Photochemical reaction kinetics in optically dense media: The influence of thermal reactions

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Abstract

The kinetics of photochemical reactions in optically dense media essentially free from diffusion was considered. The photochromic isomerization $A \leftrightarrow B$ was studied as an example. If thermal isomerization is possible, a stationary state is achieved in time determined by rate constants for the thermal reactions. The concentration wave profile is changed during the photochemical reaction propagation. Low values of thermal reaction constants and decrease in sample optical density during photochemical isomerization were found to be essential for maximal wave penetration into the sample. Sharp concentration gradients of A and B can be observed when both the optical density is increased during photochemical isomerization and the quantum yield of the direct photochemical reaction $A \rightarrow B$ is higher than that of the reverse photochemical reaction $B \rightarrow A$.
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1. Introduction

Photochemical reactions in optically dense media are of interest in a wide variety of applications. Examples range from optical data recording to polymer degradation, solar energy capture and biological systems (photosynthesis and photodynamic therapy).

The kinetics of photochemical reactions in optically dense media essentially free from diffusion has been examined in several papers [1–14]. A decrease of light intensity within the sample has been found to constitute a significant feature of such systems. The outermost layers absorb light significantly, therefore the light intensity and the photochemical reaction rate depend on the distance from the irradiated surface. As a result, the reagent and reaction product concentrations are described by a wave-like distribution along the irradiation direction.

Evolution of the wave-like distribution shall be described by a system of partial differential equations (PDE) (1). The first equation is a differential form of the Beer–Lambert law. The next equations are kinetic:

$$\frac{\partial I(l, t)}{\partial l} = -I(l, t)\sum_i \varepsilon_i c_i(l, t)$$

$$\frac{\partial c_i(l, t)}{\partial l} = I(l, t)F(\phi_1, \varepsilon_1, c_1, \ldots, \phi_n, \varepsilon_n, c_n) + k(c_1, \ldots, c_n) \tag{1}$$

where $I(l, t)$: light intensity; $c_i(l, t)$: concentration of ith substance; ε_i: absorption coefficient for ith substance; φ_i: quantum yield of ith reaction. Function F describes the photochemical reaction, and function k describes thermal reactions, which take part in the system.

Thermal reactions have normally been neglected in study of the kinetics of photochemical reactions in optically dense media [1–8,12–14]. To this approximation, the method of complete primitive determination has been applied [4,12–14]. In some special cases, the primitive has been integrated analytically. The reverse thermal reaction has been taken into account in some papers [9–11]. An analytical solution for the distribution of A and B in the stationary state, in presence of both the photochemical reaction $A \rightarrow B$ and the reverse thermal reaction $B \rightarrow A$, has been found in [11]. In general, a kinetic description of photochemical reactions in the presence of thermal reactions has not been thoroughly developed at this time. Therefore, the aim of

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this work is an examination of the influence of thermal reactions on the photochemical reaction wave front propagation in optically dense media.

2. Mathematical model

Let us examine photochromic reversible transformation, which includes both direct thermal and photochemical reactions, and also reverse thermal and photochemical reactions, according to the scheme $A_1 \underset{h\nu,k}{\overset{h\nu,k}{\rightleftarrows}} A_2$. In this case PDE system (1) is transformed to (2):

$$\partial I/\partial l = -I(\varepsilon_1 A_1 + \varepsilon_2 A_2)$$
$$\partial A_1/\partial t = -\phi_1 \varepsilon_1 I A_1 + \phi_2 \varepsilon_2 I A_2 - k_1 A_1 + k_2 A_2 \quad (2)$$
$$\partial A_2/\partial t = \phi_1 \varepsilon_1 I A_1 - \phi_2 \varepsilon_2 I A_2 + k_1 A_1 - k_2 A_2$$

where ε_1, ε_2: absorption coefficients of substances A_1 and A_2, respectively; φ_1, φ_2: quantum yields of forward and reverse photochemical reactions, respectively; k_1, k_2: constants of thermal monomolecular forward and reverse reactions, respectively. If a uniform initial distribution is assumed, entry conditions are as follows: $A_1(l,0) = k_2/(k_1+k_2)$, $A_2(x,0) = k_1/(k_1+k_2)$, $I(0,t) = I^0$.

