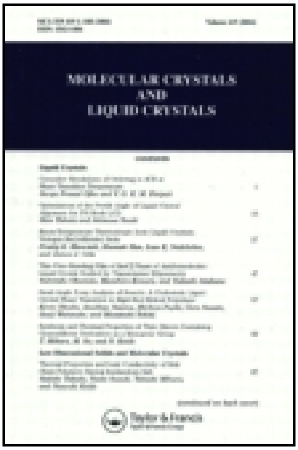

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Pathways of Triplet-Triplet Annihilation in Ethanolic Solutions of Pyrene

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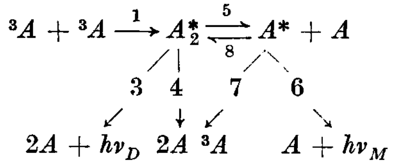
Abstract—The ratio of excimer to molecular fluorescence intensities in both the delayed and total emission spectra of pyrene in ethanol has been measured as a function of solute concentration and temperature from 150–350°K. An analysis of the data in terms of triplet-triplet annihilation leading directly to excimer formation (process 1) or production of the lowest excited molecular singlet state (process 2) shows that the relative probabilities k_1/k_2 of these processes increases from zero at low temperatures to a maximum of 1.8 at higher temperatures.

1. Introduction

The observation of both molecular and excimer bands in the delayed fluorescence spectrum of dissolved pyrene A led Parker and Hatchard[1] to suggest that triplet-triplet annihilation in this system involves the formation of an excimer intermediate A_2^*, the sequence of events being represented by



where A^* and ^3A denote the lowest excited molecular states of singlet and triplet multiplicity.

Since excimer dissociation (process 5) requires an activation energy of ~ 10 kcal/mole[1] this scheme is consistent with the observation of a negative temperature-coefficient for the ratio D_D/D_M of excimer to molecular band intensities in the delayed emission spectrum recorded above room temperature (cf. Fig. 1). At lower temperatures however this

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temperature-coefficient becomes positive (Fig. 1) and at very low temperatures in rigid solution no excimer band is observed; to account for this behaviour Tanaka *et al.*[3] proposed the additional annihilation process

$$^3A + {}^3A \xrightarrow{2} A^* + A \underset{5}{\overset{8}{\rightleftharpoons}} A_2^*$$

which, they suggested, may take place at distances greater than those defining a molecular encounter since this might be expected to be followed by photoassociation (process 8) in the solvent cage and the overall effect would be that of process 1. This view has been supported by Parker[4] who observed that D_D/D_M approaches zero at low temperatures (and high viscosities) for solutions both of pyrene and of 3,4-benzpyrene, and who pointed out that the simultaneous operation of the diffusional process 1 and of a long-range viscosity-independent process 2 would explain the transition from an encounter mechanism of triplet-triplet annihilation in low-viscosity solvents to the long-range annihilation postulated to account for the delayed component of (molecular) fluorescence exhibited by dilute rigid solutions.[5, 6]

Azumi and McGlynn[7] have discussed long range triplet-triplet annihilation in terms of a dipole-dipole interaction which, as Förster points out, is not necessarily prohibited by a spin-forbidden transition in the donor (in this case $^3A \rightarrow A$) if the transition is optically allowed in the acceptor; it is doubtful whether the latter condition is fulfilled if the acceptor is excited directly to the singlet state (i.e. $^3A \rightarrow A^*$) although the reverse process often competes effectively with fluorescence emission.

Kellogg[8] has suggested an alternative mechanism based on an optically-allowed transition of the acceptor to a higher triplet state $^3A^*$ i.e.

$$^3A + {}^3A \longrightarrow A + {}^3A^*$$

which satisfies the conditions described by Förster[9] for the dipole-dipole induced radiationless transfer of energy, and has shown that the considerable overlap of the phosphorescence (donor emission) spectrum and the triplet-triplet absorption spectrum (of the acceptor) is sufficient to account for a transfer distance of 40 Å. in the case of phenanthrene[8]; however it remains to be shown that intersystem crossing from this higher triplet state to the singlet manifold ($^3A^* \rightarrow A^*$), required to complete the overall process, competes effectively with its internal conversion to ^3A.

