SHORT RANGE EFFECTS ON PYRENE-EXCIMER ENERGY TRANSFER TO 9,10-DIPHENYLANTHRACENE

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The rate constants for the energy transfer process between the pyrene-excimer and 9,10-diphenylanthracene (DPA) in solvents of different viscosities were obtained from the excimer decay curves of pyrene. The results were analysed in terms of a short-range and a long-range energy transfer processes.

1. INTRODUCTION

The probability of energy transfer $w(r)$, for a donor-acceptor pair of molecules, whose separation is $r$, can be written as a sum of two terms corresponding to the dipole-dipole and exchange contributions:

$$w(r) = \frac{\alpha}{r^6} + A \exp(-2r/L)$$  \hspace{1cm} (1)

where $\alpha$ is a characteristic constant for the dipole-dipole mechanism, $A$ is the pre-exponential factor and $L$ the mean effective Bohr radius for the exchange interaction.

In solution, the energy transfer is diffusion modulated. The radial pair distribution function obeys a modified diffusion equation\(^1\) that contains as a sink term the probability of transfer, $w(r)$. Usually only the long-range dipole-dipole term is considered as a distance dependent term. The exchange contribution is taken into account using a partially reflecting boundary condition at the encounter distance, $R_e$. In steady-state conditions, the radial pair distribution function can be obtained and from it the transfer rate constant $k$. The effective distance for the energy transfer ($R = k/4 \pi D$) is given by the following expression\(^2\) :

$$R = R_e + \frac{2 \beta(\alpha/D)^{1/4}}{(2 \pi)^{3/4} I_{3/4}(z_0^d)}$$  \hspace{1cm} (2)

where $D$ is the mutual diffusion coefficient of the donor-acceptor pair, $\beta$ a parameter that considers the effectiveness of the transfer reaction at the encounter distance,

$$R_e = \frac{2 \Gamma(3/4)}{3} \left( \frac{\alpha}{\beta} \right)^{1/4}$$  \hspace{1cm} (3)

and $I_\nu(z)$ a modified Bessel function of the first kind, $\Gamma(\nu)$ the gamma function and

$$z_0^d = \frac{1}{2 R_e} \left( \frac{\alpha}{\beta} \right)^{1/4}$$  \hspace{1cm} (4)

Recently Sipp and Voltz\(^4\) were able to solve the diffusion equation that includes the full expression for $w(r)$, using a reflecting boundary condition. In the particular case of "slow reaction" ($z_0^d << 1.0$), the effective distance is simply the sum of the contributions due to the dipole-dipole and the exchange interactions,

$$R = R_d + R_{\text{exc}}$$

The exchange contribution is given by\(^3\):
R_{exc} = R_e \left\{ 1 + \frac{L}{R_e} \left[ E + \ln \left( \frac{z_0^e}{2} \right) + \frac{L k_0(z_0^e) - z_0^e k_1(z_0^e)}{L I_0(z_0^e) + z_0^e R_e I_1(z_0^e)} \right] \right\} \quad (5)

where

\begin{align*}
2.5 & \\
2.0 & \\
1.5 & \\
1.0 & \\
0 & \end{align*}

E = 0.577 is Euler's constant and \( k_j(z), I_j(z) \) the modified Bessel functions of the first and second kind, respectively. The dipole-dipole contribution \( R_d \) is given by eq (2) with \( \varepsilon = 0 \).

2. EXPERIMENTAL

Fluorescence spectra were recorded with a home-built unity. The decay curves were obtained by a "Single-Photon Counting Technique" using an apparatus already described. Pyrene was zone refined (100 passes), 9,10-diphenylanthracene (Nuclear Enterprises-Scintillation grade), benzene (Bz), cyclohexane (Cx) (Merck-Uvasol) and cyclohexanol (Co) (Eastman Kodak, cryoscopic M.W. grade) were used without further purification. Measurements were performed at 23 ± 1°C. Deoxygenation of the samples was achieved by the freeze-pump-thaw technique (5 cycles at 10^{-5} torr).

3. RESULTS AND DISCUSSION

The excimer decay curves of concentrated solutions of pyrene (\( \sim 0.1 \) M) and DPA can be fitted as a difference of two exponentials. The rise component has a small lifetime that depends on the solvent and concentration of DPA (\( \tau_2 \leq \tau_1 \)). The long decay constant (\( \lambda_1 = 1/\tau_1 \)) obeys a linear variation with the DPA concentration:

\[ \lambda_1 = \frac{1}{\tau_0} + k C_Z \quad (7) \]

where \( \tau_0 \) is the molecular lifetime of the excimer and \( k \) the energy transfer rate constant.

