

A New Accurate Method for determining the Quantum Yields of Triplet State Production of Aromatic Molecules in Solution

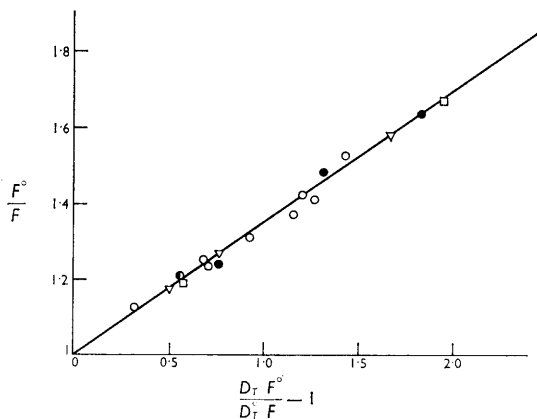
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In a recent paper¹ we showed how quantitative measurements of the relative amounts of fluorescence and of the relative initial triplet-state absorption following flash excitation in the presence and absence of bromobenzene, a fluorescence quencher containing a heavy atom, can be used to determine ϕ_T , the quantum yield of triplet-state production of aromatic molecules in solution. In order to test the applicability of this method, five different molecules containing heavy atoms have been used to quench the fluorescence of 9-phenylanthracene. Liquid paraffin (viscosity 200 centipoise) was used as solvent because the long triplet-state decay makes extrapolation to give the initial triplet-state absorbance much easier. However the method is equally applicable to less viscous solvents such as ethanol.

From the mechanism shown below,

1. ${}^1A + h\nu \rightarrow {}^1A^*$
2. ${}^1A^* \rightarrow {}^1A + h\nu_F$
3. ${}^1A^* \rightarrow {}^1A$
4. ${}^1A^* \rightarrow {}^3A^*$
5. ${}^3A^* \rightarrow {}^1A$
6. ${}^1A^* + Q \rightarrow {}^3A^* + Q$



Plot showing relationship between relative fluorescence intensities and relative initial amounts of triplet-state production for 9-phenylanthracene in liquid paraffin with various amounts of quencher, \circ , bromobenzene, \bullet , bromocyclohexane, \ominus , p-dibromobenzene, \square , ethyl iodide, and ∇ , n-propyl iodide.

where 1A , ${}^1A^*$, and ${}^3A^*$ represent the ground state, the first excited singlet state and the lowest triplet state of 9-phenylanthracene respectively, and Q the quencher containing a heavy atom, it follows that

$$\frac{F^0}{F} = 1 + k_6\tau[Q] \quad \dots \quad (1)$$

where F and F^0 are the fluorescence intensities in the presence and absence of the quencher and $\tau = 1/(k_2 + k_3 + k_4)$. If $[{}^3A]$ and $[{}^3A^0]$ are the initial concentrations and D_T and D_T^0 the initial optical densities of the triplet state following flash excitation in the presence and absence of quencher then:

$$\frac{[{}^3A]}{[{}^3A^0]} = \frac{D_T}{D_T^0} = \frac{1 + \frac{k_6}{k_4}\tau[Q]}{1 + k_6\tau[Q]} \quad \dots \quad (2)$$

Combining (1) and (2) we get

$$\frac{F^0}{F} = \left(\frac{D_T}{D_T^0} \frac{F^0}{F} - 1 \right) \phi_T + 1 \quad \dots \quad (3)$$

since $\phi_T = k_4\tau$.

Experimental details are given in Reference 1. All solutions were thoroughly outgassed. Figure 1 shows a plot based on Equation (3) for the five different quenchers at various concentrations. The line shown was drawn by the method of least squares and gives an intercept of 0.993 ± 0.012 and a slope $\phi_T = 0.3483 \pm 0.0091$. This illustrates that Equation (3) is well obeyed for all five quenchers and that the standard deviation of the ϕ_T -values is less than 3%. Lamola and Hammond have recently developed a method for measuring ϕ_T , using the sensitized *cis-trans*-isomerisation of *cis*-piperylene which gives values of ϕ_T to $\pm 5\%$.² This method would be unapplicable to 9-phenylanthracene and to other molecules with low-lying triplet levels. Preliminary measurements using inorganic iodides as fluorescence quenchers suggest that our method may not prove applicable using inorganic quenchers containing heavy atoms.

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¹ T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 620.

² A. A. Lamola and G. S. Hammond—to be published (see ref. 3).

³ A. A. Lamola, P. A. Leersmakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 2322.