Simultaneous Energy Transfer from Excited Monomer and Excimer Pyrene Molecules

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Measurements have been made of the excited monomer and excimer fluorescence intensities of pyrene when rubrene, 9,10-diphenylanthracene and perylene are used as energy acceptors. For the first time a binary system is analysed where both donor species transfer energy with comparable efficiencies. Some comments on the boundary conditions that must be applied to the differential equations are presented to clarify the problems involved. The rate constants for the energy transfer obtained from steady-state measurements and decay curves compare well with theoretical predictions. For the pyrene concentrations used there is no need to invoke energy-migration effects to interpret the results.

Let us consider a liquid system containing two fluorescent species dissolved in an inert solvent (transparent to the exciting radiation) at molar concentrations c_Y and c_Z. When the solution is irradiated with electromagnetic radiation totally absorbed by Y it is possible to verify that under appropriate conditions there is also fluorescence emission from Z, which shows the existence of an energy-transfer process between Y (the energy donor) and Z (the energy acceptor).

The following system has been considered by various authors.[1,2] Y is able to form excimers, D_Y^*, by interaction between an excited monomer, M_Y^*, and a ground-state molecule, M_Y, and the solution is excited with radiation of intensity I_0 (einstein dm^{-3} s^{-1}); both excited monomer and excimer can transfer their energy to Z (assumed not to form excimers). The reactions that can take place are condensed in table 1. Under excitation with a δ-pulse and assuming Stern–Volmer kinetics (the rate constants are independent of time) the following expressions are obtained[3,4] for the fluorescence emission intensities for both energy donors, excited monomer [$I_{MY}(t)$] and excimer [$I_{DY}(t)$]

$$I_{MY}(t) = k_{FMY}[M_Y^*] = k_{FMY} \frac{[M_Y^*]_0}{\lambda_2 - \lambda_1}[(\lambda_2 + A_x)\exp(-\lambda_1 t) - (\lambda_1 + A_x)\exp(-\lambda_2 t)] \quad (1)$$

$$I_{DY}(t) = k_{FDY}[D_Y^*] = k_{FDY} \frac{[M_Y^*]_0}{\lambda_2 - \lambda_1} k_{DMY} c_Y [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (2)$$

where $[M_Y^*]_0$ is the concentration of the initially excited molecules and λ_1, λ_2 are defined by

$$\lambda_{1,2} = -\frac{(A_x + A_y) \pm \sqrt{[(A_x - A_y)^2 + 4k_{DMY}k_{MDY}c_Y]}}{2} \quad (3)$$

with

$$A_x = -(k_{MY} + k_{DMY}c_Y + k_{ZY}^m c_Z) \quad (4)$$

$$A_y = -(k_{DY} + k_{MDY} + k_{ZY}^d c_Z). \quad (5)$$

TABLE 1.—RATE PARAMETERS FOR A SYSTEM WHERE THERE IS SIMULTANEOUS ENERGY TRANSFER FROM EXCITED MONOMER (M_Y^*) AND EXCIMER (D_Y^*) TO AN ACCEPTOR (M_Z)

$$M_Y + I_0 \longrightarrow M_Y^*$$

$$M_Y^* \xrightarrow{k_{FMY}} M_Y + h\nu_{MY}$$

$$M_Y^* \xrightarrow{k_{IMY}} M_Y$$

$$M_Y^* + M_Y \xrightarrow{k_{DMY}} D_Y^*$$

$$D_Y^* \xrightarrow{k_{MDY}} M_Y^* + M_Y$$

$$D_Y^* \xrightarrow{k_{FDY'}} 2M_Y + h\nu_{DY}$$

$$D_Y^* \xrightarrow{k_{IDY}} 2M_Y$$

$$M_Y^* + M_Z \xrightarrow{k_{ZY}^m} M_Y + M_Z^*$$

$$D_Y^* + M_Z \xrightarrow{k_{ZY}^d} 2M_Y + M_Z^*$$

Under steady-state conditions of excitation, assuming that all the exciting radiation is absorbed by pyrene ($[M_Y^*]_0 = I_0$)

$$I_{MY} = \int_0^\infty I_{MY}(t) = I_0 q_{MY} \frac{\Gamma_Y}{(1 + \sigma_{ZY}^m c_Z)\Gamma_Y + (1 + \sigma_{ZY}^d c_Z)c_Y} \tag{6}$$

$$I_{DY} = \int_0^\infty I_{DY}(t) = I_0 q_{DY} \frac{c_Y}{(1 + \sigma_{ZY}^m c_Z)\Gamma_Y + (1 + \sigma_{ZY}^d c_Z)c_Y} \tag{7}$$

where q_{MY} and q_{DY} are the quantum efficiencies of the monomer and excimer emission, and

$$\sigma_{ZY}^m = \frac{k_{ZY}^m}{k_{MY}}$$

$$\sigma_{ZY}^d = \frac{k_{ZY}^d}{k_{DY}} \tag{8}$$

are the Stern–Volmer constants for the transfer from the excited monomer and excimer. The quantity

$$\Gamma_Y = c_{hY}(1 + \gamma_Y \sigma_{ZY}^d c_Z) \tag{9}$$

represents a generalization of the half-value concentration, c_{hY},[1] for Y-excited monomer–excimer equilibrium, and

$$\gamma_Y = \frac{k_{DY}}{k_{DY} + k_{MDY}}. \tag{10}$$

If in the equations above we consider the case $c_Z = 0$ we can study the so-called unitary system[5] with the relationships that describe the behaviour of monomer and excimer equilibrium of Y.

