Reversible monomer–excimer kinetics in solution

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After summarizing a model for reversible excimer formation kinetics, with due allowance for the time-dependence of the excimer formation step, and making explicit distinction between the excimer formed from an excited monomer produced by photon absorption and that formed from an excited monomer produced by dissociation of another excimer, numerical calculations are performed, showing significant differences with respect to previous kinetic models.

1. Introduction

Since the discovery of molecular excimers by Förster and Kasper in 1954 [1], monomer–excimer kinetics in solution has been described by models of varying mathematical complexity. The original Birks model with time-independent rate coefficients [2], leading to double exponential kinetics, was followed by several attempts [3–7] to incorporate "transient effects", i.e. the time dependence of the rate coefficient for excimer formation, which is usually a diffusion controlled process. None of these treatments is appropriate, however, to the reversible (and more general) case, i.e. when the back reaction (see scheme I) is not negligible. In this communication, some illustrative numerical results are given for a model of reversible monomer–excimer kinetics previously developed [8].

2. Kinetic model and numerical results

Assuming the number of excited state molecules much smaller than the ground state ones, which is valid for low intensities of excitation light, the excited monomer (M*) and the excimer (D*) time evolutions are given by [8]

\[ [M^*] = I \otimes f_1 + I \otimes J \otimes (k_{1s} f_1) \otimes (k_{2s} f_1) \otimes f_1, \quad (1) \]

\[ [D^*] = I \otimes J \otimes (k_{1s} f_1) \otimes f_2, \quad (2) \]

where \( \otimes \) stands for convolution, \( f \otimes g = \int_0^t f(u)g(t-u) \, du \), \( I \) is the excitation pulse, \( f_1 \), and \( f_1 \) are the monomer survival probabilities after \( \delta \)-creation via light absorption and excimer dissociation, respectively, \( f_2 \) is the excimer survival probability after creation by excited-plus-unexcited monomer association and are given by

\[ f_1 = \exp(-\Gamma_1 t) \cdot \exp \left( - \int_0^t k_{1s}(u) \, du \right), \quad (3) \]

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\[ f_2 = \exp(-\Gamma_2 t) \cdot \exp(-k_2 t). \quad (5) \]

\( \Gamma_1 \) and \( \Gamma_2 \) are the sum of the intrinsic rate constants for unimolecular deactivation of monomer and excimer, respectively, \( k_{1s} \) and \( k_{1s} \) are the rate coefficients for bimolecular decay of excited monomer corresponding to uniform and non-uniform ground state monomers distribution, respectively, and \( k_2 \) is the rate constant for excimer dissociation back to the excited monomer. Finally, the quantity \( J \), which may be regarded as a secondary production rate, is given by

\[ J = \mathcal{L}^{-1} \left[ \frac{1}{1 - \mathcal{L}[k_{1s} f_1] \mathcal{L}[k_{2s} f_2]} \right], \quad (6) \]

\( \mathcal{L} \) standing for the Laplace transform operator:

\[ \mathcal{L}[f(t)] = \int_0^\infty e^{-st} f(t) \, dt. \]
The time-dependent rate coefficients $k_{18}$ and $k'_{18}$ are obtained as [8]

$$k_{18} = [M] \frac{k_a}{1 + k_a/k_d} \left[ 1 + \frac{k_a}{k_d} \exp \left( \frac{1 + k_a}{k_d} \left( \frac{Dt}{R^2} \right)^{1/2} \right) \right] \times \text{erfc} \left( \frac{1 + k_a}{k_d} \left( \frac{Dt}{R^2} \right)^{1/2} \right).$$

(7)

This is the well-known Collins–Kimball result, and

$$k'_{18} = k_{18} - \frac{d \ln k_{18}}{d t},$$

(8)

where $[M]$ is the (ground-state) monomer concentration, and $k_a$ and $k_d$ the rate constants for the activated and diffusional processes, $k_d = 4 \pi N_A R D$, $N_A$ being Avogadro’s number, $R$ the encounter radius and $D$ the mutual diffusion coefficient. The rate coefficient $k'_{18}$ differs from the Collins–Kimball result owing to the geminate pair recombination probability. This difference is important for low concentrations but decreases for high concentrations, as can be seen from eqs. (7) and (8).

The excimer time evolution, numerically computed from eq. (2), is presented in fig. 1 for two different concentrations and two different diffusion coefficients, while fixing other parameters at toluene-like values: $1/I_1 = 10$ ns, $1/I_2 = 20$ ns, $k_c = 10^{10}$ M$^{-1}$ s$^{-1}$, $k_d = 10^8$ s$^{-1}$, $R = 8$ Å. For comparison, excimer profiles are also plotted admitting that $k'_{18} = k_{18}$, i.e., neglecting the geminate pair contribution. It is seen that even at 0.1 M, differences arise for the lowest diffusion coefficient ($10^{-6}$ cm$^2$ s$^{-1}$). For concentrations below 0.1 M, the pair recombination contribution markedly affects the height and maximum of the excimer curve, for both diffusion coefficients.

3. Summary and conclusions

Excimer time evolutions were obtained in some realistic cases for a model of reversible monomer–excimer kinetics in solution and compared with a simplified model where geminate pair recombination is neglected. The importance of this last contribution is established for most conditions.

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References