Despite these limitations concerning long-range triplet-triplet annihilation, the interpretation of delayed molecular fluorescence exhibited by aromatic hydrocarbons in a rigid matrix in terms of this mechanism requires that this mutual annihilation takes place at distances of at least 15 Å, even in concentrated solutions,[10] in which case process 2 should be characteristically independent of viscosity in fluid solutions.[9] Accordingly, since process 1 undoubtedly requires an encounter of two molecules in the triplet state and the corresponding rate constant k_1 should exhibit a viscosity-dependence, the rate constant ratio k_1/k_2 might be expected to decrease with an increase in viscosity produced by lowering the temperature of the solution.

2. Experimental

The spectra of normal (unsectored) and delayed fluorescence components of carefully outgassed solutions of pyrene in ethanol were recorded photoelectrically as a function of temperature over the range 150–350°K using an Aminco-Keirs spectrophotophosphorimeter; the procedure has been described previously,[2] except that in order to obtain a sufficient intensity of the delayed component, this was excited by the 313 mμ line from a 125 watt high pressure stabilized arc (Mazda MBL/D) fitted to the instrument.

The recorded signal intensities at 395 mμ and at 465 mμ, corresponding to the molecular and excimer emission bands respectively, were corrected for the sensitivities of the detector assembly at these wavelengths, and converted to relative molecular and excimer fluorescence intensities by comparison with the corrected spectra of the individual bands obtained for dilute and concentrated solutions. No correction was made for the contribution of the very small intensity (~1%) of the delayed component to the intensity of the total (unsectored) emission spectrum.

Wire mesh screens of different transmission were used to vary the source intensity and delayed fluorescence decay curves were obtained as described previously.[12]

3. Results

The measured intensity ratios D_D/D_M and F_D/F_M are plotted for different solute concentrations as a function of temperature in Figure 1. Over the whole region the delayed fluorescence intensity was found to

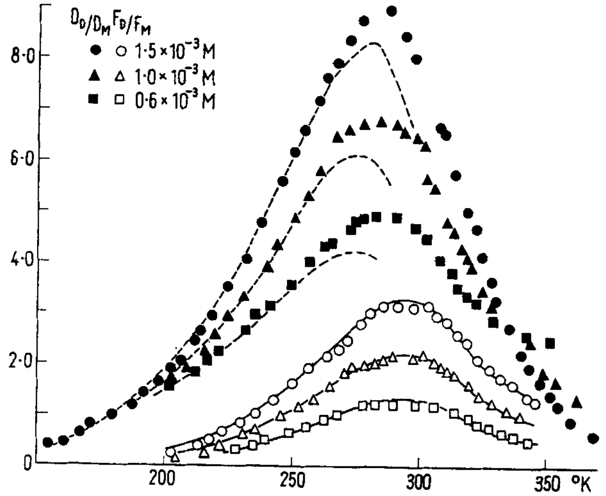

Figure 1. Temperature-dependence of D_D/D_M (solid symbols) and F_D/F_M (open symbols) for solutions of pyrene in ethanol. Solid curves drawn according to equation (1) with quoted values of rate constants; dashed curves from equations (4) and (8).

vary as the square of the incident light intensity and to decay exponentially.

4. Discussion

Under photostationary conditions the ratio F_D/F_M of excimer to molecular band intensities in the normal (unsectored) emission spectrum is given by

$$\frac{F_D}{F_M} = \frac{k_3 k_8[A]}{k_6(k_3 + k_4 + k_5)} \tag{1}$$

and the intensities of excimer and molecular bands in the delayed emission spectrum are respectively

$$D_D = \frac{k_3[^3A]^2}{k_3 + k_4 + k_5}\left\{k_1 + \frac{k_2 k_8[A]}{k_6 + k_7 + k_8[A]}\right\} \tag{2}$$

and

$$D_M = \frac{k_6[^3A]^2}{k_6 + k_7 + k_8[A]}\left\{k_2 + \frac{k_1 k_5}{k_3 + k_4 + k_5}\right\} \tag{3}$$

where [ ] denotes concentration of the enclosed species.

Since the delayed fluorescence component decays exponentially, it follows from (2) and (3) that

$$d \ln D_D/dt = 2d \ln [^3A]/dt = d \ln D_M/dt$$

i.e. the ratio $D_D(t)/D_M(t)$ of intensities recorded at an interval t following excitation out-off is independent of t and equal to the intensity ratio expected under photostationary conditions. Equations (2) and (3) lead to the expression

$$\frac{D_D}{D_M} = \frac{k_1k_3(k_6 + k_7) + k_3k_8[A]\,(k_1 + k_2)}{k_2k_6(k_3 + k_4) + k_5k_6\,(k_1 + k_2)} \tag{4}$$

from which the temperature-dependence of the ratio k_1/k_2 can be estimated provided the rate constants $k_3 - k_8$ are known as a function of temperature over the same range.

