

## DETERMINATION OF THE S\*-T TRANSITION PROBABILITIES OF SOME ACRIDINE DYES AND OF THIOPYRONINE BY THE METHOD OF SENSITIZED DELAYED FLUORESCENCE

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(Received September 12, 1980; in revised form November 10, 1980)

### Summary

Parker's method of delayed fluorescence as a means of determining the S\*-T transition probability  $\Phi_{ST}$  was extended to systems in which reversible triplet energy transfer occurs between donor and acceptor. The  $\Phi_{ST}$  values of proflavine, acriflavine and acridine orange in ethanol were determined by this extended method using anthracene or 9-methylanthracene as an acceptor and eosine as a reference donor. The  $\Phi_{ST}$  values thus obtained are  $0.45 \pm 0.05$  (proflavine),  $0.53 \pm 0.07$  (acriflavine) and  $0.30 \pm 0.05$  (acridine orange).

The  $\Phi_{ST}$  values of eosine and thiopyronine were also determined by the method in Parker's original form using perylene as an acceptor and erythrosine as a reference donor. The  $\Phi_{ST}$  values obtained,  $0.44 \pm 0.01$  (eosine) and  $0.24$  (thiopyronine), agree satisfactorily with those obtained by a chemical method,  $0.43 \pm 0.04$  (eosine) and  $0.28 \pm 0.03$  (thiopyronine).

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### 1. Introduction

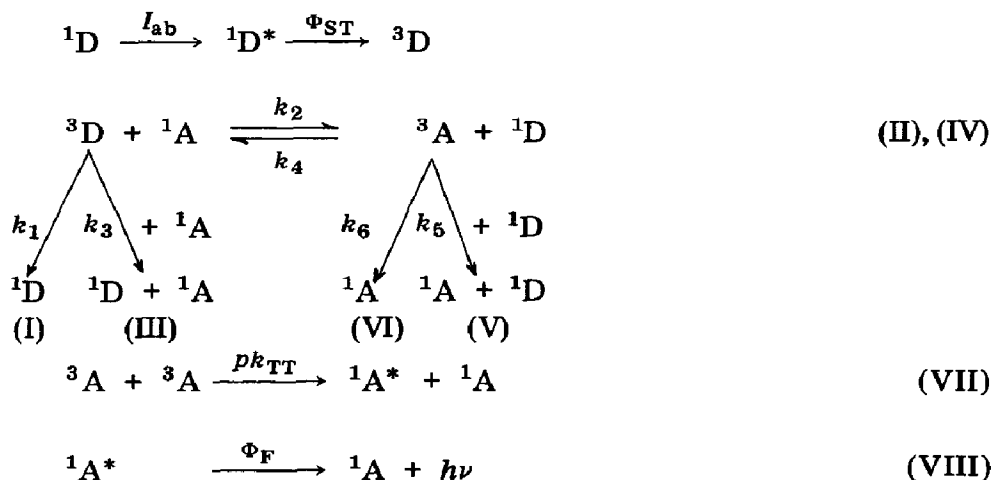
Determination of the S\*-T transition probability  $\Phi_{ST}$  is required for a quantitative interpretation of studies of photobiological effects, solar energy conversion, photochemical organic synthesis and so on. Parker [1 - 3] has developed a method of delayed fluorescence to determine the  $\Phi_{ST}$  values of some aromatic hydrocarbons. This method is considered to be particularly

useful for determining the  $\Phi_{ST}$  values of donor dyes (D) in alcohol if suitable aromatic hydrocarbons with triplet levels lower than those of the dyes are available as acceptors (A). It is rather easy to find such acceptors for which the fluorescence spectra are located in the wavelength region where donors do not absorb, because the longest wavelength absorption bands of many dyes, being located in the visible region, are far apart from those of hydrocarbons and the S\*-T separations of hydrocarbons are larger than those of dyes.

