Excited Complex formed by Mixed Triplet Interaction

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SENSITISED P-type delayed fluorescence[1] can be produced by two mechanisms, both of which require as their first stage the transfer of triplet energy from donor (D) to acceptor (A):

$$^3D + {}^1A \rightarrow {}^1D + {}^3A \quad (1)$$

The first mechanism then proceeds by interaction between two acceptor triplets:

$$^3A + {}^3A \rightarrow [^1A_2{}^*] \rightarrow {}^1A^* + {}^1A \quad (2)$$

and the second by interaction between unlike triplets:

$$^3A + {}^3D \rightarrow [(AD)^*] \rightarrow {}^1A^* + {}^1D \quad (3)$$

Process (2) can involve the intermediate formation of an excited dimer,[2] and we now present evidence that process (3) can take place *via* the formation of an excited complex, (AD)*. Such excited complexes ("exciplexes")[3] have previously been detected by measuring the prompt fluorescence spectra of relatively concentrated solutions, in which they are sometimes produced by reaction of excited and ground state singlet molecules:—

$$^1A^* + {}^1D \rightarrow (AD)^* \quad (4)$$

Process (3) is favoured in solutions containing low concentrations of acceptor, *i.e.*, solutions in which the donor triplet is only partly quenched. With high concentrations of acceptor, the donor triplet is strongly quenched [equation (1)] and delayed fluorescence is then emitted only *via* process (2). The transition from the first of these conditions to the second is illustrated by the spectra in the Figure. At −75° in ethanol, anthracene alone emits delayed fluorescence showing strong bands due to monomer, and a weak broad band due to dimer (curve 1), corresponding to the processes:

$$\begin{array}{ccc} {}^3D + {}^3D \rightarrow {}^1D_2^* & \xrightarrow{\qquad} & {}^1D^* + {}^1D \\ \downarrow & & \downarrow \\ \text{dimer emission} & & \text{monomer emission} \end{array} \qquad (5)$$

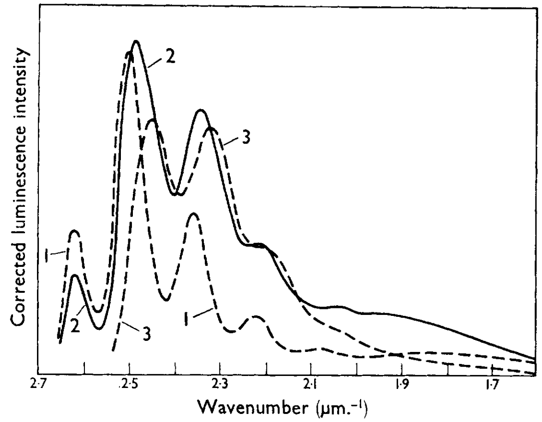

FIGURE. *Illustrating formation of excited complex. Delayed fluorescence of ethanolic solutions of* 10^{-4}M *anthracene containing the following concentrations of 9,10-diphenylanthracene: Curve 1, zero; curve 2,* 3 × 10^{-7} M; *curve* 3, 10^{-5} M. (*High wave number regions distorted by self-absorption.*)

In the presence of 3 × 10^{-7}M diphenylanthracene (curve 2) the anthracene triplet is partly quenched (as indicated by the decreased intensity of the band at ~2·6 μm.⁻¹), and the delayed fluorescence spectrum now contains components due to anthracene monomer and diphenylanthracene monomer, as well as a broad band emission (~1·9 μm.⁻¹) which is more intense than that observed from the solution containing anthracene alone. When the concentration of diphenylanthracene is increased to 10^{-5} M, the delayed fluorescence of the anthracene is almost completely quenched, process (3) can no longer occur, and the spectrum corresponds almost entirely to emission from diphenylanthracene monomer produced *via* process (2), with only a small proportion of broad band emission (curve 3).

We accordingly attribute the increased broad band emission (curve 2) to the excited complex (AD)*. From the spectra of the delayed fluorescence of solutions containing various concentrations of diphenylanthracene, we have calculated the ratios of the intensities of emissions from the excited complex (θ_C) and from the diphenylanthracene monomer (θ_M) (see Table 1). The value of θ_C/θ_M is greatest at low concentrations of diphenylanthracene and falls to zero at high concentrations, as would be expected if the delayed fluorescence of the monomer is produced *via* processes (2) and (3), but that of the excited complex *via* process (3) alone.

TABLE 1.

Relative efficiency of delayed fluorescence of excited complex

All solutions contained 10^{-4}M anthracene and were excited at 366 nm.

Concentration of 9,10-diphenylanthracene	Ratio of intensities of emission from complex and from 9,10-diphenylanthracene (θ_C/θ_M)
10^{-7}M	0·7
3 × 10^{-7}	0·32
10^{-6}	0·24
3 × 10^{-6}	0·13
10^{-5}	0·08
3 × 10^{-5}	0·02

Correction of the appropriate spectra gave spectra corresponding to the excited complex alone, and the excited dimer of anthracene alone. The wave

TABLE 2.

Delayed fluorescence of excited dimers at −75° in ethanol

Compound	Concentration	θ_D/θ_M	Wave number maximum Monomer	Wave number maximum Dimer
Pyrene	2 × 10^{-5}M	0·79	2·69 μm⁻¹	2·03 μm⁻¹
9-Methylanthracene	2 × 10^{-5}	0·23	2·57	1·77
9,10-Dimethylanthracene	5·5 × 10^{-5}	0·62	2·48	1·75
9-Phenylanthracene	2 × 10^{-5}	0·33	2·53	1·89
9,10-Diphenylanthracene	2·1 × 10^{-5}	nil	2·46	none
Anthracene	10^{-4}	0·16	2·64	1·83
Anthracene + diphenylanthracene (complex)	see Table 1	—	—	1·92

number maxima of these spectra are compared in Table 2 with the corresponding values derived from measurements of the delayed fluorescence of pyrene and 9,10-substituted anthracenes[4] at −75°.

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