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Studies on the Delayed Fluorescence by Means of a Flash Technique*[1]

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It has been shown that the delayed and normal fluorescence can be measured accurately by a usual flash apparatus. Such measurements, combined with that of T–T absorption, have enlarged the potentiality of a flash technique to a large extent. As an example, a simple method of differentiation between E-type and P-type delayed fluorescence has been presented. Detailed studies have been made on the T–T annihilation process of anthracene (A) and the probability for Process $A^T+A^T \rightarrow A+A^*$, has been decided. The value obtained is 0.077 ± 0.005. E-Type delayed fluorescence of eosine and proflavine have been studied and the value of $k_t \cdot \phi_{ST}$ (k_t, the rate constant of Process, $T \rightarrow S^*$; ϕ_{ST}, the probability of the intersystem crossing) have been evaluated, to be 3.3_6 and 2.7_8 sec^{-1} respectively. Some advantages of the present method over the sector method have been discussed.

A flash photolytic technique is now extensively used for studying the behavior of intermediates produced in the photochemical reaction of organic substances. The method, however, usually relies upon the measurement of the UV absorption spectra of transient species.

If the measurement is extended to the emission phenomena such as the normal and delayed fluorescence, the potentiality of the flash technique will largely be enlarged. Such attempts have been made by Zahlan *et al.*[1] and by Powell[2] to determine the intersystem-crossing probability of some hydrocarbons in the gaseous state. Wild *et al.*[3] also measured the delayed fluorescence of

*1 A preliminary report was published in *Photochem. and Photobiol.*, **7**, 499 (1968).

1) A. B. Zahlan, S. Z. Weisz, R. C. Jarnagin and M. Silver, *J. Chem. Phys.*, **42**, 4244 (1965).
2) G. L. Powell, *ibid.*, **47**, 95 (1967).
3) U. Wild and Hs. H. Günthard, *Helv. Chim. Acta*, **48**, 1843 (1965).

anthrancene in glycerol in the temperature range from −20 to 90°C. In spite of these reports, it does not seem that the methodology has been fully established and that its availability has been duly recognized. We believe that various kinds of process such as delayed fluorescence, quenching of fluorescence, T–T energy transfer and other elementary processes in the excited states can be attacked by combining the measurement of the emission-time relation with that of the T–T absorption.

The objective of the present paper is to report firstly, how the time dependence of the delayed fluorescence and of the normal fluorescence (during flash irradiation) can be accurately measured with an ordinary flash apparatus now generally used, and secondly how the method can be applied, as an example, to the investigation of the mechanisms of the delayed fluorescence.

Delayed fluorescence has been studied extensively by Parker and his coworkers[4]; and now it has been well established that there are two types of delayed fluorescence, *i. e.*, E-type and P-type. Choosing anthracene of which the elementary processes in the excited state have been studied in detail, we would like to show how the present method is used for studying the P-type delayed fluorescence, with some advantages over the sector method. For this purpose, the delayed fluorescence of anthracene as well as the sensitized one, using eosine, erythrosine and proflavine as sensitizers, have been studied. E-Type delayed fluorescence of proflavine and eosine have also been studied and the results have been compared with those obtained by other methods.

Experimental

A great advantage of the present method is that the time dependence of the delayed fluorescence and the triplet decay can be compared in the similar experimental condition with the same apparatus. In order to do this, it is, of course, necessary to keep the geometry of the entire apparatus rigorously fixed. It is also required that the intensity of the flash and its time dependence can be controlled reproducibly. These requirements could be achieved with some satisfaction.

In order to investigate the mechanism of the delayed fluorescence, measurement has to be performed of A) the triplet decay and the intensity of the delayed fluorescence as a function of time both in the same condition, and besides, of B) the normal fluorescence intensity (during a flash) and the yield of the triplet state under the same condition which is, however, different from A).

