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Reversibility in monomer–excimer kinetics

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A model for reversible monomer–excimer kinetics is presented, taking into account the time dependence of the excimer formation rate coefficient and making explicit distinction between the excimer formed from a monomer excited by light and the excimer formed from an excited monomer produced by the dissociation of another excimer. The respective rate coefficients of excimer formation are determined within classical diffusion theory. The results obtained, applicable to both excimer and exciplex kinetics, suggest that experimental systems should, under suitable conditions, exhibit rich kinetic behaviour not yet observed.

1. Introduction

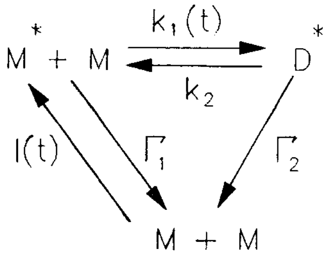
Intermolecular excimer formation appears to have been the first photophysical process where reversibility was observed [1,2]. A simple kinetic scheme (scheme I below) for the excimer formation mechanism in liquid medium was proposed by Döller and Förster [3], its general solution being given shortly afterwards by Birks, Dyson and Munro [4] [#1]. This kinetics was latter extensively applied by Birks and co-workers, both in steady-state and in time-resolved fluorescence, in a series of classical studies [6]. As the excimer formation process is known to be diffusion controlled [6], the respective rate coefficient must be time dependent [7]. In the kinetic treatment developed by Birks et al. [4] a time-independent value was nevertheless used, which although physically questionable, considerably simplified the mathematics. The time-independent rate coefficient was assumed to equal the long-time limit of the Smoluchowski relation [4,8], $4\pi N_A RD$, where N_A is Avogadro's number, R the encounter distance and D the mutual diffusion coefficient. While this may be reasonable in irreversible systems for sufficiently long times, it is doubtful that such an assumption should generally apply, as in a reversible system "transient" effects are repeatedly re-occurring. The incorporation of the transient contribution in the monomer decay for the irreversible case, i.e. no excimer reverse dissociation, is relatively straightforward [9] [#2], and was experimentally checked by Heumann [11]. Attempts to extend this treatment to the reversible system were either heuristic [12,13] or contained simplifications [13–16]. Here a model of reversible excimer kinetics is presented, where a distinction between the excimer formed from an excited monomer produced by photon absorption (external production) and that formed from an excited monomer produced by dissociation of another excimer (internal production) is made. This allows the study of the contribution of the geminate pair of monomers created by excimer dissociation on the overall kinetics. The geminate pair contribution is significant for viscous solvents at low and intermediate concentrations.

2. The kinetic model

Consider the so-called Birks kinetic scheme

[#1] Identical solutions were previously obtained by Weller [5] for the similar excited state acid–base kinetic scheme.

[#2] See however the remarks by Periasamy et al. [10].



Scheme 1

This scheme may be misleading as no explicit distinction is made between the excimer formed from a monomer excited by photon absorption and the excimer formed from an excited monomer generated by a previously dissociated excimer. That the excimer formation rate cannot be the same in both cases is easily accepted by considering a dilute solution; in the first case, the initial distribution of ground state monomers around the excited one is essentially uniform, while in the second case there is always a close neighbour, former partner in the original excimer. The total excited monomer concentration can thus be separated in two contributions,

$$[\mathrm{M}^*]=I\otimes f_1+k_2[\mathrm{D}^*]\otimes f_1' , \qquad (1)$$

where I is the number of moles of photons absorbed per unit time and unit volume, and f_1 and f_1' are the survival probabilities for excited monomers produced by photon absorption and excimer dissociation, respectively. The first term is the concentration of monomers excited by light absorption, and the second term the concentration of excited monomers created by excimer dissociation. In a very recent treatment of reversible diffusion-influenced reactions, Agmon and Szabo [17] obtained a relation similar to eq. (1) but valid only for a δ function light pulse and for stable species (i.e. infinite lifetimes for M* and D*). The use of the convolution, probably introduced in photophysics by Brody [18], amounts to an assumption of linearity, i.e. absence of saturation and interference effects, well justified for the light sources commonly employed. With low light intensities depletion of the ground state is negligible and excited monomers are, on the average, far enough apart and can be considered independent. In this case, $I(t)$ is proportional to the excitation source intensity, $E(t)$. Also, the survival probability of the excited monomer is only a function of the respective age and mode of production, but not of the time of birth. The survival probabilities can then be written as

$$f_1(t)=\exp(-\Gamma_1 t)\,\exp\left(-\int_0^t k_{1\delta}(u)\,\mathrm{d}u\right), \qquad (2)$$

$$f_1'(t)=\exp(-\Gamma_1 t)\,\exp\left(-\int_0^t k_{1\delta}'(u)\,\mathrm{d}u\right), \qquad (3)$$

where $\Gamma_1=1/\tau_1$ (τ_1 being the intrinsic monomer lifetime) accounts for unimolecular processes of decay, and $k_{1\delta}(t)$ and $k_{1\delta}'(t)$ are the δ-production rate coefficients [19] for bimolecular decay via excimer formation. The form of $k_{1\delta}(t)$ and $k_{1\delta}'(t)$ will be discussed in section 3.

