Triplet Formation Efficiencies from Delayed Fluorescence Measurements

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THE process of triplet to singlet energy transfer[1] proceeds at high encounter efficiency provided that the triplet level of the acceptor lies well below that of the donor. With high acceptor concentrations the donor triplet is completely quenched and the efficiency of the resulting sensitised delayed fluorescence[2] of the acceptor is then given by the following equation:—

$$\theta/\phi_f = \tfrac{1}{2}pk_r I_a(p_e\phi_t\tau)^2 \qquad (1)$$

in which ϕ_f and θ are the efficiencies of prompt and sensitised delayed fluorescence of the acceptor, k_r is

sensitised delayed fluorescence). The relationship between the intensities of sensitised delayed fluorescence (I_{DF}) emitted by two solutions containing the same acceptor but different donors, and measured at the same rate of light absorption in the same solvent, is thus as follows:—

$$\frac{(I_{DF})_1}{(I_{DF})_2} = \left[\frac{(p_e\phi_t)_1\,\tau_1}{(p_e\phi_t)_2\,\tau_2}\right]^2 \qquad (2)$$

Thus, if p_e is the same for all donors (it is generally assumed to be unity), measurement of the relative

TABLE

Sensitised delayed fluorescence of 4×10^{-5}M *perylene in ethanol at* 21°C
Wavelength of exciting light was 313 nm.

Donor	I_{DF} (relative)	τ_{DF} msec.	ϕ_t	ϕ_f
Anthracene	1·000	2·44	[0·70]	[0·30]
Pyrene	0·144	2·32	0·28	0·72
1-Methoxynaphthalene	0·437	2·46	0·46	0·53
Naphthalene	0·886	2·48	0·65	0·21
Acenaphthene	0·399	2·39	0·45	0·39

the bimolecular encounter rate constant, p is the probability that an encounter between two acceptor triplets will give rise to an excited singlet acceptor, I_a is the rate of light absorption by the donor, p_e is the proportion of quenching encounters between donor triplet and acceptor ground state that give rise to acceptor triplets, ϕ_t is the triplet formation efficiency of the *donor* and τ the triplet lifetime of the *acceptor* (equal to twice the lifetime of the

intensities and the lifetimes of the delayed fluorescence provides a simple method for comparing the triplet formation efficiencies of the two donors.

To avoid complications due to the additional delayed fluorescence produced by direct excitation of the acceptor, the latter should have a low triplet-formation efficiency and a low extinction coefficient at the wavelength of the exciting light. It should also have a low-lying triplet level so that

it can accept triplet energy from a wide range of donors. Perylene is almost ideal in these respects.[3] Its probability factor p is rather low[3] but is sufficient to give a readily measurable sensitised delayed fluorescence with many donors. Some preliminary values of ϕ_t obtained by comparison with anthracene ($\phi_t = 0.70$)[4] are shown in the Table, together with values of ϕ_f, also determined by comparison with anthracene.[5]

For two of the compounds $\phi_t + \phi_f$ is unity; for the other two it is somewhat less than unity. It therefore seems that internal conversion from the first excited singlet state is negligible for the former but appreciable for the latter. However, the over-all precision with which $\phi_t + \phi_f$ can be measured is probably not better than 10% and definite conclusions about the significance of internal conversion from the excited singlet state must await the accumulation of data from experiments now in progress with a variety of other compounds.

[1] G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, 1961, *A*, **264**, 1.
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[3] C. A. Parker and T. A. Joyce, *Chem. Comm.*, 1966, 108.
[4] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 620.
[5] C. A. Parker and W. T. Rees, *Analyst*, 1960, **85**, 587.