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Solving the problem of photochemical kinetics in a medium with low reagent mobilities

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Solutions of systems of partial differential equations (PDE) describing photochemical kinetics for such processes as (1) $A + h\nu \to B$; (2) $A + h\nu \to B$ and $B \to A$; (3) $A + h\nu \to B$ and $B \to C$; (4) $A + h\nu \to B$ and $B + h\nu \to C$ were found. It was established that when the intensity of UV light and the current time are used as independent derivatives, the initial PDE system will split into the set of ordinary differential equations (ODE) in combination with the boundary and initial conditions imposed. These ODE may be solved exactly. A procedure to obtain approximate solutions which are convenient to use was also proposed. Errors of the approximate solutions were estimated. An alternative method to obtain approximate solutions of the initial PDE consisting of transforming it to a system of the equations that can be easily solved using the successive iterations has been proposed. The results obtained may be useful for description photochemical kinetics in the media of low mobilities of reagents.

KEY WORDS: photochemical kinetics, mathematical models

0. Introduction

Modern photochemistry has come across the problem of studying of photochemical kinetics in the systems with low reagent mobilities. The main feature of the systems is the existence of a substantial inequality of molecules with respect to the intensity of UV light initiating a photochemical reaction. Some approaches to describe the kinetics of reactions in the said systems [1–7] have been proposed. However, a great majority of the works deals with very simplified cases or uses some approximations restricting fields of their applicability tremendously. Developing general methods of constructing of the mathematical models of photochemical kinetics and of a subsequent solution of the involved equations is an intriguing and important problem.

To take into account an inequality of molecules with respect to the UV light intensity one can replace the integral form of the Lambert–Berr law with of the differential one. Let us consider a sample irradiated by UV light as a system consisting of a large number of the "elementary photochemical reactors". The rate of a chemical reaction

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in each reactor is proportional to the photosensitive compound concentration and to the intensity of the UV light absorbed by the reactor. When there is no transfer of a photosensitive compound, i, between the "elementary reactors" one will be able to write down

$$\frac{\partial A_i}{\partial t} = -\varphi_i E A_i, \tag{1}$$

where $A_i \equiv A_i(x,t)$ is the concentration of the ith substance, $E \equiv E(x,t)$ is the intensity of the absorbed UV light, φ_i is a proportionality constant.

E can be determined using the integral form of the Lambert–Berr equation

$$E = E_0\left[1 - \exp\left(-l\sum_{i=1}^{n} a_i A_i\right)\right],$$

where a_i is the absorbance of the ith substance, E_0 is the intensity of the UV light irradiating an elementary reactor, l is thickness of the reactor.

When l is small, one can write

$$\frac{\partial E}{\partial x} = -E\sum_{i=1}^{n} a_i A_i. \tag{2}$$

Equations (1) and (2) together with differential equations of an ordinary chemical kinetics for non-photochemical steps, proper boundary and initial conditions imposed and the reagents mass conservation relationships can be used to construct mathematical models describing the variation of a reactant concentration in space and time in the course of a photochemical reaction. The similar models were used earlier [2,6,7]. But in these works the exact solutions were not obtained even for simple cases.

The need of such solutions is caused by difficulties associated with the correct processing of the photochemical kinetics results obtained in experiments. We should note that numerical procedures [8–10] are not appropriate being very time-consuming and producing output which is hard to apply and interpret.

The aim of our paper is to obtain exact and/or approximate expressions describing photochemical reaction kinetics when the UV intensity and the reagent concentrations are not constant in space along an irradiated sample.

1. Mathematical models of simple photochemical reactions

Using the differential form of the Beer–Lambert equation one can obtain the following PDE systems describing the kinetics of simple photochemical reactions.