This work was carried out with two aims in mind. One is to show the simplicity and excellence of Parker's method by comparing the  $\Phi_{ST}$  values obtained by this method with those determined by a chemical method in which the quantum yields of photoreduction of dyes with and without sensitization are compared [4]. For this purpose eosine, erythrosine and thiopyronine are used as donors and perylene is used as an acceptor. The  $\Phi_{ST}$  values for eosine and erythrosine have been determined previously by the chemical method [4] and a similar experiment for thiopyronine will be carried out in this work. The second aim is to extend this method to a system in which the donor and acceptor have almost the same triplet levels. Perylene, for example, cannot be used as a convenient acceptor for acridine dyes because acridine dyes have absorption bands located close to the fluorescence spectrum of perylene. Anthracene is a suitable acceptor in this respect but its triplet level is very close to those of the xanthene dyes which are available at present as the reference donor.

Parker has demonstrated the usefulness of his method as long as the donor triplet level is much higher than that of the acceptor. Here the more general case, in which reversible energy transfer occurs [5, 6], will be treated. The relation obtained will be reduced to Parker's as a special case.

The processes involved are summarized in the following scheme (Scheme A) where D and A are, for instance, eosine ( $E_T = 14\,900\text{ cm}^{-1}$  [7]) and anthracene ( $E_T = 14\,700\text{ cm}^{-1}$  [7]) respectively:



Scheme A.

$I_{ab}$  denotes the light quanta absorbed by D,  $\Phi_{ST}$  is the S\*-T transition probability of D,  $\Phi_F$  is the fluorescence quantum yield of A and  $p$  is the probability of the T-T annihilation reaction to produce  $^1A^*$ ;  $k_j$  is the rate constant of reaction  $j$ . Under steady state illumination the rate of process (VII) is much smaller than those of processes (I) and (VI). Although one type of mixed T-T annihilation occurs,



the other type



never occurs in such systems [8, 9]. The rate of process (IX) is of the same order of magnitude as that of process (VII) [9].

When the steady state method is applied to Scheme A, the following expression for the intensity of the delayed fluorescence from  $^1A^*$  is obtained in a straightforward manner:

$$I_{DF} = \alpha \Phi_F p k_{TT} \times \left\{ \frac{k_2[A]}{k_1 k_6 + k_1(k_4 + k_5)[D] + (k_2 + k_3)k_6[A] + (k_2 k_5 + k_3 k_4 + k_3 k_5)[A][D]} \right\}^2 \times (I_{ab} \Phi_{ST})^2 \quad (1)$$

When  $k_3$  and  $k_5$  are negligible compared with  $k_2$  and  $k_4$  respectively, eqn. (1) is reduced to

$$I_{DF} = \alpha \Phi_F p k_{TT} \left( \frac{k_2[A]}{k_1 k_6 + k_1 k_4 [D] + k_2 k_6 [A]} \right)^2 (I_{ab} \Phi_{ST})^2 \quad (2)$$

When the energy difference between the triplet states of the donor and acceptor is large,  $\Delta E_T \geq 2100 \text{ cm}^{-1}$ ,  $k_4 \approx 0 \text{ M}^{-1} \text{ s}^{-1}$  [10], and further when the concentration of acceptor is sufficiently high,  $k_2[A] \gg k_1$ , eqn. (1) is reduced to

$$I_{DF} = \alpha \Phi_F p k_{TT} \left( \frac{1}{k_6} \right)^2 (I_{ab} \Phi_{ST})^2 \quad (3)$$

This relation is the same as that derived by Parker.

## 2. Experimental

Eosine (Gluber's G.R. reagent) was recrystallized from ethanol three times. Erythrosine (Wako Junyaku G.R. reagent) was recrystallized three times from a mixed solvent of ethanol and benzene. The sample of thio-pyronine, which was kindly supplied by Professor S. Kato (Osaka University), had been used for earlier experiments [11]. Proflavine and acriflavine

