Transient Effects On Pyrene Monomer–Excimer Kinetics

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A new method of analysis of time-dependent rate phenomena in an excimer formation process is presented. The method uses a convolution relation between the monomer and excimer decay curves that includes the time-dependent rate coefficient. From the analysis of the decay curves the mutual diffusion coefficient (D) and the effective radius of interaction (R') can be calculated. The method was applied to the intramolecular excimer formation of methyl 4-(1-pyrene)butyrate (1) in toluene between -16 and 22 °C. With the help of the theory of partially diffusion controlled reactions a critical distance for reactions was calculated to be 7.6 ± 0.7 Å. The temperature dependence of the diffusion coefficient of 1 gives an activation energy of 2.5 kcal mol⁻¹.

Introduction

Excimer formation,1 particularly for pyrene,2 is a much studied subject, both in its own right and as a probe for various processes in micelles,3 bilayers,4 systems, and polymers.5 The formation step itself is diffusion controlled. Rate coefficients for diffusion-controlled processes are time dependent.6 For the presence of a transient term complicates the data analysis, normally making it very difficult to obtain an analytical solution for the decay functions.7,8 For this reason, the transient effects, which are particularly important at shorter times, are commonly neglected. Where the contribution of a transient term to the global decay kinetics is small, neglecting it does not introduce large errors into the calculation of steady-state rate coefficients from experimental data. The transient contribution to diffusion-controlled processes, however, contains important information about the system. For example, it allows the mutual diffusion coefficient of the reactants to be obtained.9 A reliable method would be welcome for extracting this information from fluorescence decay data, particularly in the case where the relative contribution of this term is small.

This paper describes a new method of data analysis that avoids the necessity of the analytical solution for the decays by using a convolution relation between the excimer and the monomer experimental decay curves. The excimer decay is considered as a convolution of the rate of excimer formation that includes the monomer decay, with a single exponential function representing the deactivation of the excimer. In this way a curve-fitting procedure enables us to calculate the time-dependent part of the rate coefficient.

We apply this method to the case of pyrene excimer formation, in the nanosecond time domain, for methyl 4-(1-pyrene)butyrate (1) in toluene at ordinary temperatures. Pyrenebutyric acid and its derivatives are commonly used as fluorescence sensors, and itself is a useful model for 1-substituted alkylypyrene derivatives. The solvent and temperatures for these experiments represent conditions where the transient term makes only a small contribution to the data.

Detailed analysis of the experimental results allows us to obtain the mutual diffusion coefficient of the reacting species and the effective distance of reaction.

The reaction scheme describing the formation of an intramolecular excimer (D*) from one molecule in the ground state (M) and another one in the first electronically excited state (M*) is presented in Scheme 1.

In this scheme k_M and k_D are reciprocals of the excited monomer (M*) and excimer (D*) lifetimes, and k_1(t) and k_2 are the rate coefficients for the excimer formation and dissociation processes, respectively.

SCHEME 1

\[
M \xrightarrow{k_M} M^* + M \xrightarrow{k_1(t)} \frac{k_1(t)}{k_D} D^* \\
\]

From the kinetic scheme a set of coupled differential equations are usually written:

\[
d[M^*]/dt = -(k_M + k_1(t)[M])[M^*] + k_1[D^*], \quad (1)
\]

\[
d[D^*]/dt = k_1(t)[M][M^*] - (k_D + k_2)[D^*], \quad (2)
\]

A very complicated analytical solution of these equations was recently obtained by Weixelbaumer et al.7 However, Hauser et al.10 have pointed out that eq 1 and 2 does not describe the physical model. These authors proposed a solution based on convolution relations between the excited monomer and excimer decays. When k_1(t) is time independent, the well-known solution1 for a δ-pulse of exciting light is

\[
[M^*]_i = \frac{[M^*]_0}{\lambda_1 - \lambda_2} \int_0^t (\lambda_2 - \lambda_1) \exp(-\lambda_2t) \exp[\lambda_1(t - \tau)] d\tau, \quad (3)
\]

\[
[D^*]_i = \frac{k_1[M^*]_0}{\lambda_2 - \lambda_1} \exp(-\lambda_2t) - \exp(-\lambda_2t) \exp[\lambda_1(t - \tau)] d\tau, \quad (4)
\]

with

\[
\lambda_{1,2} = 1/2((A_i + A_j) \pm [(A_i - A_j)^2]^{1/2} + 4k/k_{1,i}[M]), \quad (5)
\]

\[
A_i = k_i + k_M; \quad A_j = k_D + k_2, \quad (6)
\]

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(2) Birks, J. B.; Munro, I. H. Prog. React. Kinet. 1967, 4, 239.
(b) Winnik, M. A. Acc. Chem. Res. 1985, 18, 73.
and \( k_i' = \lim_{t \to \infty} k_i(t) \) is the steady-state value of the excimer formation rate coefficient.