Reaction 1 $(A + h\nu \rightarrow B)$. The process consists of the only photochemical step, $A \rightarrow B$:

$$\begin{cases} \dfrac{\partial A}{\partial t} + \varphi E A = 0, \\ B = A_0 + B_0 - A, \\ \dfrac{\partial E}{\partial x} = -E\big[a_B(A_0 + B_0) + (a_A - a_B)A\big]. \end{cases}$$

The boundary and initial conditions are $A(x,0) = A_0$, $B(x,0) = B_0$, $E(0,t) = E_0$.

Reaction 2 $(A + h\nu \rightarrow B$ *and* $B \rightarrow A)$. The process consists of two steps, photochemical, $A \rightarrow B$, and thermal, $B \rightarrow A$:

$$\begin{cases} \dfrac{\partial A}{\partial t} + (k + \varphi E)A = k(A_0 + B_0), \\ B = A_0 + B_0 - A, \\ \dfrac{\partial E}{\partial x} = -E\big[a_B(A_0 + B_0) + (a_A - a_B)A\big]. \end{cases}$$

The boundary and initial conditions to be imposed are $A(x,0) = A_0$, $B(x,0) = B_0$, $E(0,t) = E_0$.

Reaction 3 $(A + h\nu \rightarrow B$ *and* $B \rightarrow C)$. Herein, the first step, $A \rightarrow B$, is photochemical and the second one, $B \rightarrow C$, is thermal:

$$\begin{cases} \dfrac{\partial A}{\partial t} + \varphi A E = 0, \\ \dfrac{\partial B}{\partial t} + kB = \varphi E A, \\ C = A_0 - A - B, \\ \dfrac{\partial E}{\partial x} = -E\big[(a_A - a_C)A + (a_B - a_C)B + a_C A_0\big]. \end{cases}$$

The boundary and initial conditions are $A(x,0) = A_0$, $B(x,0) = 0$, $C(x,0) = 0$, $E(0,t) = E_0$.

Reaction 4 $(A + h\nu \rightarrow B$ *and* $B + h\nu \rightarrow C)$. The process consists of two photochemical steps, $A \rightarrow B$, and, $B \rightarrow C$:

$$\begin{cases} \dfrac{\partial A}{\partial t} + \varphi_1 E A = 0, \\ \dfrac{\partial B}{\partial t} + \varphi_2 E B = \varphi_1 E A, \\ C = A_0 - A - B, \\ \dfrac{\partial E}{\partial x} = -E\big[(a_A - a_C)A + (a_B - a_C)B + a_C A_0\big]. \end{cases}$$

Table 1
Parameters for a system of the first type.

Reaction No.	α_1	α_2	α_3	ε_1	ε_2
1	0	0	φ	$a_B(A_0+B_0)$	a_A-a_B
2	$k(A_0+B_0)$	k	φ	$a_B(A_0+B_0)$	a_A-a_B

Table 2
Parameters for a system of the second type.

Reaction No.	α_3	β_1	β_2	β_3	ε_1	ε_2	ε_3
3	φ	φ	k	0	a_CA_0	a_A-a_C	a_B-a_C
4	φ_1	φ_1	0	φ_2	a_CA_0	a_A-a_C	a_B-a_C

The boundary and initial conditions to be imposed are $A(x,0)=A_0$, $B(x,0)=0$, $C(x,0)=0$, $E(0,t)=E_0$.

The initial concentrations of reagents $A,\ B,\ C$ are $A_0,\ B_0,\ C_0$ (in M·m^{-3}) while the concentrations at a distance x (in m) across the sample at a current time t are $A=A(x,t),\ B=B(x,t),\ C=C(x,t)$. Monochromatic UV radiation of intensity at the surface of the sample is E_0 (in W·m^{-2}) and at a distance x across the sample at the current time t is $E=E(x,t)$. $a_A,\ a_B,\ a_C$ are absorption coefficients of $A,\ B,\ C$ (in M^{-1}·m^2). k is the first-order rate constant (in s^{-1}) and $\varphi,\ \varphi_1,\ \varphi_2$ are "effective" rate constants of the corresponding photochemical reactions (in W^{-1}·m^2·s^{-1}).