To solve PDE (2) the following dimensionless variables and parameters were introduced. $A = A_1/(A_1^0 + A_2^0)$: dimensionless concentrations; $i = I/I^0$: dimensionless light intensity; $\tau = t\phi_1\varepsilon_1 I^0$: dimensionless time; $x = l\varepsilon_1(A_1 + A_2)$: dimensionless space coordinate; $\gamma_i = \kappa_i/\phi_1\varepsilon_1 I^0$: dimensionless thermal rate constant; $\alpha = \varepsilon_2/\varepsilon_1$: absorption coefficients ratio; $\beta = \phi_2/\phi_1$: quantum yields ratio.

Using the material balance condition, the system of PDE (2) can be rewritten in dimensionless variables (3):

$$\partial i/\partial x = -i(A(1-\alpha) + \alpha)$$
$$\partial A/\partial \tau = -(1+\alpha\beta)iA + \alpha\beta i - \gamma_1 A + \gamma_2(1-A) \quad (3)$$

The following qualitative characteristics of the solution can be used. Let us designate the coordinate of inflection point x_c of the concentration wave as a wave center, and a derivative value in that point as wave slope k_f (Fig. 1).
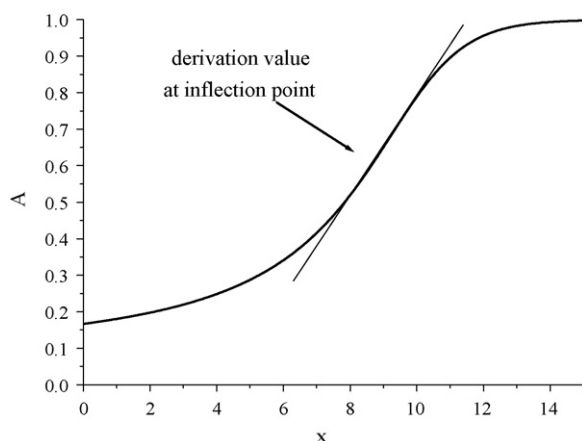

Fig. 1. Wave slope and wave center definition.

3. Results and discussion

Since PDE system (3) has no exact solution, some particular cases are examined below.

3.1. Irradiation at the isosbestic wavelength (wavelength at which species A_1 and A_2 have the same absorption coefficient), $\alpha = 1$

While the sample is irradiated at the isosbestic wavelength, light intensity distribution is constant in time and described by function $i = \exp[-x]$. In this case the solution is given by the following equation:

$$A = \frac{\{\gamma_1\gamma_2 + \gamma_2^2 + \beta(\gamma_1 + \gamma_2)e^{-x} + (\gamma_2 - \beta\gamma_1)}{\{(\gamma_1 + \gamma_2)((1+\beta)e^{-x} + \gamma_1 + \gamma_2)\}} \quad (4)$$

According to Eq. (4), at large x values compound A is uniformly distributed. The concentration of A is similar to that for thermal reactions in the absence of photochemical reactions: $A = \gamma_2/(\gamma_1 + \gamma_2)$. At small x values, the concentration of A changes with time, as in the case of irradiation in a thin layer (5):

$$A = \frac{\{\gamma_1\gamma_2 + \gamma_2^2 + \beta(\gamma_1 + \gamma_2) + (\gamma_2 - \beta\gamma_1)}{\{(\gamma_1 + \gamma_2)(1+\beta + \gamma_1 + \gamma_2)\}} \quad (5)$$

Using the method described in [3], the speed of the wave propagation in the presence of the thermal reaction can be obtained (6). One can see that wave speed depends on the x coordinate. Therefore, different points of the wave front have different speeds and the shape of the wave front is not constant and is changed in time:

$$V = \frac{\partial x}{\partial \tau} = \frac{((1+\beta)e^{-x} + \gamma_1 + \gamma_2)^2}{\{(\gamma_1 + \gamma_2)\exp[\tau((1+\beta)e^{-x} + \gamma_1 + \gamma_2)]}{\qquad -(\gamma_1 + \gamma_2) + \tau(1+\beta)(e^{-x}(1+\beta) + \gamma_1 + \gamma_2)\}} \quad (6)$$

In the absence of thermal reaction ($\gamma_1 = 0$ and $\gamma_2 = 0$) expression (6) turns into $V = 1/\tau$, which is in agreement with results obtained earlier [3,4,12,13]. In such conditions, the wave has a constant shape. The denominator of expression (6) contains the term proportional to $\exp[\tau(\gamma_1 + \gamma_2)]$. Therefore, the speed of wave propagation in presence of the thermal reactions is less than in their absence.

