NONRADIATIVE ENERGY TRANSFER. I - ENERGY MIGRATION AS A DIFFUSION PROCESS (*)

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ABSTRACT — The nonradiative energy transfer efficiency from pyrene to 9,10 diphenyl anthracene dissolved in benzene is shown to depend on pyrene concentration assuming that the transfer takes place only from the excited pyrene monomer. This result is attributed to an energy migration process taking place among pyrene molecules. A discussion of nonradiative energy transfer process is presented and the results are interpreted in terms of the available models.

1 — INTRODUCTION

It has been known for a long time [1] [2] that nonradiative energy transfer between an excited atom or molecule which is initially excited by absorption of u.v. radiation and another fluorescent species can occur, leading to fluorescence emission from the energy acceptor. It was FORSTER that first proposed a theory [3] [4] to describe this process. Although for some cases good agreement between the theoretical predictions for the transfer rate constants [5] and the experimental results was found it was soon verified that mainly when the energy donor was present at high concentrations and in liquid form the experimental values exceeded the «theoretical» ones. This led KALLMANN and FURST to propose [6] that material diffusion and/or energy migration among energy donor molecules could contribute to increase the magnitude of the energy transfer rate constant.

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As matter of fact, since the rate constant depends, according to FORSTER's theory, on the inverse sixth power of the distance between the energy donor and the energy acceptor, any process which decreases this distance would increase the energy transfer efficiency. The observed discrepancies between calculated and experimental values were interpreted in a qualitative way following FURST and KALLMANN's suggestion, although some authors tended to favour energy migration [7] while others thought that the important additional process was material diffusion [8]. In most cases, radiative energy transfer, consisting in reabsorption of the energy donor emission by the energy acceptor was considered unimportant [9] or at least accounted for [10]. However, the lack of a complete theoretical description or difficulties related with the verification of its predictions has shown the need of more experimental determinations in order to get more indications on the correct model to be used [11] [12].

The use of pyrene (Py) as an energy donor and 9,10 diphenylanthracene (DPA) as an energy acceptor has been proposed in this Laboratory [13] in the hope that by varying pyrene concentration evidence could be found for an energy migration effect. Furthermore, the fact that although pyrene is an excimer forming molecule the energy of the emissive excimer state is lower than the energy of the first excited singlet state of DPA could be invoked to assume that only pyrene monomer could transfer its energy to DPA. Obviously, this simplifies the equations used to analyse the experimental results [14].

The present work and the next one follow this line and are part of an extended study on the energy transfer processes which occur in a liquid system at room temperature containing fluorescent molecules which are excited with u.v. radiation. Experimental details have been described in previous publications [13] [14].

2 — EXPERIMENTAL RESULTS

If we consider excimer forming molecules Y which can transfer their energy to molecules Z which we assume not to form excimers, if we assume also that only excited monomers of the energy donor Y can transfer to Z, it is possible to derive the following expressions for the intensities of Y monomer emission (I_{MY}), Y excimer emission

(I_{DY}), Z emission (I_Z), when the samples are excited with u.v. radiation absorbed only by the energy donor [14].

$$I_{MY} = \frac{c_{hY}}{(1+\sigma^m_{ZY} c_Z) c_{hY} + c_Y} q_{MY} I_o \tag{1}$$

$$I_{DY} = \frac{c_Y}{(1+\sigma^m_{ZY} c_Z) c_{hY} + c_Y} q_{DY} I_o \tag{2}$$

$$I_Z = \frac{\sigma^m_{ZY} c_Z c_{hY}}{(1+\sigma^m_{ZY} c_Z) c_{hY} + c_Y} q_Z I_o \tag{3}$$

In these relationships c_Y and c_Z are the molar concentrations of Y and Z, respectively, c_{hY} is the half-value concentration for the monomer excimer Y system, q_{MY}, q_{DY} and q_Z are fluorescence quantum efficiencies, σ^m_{ZY} is the Stern-Volmer rate constant for transfer which is a measure of the transfer efficiency and is given by

$$\sigma^m_{ZY} = k^m_{ZY} \tau_{MY} \tag{4}$$

where τ_{MY} is the fluorescence decay time for the monomer emission when there is no acceptor molecules present. It is assumed that the samples are excited with light of intensity I_o (in Einstein sec^{-1}) and that the solutions do not contain oxygen or any other quenching agent.