To simplify the further considerations let us subdivide the PDE systems as being of the first (reactions 1 and 2) and second type (reactions 3 and 4).

The first type system (definitions of the parameters are shown in table 1):

$$\begin{cases} \dfrac{\partial A}{\partial t}+(\alpha_2+\alpha_3E)A=\alpha_1, \\ B=A_0+B_0-A, \\ \dfrac{\partial E}{\partial x}=-E(\varepsilon_1+\varepsilon_2A), \end{cases} \tag{3}$$

has the following boundary and initial conditions: $A(x,0)=A_0$, $B(x,0)=0$, $E(0,t)=E_0$.

The second type system (definitions of its parameters are shown in table 2):

$$\begin{cases} \dfrac{\partial A}{\partial t}+\alpha_3EA=0, \\ \dfrac{\partial B}{\partial t}+(\beta_2+\beta_3E)B=\beta_1EA, \\ C=A_0-A-B, \\ \dfrac{\partial E}{\partial x}=-E(\varepsilon_1+\varepsilon_2A+\varepsilon_3B) \end{cases} \tag{4}$$

has the following boundary and initial conditions: $A(x,0) = A_0$, $B(x,0) = 0$, $C(x,0) = 0$, $E(0,t) = E_0$.

2. Solving of the systems by the coordinate system changing

Having $\partial E/\partial x \neq 0$ for all $x \geqslant 0$ and $t \geqslant 0$, one can transform the systems from the independent variables, x and t, to the independent variables, E and t. Then the first type PDE system splits into two ordinary differential equations (ODE) and one equality, and the second type system splits into three ODEs and one equality.

Then the first type system takes form

$$\begin{cases} \dfrac{\mathrm{d}A}{\mathrm{d}t} + p_1(E)A = \alpha_1, \\ B = A_0 + B_0 - A, \\ \dfrac{\mathrm{d}x}{\mathrm{d}E} = -\dfrac{1}{Eq_1(E,t)}, \end{cases} \tag{5}$$

where

$$A(E,0) = A_0, \qquad B(E,0) = 0, \qquad x(E_0,t) = 0,$$

and

$$p_1(E) = \alpha_2 + \alpha_3 E, \qquad q_1(E,t) = \varepsilon_1 + \varepsilon_2 A(E,t).$$

Being treated in the same way, the second system splits into

$$\begin{cases} \dfrac{\mathrm{d}A}{\mathrm{d}t} + p_2(E)A = 0, \\ \dfrac{\mathrm{d}B}{\mathrm{d}t} + p_3(E)B = \beta_1 EA, \\ C = A_0 - B - A, \\ \dfrac{\mathrm{d}x}{\mathrm{d}E} = -\dfrac{1}{Eq_2(E,t)}, \end{cases} \tag{6}$$

where

$$A(E,0) = A_0, \qquad B(E,0) = 0, \qquad C(E,0) = 0, \qquad x(E_0,t) = 0,$$

and

$$p_2(E) = \alpha_3 E, \qquad p_3(E) = \beta_2 + \beta_3 E, \qquad q_2(E,t) = \varepsilon_1 + \varepsilon_2 A(E,t) + \varepsilon_3 B(E,t).$$

The exact solution of equations (5) can be easily obtained:

$$A = A(E,t) = a_1(E) + b_1(E)\exp\bigl[-p_1(E)t\bigr], \tag{7.1}$$

$$B = B(E,t) = A_0 + B_0 - A(E,t), \tag{7.2}$$

$$x = x(E,t) = \int_E^{E_0} \frac{\mathrm{d}u}{uq_1(u,t)}, \tag{7.3}$$

where

$$a_1(E) = \frac{\alpha_1}{p_1(E)},$$
$$b_1(E) = A_0 - a_1(E).$$

The exact solution of equations (6) can be written as

$$A = A(E,t) = A_0 \exp\bigl(-p_2(E)t\bigr), \tag{8.1}$$
$$B = B(E,t) = \frac{A_0\beta_1 E}{p_3(E) - p_2(E)}\bigl\{\exp\bigl[-p_2(E)t\bigr] - \exp\bigl[-p_3(E)t\bigr]\bigr\}, \tag{8.2}$$
$$C = C(E,t) = A_0 - A(E,t) - B(E,t), \tag{8.3}$$
$$x = x(E,t) = \int_E^{E_0} \frac{\mathrm{d}u}{uq_2(u,t)}. \tag{8.4}$$