3.2. Concentration distribution at infinitely long irradiation

The system reaches the stationary state and the concentrations are constant when $\tau \to \infty$:

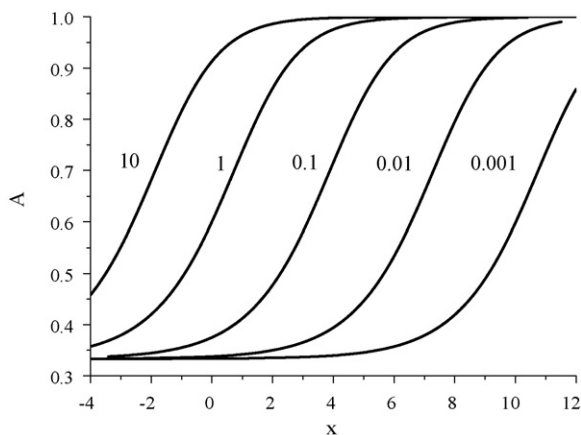$$\frac{\partial A}{\partial \tau} = 0 = -iA(1+\alpha\beta) + i\alpha\beta - \gamma_1 A + \gamma_2(1-A) \quad (7)$$

Fig. 2. Wave fronts of A in a stationary state at different rates of reverse thermal reaction γ_2. γ_2 values shown near concentration profile and $\alpha = 0.5$; $\beta = 1$ and $\gamma_1 = 0$. The concentration waves are shown at negative values of x to illustrate the constant wave shape.

Fig. 3. Dependence of wave center coordinate x_c on parameters α and β, at $\gamma_1 = 0$ and $\gamma_2 = 0.01$.

The combination of Eq. (7) with the first equation of PDE system (3) gives, after integration, the parametrically defined distribution of A in stationary state:

$$A = \frac{\alpha\beta i + \gamma_2}{i(1 + \alpha\beta) + \gamma_1 + \gamma_2}$$
$$x = -\frac{\gamma_1 + \gamma_2}{\alpha\gamma_1 + \gamma_2}\ln[i] - \frac{(-1 + \alpha)(\alpha\beta\gamma_1 - \gamma_2)}{\alpha(1 + \beta)(\alpha\beta\gamma_1 + \gamma_2)}\ln\left[\frac{i\alpha(1 + \beta)(\alpha\gamma_1 + \gamma_2)}{\alpha(1 + \beta)(\alpha\gamma_1 + \gamma_2)}\right]$$

(8)

Let us consider the case most abundant in practice, when direct thermal reaction is absent ($\gamma_1 = 0$). Distributions of the concentration of A, calculated from expression (8) at different rates of reverse thermal monomolecular reaction γ_2, are shown in Fig. 2. As it follows from Fig. 2, the concentration wave in stationary state penetrates deeper when the value of reverse thermal monomolecular reaction γ_2 decreases. The shape of the wave, however, is permanent. To obtain the distance between wave fronts with different values of thermal reaction γ_2, light intensity i is found from the first equation of system (8) and inserted into its second equation. Thus

reaction γ_2 and $\tilde{\gamma}_2$ is given by expression (10):

$$x = \tilde{x} - \ln\left[\frac{\gamma_2}{\gamma_1}\right] - \frac{1 - \alpha}{\alpha(1 + \beta)}\ln\left[\frac{\gamma_2((1 + \beta)\alpha + \tilde{\gamma}_2)}{\tilde{\gamma}_2((1 + \beta)\alpha + \gamma_2)}\right]$$

(10)

There are two qualitatively different cases of concentration distribution in the presence of direct and reverse thermal reactions. The first one implies the concentration of A in the photostationary state $A = (\beta i + \gamma_2)/(\alpha\beta i + i + \gamma_1 + \gamma_2)$ is higher than in the thermal stationary state $A = \gamma_2/(\gamma_1 + \gamma_2)$. Conversely, the second case means that the concentration of A in a photostationary state is lower than in a thermal stationary state. These situations are separated by the borderline case in which the concentration of A in a thermal stationary state is identical to that in a photostationary state. This case is realized when $\alpha\beta = \gamma_2/\gamma_1$, i.e., $k_2/k_1 = \varepsilon_2\varphi_2/\varepsilon_1\varphi_1$.