For the system Pyrene (Y) + 9,10 diphenyl anthracene (Z) dissolved in benzene, which does not absorb the radiation used to excite the samples (mainly the 3130 Å Hg line), the intensities of pyrene monomer emission, pyrene excimer emission and DPA emission were obtained experimentally, and analysed using the equations written above. From the linear relationships $1/I_{DY}$ versus c_Z, it was possible to evaluate the values ot σ^m_{ZY} (the Stern-Volmer rate constant) for a number of solutions with different pyrene concentrations (TABLE I).

It is seen that σ^m_{ZY} and so, from (4), k^m_{ZY} increases with increasing pyrene concentration Since the viscosity ot the solutions remains constant, and the relative amount of pyrene monomer and excimer has already been taken into account by the kinetic scheme, this variation can be taken as an indication that there is energy migration among pyrene molecules.

TABLE I

c_Y (mole l^{-1})	σ_{ZY}^{m} (l mole^{-1})
0.200	20264
0.180	18572
0.160	18837
0.140	17756
0.120	16958
0.100	14889
0.090	14527
0.080	10952
0.070	11727
0.060	11823
0.040	8391
0.020	5978
0.010	5327
0.008	5090
0.006	5163
0.004	4901

3 — DISCUSSION

As stated before, the theory of long range non radiative energy transfer proposed by FORSTER [3] [4] is unable to account for the magnitude of the experimentally obtained transfer rate constants. For these cases the theory of diffusion controlled reactions, [15] [16] has been invoked following KALLMANN and FURST's [6] suggestion.

Actually, two different approaches can be found in the literature. Some authors [17] [18] propose a modification of FORSTER's theory whereby the variation of the distance between energy donor and energy acceptor is introduced. For the other group of theories it is the diffusion equation that is modified to include long-range energy transfer.

The work of YOKOTA and TANIMOTO [19] and of GOSELE et al [20] [21] deserve a special reference among the latter. For YOKOTA and TANIMOTO, the transfer rate constant is given by

$$k = \frac{4 \pi \mathrm{N} \mathrm{D}}{1000} r_{\mathrm{F}} \tag{5}$$

where D is the diffusion coefficient, N is Avogadro's number and r_{F} (FORSTER's radius) is

$$r_{\mathrm{F}} = k' \left(\frac{\alpha}{\mathrm{D}} \right)^{1/4} \tag{6}$$

k' being 0.676 or 0.910 according to the method used to solve the equations and α is

$$\alpha = \frac{\mathrm{R}_o}{\tau_o} \tag{7}$$

where R_o is FORSTER's critical radius for transfer and τ_o the decay constant for monomer emission in the absence of acceptor.

In more recent work GOSELE has given the following expression for the energy transfer rate constant

$$k = \frac{4 \pi \mathrm{N} \mathrm{D}}{1000} r_{\mathrm{eff}} \tag{8}$$

with

$$r_{\mathrm{eff}} = r_{\mathrm{F}} + \mathrm{R}_e f(\mathrm{Z}_o) \tag{9}$$

where

$$\mathrm{Z}_o = \frac{1}{2\, \mathrm{R}_e^{2}} \times \left(\frac{\alpha}{\mathrm{D}} \right)^{1/2} \simeq \left(\frac{r_{\mathrm{F}}}{\mathrm{R}_e} \right)^{2} \tag{10}$$

$f(\mathrm{Z}_o)$ being a complex funcion which is given graphically by the authors in the original paper, and R_e is the encounter distance.

In neither of those papers energy migration is taken into account. For this process two different models have been proposed one involving a resonance transfer between neighbouring molecules [22], which follows FORSTER's early suggestion [3], the other involving successive monomer and excimer formation and dissociations [23] [24]. In this case it is possible to define an energy migration coefficient with the form

$$\Lambda = \frac{<a>^2}{6\,\bar{t}_{\text{mig}}} \tag{11}$$

$<a>$ being the r.m.s. of the distance between molecules, and

$$\bar{t}_{\text{mig}} = \frac{1}{k_{\text{DMY}}\ c_{\text{Y}}} + \frac{1}{k_{\text{MDY}}} \tag{12}$$

the «mean time» for the migration, i.e., the time taken for a monomer to interact with a ground state molecule and form an excimer plus the time taken for the excimer to dissociate, k_{DMY} and k_{MDY} being the rate constants for excimer formation and dissociation, according to the equation

$$\mathrm{M_Y} + \mathrm{M_Y^*} \underset{k_{\text{MDY}}}{\overset{k_{\text{DMY}}}{\rightleftarrows}} \mathrm{D_Y^*} \tag{13}$$

