approximate equilibrium in question really holds.

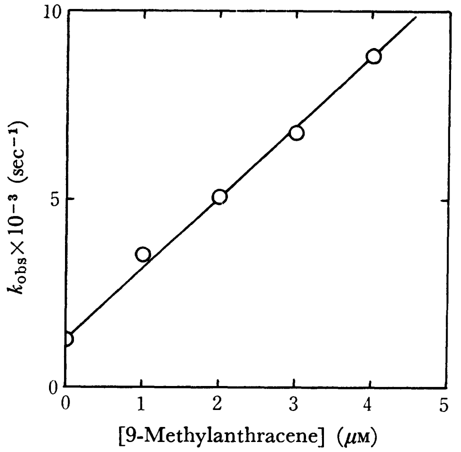


Fig. 14. Effect of 9-methylanthracene concentration on the first-order rate constant of triplet eosin.
[Eosin] = 2×10^{-6} M

Eosin-9-methylanthracene. Since the difference in triplet levels of donor and acceptor is still larger than that for erythrosin-9-methylanthracene, it is expected that the quasi-equilibrium does not hold in this case. In fact, the existence of triplet eosin could not be observed at high concentration of donor and acceptor. From the plot of decay constant of triplet eosin, k_{obs} against [9-methylanthracene] at low [eosin](2.0×10^{-6}), we obtain $k_2+k_3=(1.9+0.2)\times 10^9$ M^{-1} sec^{-1} and from a similar experiment for the decay of 9-methylanthracene $k_4+k_5=(2.1+0.4)\times 10^8$ M^{-1} sec^{-1}.

All the rate constants evaluated in the present paper are summarized in Table 1.

Discussion

In the present work it has been fully established that a quasi-equilibrium, $^3D+A\rightleftarrows D+{}^3A$ holds in eosin-anthracene and erythrosin-anthracene. It is well known that Bäckström and Sandros[5] found the reversible energy transfer between donor and acceptor with triplet levels close together. But they did not observe the establishment of a relation $[^3A]/[^3D]=\text{const}\cdot[A]/[D]$, as shown in the present paper. Besides, the present study demonstrates definitely that the rate constant for $^3D+A\rightarrow D+{}^3A$ (k_2) is smaller than that for the reverse transfer (k_4). Thus in erythrosin-anthracene where $\Delta E\sim 0$, and in eosin-anthracene

TABLE 1. RATE CONSTANTS FOR ELEMENTARY REACTIONS INVOLVED IN ENERGY TRANSFER

	Eosin Anthracene	Erythrosin Anthracene	Erythrosin 9-Methylanthracene	Eosin 9-Methylanthracene
k_1 (sec^{-1})	$(2.4\pm 0.3)\times 10^3$	$(5.5\pm 0.5)\times 10^3$	$(5.5\pm 0.5)\times 10^3$	$(2.4\pm 0.3)\times 10^3$
k_2+k_3 (M^{-1} sec^{-1})	$(5.1\pm 0.5)\times 10^8$	$(7.3\pm 1.0)\times 10^8$	$(2.2\pm 0.4)\times 10^9$	$(1.9\pm 0.2)\times 10^9$
k_4+k_5 (M^{-1} sec^{-1})	$(1.2\pm 0.2)\times 10^9$	$(1.7\pm 0.2)\times 10^9$	$(3.3\pm 0.3)\times 10^8$	$(2.1\pm 0.4)\times 10^8$
k_6 (sec^{-1})	$(7.6\pm 1.0)\times 10^2$	$(7.6\pm 1.0)\times 10^2$	$(2.5\times 0.5)\times 10^2$	$(2.5\pm 0.5)\times 10^2$
k_3 (M^{-1} sec^{-1})	$<7.6\times 10^7$	$<2.5\times 10^8$	$<2.1\times 10^9$	—
k_5 (M^{-1} sec^{-1})	$<1.9\times 10^8$	$<5.3\times 10^8$	$<3.3\times 10^8$	—
k_2/k_4	0.40 ± 0.05	0.45 ± 0.05	6.4 ± 0.7	—
$(k_2+k_3)/(k_4+k_5)$	0.43 ± 0.10	0.43 ± 0.10	6.7 ± 1.0	—

where donor triplet level is 100 cm^{-1} higher than that of acceptor, the k_2-values are about twice as small as the k_4-values. This implies that for the system where $\Delta E \lessgtr kT$, ΔE is not the only important factor for determining the transfer efficiency.

For interpreting the present results, it is helpful to refer to the results and the interpretations of other workers on the related phenomena. For the system in which the reversible energy transfer occurs, Sandros[5)] proposed that the encounter complex is formed with a diffusion controlled rate and that the probability for the forward and backward energy transfer is determined only by the energy difference between ^{3}D and ^{3}A. Thus they inferred that the rate constant for endothermic transfer is essentially determined by a factor $e^{-\Delta E/RT}$ where $\Delta E = E(^3\mathrm{D}) - E(^3\mathrm{A})$. The same assertion was made also by Stevens and Walker.[10)] Wagner,[7)] on the other hand, studied the system in which energy transfer is irreversible and obtained results which lead to the conclusion that the transfer efficiency can be much smaller than the diffusion-controlled one, on account of the competition between the transfer process and the diffusion apart of ^{3}D and A. Richtol and Belorit[11)] and also Borkman and Kearns[12)] studied the irreversible energy transfer and found that the $^3\mathrm{D}+\mathrm{A}\rightarrow\mathrm{D}+\mathrm{A}$ process occurs to some extent. Both groups proposed the following scheme where (^{3}D···A) is an encounter complex.

$$\begin{tikzcd} {}^3\mathrm{D} + \mathrm{A} \arrow[r, shift left] & ({}^3\mathrm{D}\cdots\mathrm{A}) \arrow[l, shift left] \arrow[r] \arrow[d] & \mathrm{D} + {}^3\mathrm{A} \\ & \mathrm{D} + \mathrm{A} & \end{tikzcd}$$

Their conclusion is similar to Wagner's in that the overall rate constants for energy transfer and energy dissipation are small on account of the backward reaction $(^3\mathrm{D}\cdots\mathrm{A})\rightarrow{}^3\mathrm{D}+\mathrm{A}$.

