PHOTOCHEMICAL REACTIONS WITH A PARTICIPATION OF DIFFUSION

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Influence of diffusion coefficients of reaction components on a course of simple photochemical reaction has been studied by numerical simulation. Diffusion coefficients have been varied in the range $\langle 0, \infty \rangle$. Relationships between values of diffusion coefficients and parameters of photochemical reactions (entry concentrations and absorptivities of components, intensity of incident light and quantum yield of corresponding photochemical reactions) have been shown.

Photochemical reactions have a specific feature that one of the reaction components – photons – gets into the reaction space only from its surface. Photochemical experiments are usually performed in perfectly stirred reaction vessels. But there exist some cases (e.g. flow reactor), where the reaction space is not or only partially stirred.

The problems of diffusion in photochemical experiments have attracted interest of chemists for a long time[1–4]. They discussed the kinetics of radical reactions, where a steady state was supposed, and the dependence of light intensity on the distance from a front surface was approximated by the first term of the Taylor series (it is equivalent to the presumption that the light energy is constant in the reaction volume). But this approximation is valid only for the low concentrations and the short pathlength. It is impossible to use this simplification for the case of high concentrations.

The aim of this work is to discuss the photochemical reactions with a participation of diffusion. A set of equations joining the two processes is presented. Some numerically solved examples are introduced in order to describe the influence of diffusion on the course of the photochemical process in the reaction volume. Influence of temperature on the processes in photochemical reactors (diffusion process and some photochemical or thermal reactions) is not considered in this work.

THEORETICAL

Mathematical Formulation of the Problem

Suppose a primary beam, falling at the front of the reaction volume, is homogenous and monochromatic, with the intensity I_0. There are two processes which must be considered while describing the problem. One of them is the photochemical reaction, while the other one is the diffusion. For simplicity we suppose that both processes take place only along the x-axis, which is parallel with the direction of the incident beam. The origin of the x-axis was put into the front wall of the volume.

We assume a photochemical reaction of the type

$$\mathrm{A} \underset{\varphi_{\mathrm{B}}}{\overset{\varphi_{\mathrm{A}}}{\rightleftarrows}} \mathrm{B} \qquad (1)$$

and we treat the diffusion as a transfer of molecules through a plane perpendicular to the direction of the incident radiation. If only a photochemical process is assumed (superscript f), the change of concentration of the k-th compound at the point x on the x-axis is given by

$$\left(\frac{\partial c_k}{\partial t}\right)_x^{\mathrm{f}} = I_x \sum_{s=1}^{2} \varphi_s \varepsilon_s c_{s,x} (-1)^{\delta_{s,k}}\,, \qquad (2)$$

where ε_s is the extinction coefficient of the compound s, $c_{s,x}$ is the concentration of the compound s at distance x, φ_s is the quantum yield for the compound s, $\delta_{s,k}$ is Kronecker delta, and I_x is the intensity of the light at distance x. The corresponding change of concentration due to diffusion only is given by the second Fick law (superscript d)

$$\left(\frac{\partial c_k}{\partial t}\right)_x^{\mathrm{d}} = D_k \frac{\partial^2 c_k}{\partial x^2}\,, \qquad (3)$$

where D_k is the diffusion coefficient for compound k. The total change of concentration of compound k at distance x is given by the sum of Eqs (*2*) and (*3*)

$$\left(\frac{\partial c_k}{\partial t}\right)_x = \left(\frac{\partial c_k}{\partial t}\right)_x^{\mathrm{f}} + \left(\frac{\partial c_k}{\partial t}\right)_x^{\mathrm{d}}. \qquad (4)$$

The resulting relation (*4*) represents the system of nonlinear partial differential equations of the parabolic type, for which an analytical solution is not known.