For very low concentrations of pyrene the expression for λ_1 reduces to

$$\lambda_1 = k_{MY} + k_{DMY}c_Y + k_{ZY}^m c_Z \tag{11}$$

showing how the analysis of the decay curves of the monomer can be used to obtain k_{ZY}^m. On the other hand for high values of c_Y

$$\lambda_1 = k_{DY} + k_{ZY}^d c_Z \tag{12}$$

and now it is the decay of the excimer that can be used to obtain k_{ZY}^d.

Under steady-state conditions of excitation we can also get the values of σ_{ZY}^d. In fact from eqn (6), (7) and (9)

$$\frac{I_{MY}}{I_{DY}} = \frac{q_{MY}}{q_{DY}} \frac{c_{hY}}{c_Y} (1 + \gamma_Y \sigma_{ZY}^d c_Z). \tag{13}$$

Furthermore eqn (7) predicts a quadratic variation of $1/I_{DY}$ with c_Z

$$\frac{1}{I_{DY}} = a_0 + a_1 c_Z + a_2 c_Z^2 \tag{14}$$

which can be used to obtain σ_{ZY}^m and σ_{ZY}^d.

The question of the effect of a possible energy-migration process among energy-donor molecules can be studied by verifying if the values of the Stern–Volmer rate constants σ_{ZY} do vary with c_Y. If this is not the case, an alternative way of obtaining σ_{ZY}^d is the analysis of the variation of c_Y/I_{DY} with c_Y for constant c_Z. From the angular coefficient of the "predicted" linear variation, σ_{ZY}^d can be obtained.

In the past, this problem was considered in some limiting cases either using very dilute solutions to minimize the contribution of the excimer,[6,7] or using solid solutions[8,9] to avoid the effect of monomers. In systems where monomer–excimer equilibrium is fast, only an "average rate constant" for the transfer can be evaluated.[10,11]

What has been lacking is an unambiguous demonstration, with a carefully chosen system, of simultaneous transfer from the excimer and excited monomer, together with possible correlations between the transfer properties, including energy-migration processes, with the available theoretical treatments.

It is the purpose of this work to contribute to a better understanding of the problem. Pyrene was chosen as the energy donor since it is an excimer-forming molecule whose properties are well-known. Different acceptors, viz. rubrene, 9,10-diphenylanthracene (DPA) and perylene, were considered in order to examine differences in the magnitudes of the transfer constants as the overlap between donor emission and acceptor absorption was varied.

Once the Stern–Volmer rate constants for transfer are obtained from the experimentally measured emission intensities they must be compared with the values predicted by theory. Let us see briefly how this can be done.

The transfer probability for dipole–dipole interactions between an excited energy donor D^*, and an acceptor A, whose separation is r is given by[12]

$$\omega(r) = \frac{1}{\tau_0^D} \left(\frac{R_0}{r} \right)^6 = \frac{\alpha}{r^6} \tag{15}$$

where τ_0^D is the decay time of the donor in the absence of acceptor. Förster's critical distance, R_0, is given by

$$R_0^6 = \frac{9000\chi^2 q_D \ln 10}{128\pi^5 n^4 N} \int \frac{F_D(\bar{\nu})\varepsilon_A(\bar{\nu})}{\bar{\nu}^4} \, d\bar{\nu} \tag{16}$$

q_D being the quantum efficiency of the energy donor emission, n the refractive index, χ^2 an orientation factor whose value is $\frac{2}{3}$ for solutions of low viscosity, N Avogadro's number, $F_D(\bar{\nu})$ the normalized molecular fluorescence emission of the donor and $\varepsilon_A(\bar{\nu})$ the absorption spectrum of the acceptor.

The rate constant for the energy-transfer process in a fluid medium is given by[13]

$$k(t) = 4\pi D R_e^2 \left(\frac{\partial U}{\partial r}\right)_{r=R_e} + \int_{r=R_e}^{\infty} w(r)U(r)4\pi r^2 \, dr \tag{17}$$

where D is the sum of diffusion coefficients of the donor and acceptor molecules and U is the solution of the differential equation

$$\frac{\partial U}{\partial t} = D\Delta U - w(r)U. \tag{18}$$

The rate constant $k(t)$ turns out to be the sum of two terms. The first gives the transfer component at the encounter distance, R_e, and the second one the transfer component due to Förster's mechanism for distances greater than R_e. To obtain $k(t)$ it is necessary to solve eqn (18). Unfortunately this equation has no analytical solution,[14] and so approximate methods must be used. For large values of time it is reasonable to consider $\partial U/\partial t = 0$ (stationary conditions). Then eqn (18) can be solved under adequate boundary conditions. We make two assumptions: (1) for $t = 0$ there is uniform distribution of molecules; (2) for the encounter distance the so-called radiation boundary condition[15] can be set, $viz.$