In the general case integrals (7.3) and (8.4) are not easy to evaluate. However, they can serve as the starting point to construct a family of approximations.

At the first step functions $q_1(E,t)$ and $q_2(E,t)$ may be approximated by the first term of the series expansions

$$q_1(E,t) = q_1(E_0,t) + \frac{\partial q_1(E_0,t)}{\partial E}(E - E_0) + \cdots, \tag{8.5}$$
$$q_2(E,t) = q_2(E_0,t) + \frac{\partial q_2(E_0,t)}{\partial E}(E - E_0) + \cdots. \tag{8.6}$$

Substitution of $q_1(E,t) \approx q_1(E_0,t)$ and $q_2(E,t) \approx q_2(E_0,t)$ into equations (7.3) and (8.4) gives the approximate solutions for x, $\widetilde{x}_1$ and $\widetilde{x}_2$,

$$\widetilde{x}_1 = \widetilde{x}_1(E,t) = \int_E^{E_0} \frac{\mathrm{d}u}{uq_1(E_0,t)} = \frac{1}{q_1(E_0,t)} \ln\frac{E_0}{E}, \tag{8.7}$$
$$\widetilde{x}_2 = \widetilde{x}_2(E,t) = \int_E^{E_0} \frac{\mathrm{d}u}{uq_2(E_0,t)} = \frac{1}{q_2(E_0,t)} \ln\frac{E_0}{E}. \tag{8.8}$$

Upper estimates of the relative errors appeared due to use of the approximations given by equations (8.7) and (8.8) were obtained (see appendix):

$$\delta x_1 \leqslant A_0 V_1(\varphi t E, \varphi t E_0)\left|\frac{a_A - a_B}{q_1(E_0,t)}\right|, \tag{8.9}$$

$$\begin{aligned}\delta x_2 \leqslant \Biggl|\frac{a_A - a_B}{q_1(E_0,t)}\biggl\{&\frac{k(A_0 + B_0)\varphi(E_0 - E)}{(k + \varphi E_0)(k + \varphi E)} + A_0 V_1\bigl(t(k + \varphi E), t(k + \varphi E_0)\bigr)\\ &+ k(A_0 + B_0)\biggl\{\frac{\exp[-t(k + \varphi E_0)]}{k + \varphi E_0} + \mathrm{e}t\biggr\}\biggr\}\Biggr|.\end{aligned} \tag{8.10}$$

Here, we have e $= 2.718281828\ldots$.

$$\delta x_3 \leqslant A_0 \left| \frac{-\varepsilon_2}{q_2(E_0,t)} V(\varphi t E_0, \varphi t E) \right| + \varphi A_0 \left| \frac{\varepsilon_2}{q_2(E_0,t)} \left\{ \frac{E_0}{k-\varphi E_0} V_1(\varphi t E_0, kt) - \frac{E}{k-\varphi E} V_1(\varphi E t, kt) \right\} \right|, \tag{8.11}$$

$$\delta x_4 \leqslant A_0 \left| \frac{\varepsilon_2}{q_2(E_0,t)} V_1(\varphi_1 t E_0, \varphi_1 t E) \right| + \varphi_1 A_0 \left| \frac{\varepsilon_3}{(\varphi_2-\varphi_1) q_2(E_0,t)} \left[V_1(\varphi_1 E_0 t, \varphi_2 E_0 t) + \left(\frac{\varphi_2}{\varphi_1}\right)^{\varphi_1/(\varphi_1-\varphi_2)} \left(1 - \frac{\varphi_1}{\varphi_2}\right) \right] \right|, \tag{8.12}$$

where

$$V_1(x,y) = \exp(-x) - \exp(-y).$$

(Here and below capped symbols such as $\widetilde{x}(E,t)$, $\widetilde{E}(x,t)$ etc. denote the approximate solutions.)