To make an accurate measrement of the time dependence of the delayed fluorescence, it is necessary to remove the effect of the scattered light during a flash and to make the duration of a flash as short as possible. Use of some suitable sensitizers with appropriate filters is very effective for removing the scattered light and accordingly for separating the normal and delayed fluorescence satisfactorily.

Decay of T–T absorption and the change of delayed fluorescence with time, were measured at fixed wavelengths by means of a Nalumi-RM 23 monochromator. Photomultipliers employed, were Hamamatsu TV R106 and R132. A Iwasaki-Tsushinki SS-5004 synchroscope was used. Cells were the standard ones *i. e.*, quartz cells 10 mm in diameter, 100 mm in length or SB glass tubes 10 mm in diameter with two quartz plates pasted on both ends. Energy input to the flash lamp was selected in the region from 10 to 120 joules.

For the measurement of normal fluorescence, which is quite strong, neutral filters were inserted in between the monochromator and the cell. Measurement of the normal fluorescence from an aerated solution was of great help to examine the degree of superposition of the normal and delayed fluorescence. Because the aerated solution gives no delayed fluorescence and the profile of the emission is closely related with that of the flash.[5]

Anthracene, β-acetonaphthone, eosine, proflavine, erythrosine and ethanol were purified by the standard methods.

Method of Analysis and Results

Typical Examples for the Time Dependence of the Normal and Delayed Fluorescence. The intensity of the delayed fluorescence, I_{DF} and the second order decay constant of T–T absorption were measured at the same high energy input to the flash lamp. Figures 1 and 2 give respectively the I_{DF} *vs.* t plots for the case of direct excitation of anthracene and for the eosine-sensitized excitation. The dotted line in Fig. 1 represents the normal fluorescence from the aerated solution. It is evident that the shaded area can be used as the quantity of the delayed fluorescence during the time interval from a to b. A small peak existing

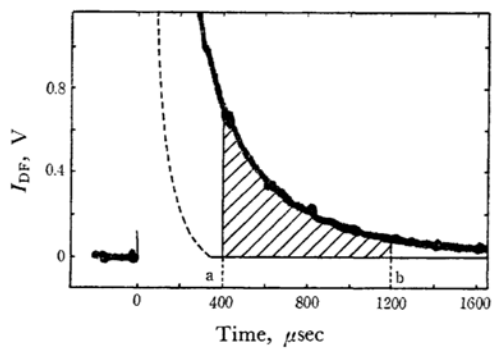

Fig. 1. Delayed fluorescence (solid line) and normal fluorescence (dotted line) of anthracene at 400 nm by direct excitation.
[Anthracene] = 1.0×10^{-4} M.

4) C. A. Parker, "Advances in Photochemistry," Vol. II, ed. by W. A. Noyes, G. S. Hammond and J. N. Fitts, Interscience Publishers, New York, N. Y. (1964). p. 305.

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

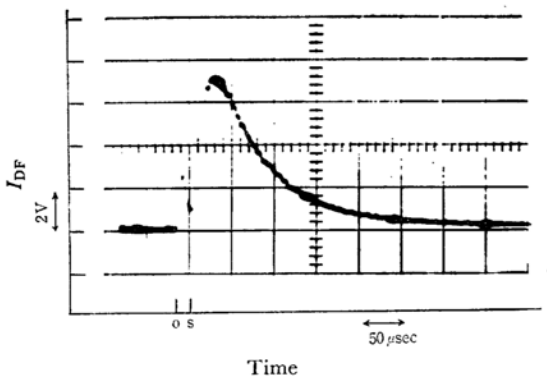

Fig. 2. Delayed fluorescence of anthracene at 400 nm sensitized by eosine.
[Anthracene]$=3.6\times10^{-5}$ M
[Eosine]$=2.0\times10^{-5}$ M

between o and s in Fig. 2 is due to the scattered light during a flash. The area after s gives the quantity of the delayed fluorescence. It is evident that in the case of the sensitized emission, rise and fall of the delayed fluorescence can be measured with enough accuracy. As will be reported elsewhere, the analysis of the rising portion of the curve enables us to evaluate the rate constant for the process of T–T energy transfer. Figure 3 gives the spectrum of the delayed fluorescence of anthracene sensitized by eosine. This was obtained by measuring the decay curves such as shown in Fig. 2, at various wavelengths, and by plotting the intensities at the peak positions against the wavelength. The spectrum agrees satisfactorily with that of the normal fluorescence; this ensures the reliability of the intensity measurement.