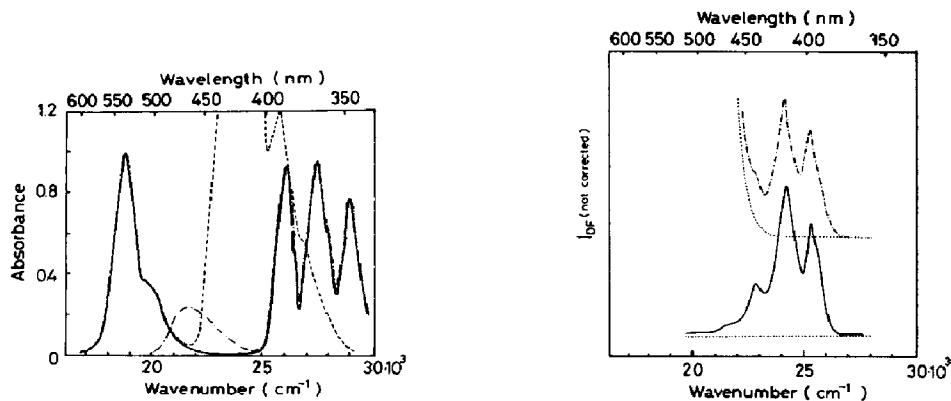


Fig. 1. Absorption spectra for sample solutions in ethanol: —, [erythrosine] =  $1.0 \times 10^{-5}$  M, [9-methylanthracene] =  $1.0 \times 10^{-4}$  M; - - - -, [proflavine] =  $4.9 \times 10^{-6}$  M, [9-methylanthracene] =  $1.0 \times 10^{-4}$  M; ····, [erythrosine] =  $1.0 \times 10^{-5}$  M, [perylene] =  $1.0 \times 10^{-4}$  M.

Fig. 2. Delayed fluorescence spectra of 9-methylanthracene sensitized by erythrosine (—) and by proflavine (- - - -) (shifted). The broken curves represent the data obtained in aerated solutions.

(Wako Junyaku) were purified using a column of activated alumina and were recrystallized from ethanol. The samples of acridine orange and anthracene were those used for experiments described in refs. 12 and 13 respectively. 9-Methylanthracene (Kanto Kagaku) and perylene (Tokyo Kasei G.R. reagent) were recrystallized several times from ethanol and toluene respectively. No impurities were found from the absorption and fluorescence spectra.

Each sample was degassed by distilling the solvent five times under vacuum. The absorption and fluorescence spectra were measured using a Hitachi EPS-3T spectrophotometer and a Hitachi MPF-2A fluorimeter respectively. The intensities of the delayed fluorescence were measured at one of the fluorescence maxima of the acceptor where there is no absorption of dye, *i.e.* at 400, 412 and 468 nm for anthracene, 9-methylanthracene and perylene respectively. The decay rate of the triplet molecule was measured with an ordinary flash apparatus.

### 3. Results and discussion

Figure 1 shows absorption spectra for ethanol solutions of erythrosine ( $1 \times 10^{-5}$  M) and 9-methylanthracene ( $1 \times 10^{-4}$  M), of erythrosine ( $1 \times 10^{-5}$  M) and perylene ( $1 \times 10^{-4}$  M) and of proflavine ( $4.9 \times 10^{-6}$  M) and 9-methylanthracene ( $1 \times 10^{-4}$  M). We can see that perylene is a suitable acceptor for xanthene dyes but not for acridine dyes. Figure 2 shows the delayed fluorescence of 9-methylanthracene which is obtained when the proflavine and erythrosine used as donors are excited at 460 nm and 510 nm respectively. On introduction of air the delayed fluorescence is

TABLE 1

$\Phi_{ST}$  values for eosine and thiopyronine in ethanol ([perylene] =  $1.0 \times 10^{-4}$  M)

	$I_{DF}/I_{DF}^S$	$\Phi_{ST}$
Eosine	0.205	0.45
( $5.0 \times 10^{-6}$ M)	0.184	0.43
	0.197	0.44
Thiopyronine	0.0554	0.24
( $5.0 \times 10^{-6}$ M)	0.0556	0.24

reduced to the broken lines and the difference between the two corresponding curves can be attributed to the sensitized delayed fluorescence.