An important relation can be established between the excited monomer and excimer decay curves. The excimer is created from the excited monomer with a rate coefficient \( k_i(t) \). Once formed, the excimer decays with a single exponential function representing the deactivation of the excimer. Therefore the excimer decay, \([D^*]+k_2(t) \), should be considered a convolution of the rate of excimer formation with its decay function, expressed by eq 4.

\[
[D^*]_i = k_i(t)[M][M^*] + \exp[-A,t] = \int_0^\infty k_i(\theta)[M^*]_i \exp[-A, (t - \theta)] \; d\theta \quad (7)
\]

This equation is satisfied by eq 3 and 4 for a time-independent rate coefficient, \( k_i \). However it can be shown that the differential and the convolution formulations for time-dependent rate coefficients are not equivalent. This is due to the presence of excited species of different “ages” created by the initial excitation and the successive processes of excimer formation and dissociation. Only the convolution description considers correctly the presence of different origins of time in \( k_i(t) \), and so is the appropriate formulation in the interpretation of the experimental results.

### Rate Coefficient

For intermolecular excimer formation, the rate coefficient \( k_i(t) \) is given by the theory of partially diffusion-controlled reactions.

\[
k_i(t) = \frac{4\pi DNR}{1000} \frac{\beta R}{1 + \beta R} \left[ 1 + \beta R \exp(x^2t) \right] \text{erfc} (xt^{1/2}) \quad (8)
\]

where

\[
x = \frac{1 + \beta R}{R} D^{1/2} \quad (9)
\]

and the complementary error function

\[
\text{erfc} (y) = \frac{2}{\pi^{1/2}} \int_y^\infty \exp(-z^2) \; dz \quad (10)
\]

Here \( D \) is the mutual diffusion coefficient \((D = D_N + D_M)\) of the monomer in the excited and ground state, \( N \) is the Avogadro number, and \( R \) is a critical distance at which the reaction takes place. The parameter

\[
\beta = \frac{k \Delta R}{D} \quad (cm^{-1}) \quad (11)
\]

measures the efficiency of excimer formation and \( \Delta R \) is the thickness of the spherical shell where the reaction takes place with a specific rate constant

\[
k_c = 4\pi R^2 \Delta R k \quad (12)
\]

due to a collision process with rate constant \( k (cm^{-1} \cdot s^{-1})\).

At sufficiently long times, a good approximation of eq 8 is obtained by using the asymptotic expansion

\[
\exp(y^2) \text{erfc} (y) = \frac{1}{\pi^{1/2}y} \left[ 1 - \frac{1}{2y^2} + \frac{3}{4y^4} - \frac{15}{8y^6} + \cdots \right] \quad (y > 1) \quad (12a)
\]

Considering only the first term of this expansion

\[
k_i(t) = \frac{4\pi DNR}{1000} \left[ 1 + \frac{R'}{(\pi Dt)^{1/2}} \right] \quad (13)
\]

where

\[
R' = \frac{\beta R}{1 + \beta R} R \quad (14)
\]

is an effective distance of reactions. The steady state is achieved for longer times \((R'(\pi D t)^{-1/2} \ll 1)\) and the rate constant is given by the familiar expression

\[
k_i' = \frac{4\pi DNR'}{1000} \quad (15)
\]

### Experimental Section

Methyl 4-(1-pyrenyl)butyrate has been prepared by esterification of pyrene butyric acid with methanol. It was purified by chromatography and recrystallized. Toluene (Aldrich) was purified by fractional distillation from sodium.

The fluorescence spectra were run on a Spex Fluorolog 2 spectrofluorimeter. The fluorescence decay curves were obtained by utilizing the time-correlated single-photon-counting technique. As excitation source, a coaxial gated nanosecond flash lamp (Edinburgh Instruments) filled with deuterium gas and operating at 50 kHz with a 2-ns half-width was employed. The excitation wavelength was 345 nm, the monomer fluorescence was observed at 376 nm and the excimer fluorescence at 520 nm. For analysis of the decay curves the \( \delta \) function convolution method was used. The reference decay curves were obtained using degassed solutions of BBOT (2,5-bis(5-tert-butyl-2-benzo-axazolyl)thiophene) in ethanol \((\tau = 1.47 \text{ ns})\) for excimer and POPPO (p-bis(5-phenylxazol-2-yl)benzene) in cyclohexane \((\tau = 1.1 \text{ ns})\) for monomer decay curves. The samples were degassed by the freeze-pump-thaw technique (five cycles). The temperature was controlled \((\pm 0.5 \text{ °C})\) by using a home-built thermostated cell holder.