The effect of energy migration is then introduced adding Λ to the diffusion coefficient in the expression of the diffusion equation, the «theoretical» value of the rate constant being

$$k_{\text{theor.}} = \frac{4\pi\mathrm{N}(\mathrm{D}+\Lambda)}{1000}\ r_{\text{eff}} \tag{14}$$

Both models lead to similar analytical expressions [25]. However it was found that VOLTZ model did not fit the experimental results reported here. Accordingly the results were analysed in terms of (14) and (11).

Taking D (the sum of diffusion coefficients for Py and DPA) to be 2.5×10^{-5} cm^{2}s^{-1}, $\tau_{\text{MY}} = 320$ ns, $\mathrm{R}_e = 6$ Å, $k' = 0.676$, one obtains, from (6) $r_{\mathrm{F}} \simeq 7$ Å and taking from the curve given by GOSELE the value 0.08 for $f(\mathrm{Z}_o)$, k given by (5) is 1.40×10^{10} l mole^{-1} sec^{-1}.

Now if we plot k^m_{ZY} calculated from the values in table I and extrapolate to $c_Y = 0$ it is possible to obtain $k^m_{ZY} \simeq 1.20 \times 10^{10}$ l mole^{-1} sec^{-1} which is in fair agreement with the calculated value (it is worth noting that no correction for radiative transfer was made here). Taking now $<a> = 4$ Å, $k_{DMY} = 3.9 \times 10^{11}$ mole. l sec^{-1}, $k_{MDY} = 9.8 \times 10^{10}$ sec^{-1} it is possible to calculated k_{theor} from (14). In the figure, the values of k^m_{ZY} obtained from the experimental values in Table I together with the calculated curve are indicated. The fitting is quite good. However the values of k_{DMY} and k_{MDY} neded are quite high when compared with published values ($k_{DMY} = 4.2 \times 10^9$ mole^{-1} l sec^{-1}, $k_{MDY} = 3.7 \times 10^6$ sec^{-1}). This discrepancy has already been verified in cases where this model for migration has been invoked [23]. This fact is taken as an indication that the model used needs to be modified although its form seems to be adequate. Work is in progress to elucidate this problem and the results will be published soon.

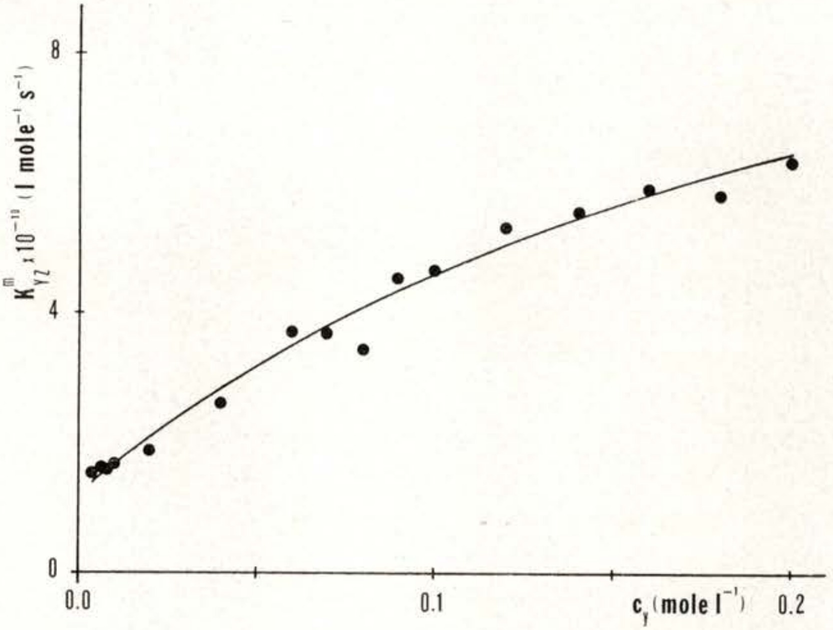

Fig. 1 — The rate constant for the energy transfer from Pyrene monomer to DPA as a function of Pyrene concentration for deoxygenated solutions. Circles: Experimental values. Full curve: calculated from (11) (12) and (14).

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