$$U(r, t=0) = 1 \qquad r > R_e \tag{19}$$

$$\left(\frac{\partial U}{\partial r}\right)_{r=R_e} = \beta U \tag{20}$$

where β is a parameter that takes into account the fact that the reaction may be uncomplete at the encounter. We then obtain[16]

$$k_\infty = 4\pi D R_F \left(\frac{I_{3/4}(z_0)}{I_{-3/4}(z_0)} + \frac{2\beta\left(\dfrac{\alpha}{D}\right)^{1/4}}{\pi\sqrt{2}z_0 I_{-3/4}(z_0)\left[(2z_0)^{3/2}I_{-3/4}(z_0) + \beta\left(\dfrac{\alpha}{D}\right)^{1/4}I_{1/4}(z_0)\right]} \right) \tag{21}$$

where R_F is Förster's radius

$$R_F = \frac{2\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})}\left(\frac{\alpha}{D}\right)^{1/4} \tag{22}$$

I_ν being a modified Bessel function of the first kind and order ν, Γ the gamma function and

$$z_0 = \frac{1}{2R_e^2}\left(\frac{\alpha}{D}\right)^{1/2}. \tag{23}$$

From the general expression for k_∞ some limiting cases can now be obtained easily. The value for $\beta = 0$ describes the case where the barrier is a perfect reflector[17] and

$$k_\infty = 4\pi DR_F \frac{I_{3/4}(z_0)}{I_{-3/4}(z_0)}. \tag{24}$$

The so-called Smoluchowski boundary conditions[18] correspond to a perfect absorbing barrier, and occur for $U(R_e, t) = 0$. In this case the reaction is complete at R_e, and the solution[18] is the limiting case of eqn (21) for large values of β:

$$k_\infty = 4\pi D[R_F + f(z_0)R_e] \tag{25}$$

with

$$f(z_0) = \frac{4\sqrt{2}}{[\Gamma(\frac{1}{4})]^2}(z_0)^{1/2}\frac{K_{1/4}(z_0)}{I_{1/4}(z_0)}. \tag{26}$$

For values of $z_0 > 2.5$ the rate constant does not depend on the transfer of the encounter distance, and for all cases the same result is predicted

$$k_\infty = 4\pi DR_F \tag{27}$$

which is the expression obtained by Yokota and Tanimoto.[19] For values of $z_0 < 2.5$ the general eqn (21) gives intermediates values between the two extreme cases given by eqn (24) and (25), according to the value of β.

For small times the stationary condition is not valid, and Gösele[13] has proposed that

$$k(t) = 4\pi DR_{eef}\left(1 + \frac{R_{eef}}{\sqrt{(\pi Dt)}}\right) \tag{28}$$

with $R_{eef} = k_\infty/4\pi D$, which was shown[20] to be reasonably adequate.

EXPERIMENTAL

Steady-state measurements were performed as described in a previous publication.[21] Light from a Hg arc source (Bausch & Lomb, HP-100), monochromatized with a Bausch & Lomb high-intensity grating monochromator of 2700 grooves per mm, blazed at 250 nm, was used to excite the samples.

The emission was observed from the same face as that exposed to the incident radiation (measurements in reflection) and analysed with another monochromator (Bausch & Lomb, model 500 mm) with 600 grooves per mm, blazed at 300 nm. The fluorescence radiation was detected with a photomultiplier (EMI 9635 QB), and the emission recorded with a Houston–Omnigraphic type 3000 recorder, which was scanned synchronously with the analysing monochromator. The errors involved in the fluorescence intensities are $ca.$ 3%.

The decay curves were obtained on a single-photon counting apparatus (ORTEC 9200). A lamp, of the free-running type (ORTEC, model 9352), operating in air, was used to excite the samples. The full width at half-maximum intensity (f.w.h.m.) was $ca.$ 2.5 ns. The fluorescence was analysed with a monochromator (Schoeffel GM 100) and detected with a photomultiplier (RCA 8850). From the current generated on discharging the lamp an impulse (start) was directly obtained to initiate the time-sweep of a time-to-amplitude converter (t.a.c.) (ORTEC, model 457). From the anode of the photomultiplier an impulse was obtained to stop the t.a.c. The instrument is also equipped with an electronic device, analogous to that described by Schuyler and Isenberg,[22] to avoid recording multiphoton events. The output pulses of the t.a.c. were stored on a multichannel pulse height analyser (ORTEC, model 6240). The data accumulated could be read onto punched tape or onto an XY plotter.

The analysis of the decay curves was made on a computer using a non-linear least-squares analysis. The time range of the experiments was long enough to allow the experimental points to be fitted without convoluting the lamp pulse. The errors involved in evaluating the decay parameters are estimated for λ_1 as $\pm 2\%$ and for λ_2 as $\pm 5\%$.