### 3.1. Determination of $\Phi_{ST}$ for eosine and thiopyronine

Perylene was used as an acceptor and erythrosine was used as a reference donor since its  $\Phi_{ST}$  value is known to be approximately unity [4, 14]. From eqn. (3) the ratio  $I_{DF}/I_{DF}^S$  of the delayed fluorescence intensity of perylene sensitized by eosine (or thiopyronine) to that of perylene sensitized by erythrosine is given by

$$\frac{I_{DF}}{I_{DF}^S} = \frac{I_{ab}^2}{I_{ab}^S{}^2} \frac{\Phi_{ST}^2}{\Phi_{ST}^S{}^2} \frac{k_6^S{}^2}{k_6^2} \quad (4)$$

In practice the concentrations of eosine (or thiopyronine) and erythrosine were adjusted in such a way that the absorbance of the two solutions became equal at the excitation wavelength. Assuming  $k_6 = k_6^S$  and putting  $I_{ab} = I_{ab}^S$  and  $\Phi_{ST}^S = 1$ ,  $\Phi_{ST}$  can be easily determined from the value of  $I_{DF}/I_{DF}^S$ . The results obtained are summarized in Table 1. The value of eosine agrees satisfactorily with that (0.43) obtained previously using the chemical method [4]. For thiopyronine the determination of  $\Phi_{ST}$  by the chemical method was performed using 1,2,5,6-dibenzanthracene ( $\Phi_{ST}^S = 0.89$  [15],  $\Phi_{ST}^S = 1.03$  [14]) as a donor. The results are given in Table 2 and the  $\Phi_{ST}$  values in column 5 agree with the data in Table 1. The assumption  $k_6 = k_6^S$  is verified by the reproducibility of the results shown in Table 1 and by the agreement between the  $\Phi_{ST}$  values obtained using the chemical method and the sensitized delayed fluorescence method.

### 3.2. Determination of $\Phi_{ST}$ for acridine dyes

To confirm whether or not the method, even when extended to reversible energy transfer, is still reliable, anthracene and 9-methylanthracene were used as acceptors for the reference donors eosine and erythrosine.

The rate constants of the elementary processes involved in Scheme A are given in Table 3 [6] for the four combinations of donor and acceptor. The values of  $k_6$  for anthracene and 9-methylanthracene were re-examined

TABLE 2

 $\Phi_{ST}$  values of thiopyronine determined using the chemical method<sup>a</sup>

[ATU] (M)	$\Phi$	$\Phi^S$	$\Phi_{ST}$	
			$\Phi_{ST}^S = 1.03$ [14]	$\Phi_{ST}^S = 0.89$ [15]
$3.0 \times 10^{-2}$	0.046	0.17	0.28	0.24
$2.0 \times 10^{-2}$	0.041	0.13	0.32	0.28
$1.5 \times 10^{-2}$	0.033	0.11	0.31	0.27
$1.0 \times 10^{-2}$	0.028	0.08	0.36	0.31
			$0.32 \pm 0.04$	$0.28 \pm 0.03$

<sup>a</sup> [1,2,5,6-dibenzanthracene] =  $4.0 \times 10^{-5}$  M; [thiopyronine] =  $1.0 \times 10^{-5}$  M; reducing agent, allylthiourea (ATU).

$\Phi$  is the quantum yield of thiopyronine photoreduction and  $\Phi_{ST}^S$  is the quantum yield of thiopyronine photoreduction sensitized by 1,2,5,6-dibenzanthracene.  $\Phi_{ST}^S$  is the S\*–T transition probability of 1,2,5,6-dibenzanthracene.

TABLE 3

Rate constants for the elementary reactions involved in Scheme A [6]

Rate constant	Eosine		Erythrosine	
	Anthracene	9-Methylanthracene	Anthracene	9-Methylanthracene
$k_1$ (s <sup>-1</sup> )	$(2.4 \pm 0.3) \times 10^3$	$(2.4 \pm 0.3) \times 10^3$	$(5.5 \pm 0.5) \times 10^3$	$(5.5 \pm 0.5) \times 10^3$
$k_2 + k_3$ (M <sup>-1</sup> s <sup>-1</sup> )	$(5.1 \pm 0.5) \times 10^8$	$(1.9 \pm 0.2) \times 10^9$	$(7.3 \pm 1.0) \times 10^8$	$(2.2 \pm 0.4) \times 10^9$
$k_4 + k_5$ (M <sup>-1</sup> s <sup>-1</sup> )	$(1.2 \pm 0.2) \times 10^9$	$(2.1 \pm 0.4) \times 10^8$	$(1.7 \pm 0.2) \times 10^9$	$(3.3 \pm 0.3) \times 10^8$
$k_6$ (s <sup>-1</sup> )	$(7.6 \pm 1.0) \times 10^2$	$(2.5 \pm 0.5) \times 10^2$	$(7.6 \pm 1.0) \times 10^2$	$(2.5 \pm 0.5) \times 10^2$