Process 8 was shown by Birks *et al.*[15] to be diffusion-limited at 20°C; accordingly it is assumed that

$$k_8 = k_d = 8\mathrm{RT}/3000\eta \tag{5}$$

over the whole temperature range, and may be computed from published data for the solvent viscosity η.

In dilute solutions such that $(k_6 + k_7) \gg k_8[A]$ the lifetime τ_M of the excited molecule is given by

$$\frac{-d \ln F_M}{dt} = \frac{1}{\tau_M} = k_6 + k_7$$

since it has been established that internal conversion ($A^* \to A$) does not contribute to its electronic relaxation.[16] Independent measurements[13] of τ_M as a function of temperature for a 2×10^{-6} M solution of pyrene in ethanol provide the values

$$k_6 = 1.33 \times 10^6\ \mathrm{sec}^{-1}$$

$$k_7 = 3.3 \times 10^7 \exp\,(-2270/\mathrm{RT})\ \mathrm{sec}^{-1}$$

The radiative decay constant is in excellent agreement with the value $k_6 = 1.36 \times 10^6\ \mathrm{sec}^{-1}$ measured by Birks *et al.* who also find that[17]

$$k_3 = 1.3 \times 10^7\ \mathrm{sec}^{-1}.$$

The rate constants for processes 4 and 5 are estimated from the temperature dependence of the intensity ratio F_D/F_M of the same solutions for which purpose Eq. (1) is rearranged to

$$\frac{k_8[A]}{k_6F_D/F_M} - 1 = \frac{k_4 + k_5}{k_3} \tag{6}$$

The logarithm of $(k_4 + k_5)/k_3$ from (6) is plotted as a function of reciprocal temperature in Fig. 2 and a curve fitting procedure based on the approximations

$$k_4 \gg k_5 \text{ at low temperatures}$$

$$k_4 \ll k_5 \text{ at high temperatures}$$

is employed to obtain the expressions

$$k_4 = 2.9 \times 10^7 \exp(-1150/\mathrm{RT}) \sec^{-1}$$

$$k_5 = 1.5 \times 10^{16} \exp(-12700/\mathrm{RT}) \sec^{-1}$$

The latter is in good agreement with the value

$$k_5 = 2 \times 10^{16} \exp(-12600/\mathrm{RT}) \sec^{-1}$$

previously reported[17] and the activation energy corresponds to the sum of the excimer dissociation energy (9.5 kcal/mole) and the activation energy for viscous flow (3.2 kcal/mole) of the solvent. The solid curve is drawn in Fig. 2 in accordance with the quoted values for the constants k_3, k_4 and k_5 and these together with k_6 and k_8 are used to construct the theoretical temperature variation of F_D/F_M from equation (1) represented by the solid curves in Fig. 1.

At lower temperatures ($\leq$270°K) where $k_5 \ll (k_3 + k_4)$ Eq. (4) reduces to

$$\frac{D_D}{D_M} = \frac{k_3k_8[A]}{k_6(k_3 + k_4)}\left\{1 + \frac{k_1}{k_2}\right\} + \frac{k_1k_3(k_6 + k_7)}{k_2k_6(k_3 + k_4)}$$

which may be rearranged with Eq. (1) to yield

$$\frac{D_D}{D_M} - \frac{F_D}{F_M} = \frac{k_1}{k_2}\left\{\frac{F_D}{F_M} + \frac{\gamma_D}{\gamma_M}\right\} \tag{7}$$

where $\gamma_D = k_3/(k_3 + k_4)$ and $\gamma_M = k_6/(k_6 + k_7)$.