Pyrene was zone-refined (60 passes), perylene was trisublimated *in vacuo*, and DPA (Nuclear Enterprises, scintillation grade), rubrene (K&K) and benzene (Merck–Uvasol) were used without further purification. Deoxygenation of the samples was achieved by N_2-bubbling (steady-state measurements) and by the freeze–thaw method (decay curves). The experiments with rubrene were performed in the dark to avoid photoperoxidation. The solutions were excited with radiation of wavenumber $\bar{\nu}_{exc} = 2.994 \times 10^6\ m^{-1}$; the measurements were made at room temperature, $23 \pm 2\ °C$.

RESULTS

The energy transfer from pyrene (dissolved in benzene) to different acceptors was studied under steady-state and transient conditions of excitation. To analyse the results the rate parameters for pyrene solutions in the absence of acceptor are needed. Decay curves of the excited monomer and excimer were studied for emission wavenumbers of 2.604×10^6 and $2.083 \times 10^6\ m^{-1}$, respectively, and the decay constants λ_1 and λ_2 were obtained.

Fig. 1 shows the variation of λ_1 and λ_2 with pyrene concentration, c_Y. By following the well-known procedure[5] it was possible to obtain the following rate constants: $k_{MY} = (3.2 \pm 0.05) \times 10^6\ s^{-1}$; $k_{DY} = (2.0 \pm 0.04) \times 10^6\ s^{-1}$; $k_{DMY} = (4.7 \pm 0.1) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$; $k_{MDY} = (0.60 \pm 0.04) \times 10^7\ s^{-1}$. From eqn (6) and (7) and with $c_Z = 0$, the value of the half-value concentration was obtained, $c_{hY} = (8.8 \pm 0.2) \times 10^{-4}\ mol\ dm^{-3}$.
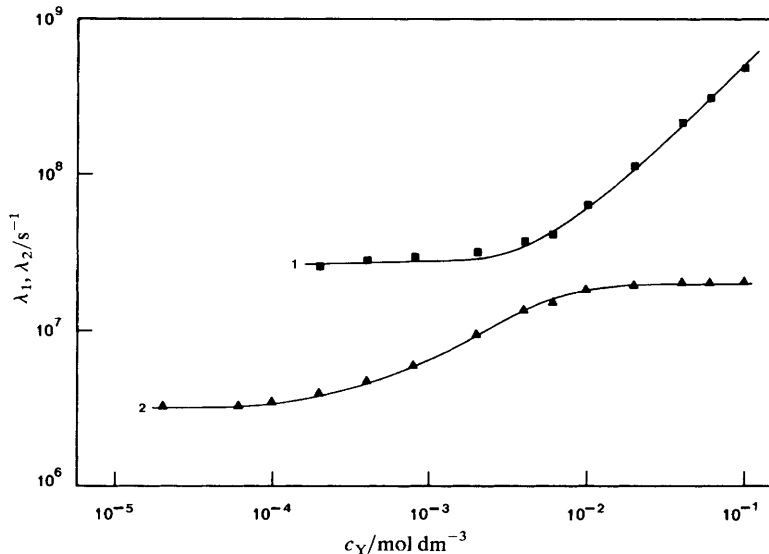

FIG. 1.—Variation of (1) λ_1 and (2) λ_2, for pyrene solutions in benzene, with pyrene concentration c_Y.

To study the transfer of energy from pyrene to rubrene, steady-state measurements were performed, and from these the intensities of pyrene excited monomer and excimer were observed at 2.604×10^6 and $2.132 \times 10^6\ m^{-1}$, respectively. The

experimentally measured intensities were corrected for the effect of radiative transfer according to the method proposed in an earlier publication.[23] However, the effect of the refractive index, n, was taken into account, and so the values of the angles in the relationships reported previously were evaluated from

$$\alpha' = \arccos\left(\frac{\cos\alpha}{n}\right) \tag{29}$$

$$\beta' = \arccos\left(\frac{\cos\beta}{n}\right) \tag{30}$$

α being the angle between the incident beam and the cell wall and β an "average" angle defined by the "emission beam" and the cell wall. (With our experimental set-up we used $\alpha = 60°$ and $\beta = 30°$.)

