Diffusion and Surface Quenching of the Triplet State of Aromatic Hydrocarbons in the Gas Phase

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UNDER conditions such that the intensity of delayed fluorescence varies as the second power of absorbed light intensity, the emission originates in a process of triplet–triplet state annihilation[1] which requires that the exponential-decay constant k_D is exactly twice that for unimolecular triplet-state relaxation k_T.[1,2] Thus a method is available for the measurement of triplet-state lifetimes of aromatic hydrocarbons in the vapour phase which is not complicated by the dominant second-order effects encountered at the relatively high triplet-state concentrations required to monitor its optical density by flash kinetic spectroscopy.[3]

During an investigation of delayed fluorescence of aromatic hydrocarbon vapours it was necessary to focus the exciting beam from a 125 w D.C. mercury arc on to the centre of the vertical cylindrical Pyrex cell, and also to focus the fluorescence radiation from this small excitation zone on to the detector to obtain an appreciable signal: noise ratio at low vapour pressures. Under these conditions the delayed component of fluorescence was found to decay exponentially with time and vary as the square of the incident light intensity[4] as required by the triplet–triplet annihilation mechanism; moreover at very low pressures the lifetime of the triplet state measured as $2/k_D$, was observed to *increase* both with vapour pressure p in a given cell and with the cell radius R at a given vapour pressure. The data for anthanthrene shown in the Figure can be expressed as

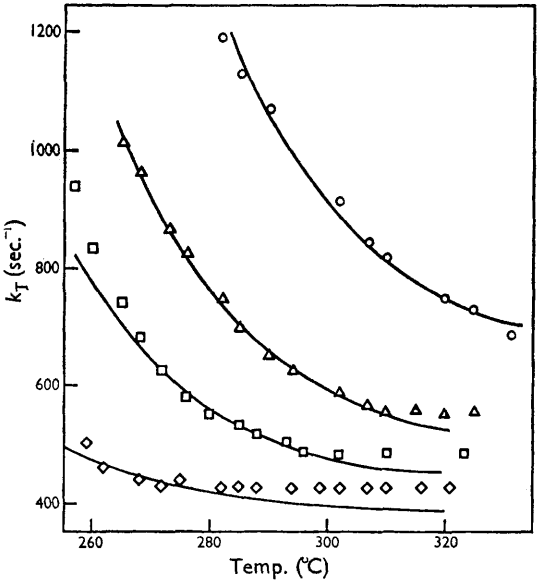
$$k_D/2 = k_T = A + B/R^2 + C/pR^2 \qquad (1)$$

where A, B, and C are constants at the particular vapour temperature.

This behaviour is qualitatively consistent with a mechanism in which the measured triplet-state decay-constant is determined by (*a*) homogeneous unimolecular triplet-state relaxation characterised by a rate constant $k_1 = A$; (*b*) quenching by an impurity Q in the solid hydrocarbon which is assumed to be vapourised completely at the lowest anthanthrene pressure and to be present at concentration $[Q] \propto R^{-2}$ in cells of uniform height containing (approximately) the same weight of anthranthrene; (*c*) diffusion of triplet states out of the observation zone under a concentration gradient maintained by quenching of the triplet state of the cell walls. Although the cylindrical symmetry of the system imposes an angular dependence of the concentration gradient which may also be determined by the rate of homogeneous relaxation, a treatment of the model system, in which diffusion of molecules from the principal axis to the curved walls of a cylinder of length $\gg R$ where they are quenched, shows[5] that the diffusion is characterised by a first-order rate constant of the form

$$2D/R^2 = \bar{C}/2\ 2^{\frac{1}{2}}\pi\sigma^2 nR^2 \qquad .. \qquad .. \qquad (2)$$

where the diffusion coefficient D is expressed in terms of the average molecular velocity $\bar{C}$,



Plot of $k_D/2 = k_T$ *measured for anthanthrene vapour delayed fluorescence as a function of temperature of liquid anthanthrene, in cylindrical cells of diameter* 0·5 *cm.* ○; 0·7 *cm.* △; 1·1 *cm.* □; *and* 1·9 *cm.* ◇. *Vapour temperature,* 340°C.

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[1] C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, 1962, **147**; *Proc. Roy. Soc.*, 1962, *A*, **269**, 574.

[2] B. Stevens and M. S. Walker, *Proc. Roy. Soc.*, 1964, *A*, **281**, 420.

[3] G. Porter and P. West, *Proc. Roy. Soc.*, 1964, *A*, **279**, 302.

[4] B. Stevens, M. S. Walker, and E. Hutton, *Proc. Chem. Soc.*, 1963, 62.

[5] *E.g.*, E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, 1957, p. 1169 ff.

collision diameter σ and molecular concentration n. This corresponds to the third term in expression (I).

The quantitative consistency of this mechanism is illustrated by the solid curves in the Figure drawn according to expression (I) with

$$A + B/R^2 = (k_{\mathrm{I}})_{p=\infty} \quad \text{and with} \quad C/p = 2D$$

by using a value of 9Å for σ and vapour pressure data for anthanthrene liquid calculated from an estimated heat of vapourisation of 26·0 kcal./mole and the vapour pressure of the solid[6] at its melting point.

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[6] H. Inokuchi, S. Shiba, T. Handa, and H. Akamatu, *Bull. Chem. Soc. Japan*, 1952, **25**, 299.