in the present study. It is known that the values of  $k_3$  and  $k_5$  respectively are less than 10% of  $k_2$  and  $k_4$  for the eosine–anthracene pair and are less than 30% of  $k_2$  and  $k_4$  for the erythrosine–anthracene pair [6]. Therefore we analysed the experimental results as an approximation by assuming that  $k_3$  and  $k_5$  are negligible compared with  $k_2$  and  $k_4$ .

### 3.2.1. Eosine–anthracene as a reference system ([eosine] = $1.2 \times 10^{-5}$ M, [anthracene] = $1.0 \times 10^{-4}$ M)

From eqn. (2) and using the data listed in Table 3, the intensity of the delayed fluorescence of anthracene sensitized by eosine is given by the following relation:

$$I_{DF}^S = \alpha \Phi_F p k_{TT} I_{ab}^S {}^2 \Phi_{ST}^S {}^2 \times 5.9 \times 10^{-7} \quad (5)$$

The intensity of the delayed fluorescence of anthracene sensitized by acridine dyes is given by eqn. (3). By substituting the value for  $k_6$ , we obtain

TABLE 4

$\Phi_{ST}$  values for acridine dyes (reference system, eosine-anthracene)

	Concentration (M)	$I_{DF}/I_{DF}^S$	$\Phi_{ST}$
Proflavine	$8.9 \times 10^{-6}$	5.7	0.53
	$6.3 \times 10^{-6}$	5.0	0.49
	$4.1 \times 10^{-6}$	4.4	0.46
	$5.4 \times 10^{-6}$	5.4	0.51
Acriflavine	$3.6 \times 10^{-6}$	7.2	0.59
	$2.5 \times 10^{-6}$	7.8	0.61
	$1.3 \times 10^{-6}$	5.4	0.51
Acridine orange	$7.5 \times 10^{-6}$	1.6	0.28
	$5.8 \times 10^{-6}$	1.2	0.24
	$4.0 \times 10^{-6}$	1.4	0.26
	$2.5 \times 10^{-6}$	1.5	0.27

TABLE 5

$\Phi_{ST}$  values for acridine dyes (reference system, eosine-9-methylantracene)

	Concentration (M)	$I_{DF}/I_{DF}^S$	$\Phi_{ST}$
Proflavine	$4.5 \times 10^{-6}$	1.1	0.42
	$1.8 \times 10^{-6}$	0.92	0.38
	$1.0 \times 10^{-6}$	1.0	0.40
Acriflavine	$3.6 \times 10^{-6}$	1.4	0.47
	$1.3 \times 10^{-6}$	1.6	0.51
Acridine orange	$1.1 \times 10^{-5}$	0.66	0.32
	$7.9 \times 10^{-6}$	0.89	0.38
	$5.4 \times 10^{-6}$	0.68	0.33
	$2.8 \times 10^{-6}$	0.92	0.38

$$I_{DF} = \alpha \Phi_F \rho k_{TT} I_{ab}^2 \Phi_{ST}^2 \times 1.74 \times 10^{-6} \quad (6)$$

From eqns. (5) and (6), and substituting  $I_{ab} = I_{ab}^S$  and  $\Phi_{ST}^S = 0.43$ , we obtain the following for the  $\Phi_{ST}$  values for acridine dyes:

$$\Phi_{ST} = 0.22 (I_{DF}/I_{DF}^S)^{1/2} \quad (7)$$

The results are given in Table 4.