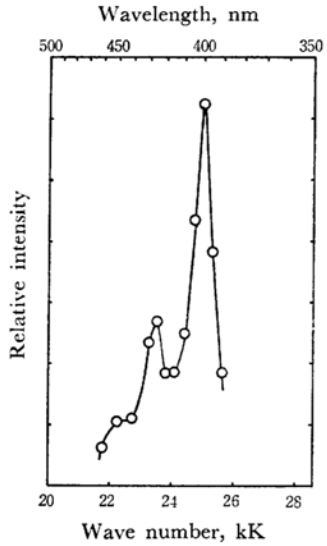

Fig. 3. Delayed fluorescene spectrum of anthacene sensitized by eosine.
[Anthracene]$=3.6\times10^{-5}$ M
[Eosine]$=2.0\times10^{-5}$ M

Normal fluorescence was measured at a low energy input to the flash lamp. Under such a condition, the yield of triplet state could be determined precisely because the decay was practically first order. Figure 4 is an example of the profile

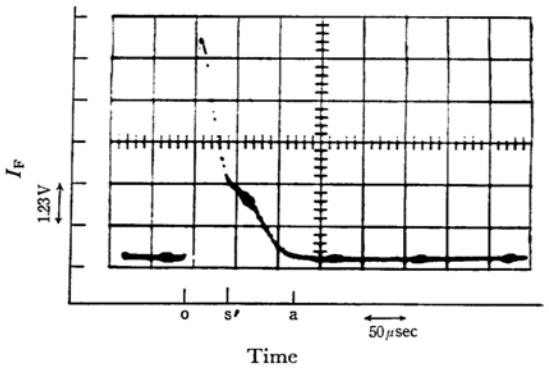

Fig. 4. Normal fluorescence of anthracene during a flash.
[Anthracene]$=1.0\times10^{-4}$ M
Flash energy 80 joule

of the normal fluorescence of anthracene in the aerated solution. Since this reflects the profile of the flash, the reproducibility of flashing can be checked by making such measurements from time to time. It was found that the reproducibility was quite excellent. The optical density of T–T absorption corresponding to the yield of triplet state, $(D_T)_0$, was decided by extrapolation of the decay curve of T–T absorption to the time-point S'. This is somewhat conventional but was found to be most satisfactory.

In the case of E-type delayed fluorescence, the intensity was so weak that it was very difficult to distinguish the delayed fluorescence from the normal one. This was almost impossible in the case of direct excitation. An example of the

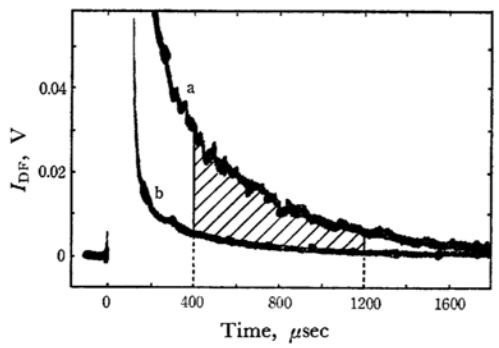

Fig. 5. Delayed fluorescence of eosine sensitized by β-acetonaphthone.
[Eosine]$=6.8\times10^{-6}$ M
[β-Acetonaphthone]$=5.0\times10^{-4}$ M
Curve a, deaerated soln.; b, aerated soln.

delayed fluorescence of eosine in the case of sensitized emission, by β-acetonaphthone, is shown in Fig. 5. Curve a in Fig. 5 is a plot of emission intensity from the deaerated solution and curve *b*, from the aerated solution. Since the latter is due mainly to the scattered light, the shaded area can be used as a measure of the delayed fluorescence. The accuracy is rather poor in this case.