Numerical Solution of the Problem

The system of equations (*4*) was solved by Crank–Nicholson method of nets[5]. The irradiated space in the direction of light was normalized to $x \in \langle 0, 1\rangle$ and the range $\langle 0,1\rangle$ was divided into $n - 1$ equal parts, $x_0 = 0$, $x_1 = h$, $x_2 = 2h, \ldots, x_n = 1$, where the step is $h = 1/n$ and point x_i is $x_i = (i - 1)h$, $i = 1, 2, \ldots, n$. In a similar way the total irradiation time was divided into r equal parts,

$$t_0 = 0,\ t_1 = p,\ t_2 = 2p, \ldots, t_r = T,$$

where the step is $p = T/r$ and the point t_j is $t_j = jp$, $j = 0, 1, \ldots, r$. The set of points obtained by intersections of lines $x = i \,.\, h$ and $t = j \,.\, p$ forms a rectangular net. Expression of derivatives by approximate formulae

$$\left(\frac{\partial c_k}{\partial t}\right)_{(x_i,\, t_j)} = (c_{k,i}^{j+1} - c_{k,i}^{j})/p \tag{5}$$

and

$$\left(\frac{\partial^2 c_k}{\partial x^2}\right)_{(x_i,\, t_j)} = \tfrac{1}{2}(c_{k,i-1}^{j} - 2c_{k,i}^{j} + c_{k,i+1}^{j})/h^2 + \tfrac{1}{2}(c_{k,i-1}^{j+1} - 2c_{k,i}^{j+1} + c_{k,i+1}^{j+1})/h^2 \tag{6}$$

gives us the final equation which in a matrix notation may by written as

$$\boldsymbol{A}_k \,.\, \boldsymbol{c}^{j+1} = \boldsymbol{B}_k \,.\, \boldsymbol{c}_k^{j} + 2 \,.\, \boldsymbol{f}_k^{j}\,, \tag{7}$$

where for $i = 2, 3, \ldots, n - 1$ the matrix $\boldsymbol{A}_k$ have the following form

$$\left|\begin{array}{cccccc} -\alpha_k & 2 + 2\alpha_k & -\alpha_k & 0 & 0 & \ldots \\ 0 & -\alpha_k & 2 + 2\alpha_k & -\alpha_k & 0 & \ldots \\ 0 & 0 & -\alpha_k & 2 + 2\alpha_k & -\alpha_k & \ldots \\ & & \vdots & & & \end{array}\right|$$

and the matrix $\boldsymbol{B}_k$ is

$$\left|\begin{array}{cccccc} \alpha_k & 2 - 2\alpha_k & \alpha_k & 0 & 0 & \ldots \\ 0 & \alpha_k & 2 - 2\alpha_k & \alpha_k & 0 & \ldots \\ 0 & 0 & \alpha_k & 2 - 2\alpha_k & \alpha_k & \ldots \\ & & \vdots & & & \end{array}\right|$$

with

$$\alpha_k = pD_k/h^2\,. \tag{8}$$

The vector $\boldsymbol{f}^j$ is a vector of photochemical contributions for compound k and time j.

For layer i (distance from the front wall) the element of this vector is

$$f^j_{k,i} = I^j_i \sum_{s=1}^{2} \varphi_s \varepsilon_s c^j_{s,i} (-1)^{\delta_{s,k}} , \tag{9}$$

where

$$I^j_i = I^j_{i-1}\left(1 - \sum \varepsilon_{sa} c^j_{sa,i} h\right) . \tag{10}$$

The summation in Eq. (*10*) is over all absorbing components. The irradiated solution is closed and therefore there is no exchange of mass with the outside space. The boundary conditions are of the second type

$$\left(\frac{\partial c_k}{\partial x}\right)_{x=0,1} = 0 . \tag{11}$$

The boundary concentrations were computed by nonsymmetric differentiation

$$\left(\frac{\partial c_k}{\partial x}\right)_{\substack{x=0\\ t=(j+1)p}} = \left(-3c^{j+1}_{k,1} + 4c^{j+1}_{k,2} - c^{j+1}_{k,3}\right)/2h = 0 \tag{12}$$

$$\left(\frac{\partial c_k}{\partial x}\right)_{\substack{x=1\\ t=(j+1)p}} = \left(-3c^{j+1}_{k,n} + 4c^{j+1}_{k,n-1} - c^{j+1}_{n-2}\right)/2h = 0 . \tag{13}$$

For the time $t = 0$ the concentrations $c_{k,i}$ are known: $c_{k,i} = c^0_k$, $i = 1, 2, \ldots, n$. Thus the concentration gradient and the following diffusion arises from the photochemical process, which changes the entry constant distribution of concentrations. Since the matrices ***A*** and ***B*** are tridiagonal the unknown parameters c^{j+1} were computed by the factorization of the set of equations (*7*).