The excimer, once created, has a survival probability given by

$$f_2(t)=\exp(-\Gamma_2 t)\,\exp(-k_2 t)\,. \qquad (4)$$

The total excimer concentration can also be written as the sum of two separate contributions,

$$[\mathrm{D}^*]=[k_1(I\otimes f_1)]\otimes f_2+[k_1'(k_2[\mathrm{D}^*]\otimes f_1')]\otimes f_2\,, \qquad (5)$$

Γ_2 being the inverse of the intrinsic excimer lifetime and k_2 being the rate constant for dissociation. In eq. (5), the first term corresponds to excimers created by monomers excited by light absorption, while the second term corresponds to excimers created by excited monomers produced by excimer dissociation.

The rate coefficients k_1 and k'_1 are related to the rate coefficients $k_{1\delta}$ and $k'_{1\delta}$ derived for δ-production by the equation [19,20]

$$k=\frac{P\otimes(k_\delta f)}{P\otimes f}, \tag{6}$$

where P is the production rate, which is I for k_1 and $k_2[\mathrm{D}^*]$ for k'_1, hence

$$k_1=\frac{I\otimes(k_{1\delta}f_1)}{I\otimes f_1}, \tag{7}$$

$$k'_1=\frac{k_2[\mathrm{D}^*]\otimes(k'_{1\delta}f'_1)}{k_2[\mathrm{D}^*]\otimes f'_1}. \tag{8}$$

substitution of eqs. (7) and (8) in eq. (4) for k_1 and k'_1, respectively, yields

$$[\mathrm{D}^*]=[I\otimes(k_{1\delta}f_1)+k_2[\mathrm{D}^*]\otimes(k'_{1\delta}f'_1)]\otimes f_2\,. \tag{9}$$

Application of Laplace transforms to both sides of eqs. (1) and (9) allows the separation of [M*] from [D*]. The result, after inverse Laplace transformation, is

$$[\mathrm{M}^*]=I\otimes f_1+I\otimes J\otimes(k_{1\delta}f_1)\otimes(k_2f_2)\otimes f'_1\,, \tag{10}$$

$$[\mathrm{D}^*]=I\otimes J\otimes(k_{1\delta}f_1)\otimes f_2\,, \tag{11}$$

where

$$J=\mathscr{L}^{-1}\left[\frac{1}{1-\mathscr{L}[k'_{1\delta}f'_1]\mathscr{L}[k_2f_2]}\right], \tag{12}$$

J playing the role of a secondary production rate. Eqs. (10) and (11) are the main relations of the kinetic model and from which monomer and excimer time profiles can be computed. The remaining part of this paper will be concerned with the rate coefficients $k_{1\delta}$ and $k'_{1\delta}$, which determine f_1 and f'_1 and therefore the time evolution of [M*] and [D*].

3. The excimer formation rate coefficients

Within the independent pair approximation, the survival probability of the excited monomer surrounded by $M=[\mathrm{M}]VN_\mathrm{A}$ ground state monomers at initial distances $r_{01}, r_{02}, ..., r_{0M}$ is

$$s(t)=\exp(-\Gamma_1 t)\prod_{i=1}^{M}P(t|r_{0i})\,, \tag{13}$$

V being the vessel volume and $P(t|r_{0i})$ the probability that the reaction between the pair has not occurred until time t, given that the initial distance was r_{0i}. The average survival probability is obtained by weighing eq. (13),

$$S(t)=\exp(-\Gamma_1 t)\prod_{i=1}^{M}\int_R^\infty g_i(r_0)P(t|r_0)\,\mathrm{d}r_0\,, \tag{14}$$

where $g_i(r_0)$ is the distance distribution function for the ith pair at $t=0$. Defining further a probability of reaction between t and $t+\mathrm{d}t$, given an initial distance r_0, $p(t|r_0)$, one has

$$P(t|r_0)=1-\int_0^t p(t'|r_0)\,\mathrm{d}t' . \tag{15}$$

The general rate coefficient k_δ, is, by definition, related to $S(t)$ by

$$k_\delta=-\Gamma_1-\frac{\mathrm{d}\ln S}{\mathrm{d}t}, \tag{16}$$

hence,

$$k_\delta=\sum_{i=1}^{M}\frac{\int_R^\infty g_i(r_0)p(t|r_0)\,\mathrm{d}r_0}{\int_R^\infty g_i(r_0)P(t|r_0)\,\mathrm{d}r_0} . \tag{17}$$

