Activation-controlled Delayed Fluorescence of Benzil

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The phosphorescence spectra of benzil in benzene recorded by Bäckström and Sandros[1], and in n-heptane, by Almgren[2] both show a weak band in the position corresponding to the prompt fluorescence. We have found a similar weak band in the spectrum of the long-lived photoluminescence of benzil in perfluoromethylcyclohexane (see curve B). The position of the weak band corresponded with the maximum in the prompt fluorescence spectrum (curve D) and its quantum efficiency at 20° was approximately one half of that of the corresponding band in the spectrum of directly excited total luminescence (see Table). The intensity of the weak band (at 1·99 μm.$^{-1}$) was proportional to the first power of the intensity of the exciting light and increased with temperature relative to the intensity of the phosphorescence band (at 1·78 μm.$^{-1}$) (compare curves A, B, and C). The slope of the logarithmic plot[3] gave an activation energy corresponding to $0{\cdot}20 \pm 0{\cdot}02$ μm.$^{-1}$, *i.e.* close to the spectroscopic value derived from the separation between the maxima of the delayed fluorescence and phosphorescence bands. The weak band is thus identified as *E*-type delayed fluorescence.[3]

The ratio ϕ_e/ϕ_f (see Table) is far greater than in systems previously investigated (*e.g.* ϕ_e/ϕ_f ~0·005 for eosin in glycerol at 20°[4]) and it is of interest to know what factors contribute to high values of this parameter. For this purpose the

Table

Quantum efficiencies and lifetimes of photoluminescence of benzil in de-aerated perfluoromethylcyclohexane at 20°

Prompt fluorescence:	$\phi_f = 0{\cdot}0012$
Delayed fluorescence:	$\phi_e = 0{\cdot}0015$
Phosphorescence (directly excited):	$\phi_p = 0{\cdot}034$; $\tau = 0{\cdot}50$ msec.
Phosphorescence (sensitised by benzophenone):	$\phi_p = 0{\cdot}034$; $\tau = 0{\cdot}44$ msec.
Radiative lifetime of triplet ($=\tau/\phi_p$): (assuming $\phi_t \sim 1$)	15 ± 1; 13 ± 1 msec.

kinetic scheme previously used[3] to describe E-type delayed fluorescence must be extended to take account of the fraction (ϕ_t) of the singlet excited molecules produced by thermal activation that return to the triplet state. The overall rate of depletion of the triplet state by thermal activation is then k_e $(1 - \phi_t)$ and equation 120 in ref. 3 then becomes:—

$$\phi_e/\phi_f = k_e\phi_t\tau = k_e\phi_t/[k_p + k_m + k_q[q] + k_e(1 - \phi_t)] \quad (1)$$

in which k_e is the rate constant for the process $S_1 \longleftarrow T_1$ and the other rate constants in the denominator refer to the processes $T_1 \longrightarrow S_0$. The ratio ϕ_e/ϕ_f has a maximum value equal to $\phi_t/(1 - \phi_t)$ when:—

$$k_e(1 - \phi_t) >> (k_p + k_m + k_q[q]) \quad (2)$$

We propose the name activation-controlled delayed fluorescence for emission under the conditions represented by equation (2). Clearly, with compounds having high triplet-formation efficiencies the ratio ϕ_e/ϕ_f can rise to very high values when the conditions for activation-controlled delayed fluorescence are approached. If in addition the sum of ϕ_f and ϕ_t is unity, the value of ϕ_e becomes equal to ϕ_t and it is thus possible, in principle, to observe activation-controlled delayed fluorescence at near unit-quantum efficiency from compounds having low efficiencies of prompt fluorescence.

Benzil in solution falls far short of exhibiting activation-controlled delayed fluorescence because of its relatively large triplet–singlet separation (giving a relatively low value of k_e) and the relatively high values of the other triplet–decay constants. Activation-controlled delayed fluorescence is most likely to be observed with compounds having a small triplet–singlet separation. Some of the charge-transfer complexes investigated by Iwata, Tanaka, and Nagakura[5] appear to satisfy this condition. We suggest therefore that the long-lived emissions from such complexes (*e.g.* those of hexamethylbenzene with tetrachlorophthalic anhydride or pyromellitic dianhydride) at 77° K are in fact E-type delayed fluorescence emitted under conditions approaching those of activation control. The lifetimes of the triplets would then be controlled mainly by the values of $k_e(1 - \phi_t)$ [see equation (1)] and would be expected to have much lower values than those of the charge-transfer complexes showing large triplet–singlet separations. This was indeed found to be the case with hexamethylbenzenete–trachlorophthalic anhydride.[5]

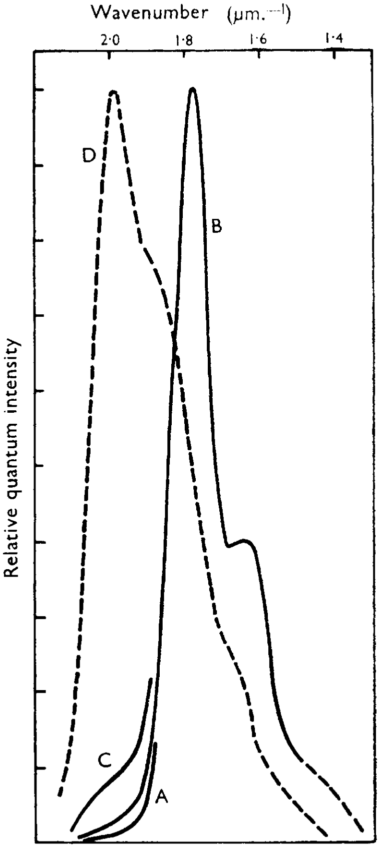

FIGURE. *Photoluminescence emission spectra of* 2×10^{-4}M-*benzil in perfluoromethylcyclohexane.* (A)(B)(C) *long-lived emission in de-aerated solutions:* (A) *directly excited by* 313 *nm. at* −19°; (B) *both directly excited* (313 *nm.*) *and sensitised by benzophenone* (366 *nm.*) *at* +20°; (C) *sensitised by benzophenone at* +60°: (D) *prompt fluorescence of an aerated solution. Intensity scale of* (D) *is not comparable with remainder.*

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