Fig. 2 shows the variation of I_{MY}/I_{DY} with c_Z, giving a linear dependence in accordance with eqn (13). For $c_Y = 0.01$ mol dm^{-3} the uncorrected values for radiative transfer are also shown. The correction depends on c_Y, but at $c_Y = 0.15$ mol dm^{-3} it becomes negligible. Since for pyrene γ_Y [given by eqn (10)] can be evaluated as 0.77, it is now easy to obtain the values of σ_{ZY}^d for different concentrations of the energy donor. These values are noted in table 2. They do
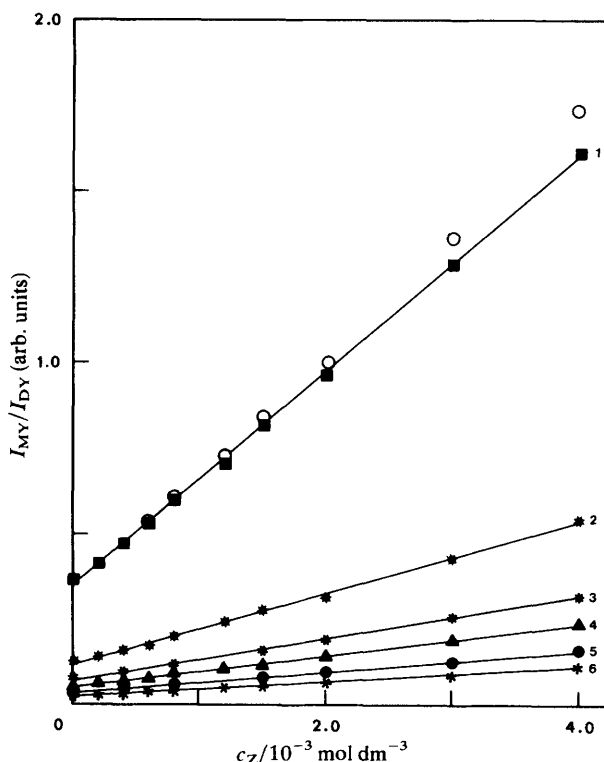

FIG. 2.—Relative monomer to excimer intensities of pyrene as a function of acceptor concentration: (1) $c_Y = 1.0 \times 10^{-2}$ mol dm^{-3}; (2) $c_Y = 3.0 \times 10^{-2}$ mol dm^{-3}; (3) $c_Y = 5.0 \times 10^{-2}$ mol dm^{-3}; (4) $c_Y = 7.0 \times 10^{-2}$ mol dm^{-3}; (5) $c_Y = 1.0 \times 10^{-1}$ mol dm^{-3}; (6) $c_Y = 1.5 \times 10^{-1}$ mol dm^{-3}. $\bigcirc$, Values not corrected for radiative transfer for $c_Y = 1.0 \times 10^{-2}$ mol dm^{-3}.

TABLE 2.—STERN–VOLMER CONSTANTS σ_{ZY}^d, FOR PYRENE-EXCIMER-RUBRENE TRANSFER, FOR VARIOUS CONCENTRATIONS OF PYRENE, c_Y

$c_Y/10^{-2}$ mol dm^{-3}	$\sigma_{ZY}^d/10^2$ dm^3 mol^{-1}
1.0	1.17 ± 0.05
3.0	1.19 ± 0.05
5.0	1.17 ± 0.05
7.0	1.18 ± 0.05
10.0	1.15 ± 0.05
15.0	1.19 ± 0.05

not vary with pyrene concentration, at least for the concentrations used, which can be taken as an indication that an energy-migration process is unimportant here. An average value for σ_{ZY}^d of $(1.15 \pm 0.05) \times 10^3$ dm^3 mol^{-1} can then be extracted from the values in table 2.

As suggested previously, an alternative way of obtaining σ_{ZY}^d is the study of the linear variation of c_Y/I_{DY} with c_Y for each c_Z, followed by a study of the variation of the angular coefficients b_1 with c_Z. These relationships are well verified (fig. 3 and 4), yielding $\sigma_{ZY}^d = (1.09 \pm 0.05) \times 10^3$ dm^3 mol^{-1}.