If all monomers are randomly distributed, as is the case for $k_{1\delta}$, then $g_i(r_0)=4\pi r_0^2/V$ and eq. (17) becomes

$$k_{1\delta}=[\mathrm{M}]N_\mathrm{A}\frac{\int_R^\infty 4\pi r_0^2 p(t|r_0)\,\mathrm{d}r_0}{\int_R^\infty g(r_0)P(t|r_0)\,\mathrm{d}r_0} . \tag{18}$$

The denominator of this equation is very close to unity for all times, and $k_{1\delta}$ can then be approximated by

$$k_{1\delta}=[\mathrm{M}]N_\mathrm{A}\int_R^\infty 4\pi r_0^2 p(t|r_0)\,\mathrm{d}r_0 . \tag{19}$$

The probability of instantaneous reaction $p(t|r_0)$ can be written as

$$p(t|r_0)=4\pi R^2 f(R,t|r_0)k , \tag{20}$$

where $f(R,t|r_0)$ is the probability of finding the pair at the encounter distance at time t, given an initial separation r_0, and k is the intrinsic rate of reaction for the pair. Substitution of eq. (20) in eq. (19) gives

$$k_{1\delta}=[\mathrm{M}]4\pi N_\mathrm{A}R^2k\int_R^\infty 4\pi r_0^2 f(R,t|r_0)\,\mathrm{d}r_0 , \tag{21}$$

however, by symmetry (isotropy),

$$f(R,t|r_0)=f(r_0,t|R) , \tag{22}$$

hence,

$$k_{1\delta}=[\mathrm{M}]4\pi N_\mathrm{A}R^2k\int_R^\infty 4\pi r_0^2 f(r_0,t|R)\,\mathrm{d}r_0 . \tag{23}$$

The rate coefficient can therefore be written as

$$k_{1\delta}=[\mathrm{M}]k_\mathrm{a}P(t|R)=[\mathrm{M}]k_\mathrm{a}\left(1-\int_0^t p(t'|R)\,\mathrm{d}t'\right), \tag{24}$$

where $k_\mathrm{a}=4\pi N_\mathrm{A}R^2k$ and has units m^3 mol^{-1} s^{-1}. Eq. (24) is Noyes' equation [21], although differently derived.

The probability $f(r,t|r_0)$ of finding the pair of particles at distance r and time t given an initial separation

r_0, obeys, for spherical symmetry and in the absence of an interaction potential and hydrodynamic effects, the diffusion equation

$$\frac{\partial f}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right), \tag{25}$$

whose solution with the boundary condition at the sink surface

$$4\pi R^2 D \frac{\partial f}{\partial r} = kf, \quad r = R, \tag{26}$$

and the initial condition

$$f(r, 0 \,|\, r_0) = (4\pi r_0^2)^{-1} \delta(r - r_0) \tag{27}$$

is [22]

$$\begin{aligned} f(r, t \,|\, r_0) = \frac{1}{4\pi r r_0} \Bigg\{ & (4\pi D t)^{-1/2} \left[\exp\left(-\frac{(r-r_0)^2}{4Dt}\right) + \exp\left(-\frac{(r-2R+r_0)^2}{4Dt}\right)\right] \\ & - \frac{1}{R}\left(1 + \frac{k}{4\pi R D}\right) \exp\left[\left(1 + \frac{k}{4\pi R D}\right)^2 \frac{Dt}{R^2} + \left(1 + \frac{k}{4\pi R D}\right)(r - 2R + r_0)\frac{1}{R}\right] \\ & \times \operatorname{erfc}\left[\frac{(r-2R+r_0)}{(4Dt)^{1/2}} + \left(1 + \frac{k}{4\pi R D}\right)\left(\frac{Dt}{R^2}\right)^{1/2}\right]\Bigg\}. \end{aligned} \tag{28}$$