Differentiation between P-Type and E-Type Delayed Fluorescence. It is well known that the delayed fluorescence of aromatic hydrocarbons occurs through the T–T annihilation, $T+T\xrightarrow{k_1}S^*+S$. The details of other processes simultaneously occurring, however, still remain to be studied in future. Here the following scheme is conventionally assumed.

$$T + T \begin{cases} \xrightarrow{k_1} S^* + S \\ \xrightarrow{k_2} T + S \end{cases} \qquad k_{TT} = k_1 + k_2$$

Putting $p=(k_1/k_{TT})$, the intensity of the delayed fluorescence can be written as follows,

$$I_{DF} = \alpha\phi_F p k_{TT}[T]^2 = \alpha\phi_F p k_{TT}[D_T/\varepsilon_T d]^2 \qquad (1)$$

where α is a constant depending upon the apparatus and upon the entire experimental conditions, where ϕ_F is a quantum yield of the fluorescence and where D_T, ε_T and d are respectively the optical density for T–T absorption, molar absorbance for it and the light path of a cell (100 mm in the present case).

Taking logarithm of Eq. (1), one obtains

$$\log I_{DF} = 2\log D_T + \log(\alpha\phi_F p k_{TT}/(\varepsilon_T)^2 d^2) \qquad (2)$$

Eq. (2) requires that the plot of $\log I_{DF}$ *vs.* $\log D_T$ should have a slope of 2. Figure 6 shows that this relation really holds very satisfactorily. This is perhaps the simplest method for verifying the P-type delayed fluorescence. It is somewhat disappointing that the four lines do not coincide. This is, of course, due to the fluctuation in α-values. The smallest value for proflavine may perhaps be attributed to a large value of its molar absorbance at 400 nm, which reaches $8.5\times10^3\ M^{-1}\,cm^{-1}$. For the other three cases the deviation of α from the average is within ±40%.

E-Type delayed fluorescence was more difficult to study because of its very weak intensity. Moreover, since both eosine and proflavine have more or less absorption in the entire UV region, the dye concentrations should be less than $\sim10^{-5}$ M in order to reduce the perturbing effect of the normal fluorescence.

It is therefore necessary to examine how the energy transfer from β-acetonaphthone to a dye occurs at such a low concentration. Figure 7 shows the decay of T–T absorption of β-acetonaphthone in the presence and in the absence of eosine.

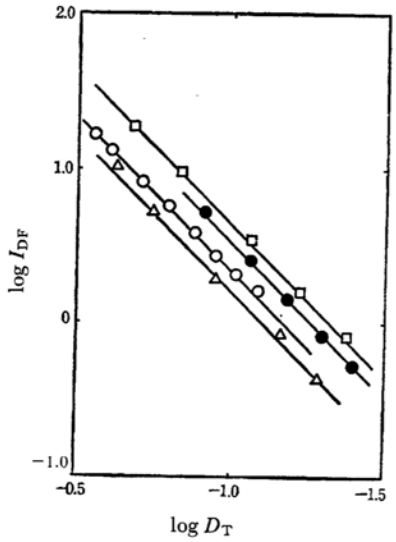

Fig. 6. Confirmation of Eq. (2).
[Anthracene] = 1.0×10^{-4} M
● Direct excitation
□ [Eosine] = 5.0×10^{-6} M
△ [Proflavine] = 1.2×10^{-5} M
○ [Anthracene] = 8.0×10^{-5} M
[Erythrosine] = 8.0×10^{-6} M