### 3.2.2. Eosine-9-methylantracene as a reference system ([eosine] = $3.5 \times 10^{-6}$ M, [9-methylantracene] = $1.0 \times 10^{-4}$ M)

The results given in Table 5 were obtained by a process similar to that described in Section 3.2.1.

TABLE 6

 $\Phi_{ST}$  values for acridine dyes

	Concentration (M)	$I_{DF}/I_{DF}^S$	$\Phi_{ST}$
<i>Reference system, erythrosine-anthracene</i>			
Proflavine	$9.0 \times 10^{-6}$	11.8	1.23
	$6.3 \times 10^{-6}$	12.0	1.24
	$4.1 \times 10^{-6}$	11.0	1.18
	$2.0 \times 10^{-6}$	11.0	1.18
Acriflavine	$4.9 \times 10^{-6}$	9.0	1.07
	$3.6 \times 10^{-6}$	9.0	1.07
	$2.5 \times 10^{-6}$	10.0	1.13
<i>Reference system, erythrosine-9-methylanthracene</i>			
Proflavine	$4.7 \times 10^{-6}$	1.1	0.74
	$2.9 \times 10^{-6}$	0.99	0.70

TABLE 7

Average values of  $\Phi_{ST}$  for acridine dyes and values of  $\beta$ 

<i>Reference system</i>	$\Phi_{ST}$		
	<i>Proflavine</i>	<i>Acriflavine</i>	<i>Acridine orange</i>
Eosine-anthracene	$0.49 \pm 0.04$	$0.56 \pm 0.06$	$0.26 \pm 0.02$
Eosine-9-methylanthracene	$0.40 \pm 0.02$	$0.49 \pm 0.02$	$0.35 \pm 0.03$
Erythrosine-anthracene	$1.21 \pm 0.03$ ( $\beta = 0.76 - 0.86$ )	$1.09 \pm 0.04$ ( $\beta = 0.89 - 0.93$ )	—
Erythrosine-9-methylanthracene	$0.72 \pm 0.02$ ( $\beta = 0.99$ )	—	—

### 3.2.3. Erythrosine-anthracene as a reference system ([erythrosine] = $1.03 \times 10^{-5}$ M, [anthracene] = $1.0 \times 10^{-4}$ M)

The results given in Table 6 were obtained for proflavine and acriflavine. The data for acridine orange were omitted because of large experimental errors.

### 3.2.4. Erythrosine-9-methylanthracene as a reference system ([erythrosine] = $1.2 \times 10^{-5}$ M, [9-methylanthracene] = $1.0 \times 10^{-4}$ M)

The results given in Table 6 were obtained for proflavine and acriflavine. acriflavine and acridine orange were omitted because of large experimental errors.

The average values of  $\Phi_{ST}$  for each acridine dye determined using the various reference systems are summarized in Table 7.



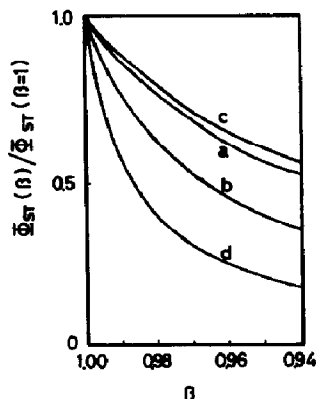


Fig. 3. Plots of  $\Phi_{ST}(\beta)/\Phi_{ST}(\beta = 1)$  vs.  $\beta$  for the various reference systems: curve a, eosine-anthracene; curve b, eosine-9-methylanthracene; curve c, erythrosine-anthracene; curve d, erythrosine-9-methylanthracene.

The  $\Phi_{ST}$  values obtained for the eosine-anthracene reference system agree satisfactorily with those for the eosine-9-methylanthracene reference system. However, the  $\Phi_{ST}$  values obtained for the erythrosine-anthracene and erythrosine-9-methylanthracene reference systems are much larger than those obtained for the other reference systems. It is unusual that the  $\Phi_{ST}$  values obtained for the erythrosine-anthracene reference system are larger than unity for both proflavine and acriflavine. The differences of the  $\Phi_{ST}$  values from unity are significant even when errors in the determination of the rate constants listed in Table 3 are taken into account. These results indicate that the assumption  $k_3 \ll k_2$  and  $k_5 \ll k_4$  is not necessarily valid for the erythrosine-anthracene and erythrosine-9-methylanthracene pairs.