Wave penetration into a sample in a stationary state depends on the parameters α and β. Wave center coordinate x_c induced above is defined by expression (11):

$$x_c = -\frac{\alpha\beta i_c + \gamma_2}{\gamma_1 + \gamma_2 + (1 + \alpha\beta)i_c}\ln[i] - \frac{(-1 + \alpha)(\alpha\beta\gamma_1 - \gamma_2)}{\alpha(1 + \beta)(\alpha\gamma_1 + \gamma_2)}\ln\left[\frac{\alpha(1 + \beta)i_c + \alpha\gamma_1 + \gamma_2}{\alpha\gamma_1 + \gamma_2 + (1 + \beta)i_c}\right]$$
$$i_c = \left(\frac{\alpha\beta\gamma_1 - \alpha^2\beta\gamma_1 - \gamma_2 + \alpha\gamma_2 + \sqrt{(\alpha(1 + \beta)(1 + \alpha\beta)(\gamma_1 + \gamma_2)(\alpha\gamma_1 + \gamma_2) + (\alpha - 1)^2(\gamma_2 - \alpha\beta\gamma_2)^2)}}{\alpha(1 + \beta)(1 + \alpha\beta)}\right)$$

(11)

obtained, expression (9) connects, in a stationary state, the concentration of A and light intensity i. The denominator of expression (9) does not vanish at any physically feasible values of A, $(\alpha\beta + \gamma_2)/(\alpha\beta + \gamma_2 + 1) < A < 1$:

$$x = -\ln\left[\frac{\gamma_2(1 - A)}{A(1 + \alpha\beta) - \alpha\beta}\right] - \frac{(-1 + \alpha)}{\alpha(1 + \beta)}$$
$$\ln\left[\frac{(A(1 - \alpha) + \alpha)\gamma_2}{A(1 + \alpha\beta) - \alpha\beta)(\alpha + \alpha\beta + \gamma_2)}\right]$$

(9)

In the absence of a direct thermal reaction, expression (9) characterizes the distribution of substance A in stationary state. The difference between the x values at various rates of thermal
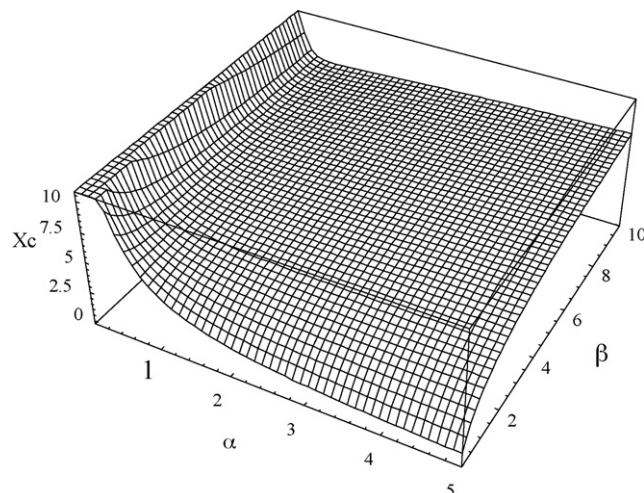
The dependence of the wave center coordinate on parameters α and β is presented in Fig. 3. One can see that the wave center coordinate is close to zero at large values of $\alpha(\varepsilon_1 < \varepsilon_2)$ and small values of $\beta(\varphi_1 > \varphi_2)$, i.e., the wave does not actually penetrate into the sample. This conclusion is consistent with the physical meaning, since in this case the photo-generated product absorbs the light but does not undergo chemical transformation. At low α values, independently of β values, a bleaching wave is observed. Fig. 3 is plotted at $\gamma_2 = 0.01$ and $\gamma_1 = 0$. The entire graph moves up along x_c axes when γ_2 decreases, and moves down when γ_2 increases in the agreement with expression (10).

The wave slope introduced above is determined by expression (12). In the absence of the direct thermal reaction, wave
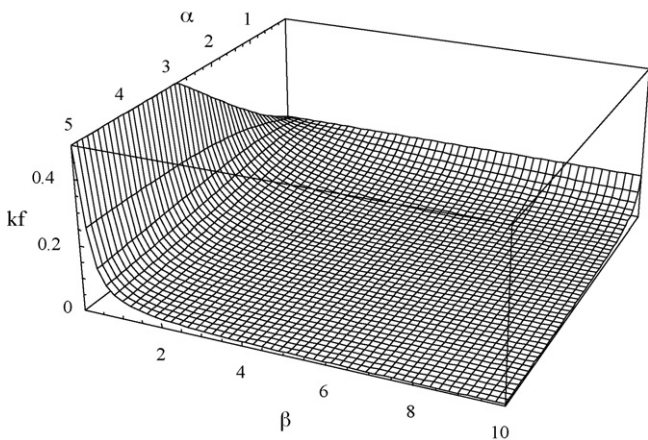
Fig. 4. Dependence of wave slope on parameters α and β. Direct thermal reaction is absent ($\gamma_1 = 0$).