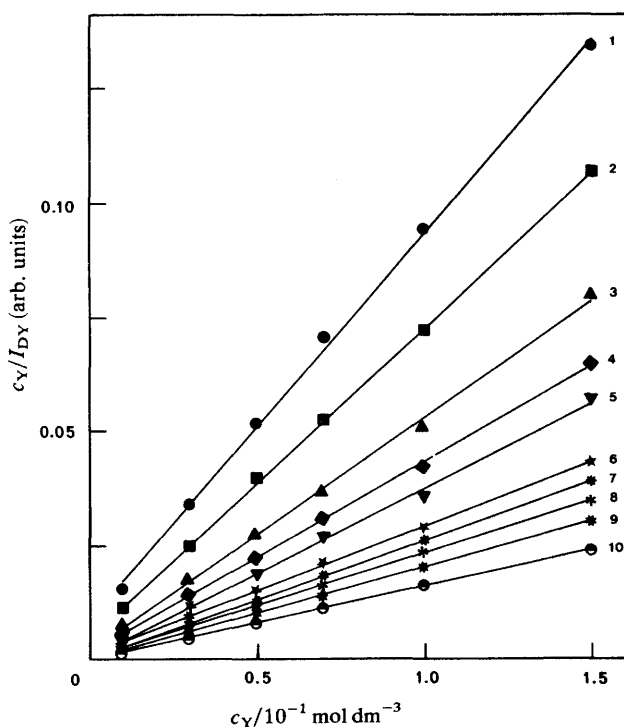

FIG. 3.—Variation of c_Y/I_{DY} with donor concentration: (1) $c_Z = 4.0 \times 10^{-3}$ mol dm^{-3}; (2) $c_Z = 3.0 \times 10^{-3}$ mol dm^{-3}; (3) $c_Z = 2.0 \times 10^{-3}$ mol dm^{-3}; (4) $c_Z = 1.5 \times 10^{-3}$ mol dm^{-3}; (5) $c_Z = 1.2 \times 10^{-3}$ mol dm^{-3}; (6) $c_z = 0.8 \times 10^{-3}$ mol dm^{-3}; (7) $c_Z = 0.6 \times 10^{-3}$ mol dm^{-3}; (8) $c_Z = 0.4 \times 10^{-3}$ mol dm^{-3}; (9) $c_Z = 0.2 \times 10^{-3}$ mol dm^{-3}; (10) $c_Z = 0$.
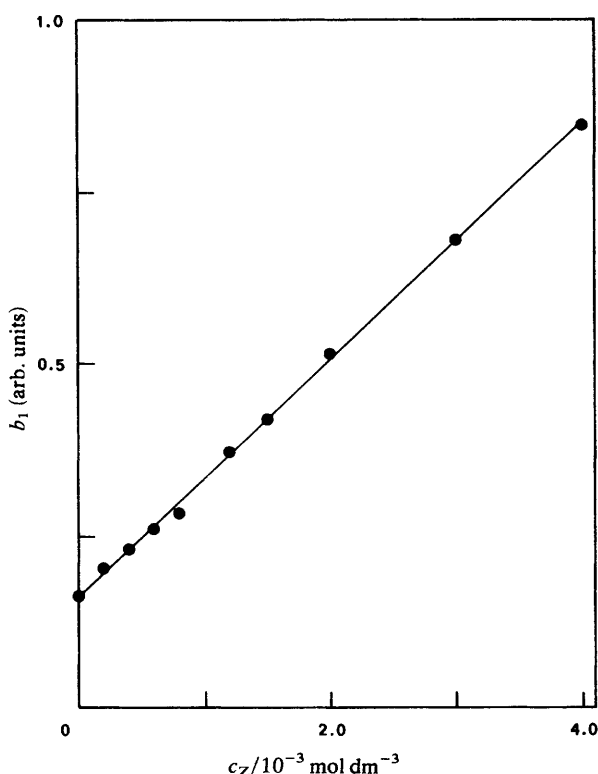
FIG. 4.—Angular coefficients of the straight lines in fig. 3 plotted against acceptor concentration.

The values of σ_{ZY}^{m} were obtained, for each concentration c_Y, by fitting the experimental results to the variation of $1/I_{DY}$ with c_Z (fig. 5) using $\sigma_{ZY}^{d} = 1.10 \times 10^3 \, dm^3 \, mol^{-1}$, $\gamma_Y = 0.77$ and $c_{hY} = 8.8 \times 10^{-4} \, mol \, dm^{-3}$. A value of $\sigma_{ZY}^{m} = (2.9 \pm 0.1) \times 10^3 \, dm^3 \, mol^{-1}$ was obtained, again with no indication of any noticeable variation with pyrene concentration.

The rate constants for transfer were also obtained from decay curves. The transfer from the monomer was extracted from the excited monomer decay curves, $I_{MY}(t)$, observed at $\bar{\nu}_{em}^{Y} = 2.604 \times 10^6 \, m^{-1}$ using solutions of low pyrene concentration ($c_Y = 2 \times 10^{-5} \, mol \, dm^{-3}$). Fig. 6 shows the linear variations of λ_1 with c_Z for the acceptors in accordance with eqn (11). From a least-squares analysis we could obtain the rate constants for the transfer as indicated in table 3.

Considering that there is no energy migration between energy-donor molecules the rate constant for transfer from the excimer can be obtained from an analysis of the decay curves of the excimer, $I_{DY}(t)$, if there is no overlap between the excimer fluorescence spectrum and the fluorescence emission of the acceptor. This overlap does exist for perylene and so the rate constant cannot be obtained. For DPA and rubrene excimer emission was observed at $\bar{\nu}_{em}^{Y} = 1.786 \times 10^6$ and $2.083 \times 10^6 \, m^{-1}$, respectively. The concentration of pyrene was $c_Y = 0.1 \, mol \, dm^{-3}$. Fig. 7 shows the linear variation of λ_1 with c_Z, in accordance with eqn (12). In table 3 we include the values of the rate constants.
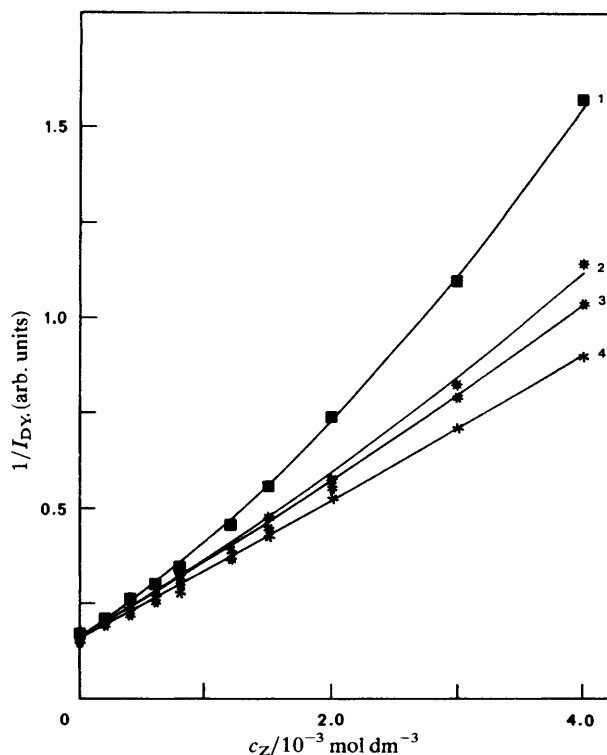
FIG. 5.—Variation of $1/I_{DY}$ with acceptor concentration: (1) $c_Y = 0.01$ mol dm^{-3}; (2) $c_Y = 0.03$ mol dm^{-3}; (3) $c_Y = 0.05$ mol dm^{-3}; (4) $c_Y = 0.15$ mol dm^{-3}.

