React. Kinet. Catal. Lett., Vol. 15, No. 2, 159–166 (1980)

KINETICS OF PARTLY DIFFUSION CONTROLLED REACTIONS

VI. FLUORESCENCE QUENCHING IN THE CASE OF A MODEL OF CYLINDRICAL SYMMETRY

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Received March 25, 1980
Accepted July 10, 1980

We propose a simple kinetic model in which two types of processes between two reactants occur: diffusional processes for distances greater than σ', the "reaction" distance, and static quenching for distances smaller than σ'. This model might be useful in the studies of diffusion in membrane systems.

Была предложена простая кинетическая модель, заключающая в себе два типа процессов, протекающих между двумя реагентами: диффузионные процессы для расстояний, превышающих расстояние „реакции" σ', и статическое гашение для расстояний, меньших σ'. Эта модель может быть использована при исследовании диффузии в мембранных системах.

INTRODUCTION

Diffusion controlled reactions have been studied by several authors who have given both theoretical treatments and experimental results in various systems of spherical symmetry /1-7/. With the extension of the formalism which is described here, such reactions can be used for studying diffusion in systems which are effectively two-dimensional, like lipid bilayer membranes.

EQUATIONS OF DIFFUSION FOR CYLINDRICAL SYMMETRY

Let us consider a homogeneous population of molecules B dissolved in membranes and the generation at the time t = 0 of reacting molecules A (produced by light excitation, for example)

$$A + B \longrightarrow C$$

Let us assume that every encounter leads to a chemical reaction. Then, we can determine the apparent rate constant of the reaction, $k_a(t)$ using the following relation /5, 6/:

$$\frac{\delta \phi (r,t)}{\delta t} + \mathcal{G} \phi (r,t) = 0 \qquad (1)$$

where

ϕ – distribution function, ratio of the local concentration of B to the mean concentration of B, $<(B)>$,

r – distance between molecules A and B,

$\mathcal{G}$ – time evolution operator equal to $- D \ \nabla^2$,

D – sum of the diffusion coefficients of A and B for cylindical symmetry,

∇^2 – Laplace operator.

We propose here a diffusion model by considering two distinct areas in the reacting system both centered on A towards which B diffuses.

(i) An area defined by two circles of radius δ the time collisional distance and σ', the "reaction" distance wherein the chemical reaction occurs with a practically infinite chemical rate constant. We assume that no diffusion occurs in this range: $(r,t) = 0$ for $r \in (\sigma, \sigma')$.

(ii) An external area $(t > \sigma')$ in which no chemical reaction, but only diffusion occurs.

Under these conditions, the value of the apparent rate constant is expressed by /2/:

$$k_a(t) = 2\ \pi N \sigma'\ D \left(\frac{\delta\phi(r,t)}{\sigma r} \right)_\sigma \tag{2}$$

where N represents the Avogadro number.

An analytical expression of eq. (1) has been reported, which is not routinely useful /3/. A numerical solution has been proposed and an approximate relationship of the form a + $b/\sqrt{t}$ has been obtained by seeking the best fitting curve by the least squares method. If, after a Dirac excitation, a reaction occurs between electronically excited molecules A and inhibitors B, excited molecules naturally disappear from the region around B. The shorter the time, the more important is the concentration of molecules B and, consequently, the rate of reaction between A and B. Thus, a precise knowledge of $k_a(t)$ for short times is necessary for an accurate determination of the reaction rate. The solution proposed in Ref. /4/ does not exactly allow it.

Using the Laplace transform for the solution of the system, we have:

$$y(\rho,\ s) = \int_0^\infty e^{-s\tau}\ \phi(\rho,\ \tau)\ d\tau$$

where $\rho = \frac{r}{\sigma'}$ and $\tau = \frac{Dt}{\sigma'^2}$

and $sy - 1 = y'' + \frac{1}{\rho}\ y'$ with $y\ (1,s) = 0$

The solution of the equation is:

$$y(\rho,s) = \frac{1}{s} \left[1 - \frac{K_o(\rho\sqrt{s})}{K_o(\sqrt{s})} \right] \tag{3}$$

where K_o is a modified Bessel function.

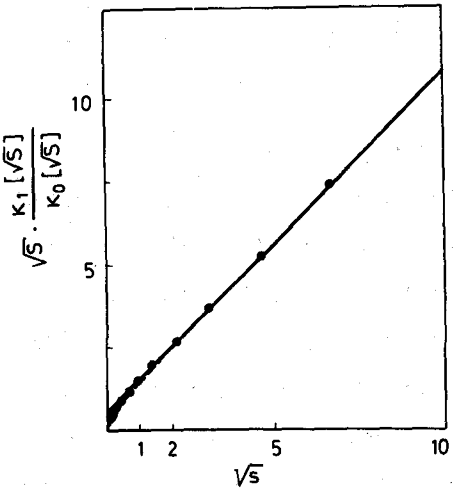

Fig. 1. Variations of $y = \sqrt{s} \times K_1(\sqrt{s})/K_0(\sqrt{s})$ versus $\sqrt{s}$, — calculated curve, --- corresponding asymptote: $1/2 + \sqrt{s}$

We finally arrive at:

$$\left[\frac{dy}{d\rho}(\rho, s)\right]_1 = \frac{1}{\sqrt{s}}\,\frac{K_1(\sqrt{s})}{K_0(\sqrt{s})} \qquad (4)$$

The product of the function with s is displayed in Fig. 1.