shape and wave slope are independent from the reverse thermal reaction rate (Fig. 2). Dependence of wave slope on parameters α and β in the absence of the direct thermal reaction is presented in Fig. 4. Maximum wave slope is observed at large values of α ($\varepsilon_1 < \varepsilon_2$) and small values of β ($\varphi_1 > \varphi_2$):

$$k_f = \frac{\partial A/\partial i}{\partial x/\partial i} = -\frac{i_c(\alpha\beta\gamma_1 - \gamma_2)(\alpha(i_c + i_c\beta + \gamma_1) + \gamma_2)}{(i_c + i_c\alpha\beta + \gamma_1 + \gamma_2)^3}$$

$$i_c = \left(\frac{\alpha\beta\gamma_1 - \alpha^2\beta\gamma_1 - \gamma_2 + \alpha\gamma_2 + \sqrt{(\alpha(1+\beta)(1+\alpha\beta)(\gamma_1+\gamma_2)(\alpha\gamma_1+\gamma_2) + (\alpha-1)^2(\gamma_2 - \alpha\beta\gamma_2)^2}}{\alpha(1+\beta)(1+\alpha\beta)} \right) \tag{12}$$

Substance distribution in a stationary state can be calculated for a sequence of thermal and photochemical reactions $A_1 \Leftrightarrow A_2 \Leftrightarrow \ldots A_n$.

Concentrations of substances in stationary state are given by the following expressions:

$$A_1 = \left(1 + \sum_{j=1}^{n-2}\prod_{k=1}^{j-2} \frac{\alpha_k\beta_\kappa i + \gamma_{\kappa+1}}{\alpha_k\beta'_\kappa i + \gamma'_\kappa} + \prod_{k=1}^{j-2} \frac{\alpha_k\beta_\kappa i + \gamma_{\kappa+1}}{\alpha_k\beta'_\kappa i + \gamma'_\kappa} \frac{\alpha_{n-1}\beta_{n-1}i + \gamma_{n-1}}{\alpha_n\beta'_{n-1}i + \gamma'_{n-1}} \right)^{-1}$$

$$A_j = A_1 \prod_{k=1}^{j-1} \frac{\alpha_k\beta_\kappa i + \gamma_{\kappa+1}}{\alpha_k\beta'_\kappa i + \gamma'_{\kappa+1}}, \quad j = 2, n-1 \tag{13}$$

$$A_n = A_1 \prod_{k=1}^{j-2} \frac{\alpha_k\beta_\kappa i + \gamma_{\kappa+1}}{\alpha_k\beta'_\kappa i + \gamma'_{\kappa+1}} \frac{\alpha_{n-1}\beta_{n-1}i + \gamma_{n-1}}{\alpha_n\beta'_{n-1}i + \gamma'_{n-1}}$$

Light intensity depends on coordinate x, as follows:

$$x = \int_0^i \left(z \left(\sum_{j=1}^{n-2} (\alpha_i - \alpha_n) A_1 \prod_{k=1}^{j-1} \frac{\alpha_k\beta_k i + \gamma_{k+1}}{\alpha_k\beta'_k + \gamma'_k} \right) + z\alpha_n \right)^{-1} dz \tag{14}$$

Expression (14) can be integrated when A_1 is substituted by the first expression from system (13), since it factorizes to common fractions.

The solutions shown above are consistent with those previously obtained for special cases. In particular expression (8) for substance distribution in the sample in the stationary state at parameters values $\alpha = 0$ ($\varepsilon_B = 0$) and $\gamma_2 = 0$ ($k_2 = 0$) is similar to the expression obtained in [11]. Expression (5) for wave propagation under irradiation at isosbestic wavelength in the absence of the thermal reaction ($\gamma_2 = 0$ and $\gamma_1 = 0$) is similar to the expression in paper [4]. Expression (6) for the speed of photochemical reaction wave propagation is similar to the expression obtained in [3] in the absence of thermal reactions ($\gamma_2 = 0$ and $\gamma_1 = 0$). In papers [9,10] a method for solving PDE Eq. (3) in the presence of reverse thermal reaction is proposed. However, the application of this method gives results that conflict with both the analytical results presented above, as well as the numerical simulation presented below.