### Results and Discussion

The experimental decay curves of monomer and excimer emission of methyl 4-(1-pyrenyl)butyrate (1) in toluene between -16 and 22 °C can be qualitatively described as follows: the excimer decay curves can be well fitted with a difference of two exponentials, according to eq 4, but with a ratio of preexponential factors different from unity. The monomer curve can be fitted with a sum of two exponentials (eq 3) only if analyzed after several channels from the beginning of the decay. The lifetimes \((\tau_i = 1/\lambda_i)\) recovered from the monomer and excimer decay curves show some small differences: the shortest lifetime recovered from the monomer decay is greater than the one from the excimer decay, and with the long lifetime the reverse usually happens. In the past such small differences were considered experimental error. Here the differences persist from sample to sample and become more important at lower temperatures or in solvents of higher viscosity. They provide a clue that eq 3 and 4 do not adequately describe the kinetics of excimer forming process. Similar observations were reported by O'Connor et al. in the kinetic study of the exciplex formation between \( \alpha \)-cyanonaphthalene and dimethylcyclopentene.

In Figures 1 and 2 are shown two typical excimer and excited monomer decay curves of a 2.0 \( \times 10^{-2} \text{ M} \) solution of 1 measured at 0 °C. As stated above the excimer decay curve is well fitted with a difference of two exponentials \((\tau_i^\text{M} = 15.8 \text{ ns}; \tau_i^\text{E} = 54.8 \text{ ns})\) with a ratio of the preexponential factors \( A_i^\text{M}/A_i^\text{E} = 0.976\), a value different from unity as predicted by eq 4. The monomer decay is well fitted with a sum of two exponentials \((\tau_i^\text{M} = 17.1 \text{ ns}; \tau_i^\text{E} = 50.9 \text{ ns})\) and with a ratio of the preexponential factors \( A_i^\text{M}/A_i^\text{E} = 61.0\).

The differences between the experimental results and the predictions of the classic monomer–excimer kinetic scheme (i.e., without transient effects) were attributed to the presence of a transient term in \( k_i \).

The experimental decay curves are given by

\[
P^{\text{M}(t)} = L(t) \odot f(t) = \int_0^\infty L(t - \theta) \times f(t) \; d\theta \quad (16)
\]
where \( L(t) \) is the instrumental response function (lamp profile) and \( I(t) \) is the decay that should be observed with a single pulse of excitation. With this taken into account, relation 7 should be written

\[
I_{D_{\text{exp}}} = I_{E_{\text{exp}}} \otimes \exp(-A \times t)
\]  

(17)

And for a time-independent rate coefficient

\[
I_{D_{\text{exp}}} = k_1 I_{M_{\text{exp}}} \otimes \exp(-A \times t)
\]  

(18)

As the value of \( k_1 \) can be included in the normalization constant, the excimer decay can be analyzed by using eq 17 as a single exponential decay replacing the lamp profile by \( I_{M_{\text{exp}}}(t) \). In Figure 3 is shown the best fit of \( I_{D_{\text{exp}}}(t) \) using relation 18. The fit is poor (\( \chi^2 = 3.2 \)), and we observe large deviations at the beginning of the decay. These suggest that the deviations might be due to the time dependence of \( k_1 \).

To take into account the transient effects, the values of \( I_{M_{\text{exp}}}(t) \) should be multiplied by \( k_1(t) \), according to eq 17. In order to perform the analysis the monomer decay curves were modified by the following procedure: (1) the centroid of the lamp profile was taken for time zero; (2) for \( t > 1 \) ns, the approximate expression, \( k_1(t) = a(1 + b \exp(-c \times t)) \), given by eq 13, was used for the excimer formation rate coefficient; (3) the values of \( I_{M_{\text{exp}}}(t) \) were multiplied by \( k_1(t) \) or as the channels were after or before the lamp centroid; (4) the analysis of the excimer decay curve begins two or three channels after the lamp centroid.