Apparently, it approaches asymptotically a value equal to $\sqrt{s} + 1/2$, leading to a good approximation of (dy/dp). Therefore, eq. (2) may be given by:

$$k_a(t) \simeq 2\pi\ ND\left(\frac{1}{2} + \frac{\sigma'}{\sqrt{\pi Dt}}\right)\ \mathrm{mol}^{-1}\ \mathrm{dm}^{2}\ \mathrm{sec}^{-1} \qquad (5)$$

The true calculated $k_a(t)$ value (numerical integration with a computer) is very close to $k_a(t)$ from eq. (5) for times smaller than about 1000 nsec in viscous solvents. Relation (5) is therefore really suitable for quenching studies of electronically excited singlet molecules with lifetimes shorter than 500 nsec. In contrast, for longer times, relation (5) is less precise, but often remains useful.

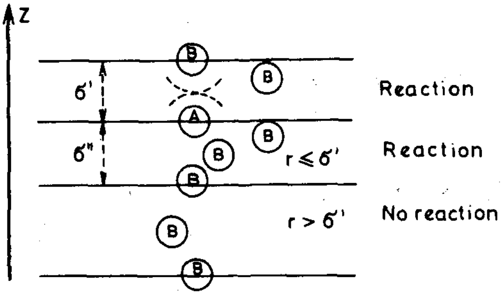

Fig. 2. Geometry of a pseudo two-dimensional diffusion reaction system

AMPLIFICATION FACTOR

The above relation leads to a $k_a(t)$ value expressed in $mol^{-1}\ dm^2\ sec^{-1}$. However, we thought that $k_a(t)$ could be better expressed in classical units of $mol^{-1}\ dm^3\ sec^{-1}$.

Considering Fig. 2, we can assume that a reaction occurs if the distance between the planes which contain molecules A and B, respectively, is smaller than σ', despite the fact that diffusion coefficient D_z is zero in this region. Hence:

$$k'_a(t) \simeq 2\pi\ N\sigma' D\left(1 + \frac{2\sigma'}{\sqrt{\pi Dt}}\right)\ mol^{-1}\ dm^3\ sec^{-1} \qquad (6)$$

In fact, biological membranes constitute three-dimensional systems. Taking into account the fact that $D_z \neq 0$, it may be assumed that a reaction occurs with a number of molecules B greater than those found between planes located at a distance $d = \pm\sigma'$ from molecule A. Especially, if $D_z \gg D$, all the molecules B in the membranes will be able to react with A. Thus, there is an amplification of the rate constant by a factor of f. Hence:

$$k'_a(t) \simeq 2\pi N\ \ '\ fD\left(1 + \frac{2\sigma'}{\sqrt{\pi Dt}}\right) = k_o\left(1 + \frac{2\sigma'}{\sqrt{\pi Dt}}\right) \qquad (7)$$

CONSEQUENCES

Let us consider the scheme of deactivation of A by B after a Dirac excitation ((δ function):

$$A \xrightarrow{k = \frac{1}{\tau}} \qquad \text{natural relaxation}$$

$$A + B \xrightarrow{k'_a(t)} C \qquad \text{deactivation}$$

If A is an emissive singlet state, it is possible to measure the quantum yield of fluorescence in the absence (ϕ_o) and presence (ϕ) of B, all other experimental parameters being equal.

As previously reported /5/, we can determine the variations of ϕ with (B), taking into account the fact that at time t = 0, the probability p of finding molecules B inside the chemical reaction volume V_1 is

$$V_1 \simeq \pi(\sigma'^2 - \sigma^2)\ \sigma' f \qquad (8)$$

Then, we observe:

(i) A nearly instantaneous deactivation of A if at least one molecule B is to be found in volume V_1,

(ii) A deactivation of A and B reaching σ' after diffusion.

As previously calculated /5/, p is given by:

$$p = \exp\ [- NV_1\ (B)] \qquad (9)$$

Then, if $(A)_o$ molecules are excited at t = 0, we get $p(A)_o$ molecules after the fast deactivation process.

For t > 0, the deactivation leads to:

$$\frac{d(A)}{(A)} = - \ [k + k'_a(t).\ (B)]$$

and to:

$$(A) = (A)_0 \exp(-NV_1B) \exp\left[-\left[k + k_0(B)\left(1 + \frac{4\sigma'}{\sqrt{\pi Dt}}\right)\right] t\right] \tag{10}$$

which leads to:

$$\frac{\phi_0}{\phi} = \exp(NV_1B)\left[\frac{1 + k_0\,\tau(B)}{I(\lambda)}\right] \tag{11}$$

where

$$\lambda = \frac{4}{\sqrt{\pi}} \cdot \frac{k_0\,\tau(B)}{[1 + k_0\,\tau(B)]^{1/2}} \cdot \frac{\sigma'}{\sqrt{D\tau}} \tag{12}$$

and

$$I(\lambda) = \int_0^\infty \exp(-u - \lambda u^{1/2})\,du =$$

$$= 1 - \frac{\lambda}{2}\sqrt{\pi}\,\exp\left(\frac{\lambda^2}{4}\right) \mathrm{Erfc}\left(\frac{\lambda}{2}\right) \quad /5,6/ \tag{13}$$

For small quencher concentrations, the first and the second term of the Taylor series of ϕ_0/ϕ versus B are:

$$\frac{\phi_0}{\phi} = 1 + \left[NV_1 + k_0\,\tau\left(1 + \frac{2\sigma'}{\sqrt{D\tau}}\right)\right](B) + \ldots \tag{14}$$

and all other terms of this expansion can be neglected.

CONCLUSIONS

Considering the fact that a more precise estimation of $k'_a(t)$ is proposed for short times and a term of steady-state inhibition is introduced, the calculations presented here notably modify the results reported by other authors /4/. From experimental data of partly diffusion controlled reactions in membrane systems, these results should allow the determination of the diffusion coefficient which represents an essential information in the understanding of numerous biological phenomena.

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