Introducing this equation with $r = R$ into eq. (21) and after integration over r_0 one obtains

$$k_{1\delta} = \frac{[\mathrm{M}] N_{\mathrm{A}} 4\pi R^2 k}{1 + Rk/D}\left\{1 + \frac{Rk}{D} \exp\left[\left(1 + \frac{Rk}{D}\right)^2 \left(\frac{Dt}{R^2}\right)\right] \operatorname{erfc}\left[\left(1 + \frac{Rk}{D}\right)\left(\frac{Dt}{R^2}\right)^{1/2}\right]\right\}, \tag{29}$$

or, in terms of the rate constants k_{a} and $k_{\mathrm{d}} = 4\pi N_{\mathrm{A}} R D$,

$$k_{1\delta} = [\mathrm{M}] \frac{k_{\mathrm{a}}}{1 + k_{\mathrm{a}}/k_{\mathrm{d}}}\left\{1 + \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}} \exp\left[\left(1 + \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}}\right)^2 \left(\frac{Dt}{R^2}\right)\right] \operatorname{erfc}\left[\left(1 + \frac{k_{\mathrm{a}}}{k_{\mathrm{d}}}\right)\left(\frac{Dt}{R^2}\right)^{1/2}\right]\right\}, \tag{30}$$

this being the well-known Collins–Kimball rate coefficient [23].

If all the monomers but one are randomly distributed [#3], and that one is initially at the encounter distance, as is the case with $k'_{1\delta}$, one has for large M, and directly from (17),

$$k'_{1\delta} = k_{1\delta} + \frac{p(t \,|\, R)}{P(t \,|\, R)}, \tag{31}$$

the contribution of the pair of monomers created by excimer dissociation being

$$k^{\mathrm{P}}_{1\delta} = \frac{p(t \,|\, R)}{P(t \,|\, R)}. \tag{32}$$

But, by eq. (24), eq. (31) becomes

$$k'_{1\delta} = k_{1\delta} - \frac{\mathrm{d} \ln k_{1\delta}}{\mathrm{d}t}. \tag{33}$$

The rate coefficient appropriate for excited monomers produced by excimer dissociation is therefore higher

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[#3] In the absence of a potential, it appears reasonable to assume an uniform distribution for the monomers around the dissociating excimer. This approximation will be the better the higher the excimer effective lifetime.

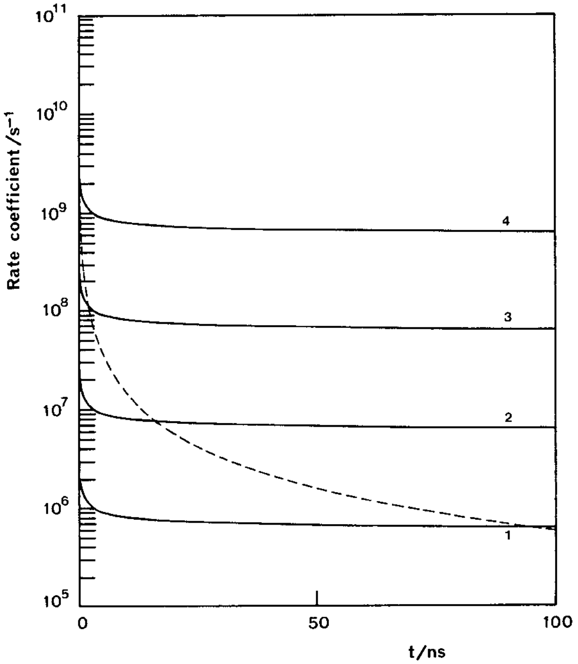

Fig. 1. Excimer formation rate coefficient versus time computed with $R=8$ Å, $k_a=10^{10}$ M^{-1} s^{-1} and $D=10^{-6}$ cm^2 s^{-1}. (---) geminate pair recombination rate coefficient, $k^{\mathrm{P}}_{1\delta}$; (—) rate coefficient for initial uniform distribution, $k_{1\delta}$. (1) [M]$=10^{-3}$ M; (2) [M]$=10^{-2}$ M; (3) [M]$=10^{-1}$ M; (4) [M]$=1$ M.