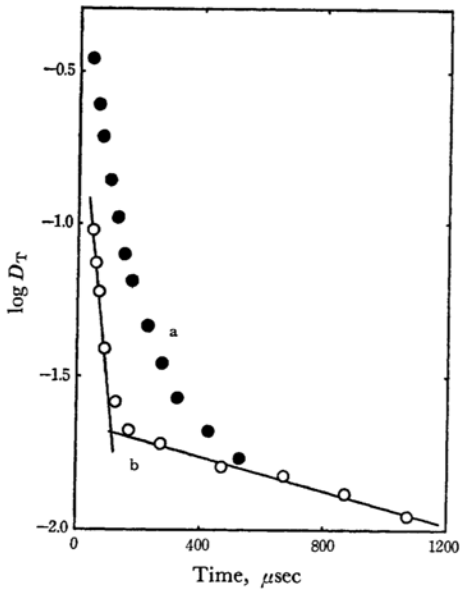

Fig. 7. Decay of T–T absorption of β-acetonaphthone at 430 nm.
● [Eosine] = 0 M
○ [Eosine] = 6.0×10^{-6} M
[β-Acetonaphthone] = 5×10^{-4} M

One can say that the energy transfer is practically complete in 200 μsec. Thus in the present system, the experimental data after 200 μsec should be used. The slow decay in the later stage of curve b, is related with another intermediate produced

by the reaction of the eosine triplet state with ethanol.[5]

It is well-known that the process T→S* for the E-type delayed fluorescence, is a monomolecular thermal activation. Thus I_{DF} is given by the following relation,

$$I_{DF} = \alpha\phi_F k_t[T] = \alpha\phi_F k_t \frac{D_T}{\varepsilon_T d} \qquad (3)$$

where k_t is the rate constant of the T→S* process. Figure 8 gives the plots of $\log D$ and $\log I_{DF}$ against time for the case of eosine, and Fig. 9 gives the similar plots for proflavine. As seen from these figures, the delayed fluorescence and the T–T absorption decay with essentially the same rate constant. This verifies that the delayed fluorescence of these dyes is mainly of E-type. However, there is a tendency, in the case of eosine, that the decay of the T–T absorption is appreciably smaller in the later stage. This is due to the existence of the absorption of another transient intermediate which is produced in the reaction between T and ethanol.[5] In the case of proflavine, the slopes for the $\log D_T$ and $\log I_{DF}$ plots agree quite well in the later stage. In both eosine and proflavine, the slopes of $\log I_{DF}$ at the early stage are somewhat larger. This suggests

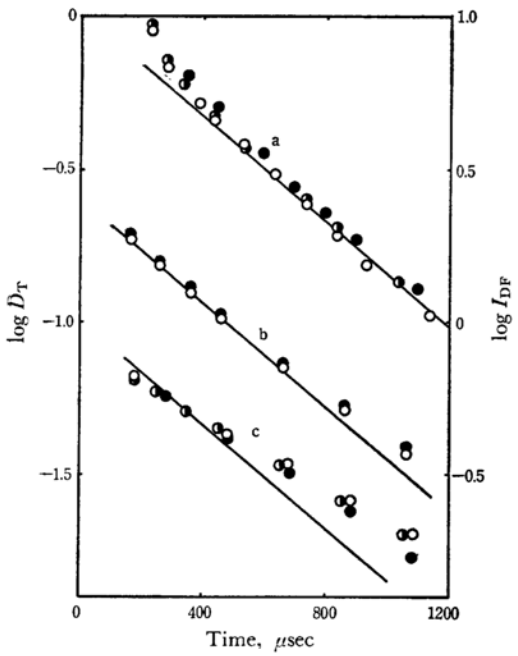

Fig. 8. Decay of T–T absorption at 580 nm and delayed fluorescence at 570 nm of eosine. a) Delayed fluorescence sensitized by β-acetonaphthone, b) T–T absorption by direct excitation, c) T–T absorption sensitized by β-acetonaphthone.
[Eosine] = 6.0×10^{-6} M
[β-Acetonaphthone] = 5.0×10^{-4}