It has been suggested [6] that both the forward and the backward energy transfers occur through an intermediate in which the excitation energy is delocalized to D and A, so that energy dissipation occurs from the intermediate to D and to A with almost the same rate constant:  $k_3 = k_5$ . According to this model eqn. (1) is reduced to

$$I_{DF}^S = \alpha \Phi_F p k_{TT} \left\{ \frac{\beta k'_2 [A]}{k_1 k_6 + k_1 k'_4 [D] + k'_2 k_6 [A] + (1 - \beta) k'_2 (\beta k'_2 + k'_4) [A] [D]} \right\}^2 \times (I_{ab} \Phi_{ST})^2 \quad (8)$$

where  $\beta = k_2/(k_2 + k_3)$ ,  $k'_2 = k_2 + k_3$  and  $k'_4 = k_4 + k_5$ . Using eqn. (8) and the rate constants listed in Table 3, the relative  $\Phi_{ST}$  values were calculated as functions of  $\beta$  as shown in Fig. 3. It is obvious that the large value of  $\Phi_{ST}$  was obtained when  $\beta = 1$  was assumed for the case of  $\beta \neq 1$ . This is the situation for the erythrosine-anthracene and erythrosine-9-methylanthracene pairs. Therefore a donor and acceptor pair in which triplet energy transfer occurs reversibly is not suitable for a reference system when energy dissipation competes with energy transfer.

For the eosine–anthracene pair  $k_3$  and  $k_5$  have been estimated [6] to be less than 10% of  $k_2$  and  $k_4$  respectively. The  $\Phi_{ST}$  values obtained for the eosine–anthracene reference system agree with those obtained for the eosine–9-methylanthracene pair in spite of the fact that reverse energy transfer is harder to achieve in the latter than in the former. The  $\Phi_{ST}$  value for acridine orange was determined to be 0.37 by a direct method [16] and agrees with that obtained earlier. Therefore the assumptions  $k_3 \ll k_2$  and  $k_5 \ll k_4$  are reasonable for the eosine–anthracene and eosine–9-methylanthracene reference systems and the  $\Phi_{ST}$  values obtained using these reference systems are reliable.

Using eqn. (8), the  $\Phi_{ST}$  values obtained for the eosine–anthracene and eosine–9-methylanthracene reference systems and the data listed in Tables 5 and 6, we can estimate the values of  $\beta$  for the erythrosine–anthracene and erythrosine–9-methylanthracene reference systems. The results are listed in Table 7. The values of  $\beta$  obtained for the erythrosine–anthracene pair are consistent with the previous estimation [6] that  $k_3$  and  $k_5$  are less than 30% of  $k_2$  and  $k_4$  respectively.

Parker's method requires in principle a condition that the triplet energy transfer between donor and acceptor ( $k_2$  and  $k_4$ ) is not accompanied by energy dissipation ( $k_3$  and  $k_5$ ). The effect of energy dissipation on the sensitized delayed fluorescence was found to be much larger for reversible energy transfer than for irreversible energy transfer. Therefore care must be taken when a reference system consisting of donor and acceptor with almost the same triplet levels is used. In the present work it was found that the eosine–anthracene and eosine–9-methylanthracene pairs are suitable for the reference system whereas the erythrosine–anthracene and erythrosine–9-methylanthracene pairs are not.