than $k_{1\delta}$ by the term $-\mathrm{d}\ln k_{1\delta}/\mathrm{d}t$, which is the geminate pair recombination contribution. This term, independent of [M], is only a small correction for high [M], but predominates for low [M]. In fig. 1, are plotted the contributions $k_{1\delta}$ and $k^{\mathrm{P}}_{1\delta}$ of the rate coefficient for several values of [M], using a mutual diffusion coefficient $D=10^{-6}$ cm^2 s^{-1}, $k_a=10^{10}$ M^{-1} s^{-1} and $R=8$ Å. The geminate pair recombination contribution is still important for concentrations higher than 10^{-2} M, the contribution being more pronounced the shorter the time. The effect of the diffusion coefficient is also important since a decrease of D enhances the geminate pair recombination contribution to the global rate coefficient. Indeed, when the recombination of the geminate pair of monomers increases by this reason, $k_{1\delta}$ simultaneously decreases, since both the separation of the geminate pair and the movement of the ground state monomers towards the excited one are slowed down by the decrease of D. This can be seen in figs. 2 and 3 where $k'_{1\delta}$ and the geminate pair recombination contribution, $k^{\mathrm{P}}_{1\delta}$ are plotted versus time for $D=10^{-5}$ cm^2 s^{-1}, $D=10^{-6}$ cm^2 s^{-1} and [M]$=10^{-2}$ M. As expected the geminate pair recombination contribution decreases with the increase of the diffusion coefficient, being negligible for times longer than 10 ns when $D=10^{-5}$ cm^2 s^{-1} and [M]$=10^{-2}$ M.

4. Conclusions

A model of monomer–excimer kinetics was developed, taking into consideration the two different modes of excited monomer production: light absorption and excimer dissociation. The appropriate rate coefficients were also obtained within the framework of classical diffusion theory (independent pair approximation). The results obtained, applicable to both excimer and exciplex kinetics, suggest that experimental systems should display, under suitable conditions, rich kinetic behaviour yet to be explored experimentally.

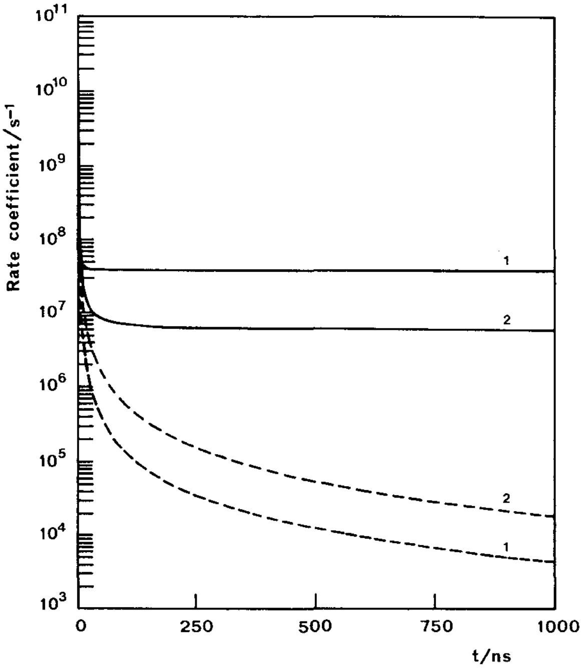

Fig. 2. Excimer formation rate coefficient versus time computed with $R=8$ Å, $k_a=10^{10}$ M^{-1} s^{-1}, $D=10^{-5}$ cm^2 s^{-1} (1) and $D=10^{-6}$ cm^2 s^{-1} (2). (---) geminate pair recombination rate coefficient, $k^{P}_{1\delta}$; (—) global rate coefficient, $k'_{1\delta}=k_{1\delta}+k^{P}_{1\delta}$.

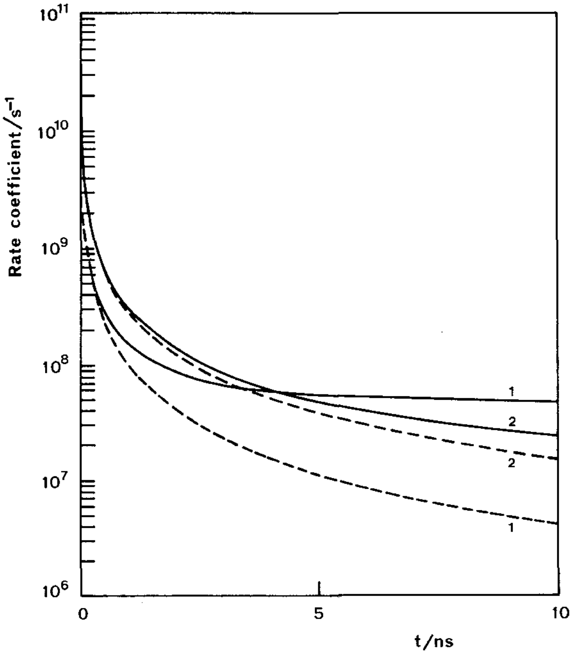

Fig. 3. Same as in fig. 2 but with a smaller time span.

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