Journal of Luminescence 48 & 49 (1991) 456-458
North-Holland

Reversible monomer–excimer kinetics in solution

M.N. Berberan-Santos, J.P. Pinheiro, J.P. Farinha and J.M.G. Martinho

Centro de Química-Física Molecular da U.T.L. (INIC), Instituto Superior Técnico, 1096 Lisboa Codex, Portugal

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]

$$[\mathrm{M}^*] = I\otimes f_1 + I\otimes J\otimes(k_{1\delta}f_1)\otimes(k_2 f_2)\otimes f_1', \qquad (1)$$

$$[\mathrm{D}^*] = I\otimes J\otimes(k_{1\delta}f_1)\otimes f_2, \qquad (2)$$

where $\otimes$ stands for convolution, $f\otimes g = \int_0^t f(u)g(t-u)\,\mathrm{d}u$, I is the excitation pulse, f_1, and f_1' are the monomer survival probabilities after δ-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

$$f_1 = \exp(-\Gamma_1 t)\cdot\exp\left(-\int_0^t k_{1\delta}(u)\,\mathrm{d}u\right), \qquad (3)$$

$$f_1' = \exp(-\Gamma_1 t)\cdot\exp\left(-\int_0^t k_{1\delta}'(u)\,\mathrm{d}u\right), \qquad (4)$$

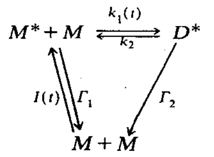
$$f_2 = \exp(-\Gamma_2 t)\cdot\exp(-k_2 t). \qquad (5)$$

Γ_1 and Γ_2 are the sum of the intrinsic rate constants for unimolecular deactivation of monomer and excimer, respectively, $k_{1\delta}$ and $k_{1\delta}'$ 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

$$J = \mathscr{L}^{-1}\left[\frac{1}{1-\mathscr{L}[k_{1\delta}'f_1']\mathscr{L}[k_2 f_2]}\right], \qquad (6)$$

$\mathscr{L}$ standing for the Laplace transform operator: $\mathscr{L}[f(t)] = \int_0^\infty \mathrm{e}^{-st}f(t)\,\mathrm{d}t$.

0022-2313/91/$03.50 © 1991 - Elsevier Science Publishers B.V. (North-Holland)



Scheme I.

The time-dependent rate coefficients $k_{1\delta}$ and $k'_{1\delta}$ are obtained as [8]

$$k_{1\delta}=[\mathrm{M}]\frac{k_{\mathrm{a}}}{1+k_{\mathrm{a}}/k_{\mathrm{d}}}\left\{1+\frac{k_{\mathrm{a}}}{k_{\mathrm{d}}}\exp\left[\left(1+\frac{k_{\mathrm{a}}}{k_{\mathrm{d}}}\right)^2\left(\frac{Dt}{R^2}\right)\right]\right.$$
$$\left.\times\,\mathrm{erfc}\left[\left(1+\frac{k_{\mathrm{a}}}{k_{\mathrm{d}}}\right)\left(\frac{Dt}{R^2}\right)^{1/2}\right]\right\}. \qquad (7)$$

This is the well known Collins-Kimball result, and

$$k'_{1\delta}=k_{1\delta}-\frac{\mathrm{d}\ln k_{1\delta}}{\mathrm{d}t}, \qquad (8)$$

where [M] is the (ground-state) monomer concentration, and k_{a} and k_{d} the rate constants for the activated and diffusional processes, $k_{\mathrm{d}}=4\pi N_{\mathrm{A}}RD$, N_{A} being Avogadro's number, R the encounter radius and D the mutual diffusion coefficient. The rate coefficient $k'_{1\delta}$ 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: $1/\Gamma_1=10$ ns, $1/\Gamma_2=20$ ns, $k_{\mathrm{a}}=10^{10}\ \mathrm{M^{-1}\,s^{-1}}$, $k_2=10^8\ \mathrm{s^{-1}}$, $R=8$ Å. For comparison, excimer profiles are also plotted admitting that $k'_{1\delta}=k_{1\delta}$, i.e. neglecting the geminate pair contribution. It is seen that even at 0.1 M, differences arise for the lowest diffusion coefficient ($10^{-6}\ \mathrm{cm^2\,s^{-1}}$). 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.

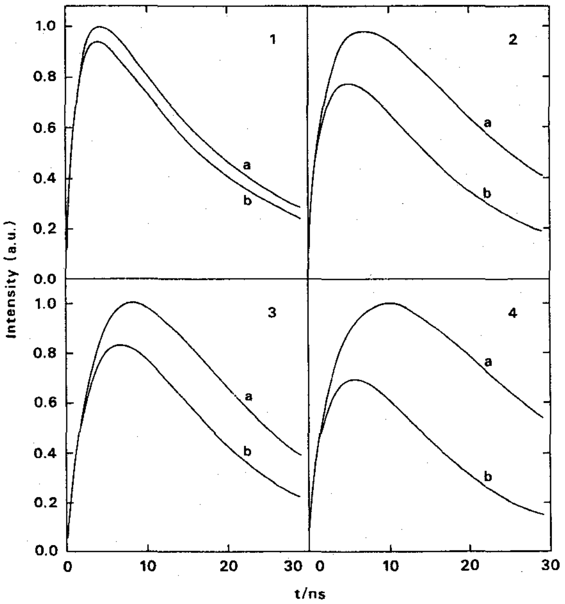


Fig. 1. Excimer concentration time evolution computed with (a) and without (b) the geminate pair recombination contribution. (1) $[\mathrm{M}]=0.1$ M, $D=10^{-5}\ \mathrm{cm^2\,s^{-1}}$; (2) $[\mathrm{M}]=0.1$ M, $D=10^{-6}\ \mathrm{cm^2\,s^{-1}}$; (3) $[\mathrm{M}]=10^{-2}$ M, $D=10^{-5}\ \mathrm{cm^2\,s^{-1}}$; (4) $[\mathrm{M}]=10^{-2}$ M, $D=10^{-6}\ \mathrm{cm^2\,s^{-1}}$.

Acknowledgement

This work was supported by JNICT (Junta Nacional de Investigação Científica e Tecnológica) and INIC (Instituto Nacional de Investigação Científica).

References

[1] T. Förster and K. Kasper, Z. Phys. Chem. NF1 (1954) 275.
[2] J.B. Birks, D.J. Dyson and I.H. Munro, Proc. Roy. Soc. A275 (1963) 575.
[3] J.M. Vanderkooi and J.B. Callis, Biochemistry 13 (1974) 4000.
[4] W. Weixelbaumer, J. Bürbaumer and H.F. Kauffman, J. Chem. Phys. 83 (1985) 1980.

[5] J.M.G. Martinho and M.A. Winnik, J. Phys. Chem. 91 (1987) 3640.

[6] D.J.S. Birch, A.D. Dutch, R.E. Imhof, B. Nadolski and I. Soutar, J. Photochem. 38 (1987) 239.

[7] K. Sienicki and M.A. Winnik, J. Chem. Phys. 87 (1987) 2766.

[8] M.N. Berberan-Santos and J.M.G. Martinho, to be published.