3.3. Numerical simulation

PDE system (3) solution, describing photochrome A transformation under irradiation in optically dense sample, cannot be found analytically. Numerical integration of PDE system (3) was used to find the substance distribution in the sample during irradiation by a finite difference method. Concentration profiles of substance A at a distinct time are presented in Fig. 5(a).

Parameter values are $\alpha = 0.1$; $\beta = 10$; $\gamma_1 = 0$; $\gamma_2 = 0.05$. It is clear that complete wave penetration into the sample can be observed at these parameters values. The wave slope value is $k_f = 0.1$. The stationary state found numerically is in agreement with the stationary state obtained analytically from expression (8).

Fig. 5(b) shows the concentration profiles of substance A at distinct points in time. Parameter values are $\alpha = 100$; $\beta = 0.05$; $\gamma_1 = 0$; $\gamma_2 = 0.05$. One can see that the reaction wave penetrates into the sample significantly less and that wave slope value $k_f = 0.5$ is significantly higher than in Fig. 5(a). A stationary state is reached in both cases at $\tau \sim 1000$. Such a large time value allows one to neglect those denominator components in (6) that are not proportional to $\exp[\tau]$. In this case wave velocity
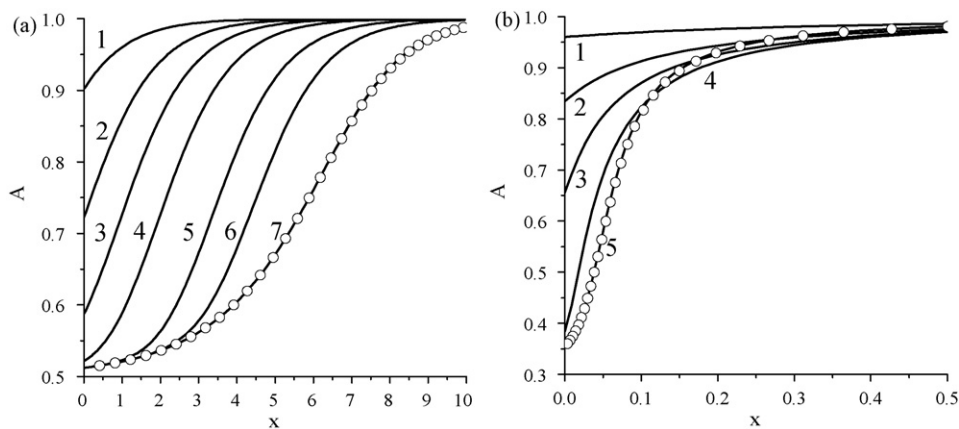
Fig. 5. Concentration profile at different irradiation times. Solid lines: numerically calculated profiles; scattered lines: analytically calculated profiles. (a) $\alpha = 0.1$; $\beta = 10$; $\gamma_1 = 0$; $\gamma_2 = 0.05$. $1 - \tau = 2$; $2 - \tau = 5$; $3 - \tau = 10$; $4 - \tau = 20$; $5 - \tau = 50$; $6 - \tau = 100$; $7 - \tau = 1000$. (b) $\alpha = 100$; $\beta = 0.005$; $\gamma_1 = 0$; $\gamma_2 = 0.05$. $1 - \tau = 5$; $2 - \tau = 20$; $3 - \tau = 50$; $4 - \tau = 200$; $5 - \tau = 1000$.

decreases proportionally to $\exp[-\tau(\exp(-x)(1+\beta)+\gamma_1+\gamma_2)]$ and does not depend on α.

4. Conclusion

Thermal reactions significantly influence photochemical reaction kinetics in optically dense media. The wavefront changes its shape on penetration into the sample in the presence of thermal reactions. The penetration depth decreases as the reverse thermal reaction rate increases. The time necessary to reach a stationary state is determined by the thermal reaction rate constants γ_1 and γ_2. The wave slope in the stationary state is determined by the ratio of the extinction coefficients of initial and product substances α, and by the ratio of the quantum yield values of direct and reverse photoreactions β. The highest slope is observed at high values of α and low values of β.

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