Values of k_1/k_2 obtained from Eq. (7) are found to increase with temperature approaching a maximum value (α) above 230°K as shown in Fig. 3. This behaviour is consistent with the operation of two triplet-

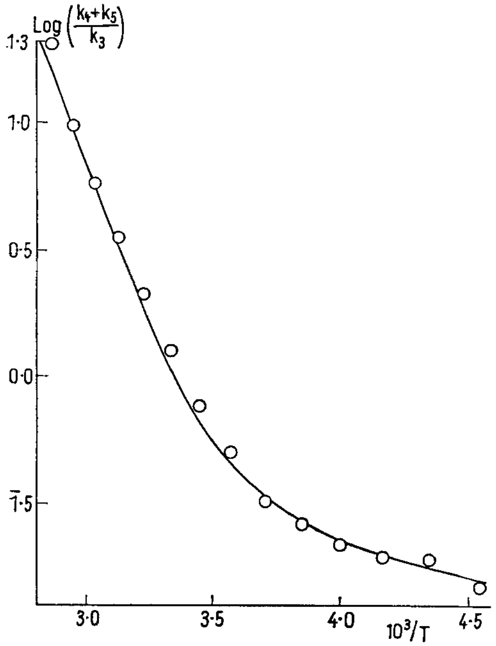

Figure 2. Plot of log (k_8 [A] F_D/k_6 F_M − 1) against $1/T$ to obtain k_4 and k_3. Solid curve drawn with values of k_4 and k_5 quoted in text.

triplet annihiliation processes to generate the excited singlet state (process 2) one of which is temperature independent and the other varying with temperature as process 1. Accordingly

$$\frac{k_1}{k_2} = \frac{k_1(T)}{k_2^0 + k_2(T)} = \frac{\alpha}{1 + k_2^0/k_2(T)} \tag{8}$$

where $\alpha = k_1(T)/k_2(T)$ is the temperature-independent limiting ratio at higher temperatures, and k_2^0 is the rate constant for the temperature-independent component of process 2. The curve drawn in Fig. 3 is a quantitative expression of Eq. (8) with $\alpha = 1.8$, (cf. the value of $\alpha = 2.0$ computed from the data at room temperature[11]), $k_2^0 = 8 \times 10^7$ lit. mole^{-1} sec^{-1} and $k_2(T) = k_d$, and the ratio k_1/k_2 computed from Eq. (8) is used in Eq. (4) to obtain the theoretical temperature-dependence of D_D/D_M represented by the broken curves in Fig. 1.

The nature of the temperature-independent biphotonic process responsible for delayed molecular fluorescence at low temperatures

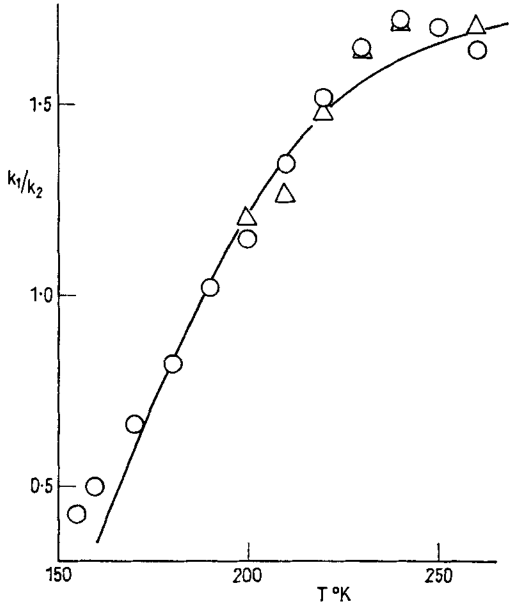

Figure 3. Temperature dependence of k_1/k_2 estimated from Eq. (7) for 1.5 × 10^{-3} *M* solution of pyrene at lower temperatures.

remains obscure. It is unlikely to involve the triplet-triplet state resonance transfer discussed by Kellogg[8] since this would depend on the triplet state lifetime $^3\tau$ which is limited by temperature-dependent diffusional quenching by impurities in this region;[13] ion-electron recombination following photooxidation of the triplet state could account for the delayed molecular fluorescence component[14] but would be subject to the same objection and would not be expected to give rise to an exponential decay. There remains however the possibility that thermal equilibration of the triplet-triplet annihilation product A_2^* is not sufficiently rapid to prevent its immediate dissociation to ground and excited singlet states at lower temperatures in which case processes 1 and 2 involve the same vibrationally-excited intermediate A_2^{*1} which is effectively stabilised at higher temperatures i.e.

$$^3A + {}^3A \rightarrow A_2^{*1} \begin{array}{l} \nearrow {}^1A_2^* \\ \searrow {}^1A^* + A \end{array}$$

The failure of Eq. (4) to account for the observed intensity ratios D_D/D_M at higher temperatures is attributed to a rapid recombination of excited and unexcited singlet states produced by process 2; dissociation annihilation in this case should increase the solute concentration in the region of electronically-excited singlet states.

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