An iterative program that minimizes \( \chi^2 \) was used to obtain the best values of \( a, b, \) and \( A_r \). As there is a normalization factor in the fitting procedure, only the values of \( b \) and \( A_r \) can be recovered. In Figure 4 is shown a good fit (\( \chi^2 = 1.20 \)) obtained by using the procedure described above. From this fit the values of \( A_r = 1.93 \times 10^7 \) s\(^{-1} \) and \( b = 0.34 \) ns\(^{-1/2} \) were obtained. The same kind of analysis was performed for the decay curves of
Figure 4. Time-dependent fit of the excimer decay curve obtained by using relation 17. \( A_p = 1.93 \times 10^5 \text{s}^{-1}; \beta = 0.34 \text{ ns}^{-1/2}; \chi^2 = 1.20. \)

![Figure 4](image)

**TABLE I: Kinetic Parameters for Excimer Formations in Methyl 4-(1-Pyrene)butyrate in Toluene**

<table>
<thead>
<tr>
<th>( T/\degree C )</th>
<th>( k_p/10^9 \text{ M}^{-1} \text{s}^{-1} )</th>
<th>( b/\text{ns}^{1/2} )</th>
<th>( A_p/10^7 \text{s}^{-1} )</th>
<th>( R'/\text{A} )</th>
<th>( D/10^{-6} \text{ cm}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-16</td>
<td>2.2</td>
<td>0.40 ± 0.05</td>
<td>1.80 ± 0.05</td>
<td>5.3 ± 0.5</td>
<td>5.5 ± 0.4</td>
</tr>
<tr>
<td>-9</td>
<td>2.6</td>
<td>0.34 ± 0.04</td>
<td>1.82 ± 0.05</td>
<td>5.0 ± 0.5</td>
<td>6.9 ± 0.6</td>
</tr>
<tr>
<td>0</td>
<td>3.0</td>
<td>0.31 ± 0.04</td>
<td>1.87 ± 0.06</td>
<td>4.9 ± 0.5</td>
<td>8.0 ± 0.6</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>0.25 ± 0.03</td>
<td>1.99 ± 0.07</td>
<td>4.4 ± 0.3</td>
<td>10.0 ± 1.0</td>
</tr>
<tr>
<td>20</td>
<td>4.0</td>
<td>0.17 ± 0.02</td>
<td>2.20 ± 0.08</td>
<td>3.6 ± 0.3</td>
<td>15.0 ± 1.5</td>
</tr>
</tbody>
</table>

To obtain individual values of \( R' \) and \( D \) one needs an independent determination of the steady-state rate coefficient \( k_1' \). What we propose and wish to examine is that these values can be obtained reliably from the same fluorescence decay curves in a time regime where the contribution of the transient term is negligible. For example analysis of the data in Figure 2 for times 10 and 20 ns after the lamp maximum gives stable values of \( \lambda_1' \) and \( \lambda_2' \). From these values the rate coefficient \( k_1' \) was obtained. This value can also be obtained from the predicted linear plot of \((\lambda_1 + \lambda_2) vs. the concentration of 1. \)

\[ \lambda_1 + \lambda_2 = k_M + k_D + k_{-1} + k_1'M \]  

(20)

The experimental values of \((\lambda_1 + \lambda_2) obtained from the monomer and/or excimer decay curves at different temperatures are shown in Figure 5. Relation 20 is well obeyed and from the slope the values of \( k_1' \) presented in Table I were obtained. The two different methods of analysis given \( k_1' \) values that differ by less than 3% from each other. In Table I are shown the calculated values of \( D \) and \( R' \), using eq 13 and 20. A linear relationship can be established between \( 1/R' \) and \( D \) by using eq 11, 12, and 14.
In Figure 6 we plot the experimental values of $1/R$ vs. $D$. The predicted linear variation is well obeyed; from the intercept we obtain a value of $R = 7.6 \pm 0.7$ Å, and from the slope, the value $k_c = (1.2 \pm 0.5) \times 10^{-11}$ cm$^2$ s$^{-1}$.