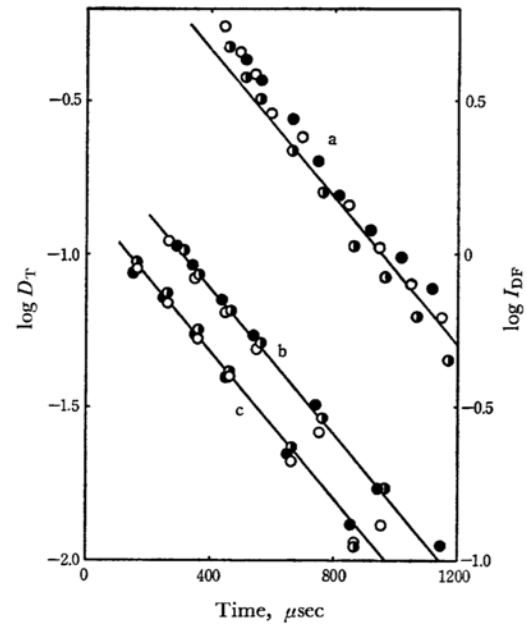

Fig. 9. Decay of T–T absorption at 550 nm and delayed fluorescence at 500 nm of proflavine. a) Delayed fluorescence sensitized by β-acetonaphthone, b) T–T absorption by direct excitation, c) T–T absorption sensitized by β-acetonaphthone.
[Proflavine] = 1.66×10^{-5} M
[β-Acetonaphthone] = 5.0×10^{-4} M

the occurrence of P-type delayed fluorescence, as has been established by Parker *et al.*[6]

Experimental Verification of the Relation between the Normal Fluorescence and the Triplet Yield. The intensity of the normal fluorescence is proportional to the absorption of light (per unit time) and can be written as follows,

$$I_F = \alpha\phi_F I_{ab} \qquad (4)$$

Integrating Eq. (4),

$$\int I_F dt = \alpha\phi_F \int I_{ab}\, dt \qquad (5)$$

The yield of the triplet state, on the other hand, can be given by the following equation,

$$[T_0] = \frac{[D_T]_0}{\varepsilon_T d} = \phi_{ST} \int I_{ab}\, dt \qquad (6)$$

where $[T]_0$ and $[D_T]_0$ are respectively the concentration of T and the corresponding optical density immediately after flashing and where ϕ_{ST} is the probability of the intersystem crossing. It is to be noted that this equation holds only when the decay of the triplet state is negligible during a flash. When the flash intensity is set rather weak,

6) C. A. Parker, C. G. Hatchard and T. A. Joyce, *Nature*, **205**, 1282 (1965); *J. Mol. Spectry.*, **14**, 311 (1964).

this holds practically and furthermore, the extrapolation of the triplet decay is easy. From Eqs. (5) and (6), one gets

$$[D_T]_0 = \frac{\varepsilon_T d \phi_{ST}}{\alpha \phi_F} \int I_F \, dt \qquad (7)$$

Figure 10 shows that this relation really holds in the case of anthracene. This is considered to be one of the most fundamental relations in the present method. If, ε_T, ϕ_{ST} and ϕ_F are all known, the value of α can be decided from the slope of the plot in Fig. 10.

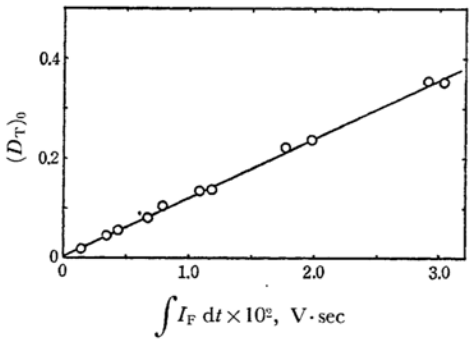

Fig. 10. Confirmation of Eq. (7).
[Anthracene] $= 1.0 \times 10^{-4}$ M

Putting $\varepsilon_T = 6.2 \times 10^4$ M^{-1} cm^{-1},[7] $\phi_{ST} = 0.7$,[8] $\phi_F = 0.27$,[9,10] one obtains a value of α to be 1.36×10^5 (at 400 nm). The value of α perhaps depends only on the wavelength when all the other experimental conditions are kept constant. It is most desirable to decide the reliable α-values at various wavelengths.