### 3.3. Sensitized oxidation of anthracenes in aerated solution following Scheme A

In aerated solutions of eosine–anthracene systems delayed fluorescence from the anthracenes is not observed, as mentioned previously; however, dye-sensitized photooxidation of the anthracenes occurs. Singlet oxygen produced by energy transfer from triplet eosine reacts with anthracene (An) to produce the endoperoxide. The quantum yield of An disappearance for the solution containing An in such a low concentration that triplet energy transfer from eosine to An almost does not occur can be expressed as

$$\Phi_A = \Phi_{^1O_2} \frac{\gamma [\text{An}]}{\delta + [\text{An}]} \quad (9)$$

where  $\Phi_{^1O_2}$  is the yield of singlet oxygen formation by eosine.  $\gamma$  and  $\delta$  are rate constant parameters [17]. At higher concentrations of An (or 9,10-dimethylanthracene (DMA)) triplet energy transfer from eosine to An occurs according to Scheme A and  $^3\text{An}$  is photooxidized by dissolved oxygen [18]; the  $\Phi_A$  value cannot be expressed by eqn. (9). In chloroform

the quantum yield of DMA disappearance at the lower concentration is experimentally expressed as

$$\Phi_{\text{DMA}} = 3.0[\text{DMA}]/(1.01 \times 10^{-3} + [\text{DMA}]) \quad (10)$$

However, at higher concentrations ( $1.1 \times 10^{-3}$  M and  $2.2 \times 10^{-3}$  M) the  $\Phi_{\text{DMA}}$  values are 0.99 and 0.24 respectively; these are considerably lower than the values of 1.57 and 2.07 calculated using eqn. (10). Such depression of the values of  $\Phi_{\text{A}}$  or  $\Phi_{\text{DMA}}$  were observed for the systems eosine- $\text{O}_2$ -DMA in ethanol and eosine- $\text{O}_2$ -An in chloroform. Comparing the value of  $k_2$  in Table 3 with the rate constant (approximately  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) for the reaction of triplet eosine and oxygen, it is understandable that the concentration of DMA which starts the depression of the  $\Phi_{\text{DMA}}$  value is approximately the same as the concentration of dissolved oxygen.

When methylene blue ( $E_{\text{T}} = 11\,650 \text{ cm}^{-1}$  [19]) was used as a singlet oxygen sensitizer the value of  $\Phi_{\text{DMA}}$  observed (3.57) was coincident with that calculated even at the higher concentration of DMA ( $2.2 \times 10^{-3}$  M). This result suggests that DMA oxidation with singlet oxygen produced by triplet methylene blue is the only reaction path. Triplet energy transfer by Scheme A cannot occur in the methylene blue- $\text{O}_2$ -DMA(or An) system because of the lower value of  $E_{\text{T}}$  for methylene blue.

## References

- 1 C. A. Parker and T. A. Joyce, *Chem. Commun.*, (1966) 234.
- 2 C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, 62 (1966) 2785.
- 3 C. A. Parker, *The Triplet State*, Cambridge University Press, London, 1967, p. 386.
- 4 M. Nemoto, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 42 (1969) 1223.
- 5 K. Sandros, *Acta Chem. Scand.*, 18 (1964) 2355.
- 6 K. Kikuchi, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 43 (1970) 2732.
- 7 K. Gollnick, *Adv. Photochem.*, 6 (1968) 40.
- 8 C. A. Parker, C. G. Hatchard and T. A. Joyce, *Nature (London)*, 205 (1965) 1282.
- 9 K. Kikuchi, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 44 (1971) 1527.
- 10 S. Nordin and R. L. Strong, *Chem. Phys. Lett.*, 2 (1968) 429.
- 11 M. Morita and S. Kato, *Bull. Chem. Soc. Jpn.*, 42 (1969) 256.
- 12 T. Komiyama, T. Miwa and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 39 (1966) 2597.
- 13 T. Miwa and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 36 (1963) 1619.
- 14 P. G. Bowers and G. Porter, *Proc. R. Soc. London, Ser. A*, 299 (1967) 348.
- 15 A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43 (1965) 2129.
- 16 B. Soep, A. Kellmann, M. Martin and L. Lindqvist, *Chem. Phys. Lett.*, 13 (1972) 241.
- 17 Y. Usui, M. Tsukada and H. Nakamura, *Bull. Chem. Soc. Jpn.*, 51 (1978) 379.
- 18 B. Stevens, *Acc. Chem. Res.*, 6 (1973) 60.
- 19 D. R. Kearns, R. A. Hollins, A. U. Khan and P. Radlick, *J. Am. Chem. Soc.*, 89 (1967) 5456.