The value of $R = 7.6$ Å is very close to the sum of the van der Waals radii of two pyrene molecules ($R = 7.1$ Å). The value of $R$ obtained compares very well with the published value by Heuman,$^7$ $7.0 \AA < R < 9.0 \AA$, for the pyrene excimer formation reaction in different solvents at room temperature. Also our value for the diffusion coefficient of the pyrene derivative ($D_M = D/2$) at room temperature agrees very with the Heuman’s values for the pyrene diffusion coefficient. The value of $R$ obtained does not support the assumption made by Donner et al.$^8$ of a critical radius of 10 Å for excimer formation in membranes. The value

$$\frac{1}{R^2} = \frac{1}{R} + \frac{D(4\pi)}{k_c}$$

(21)

of $k_c$ is usually compared with the predicted value from the kinetic theory of gases. The calculated value $k_c = 1.2 \times 10^{11}$ cm$^2$ s$^{-1}$ is lower than $k_{\text{gas}} = 1.0 \times 10^{12}$ cm$^2$ s$^{-1}$. The difference can be attributed to the steric effect of the side chain of our pyrene derivative molecule. An Arrhenius plot of $D_M/T$ is shown in Figure 7. A reasonable straight line can be drawn through the experimental points and an activation energy of 2.5 kcal mol$^{-1}$ could be obtained. In the same figure are also plotted the values of the reciprocal of viscosity $(1/\eta)$. The same slope should be expected from the two plots. A small difference (2.2 vs. 2.5 kcal mol$^{-1}$) can be attributed to the failure of the Stokes equation$^9$ relating the diffusion coefficient with the macroscopic viscosity of the medium.

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Fluorescence Quenching of 9,10-Dicyanoanthracene by Dienes and Alkenes

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The fluorescence of 9,10-dicyanoanthracene (DCNA) is quenched by a variety of acyclic and cyclic dienes and alkenes. The observed quenching rate constants are consistent with values calculated for an electron-transfer process. Solvent-dependent exciplex emission was observed for DCNA with 1,3-cycloheptadiene, 2,3-dimethyl-2-butene, and 1,3-cyclohexadiene, giving calculated exciplex dipole moments of 10.8, 13.5, and 11.2 D, respectively.

Introduction

Quenching by dienes of the fluorescence of arenes was originally rationalized by the formation of arene/diene exciplexes,$^1$ which was later confirmed by the observation of exciplex fluorescence in several systems.$^2$ Compelling evidence for the intermediacy of such exciplexes in photocycloaddition reactions was first obtained for phenanthrene/olefin systems by Caldwell,$^3$ and indirect evidence for the intermediacy of reversibly formed exciplexes in anthracene/diene systems has been reported by Yang$^4$ and Saltiel.$^5$ Woodward–Hoffmann rules$^6$ predict that concerted suprafacial [4 + 4] and [2 + 2] cycloadditions are photochemically allowed, while similar [4 + 2] cycloadditions are photochemically forbidden. The simultaneous occurrence of both forbidden and allowed reaction pathways was interpreted by Yang in terms of competing concerted and stepwise reactions of the intermediate exciplexes.$^6$ Yang et al.$^6$ found a correlation between the polarity of the arene/diene exciplexes and the mode of cycloaddition: for exciplexes with relatively little polarity, the presumably concerted [4 + 4] cycloaddition process was predominant, while for relatively polar exciplexes, the stepwise [4 + 2] pathway was observed. Triplet pathways for cycloadditions are possible, as demonstrated by Saltiel for additions of benz[a]anthracene to 1,3-pentadienes,$^8$ but the singlet pathway has been shown to operate in the anthracene/diene systems.$^6$

The polarity of the diene/exciplex exciplex depends in large part on the donor–acceptor characteristics of the diene and anthracene, respectively. Thus, when an electron-rich diene such

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The polarity of the diene/exciplex exciplex depends in large part on the donor–acceptor characteristics of the diene and anthracene, respectively. Thus, when an electron-rich diene such as 2,5-dimethyl-2-hexadiene and an electron-deficient anthracene such as 9,10-dicyanoanthracene (DCNA) were employed, a polar exciplex was formed which led in a stepwise manner to a 4a,4b cycloaddition process.21 Pathway 21 is usually compared$^6$ with the predicted value from the kinetic theory of gases. The calculated value $k_c = 1.2 \times 10^{11}$ cm$^2$ s$^{-1}$ is lower than $k_{\text{gas}} = 1.0 \times 10^{12}$ cm$^2$ s$^{-1}$. The difference can be attributed to the steric effect of the side chain of our pyrene derivative molecule. An Arrhenius plot of $D_M/T$ is shown in Figure 7. A reasonable straight line can be drawn through the experimental points and an activation energy of 2.5 kcal mol$^{-1}$ could be obtained. In the same figure are also plotted the values of the reciprocal of viscosity $(1/\eta)$. The same slope should be expected from the two plots. A small difference (2.2 vs. 2.5 kcal mol$^{-1}$) can be attributed to the failure of the Stokes equation$^9$ relating the diffusion coefficient with the macroscopic viscosity of the medium.

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