Analysis of the P-Type Delayed Fluorescence. Integration of Eq. (1) gives

$$\int I_{DF} \, dt = \frac{\alpha \phi_F p k_{TT}}{(\varepsilon_T d)^2} \cdot \int (D_T)^2 \, dt \qquad (8)$$

Elimination of α from Eqs. (7) and (8) gives the following relation,

$$\frac{\int I_{DF} \, dt}{\int I_F \, dt} = \phi_{ST} p \frac{k_{TT}}{\varepsilon_T d} \frac{\int (D_T)^2 \, dt}{(D_T)_0} \qquad (9)$$

In this equation, the values of $\int I_{DF} \, dt$, $\int (D_T)^2 \, dt$, $\int I_F \, dt$ and $(D_T)_0$ can be obtained experimentally. It is to be noted that the upper and lower limit of the first and the second integrals should respectively be set equal. The k_{TT}/ε value can be obtained by analysing the decay curve of T–T absorption. There is no need to know the value of ε_T. Thus the value of the product $p \cdot \phi_{ST}$ can be evaluated from the data obtained in the flash experiments. The value of ϕ_{ST} is 0.70 according to Medinger and Wilkinson.[8] The values of $p \cdot \phi_{ST}$ and p thus obtained from five different sets of experiments are given in Table 1 along with Parker's value of p.[6] The agreement is satisfactory. We believe that our value is more reliable since it is based only on the experimental data whereas Parker's value was evaluated by using as the k_{TT} value, the diffusion controlled rate constant theoretically calculated.

It is to be added that when the value of α is known (as in the present case), simple insertion of its value into Eq. (2) or into the intercepts of the plots in Fig. 6, gives the value of p. Of course, the same equation can be used to decide the α value if p is a known quantity.

Analysis of the E-Type Delayed Fluorescence. Integration of Eq. (3) gives

$$\int I_{DF} \, dt = \frac{\alpha \phi_F k_t}{\varepsilon_T d} \int D_T \, dt \qquad (10)$$

By eliminating α from Eqs. (7) and (10), one gets

$$\frac{\int I_{DF} \, dt}{\int I_F \, dt} = k_t \phi_{ST} \frac{\int D_T \, dt}{(D_{OT})_0} \qquad (11)$$

The upper and lower limits of the integrals $\int I_F \, dt$ and $\int D_T \, dt$ were suitably chosen by taking the perturbing effect of the scattered light into consideration. Thus the value of the product $k_t \cdot \phi_{ST}$ can be obtained in this case; for eosine 3.36 sec^{-1} and for proflavine 2.78 sec^{-1}. The values of the first order triplet decay constant for eosine and proflavine are respectively 1.98×10^3 sec^{-1} and 5.64×10^3 sec^{-1}. The value of ϕ_{ST} for eosine is 0.71 according to Porter.[11] Our recent experiment has given a value of 0.4.[12] Thus the value of k_t for eosine is 8.4 sec^{-1} (at room temperature). This value is compared with 3.77 sec^{-1} at 288°K calculated from the following relation reported by Parker.[9]

$$k_t = 7.4 \times 10^7 \exp\left(-\frac{9.6 \text{ kcal}}{RT}\right)$$

7) G. Porter and M. W. Windsor, *Discussions Faraday Soc.*, **17**, 178 (1954).
8) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).
9) C. A. Parker and C. G. Hatchard, *ibid.*, **57**, 1894 (1961).
10) E. J. Bowen and J. Sahu, *J. Phys. Chem.*, **63**, 4 (1959); G. Weber and F. Teale, *Trans. Faraday Soc.*, **53**, 646 (1957); W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).
11) P. G. Bowers and G. Porter, *Proc. Roy. Soc. London*, **A296**, 435 (1967).
12) To be published.