![Figure 1](image)

Variation of \( \lambda_1 \) with the DPA concentration for two solvents. (1) - Benzene; (2) mixtures of Benzene and Cyclohexanol (40/60).

The concentration dependence of \( \lambda_1 \) for two different mixtures of solvents is shown in fig 1.

From these variation the \( \tau_0 \) and \( k \) values presented in table 1 were recovered. In the same table are included the effective distances, \( R \), calculated using the D values evaluated from the Scheibel equation. These values are lower than the encounter radius (\( R_e = 8.8 \) Å), indicating a very inefficient energy transfer process that in these conditions is mainly influenced by short-range effects. The excimer, which doesn't have a stable ground state, is a very interesting energy donor because the possibility of back energy transfer is ruled out.

The analysis of the \( R \) values in terms of eq (2) using \( \alpha = R_0^0/\tau_0 \) with \( R_0 = 11.3 \) Å, gives the intrinsic rate constant values (\( k = 4\pi D\delta R_e^2 \)) for the reaction at the encounter distance presented in the table. The increase of these values with decreasing D indicates that a distance dependent short-range term should be considered.

Henceforth, we performed the analysis of the results using the Sipp and Voltz approach.
TABLE 1 - Values of lifetime of pyrene-excimer ($\tau_0$), transfer rate constant to DPA ($k$), mutual diffusion coefficient ($D$), experimental effective distance for the energy transfer ($R$), intrinsic rate constants at the encounter ($k_e$), effective distance of transfer for the dipole-dipole mechanism ($R_1$), pre-exponential factor for the exchange mechanism ($A$) in Benzene (Bz) Cyclohexane (Cx) and mixtures in % volume of Benzene and Cyclohexanol (Co).

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>$\tau_0$/ns</th>
<th>$k/10^9$ M$^{-1}$ s$^{-1}$</th>
<th>$D/10^{-5}$ cm$^2$ s$^{-1}$</th>
<th>$R$/Å</th>
<th>$k_e/10^9$ s$^{-1}$</th>
<th>$R_d$/Å</th>
<th>$A/10^{10}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bz</td>
<td>49</td>
<td>2.2</td>
<td>1.9</td>
<td>1.5</td>
<td>2.3</td>
<td>0.11</td>
<td>12</td>
</tr>
<tr>
<td>Cx</td>
<td>47</td>
<td>1.9</td>
<td>1.3</td>
<td>1.9</td>
<td>2.2</td>
<td>0.17</td>
<td>9.1</td>
</tr>
<tr>
<td>Bz/Co (70/30)</td>
<td>47</td>
<td>1.9</td>
<td>1.3</td>
<td>2.3</td>
<td>2.4</td>
<td>0.20</td>
<td>11</td>
</tr>
<tr>
<td>Bz/Co (50/50)</td>
<td>47</td>
<td>1.6</td>
<td>0.60</td>
<td>3.8</td>
<td>2.6</td>
<td>0.37</td>
<td>9.9</td>
</tr>
<tr>
<td>Bz/Co (40/60)</td>
<td>48</td>
<td>1.4</td>
<td>0.38</td>
<td>4.9</td>
<td>2.9</td>
<td>0.55</td>
<td>9.2</td>
</tr>
<tr>
<td>Bz/Co (30/70)</td>
<td>47</td>
<td>1.1</td>
<td>0.21</td>
<td>6.9</td>
<td>4.4</td>
<td>0.98</td>
<td>8.3</td>
</tr>
</tbody>
</table>

From the fitting of $R_{exc} = R - R_d$ values with eq (5), assuming the value of $L = 4$ Å found in the naphthalene-anthracene system, the $A$ values presented in the table were recovered. These values are nearly constant and lower than the value obtained by Sipp and Voltz ($A=6.7\times10^{11}$ s$^{-1}$). This result was expected on the basis of a smaller overlap integral between the donor fluorescence spectrum and the absorption spectrum in our system when compared with the naphthalene-anthracene system studied by Sipp and Voltz.

4. CONCLUSIONS

The results presented in this paper show that a distance dependent term should be included in order to describe the short-range exchange contribution to the transfer rate constant. Small differences for the $A$ values with the solvent composition can be contributed to the short-range cage effects that were not considered in the analysis. These effects increase the expected value for the transfer rate constant and so the obtained $A$ values must be considered as an upper limit for the present system.

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REFERENCES