In view of all the previous results, it is quite reasonable to assume the following scheme for the present system.

$$\begin{tikzcd} {}^3\mathrm{D} + \mathrm{A} \arrow[r, shift left, "k'_{\mathrm{DI}}"] & {}^3(\mathrm{D}\cdots\mathrm{A}) \arrow[l, shift left, "k'_{\mathrm{ID}}"] \arrow[r, shift left, "k'_{\mathrm{IA}}"] \arrow[d, "k'_d"] & \mathrm{D} + {}^3\mathrm{A} \arrow[l, shift left, "k'_{\mathrm{AI}}"] \\ & \mathrm{D} + \mathrm{A} & \end{tikzcd}$$

In this scheme, ^{3}(D···A) is an intermediate (I) with perhaps a specific configuration by way of which the forward and backward energy transfer ($^3\mathrm{D}+\mathrm{A}\rightarrow\mathrm{D}+{}^3\mathrm{A}$ and $\mathrm{D}+{}^3\mathrm{A}\rightarrow{}^3\mathrm{D}+\mathrm{A}$) and also the energy dissipation process ($^3\mathrm{D}+\mathrm{A}\rightarrow\mathrm{D}+\mathrm{A}$, $^3\mathrm{A}+\mathrm{D}\rightarrow\mathrm{A}+\mathrm{D}$) can occur.[*3]

As to the interchange between I and the encounter complex, two typical models are to be discriminated. The first is a model in which the intermediate is very easy to reach from the encounter state, (^{3}D···A) and (D···^{3}A). In this case the forward and backward energy transfer is repeated and a certain equilibrium state is realized during the encounter state. If one assumes that the encounter rate k_e controlled by diffusion is the same for forward and backward reactions, k_2 and k_4 can be written as

$$k_2 = k_e k_{\mathrm{IA}}/(k_{\mathrm{IA}} + k_{\mathrm{ID}} + k_d)$$
$$k_4 = k_e k_{\mathrm{ID}}/(k_{\mathrm{IA}} + k_{\mathrm{ID}} + k_d)$$

where k_{IA} and k_{ID} is the rate constant for processes $\mathrm{I}\rightarrow(\mathrm{D}\cdots{}^3\mathrm{A})$ and $\mathrm{I}\rightarrow({}^3\mathrm{D}\cdots\mathrm{A})$, respectively. Then the equilibrium constant $K=k_2/k_4$ is reduced to $k_{\mathrm{IA}}/k_{\mathrm{ID}}$ and this reflects the equilibrium state in the encounter complex. It should be added that this model requires $k_3 \approx k_5$.

The second is a model in which the intermediate is difficult to reach from the encounter state and only a small fraction α_f and α_r, respectively of (^{3}D···A) and of (D···^{3}A) goes to the ^{3}(A···D) state. In this case, k_2 and k_4 are written, respectively as follows.

$$k_2 = k_e \alpha_f k_{\mathrm{IA}}/(k_{\mathrm{IA}} + k_{\mathrm{ID}} + k_d)$$
$$k_4 = k_e \alpha_r k_{\mathrm{ID}}/(k_{\mathrm{IA}} + k_{\mathrm{ID}} + k_d)$$

Thus the equilibrium constant $K=k_2/k_4$ depends not only on $k_{\mathrm{IA}}/k_{\mathrm{ID}}$ but also on α_f/α_r. k_3/k_5 is then expected to be equal to α_f/α_r. If this model fits the truth, the result $k_2/k_4 < 1$ suggests that the intermediate has a configuration closely resembling that of an encounter compex (D···^{3}A) because the value of k_2/k_4 depends most likely on α_f/α_r much more than $k_{\mathrm{IA}}/k_{\mathrm{ID}}$.

Of the two models described above, the first appears to interpret the present results better than the second. Thus according to the first model, the sum of (k_2+k_3) and (k_4+k_5) should be the diffusion rate constants, and the experimental values are really very near them.

Apart from the argument as to which model is more suitable, it should be noted that the equilibrium state in the present system, contrary to Sandros' system,[5)] is not determined only by an energy factor. As a possible factor, an overlap integral $\int^{\infty} f_{\mathrm{D}}(\nu)\varepsilon(\nu)\,\mathrm{d}\nu$ involved in Dexter's theory[13)] is conceivable. Since the longest absorption band of donor is located in the longer wavelength region than that of acceptor, this factor is expected to be favorable to k_{ID} than k_{IA}, resulting in a larger k_4 than k_2 according to the first model.

One of the authors (H.K.) wishes to thank Matsunaga Science Foundation for financial support.

[10)] B. Stevens and M. S. Walker, *Proc. Chem. Soc.*, **1964**, 26, 109.

[11)] H. H. Richtol and A. Belorit, *J. Chem. Phys.*, **45**, 35 (1966).

[12)] R. H. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

[*3] It is possible that the forward and backward reaction occurs via a different intermediate state. Even in this case the conclusions for $K=k_2/k_4$ described below will be essentially the same.

[13)] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).