From an analysis of steady-state measurements similar to that presented for pyrene and rubrene, we obtain rate constants for the other systems which, within experimental error, are in fair accord with the values calculated from the decay curves.

DISCUSSION

The transfer rate constants are given in table 3, which also includes the rate parameters needed to interpret the results.

The diffusion coefficients were evaluated using the relationship proposed by Scheibel[24]

$$D = \frac{kT}{\eta V^{1/3}} \tag{31}$$

where k is a constant dependent on solvent and solute properties, T is the absolute temperature, η is the viscosity of the solvent and V the molar volume of the solute, which was obtained from Le Bas' increments.[25] For the excimer it was assumed that the molar volume was twice the volume of the monomer. The errors involved in calculating the diffusion coefficients are $ca.$ 15%.
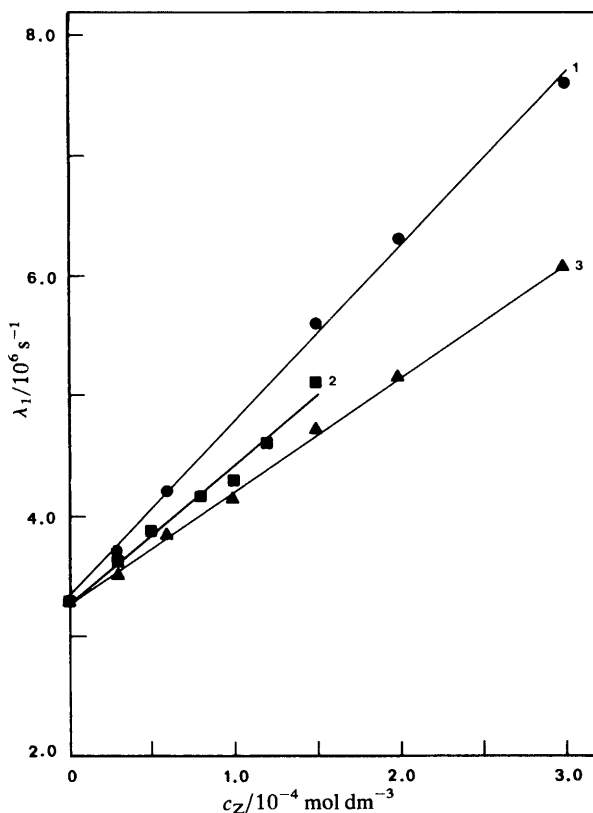
FIG. 6.—Variation of λ_1 with acceptor concentration ($c_Y = 2.0 \times 10^{-5}$ mol dm^{-3}): (1) pyrene–perylene; (2) pyrene–DPA; (3) pyrene–rubrene.

To evaluate the molecular radius it was assumed that the molecules are packed in an orderly cubic array; then

$$r = \tfrac{1}{2}(V/N)^{1/3}.$$

The values of R_0 were evaluated using eqn (16) with $q_{MY} = 0.60$ [26] and $q_{DY} = 0.55$.

TABLE 3.—VALUES OF THE ENERGY-TRANSFER RATE CONSTANTS (k_∞), DIFFUSION COEFFICIENTS (D), CRITICAL DISTANCES (R_0), ENCOUNTER DISTANCES (R_e) AND EXPERIMENTAL EFFECTIVE DISTANCES (R_{eef})