RESULTS AND DISCUSSION

Simple photochemical reactions $A \xrightarrow{\varphi} B$ are often used for actinometric determination of the intensity of light sources. To describe the kinetics of such a reaction, the following set of entry parameters may bey used: I_0, φ, c^0_A, ε_A, ε_B, D_A, D_B. Suppose first that the rates of diffusion of both A and B are equal ($D_A = D_B = D$), and furthermore, that the reaction product (compound B) does not absorb the incident light ($\varepsilon_B = 0$). In this case (see Fig. 1) the result of irradiation slightly depends on the diffusion coefficient D. Assuming that all the radiation is absorbed, the relationship between the incident light intensity I_0 and the concentration of reaction product c_B is linear.

If the reaction product B absorbs the incident radiation ($\varepsilon_B \neq 0$) (see Fig. 2) then the kinetics of the photochemical process depends on diffusion coefficient D significantly. For higher values of the extinction coefficients and the entry concentrations, the dependence of the photochemical process on the diffusion coefficient is significant. The relation between I_0 and c_B is nonlinear for both unstirred and partially stirred reactors.

For the flow reactors (in general for unstirred reaction vessels) the following important conclusion may be formulated. If the light intensity in a photochemical reaction space is to be determined, one should prefer such actinometers, for that the product of irradiation B does not absorb the incident radiation or, compared to A, absorbs it very little. Use of actinometers of the "modified ferrioxalate"[6] or azobenzene[7] types should be therefore avoided.

Consider now a photochemical reaction, represented by Eq. (*1*), e.g. the reversible photochemical *cis–trans* isomerization. Suppose first that $D_A = D_B = D$. Figures 3 and 4 describe the influence of individual parameters on the photochemical process. They demonstrate the major influence of the diffusion coefficient D. The significance of this influence increases with the increasing entry concentration of A and with the

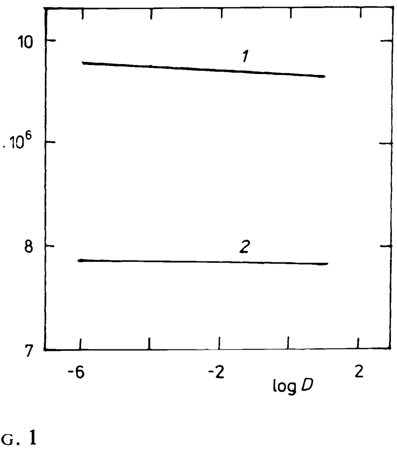

FIG. 1

The dependence of photoproduct concentration on diffusion coefficient for the A → B reaction; $\varphi = 1$, $\varepsilon_B = 0$, $I_0 = 1 . 10^{-5}$, $D_A = D_B = D$, $T = 1$, $c_B^0 = 0$, ε's are in $cm^2 mol^{-1}$, c in $mol cm^{-3}$, I in $mol s^{-1} . cm^{-2}$, and T in s. Parameter sets assumed: *1* $c_A^0 = 4 . 10^{-5}$, $\varepsilon_A = 1 . 10^5$; *2* $c_A^0 = 2 . 10^{-5}$, $\varepsilon_A = 3 . 10^5$

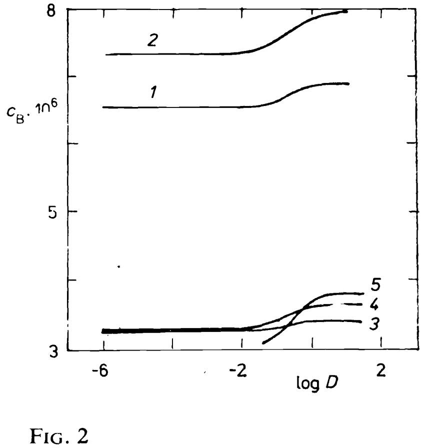

FIG. 2

As in Fig. 1, $\varphi = 1$, $T = 1$, $D_A = D_B = D$, $c_B^0 = 0$. Parameter sets assumed: *1* $c_A^0 = 2 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 1 . 10^5$, $I_0 = 1 . 10^{-5}$; *2* $c_A^0 = 3 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 1 . 10^5$, $I_0 = 1 . 10^{-5}$; *3* $c_A^0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 2 . 10^5$, $I_0 = 5 . 10^{-6}$; *4* $c_0^A = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 3 . 10^5$, $I_0 = 5 . 10^{-6}$; *5* $c_A^0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 5 . 10^5$, $I_0 = 5 . 10^{-6}$

increasing extinction of both compounds. Clearly, the effectiveness of incident photons is enhanced for higher diffusion coefficients.

