Determination of the S^*–T Transition Probability of Acridine Dyes by the Method of Sensitized Delayed Fluorescence

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Summary Φ_{ST} Values for proflavine, acriflavine, and Acridine Orange in ethanol solutions have been determined by means of the sensitized delayed fluorescence method.

THE method of sensitized delayed fluorescence has been described by Parker[1] for determining the S^*–T transition probability (Φ_{ST}) of aromatic hydrocarbons. This method is expected to be conveniently applicable to alcoholic solutions of dyes in general because the absorption spectra of dyes (donor) are generally situated in a longer-wavelength region than those of aromatic hydrocarbons and the fluorescence spectra of the latter lie in between them.

We have employed this method for determining the Φ_{ST} values of acridine dyes in ethanol by measuring the delayed fluorescence of anthracene and 9-methylanthracene, using a Hitachi MPF-2A fluorometer. There are very few dyes for which reliable Φ_{ST} values have been determined, and as reference sensitizers we have chosen eosin and erythrosin (with known Φ_{ST} values). However, these dyes have triplet energy levels very close to those of anthracene and 9-methylanthracene, and hence it is necessary to take the reverse process, $D + A_T \rightarrow D_T + A$ into account. This makes the expression for I_{DF} (intensity of the sensitized delayed fluorescence of anthracene or 9-methylanthracene) somewhat complicated. But all the necessary data for the present method to be applicable, have been evaluated by Kikuchi, Kokubun, and Koizumi.[2,3] For acridine dyes for which $E(D^T) \gg E(A^T)$ (D, acridine, A, anthracene), I_{DF} is given by the formula of Parker.[1]

In spite of the complications for eosin and erythrosin, the intensity ratio of the delayed fluorescence of anthracene for instance, sensitized by proflavine and eosin, is given by

$$\frac{I_{DF}\,(P)}{I_{DF}\,(E)} \propto \frac{(I^{P}_{ab})^2\,(\Phi^{P}_{ST})^2}{(I^{E}_{ab})^2\,(\Phi^{E}_{ST})^2} \qquad (1)$$

where a constant factor can be calculated from the known data. Since Φ_{ST} for eosin and erythrosin are known and are respectively 0·43 and 1·0, Φ_{ST} for proflavin can be evaluated from equation (1).

Figure 1 shows the absorption spectra of eosin, anthracene, and proflavine in ethanol. The fluorescence of anthracene and 9-methylanthracene lie in the region 370—450 nm, and the intensities can be measured without any interference from the dye. The fluorescence intensities for anthracene and 9-methylanthracene were measured respectively, at 400 and 412 nm. Figure 2 shows the sensitized fluorescence of 9-methylanthracene, which was completely quenched in the aerated solution, supporting the suggestion that it occurs *via* the triplet state.

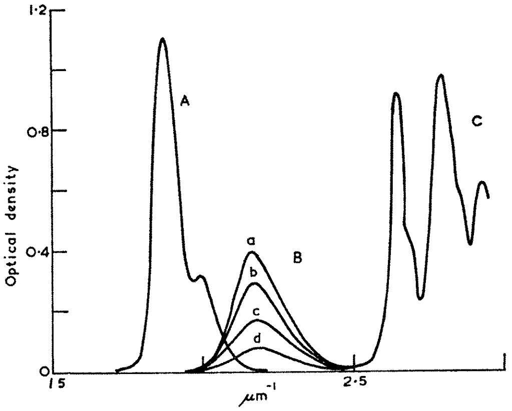

FIGURE 1. *Absorption spectra of eosin, proflavine, and anthracene in ethanol solution.*

A: *eosin* 1·25 × 10^{-5} *mole/l.*
B: *proflavine* a 8·9 × 10^{-6} *mole/l.*
b 6·33 × 10^{-6} *mole/l.*
c 4·11 × 10^{-6} *mole/l.*
d 2·0 × 10^{-6} *mole/l.*
C: *anthracene* 1 × 10^{-4} *mole/l.*

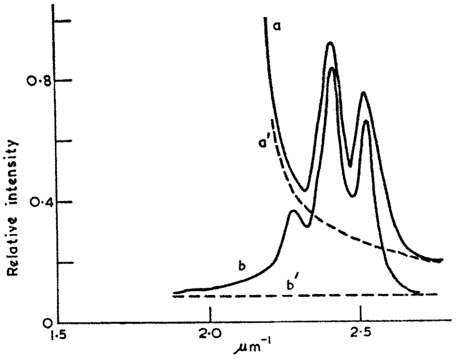

FIGURE 2. *Sensitized fluorescence of* 9-*methylanthracene.*

a *proflavine-sensitized* (*de-aerated*).
a′ *proflavine-sensitized* (*aerated*). *Excitation,* 460 *nm.*
b *erythrosine-sensitized* (*de-aerated*).
b′ *erythrosine-sensitized* (*aerated*). *Excitation,* 530 *nm.*

TABLE

Φ_{ST} *of acridine dye*

Reference system	Pro-flavine	Acri-flavine	Acridine Orange
Eosin–anthracene ..	0·49	0·56	0·28
Erythrosin–anthracene	0·50	0·46	
Eosin–9-methyl anthracene	0·40	0·42	0·32
Erythrosin–9-methyl-anthracene	0·48		
	0·47±0·07	0·47±0·09	0·30±0·02

The Table gives the Φ_{ST} values of proflavine, acriflavine, and Acridine Orange obtained by the present method using eosin or erythrosin as a reference sensitizer and anthracene or 9-methylanthracene as an acceptor. Each value is the average of several independent results.

Where perylene, whose T-level is much lower than that of eosin and erythrosin, is used as an acceptor, both eosin–perylene and erythrosin–perylene systems can be treated by Parker's equation, and the method becomes more simple. Using erythrosin as a reference substance ($\Phi^{D}_{ST} = 1$) Φ_{ST} of eosin has been determined as 0·44, which agrees with the value of 0·43 found previously by a different method.[4]

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[3] K. Kikuchi, H. Kokubun, and M. Koizumi, to be published.
[4] M. Nemoto, H. Kokubun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1969, **42**, 1223.