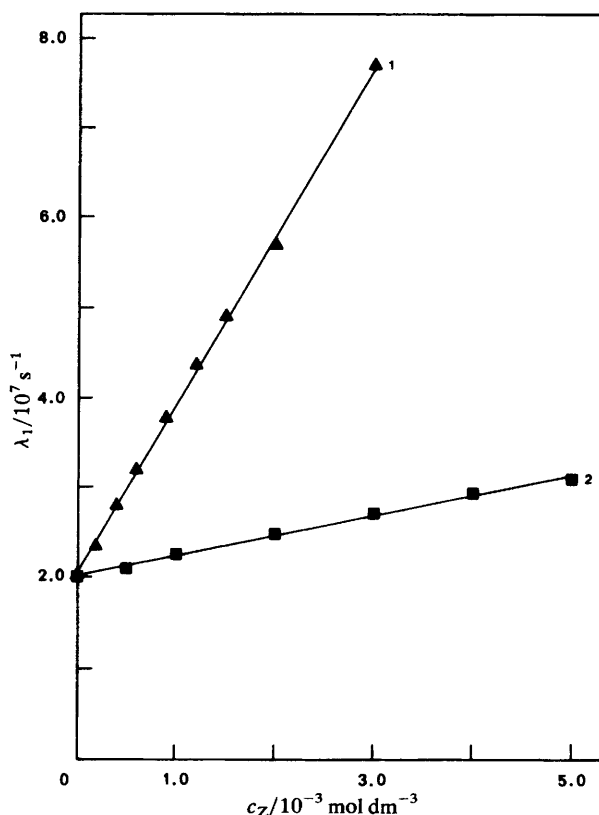| donor	acceptor	$k_\infty/10^{10}$ dm^3 mol^{-1} s^{-1}	$D/10^{-5}$ cm^2 s^{-1}	$R_0/$Å	$R_e/$Å	$R_{eef}/$Å
pyrene	DPA	1.2 ± 0.02	2.4	32.0	7.8	6.6
monomer	perylene	1.5 ± 0.02	2.6	35.4	7.3	7.6
	rubrene	0.95 ± 0.02	2.2	23.8	8.5	5.8
pyrene	DPA	0.22 ± 0.05	1.9	11.3	8.8	1.5
excimer	rubrene	1.9 ± 0.02	1.7	36.0	9.5	15.0

FIG. 7.—Variation of λ_1 with acceptor concentration ($c_Y = 0.10$ mol dm^{-3}): (1) pyrene–rubrene; (2) pyrene–DPA.

The effective distance for the transfer was evaluated from

$$R_{eef} = \frac{k_\infty \times 1000}{4\pi ND}.$$

R_{eef} depends not only on R_0 but also on the donor decay time. This fact can be observed for the pyrene-monomer–perylene and pyrene-excimer–rubrene system, where the R_0 values are almost the same (see table 3).

Let us now discuss the results in terms of the z_0 values, taking into account the different boundary conditions. In table 4 the R_{eef} values calculated from eqn (25), corresponding to the totally absorbing barrier, and from eqn (24), corresponding to the perfect reflector barrier, are presented, together with the z_0 values. We can see that only for the pyrene-excimer–rubrene system is $z_0 > 2.5$. In this case the experimental and theoretical values of R_{eef} are identical and given by eqn (22). In the other systems, ($z_0 < 2.5$) the experimental values (except for the pyrene–perylene system) are lower than those predicted from eqn (25), indicating that the reaction is not complete at the encounter distance.

From eqn (21), using the parameters of table 3, we obtain the values of β presented in table 4. These values can be related to transfer at the encounter

TABLE 4.—VALUES OF z_0, EFFECTIVE DISTANCES (R_{eef}) AND VALUES OF β FROM EQN (21)

donor	acceptor	z_0	$R_{eef}/\text{Å}^a$	$R_{eef}/\text{Å}^b$	β/cm^{-1}
pyrene monomer	DPA	0.98	8.7	5.6	1.1×10^7
	perylene	1.5	9.4	7.8	—
	rubrene	0.36	8.7	1.3	2.1×10^7
pyrene excimer	DPA	0.095	8.9	0.10	2.2×10^6
	rubrene	2.85	15.4	15.2	—

^{a} From eqn (25); ^{b} from eqn (24).

distance.[20,27] The rate constant at the encounter must include not only a dipole–dipole transfer component but also other terms related to multipolar transfer and exchange processes.[28]

Finally we may note a significant difference in the values for transfer from pyrene excimer to rubrene when measurements under transient and steady-state conditions of excitation are considered. This may be due to a variation in the transfer constant with time [eqn (28)], which could be important in evaluating rate constants obtained under steady-state conditions of excitation.[29] Assuming that, for low concentrations of rubrene, the correction factor is of the form[30] $1 + R_{eef}/(D\tau_0^D)^{1/2}$, a value of $k_{ZY}^d = 2.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} can be obtained, in good agreement with the experimental value.

CONCLUSIONS

To our knowledge we have given here the first detailed analysis of systems where both excited monomer and excimer of the donor are able to transfer their energy to an acceptor. Pyrene, which had already been used in conjunction with perylene,[31] has been shown to be an adequate energy donor. For the concentrations used there is no need to invoke energy-migration processes to interpret the results.

The discussion of the results presented here is based on the most recently published theoretical work. The need to assume adequate boundary conditions has been shown. Although for $z_0 > 2.5$ the problem may be considered as theoretically solved, since the transfer rate constants do not depend on the boundary conditions, there are still some points which are not clear.

The radiation boundary condition is considered to be a better approximation in the light of our results. The value of β is related to transfer at the encounter distance, and the problem of the solvent cage may become important. In fact excitation may be "present" at the barrier for some time, during which it can be absorbed. This would lead to an increase in the absorbing efficiency relative to absorption at a "first encounter". This possibility is under study in this laboratory both theoretically and experimentally.

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