If the diffusion coefficients D_A and D_B are different, the situation is much more complex. The molecules of the compounds A and B move with different velocities

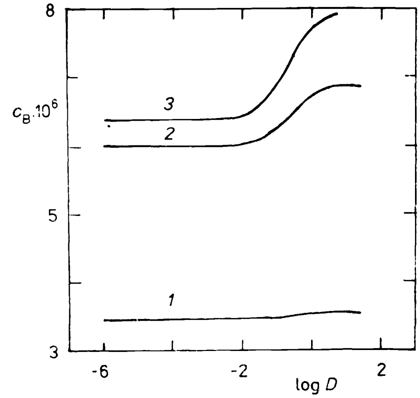

FIG. 3

The dependence of photoproduct concentration on diffusion coefficient for $A \rightleftarrows B$ reaction; $\varphi_A = \varphi_B = 1, T = 1, D_A = D_B = D$, $I_0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 1 . 10^5$, ε's are in $cm^2 mol^{-1}$, c in mol cm^{-3}, I in mol s^{-1} . cm^{-2}, and T in s. Entry concentrations assumed: *1* $c_A^0 = 1 . 10^{-5}$; *2* $c_A^0 = 3 . 10^{-5}$; *3* $c_A^0 = 5 . 10^{-5}$

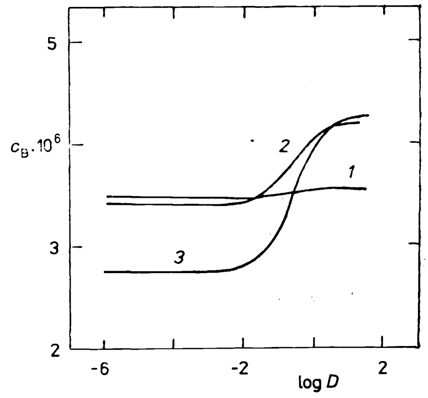

FIG. 4

As in Fig. 3, $\varphi_A = \varphi_B = 1$, $T = 1$, $D_A = D_B = D$, $I_0 = 1 . 10^{-5}$. Parameter sets assumed: *1* $c_A^0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 1 . 10^5$; *2* $c_A^0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 3 . 10^5$; *3* $c_A^0 = 1 . 10^{-5}$, $\varepsilon_A = \varepsilon_B = 5 . 10^5$

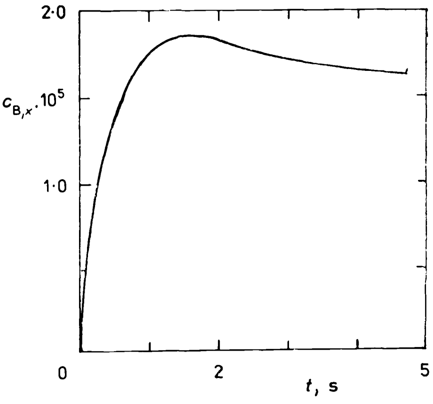

FIG. 5

Time dependence of the photoproduct concentration in the process $A \rightleftarrows B$ for $x = 0{\cdot}01$ cm; $\varepsilon_A = \varepsilon_B = 1 . 10^5$ $cm^2 mol^{-1}$, $D_A = 1, D_B = 0{\cdot}01, T = 6$ s, $c_A^0 = 3 . 10^{-5}$, $I_0 = 2 . 10^{-5}$ mol s^{-1} cm^{-2}, $\varphi_A = \varphi_B = 1$

and the relation $c_{A,x} + c_{B,x} = c_A$ is not valid any longer. If the difference between D_A and D_B is significant, a concentration wave can arise in solution (see Fig. 5). This wave moves from the front side of the irradiated space to the opposite one and the direction of this motion corresponds to the direction of the incident light. When the kinetics beam is perpendicular to the irradiation ("photochemical") beam, this wave may be observed by the increased concentration of the photoproduct B going over the equilibrium limit $((c_A/c_B)_{eq} = \varphi_B\varepsilon_B/\varphi_A\varepsilon_A)$. In such a case the photoproduct concentration c_B approaches this equilibrium limit "from up" i.e. from higher values and not "from down" (i.e. from lower values) as usual in a perfectly stirred photoreactor.

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