TABLE 1. P-TYPE DELAYED FLUORESCENCE OF ANTHRACENE

Sensitizer			Proflavine 1.2×10^{-5} M	Eosine 5.0×10^{-6} M	Erythrosine 8.0×10^{-6} M
Anthracene	1.0×10^{-4} M	1.0×10^{-4} M	1.0×10^{-4} M	1.0×10^{-4} M	8.0×10^{-5} M
$(D_T)_0$	0.080	0.289	0.151	0.203	0.347
$\int I_F\,dt$	6.7×10^{-3}	6.3×10^{-2}	2.3×10^{-2}	4.9×10^{-2}	4.8×10^{-2}
$\int (D_T)^2 dt$	1.4×10^{-4}	7.9×10^{-6}	1.4×10^{-5}	1.5×10^{-5}	5.3×10^{-5}
$\int I_{DF}\,dt$	3.7×10^{-4}	5.2×10^{-4}	7.2×10^{-4}	1.1×10^{-3}	2.5×10^{-3}
$k_{TT}/\varepsilon_T d$ (sec^{-1})		6.0×10^{3}			
$p\cdot\phi_{ST}$	5.4	5.1	5.5	5.0	5.8
ϕ_{ST}[a]		0.70			
$p\times10^2$	7.7	7.3	7.9	7.1	8.3
p (average)		0.07			
p (Parker)[b]		0.09			

a) Ref. 8 b) Ref. 6

TABLE 2. E-TYPE DELAYED FLUORESCENCE OF EOSINE AND PROFLAVINE

Sensitizer / Acceptor	5.0×10^{-4} M β-acetonaphthone	
	Eosine 6.8×10^{-6} M	Proflavine 1.66×10^{-5} M
$(D_T)_0$	0.248	0.227
$\int I_F\,dt$	9.6×10^{-2}	1.7×10^{-1}
$\int (D_T)\,dt$	1.3×10^{-5}	3.6×10^{-6}
$\int (I_{DF})\,dt$	1.5×10^{-5}	7.5×10^{-6}
$k_t\phi_{ST}$ (sec^{-1})	3.36	2.78
k_t (sec^{-1})	8.4	
ϕ_{ST}[a]	0.4	
k_{total} (sec^{-1})	1.98×10^{3}	5.64×10^{3}

a) Ref. 12)

Concluding Remarks

In the present paper it has been shown that in suitable systems both the normal and delayed fluorescence can be accurately measured by a flash apparatus. E-Type and P-type delayed fluorescence have been studied to demonstrate the availability of the present method. In particular, the value of p for anthracene (P-type) and the values of $k_t\cdot\phi_{ST}$ for eosine and proflavine (E-type) have been decided. Although there are reliable values for ϕ_{ST} and k_{TT} of anthracene reported in the literature, Parker's p-value for anthracene is the only one ever reported.

A brief description will be added on some advantages of the present method over the sector method.

1) It is possible to compare the triplet decay and the time dependence of the delayed fluorescence, with the same one apparatus and accordingly under quite the similar condition.

2) Since the triplet yield is very high in the flash experiment it is rather easy to make the intensity of the delayed fluorescence large enough to be measureable.

3) P-Type and E-type can be distinguished rather easily by examining the applicability of Eqs. (2) and (3). In the sector method on the other hand, the decay constant of the delayed fluorescence, becomes twice that of the triplet decay, only when the triplet concentration is low enough.

4) In evaluating the $p\cdot\phi_{ST}$ values of the P-type delayed fluorescence, it is unnecessary to know the absolute value of the second order rate constant of the triplet state decay. The knowledge of the apparent second order decay constant of the T-T absorption is enough for this purpose.

There will be no need to say that the present method can be used to investigate other elementary processes pertaining to the excited state. In particular, studies on the mixed T–T annihilation are expected to afford detailed information. Medinger's method for determining ϕ_{ST}[8] also will be easily modified for the present method. Lastly the application of Eq. (7) seems to be very promising, provided the dependence of α upon wavelength is systematically investigated. Studies upon these problems are now in progress.