To simplify the usage of the results obtained we have written them down for both (E,t) and (x,t) sets of the independent variables.

In the case of reaction 1 one can write down for the E and t variables

$$A(E,t) = A_0 \exp(-\varphi E t), \tag{9.1}$$

$$B(E,t) = A_0 + B_0 - A(E,t), \tag{9.2}$$

$$\widetilde{x}(E,t) = \frac{1}{q_1(E_0,t)} \ln \frac{E_0}{E}, \tag{9.3}$$

where

$$q_1(E_0,t) = a_B(A_0+B_0) + A_0(a_A - a_B)\exp(-\varphi E_0 t); \tag{9.4}$$

and for the x and t variables

$$\widetilde{E}(x,t) = E_0 \exp\bigl[-q_1(E_0,t)x\bigr], \tag{9.5}$$

$$\widetilde{A}(x,t) = A_0 \exp\bigl[-\varphi \widetilde{E}(x,t)t\bigr], \tag{9.6}$$

$$\widetilde{B}(x,t) = B_0 + A_0 - \widetilde{A}(x,t). \tag{9.7}$$

In the case of reaction 2 one can write down for E and t variables

$$A(E,t) = \frac{k(A_0+B_0)}{k+\varphi E} + \frac{\varphi E A_0 - k B_0}{k+\varphi E} \exp\bigl[-(k+\varphi E)t\bigr], \tag{10.1}$$

$$B(E,t) = A_0 + B_0 - A(E,t), \tag{10.2}$$

$$\widetilde{x}(E,t) = \frac{1}{q_1(E_0,t)} \ln \frac{E_0}{E}, \tag{10.3}$$

where

$$q_1(E_0, t) = a_B(A_0 + B_0) + (a_A - a_B)\left\{\frac{k(A_0 + B_0)}{k + \varphi E_0} + \frac{\varphi E_0 A_0 - kB_0}{k + \varphi E_0} \exp\bigl[-(k + \varphi E_0)t\bigr]\right\}, \tag{10.4}$$

and for the x and t variables

$$\widetilde{E}(x, t) = E_0 \exp\bigl[-q_1(E_0, t)x\bigr], \tag{10.5}$$

$$\widetilde{A}(x, t) = \frac{k(A_0 + B_0)}{k + \varphi \widetilde{E}(x, t)} + \frac{\varphi A_0 \widetilde{E}(x, t) - kB_0}{k + \varphi \widetilde{E}(x, t)} \exp\bigl[-\bigl(k + \varphi \widetilde{E}(x, t)\bigr)t\bigr], \tag{10.6}$$

$$\widetilde{B}(x, t) = A_0 + B_0 - \widetilde{A}(x, t). \tag{10.7}$$

In the case of reaction 3 one can write down for the E and t variables

$$A(E, t) = A_0 \exp(-\varphi E t), \tag{11.1}$$

$$B(E, t) = \frac{\varphi E A_0}{k - \varphi E} V_1(\varphi E t, kt), \tag{11.2}$$

$$C(E, t) = A_0 - A(E, t) - B(E, t), \tag{11.3}$$

$$\widetilde{x}(E, t) = \frac{1}{q_1(E_0, t)} \ln \frac{E_0}{E}, \tag{11.4}$$

where

$$q_1(E_0, t) = a_C A_0 + A_0(a_A - a_C) \exp(-\varphi E_0 t) + \frac{\varphi E_0 A_0 (a_B - a_C)}{k - \varphi E_0} V_1(\varphi E_0 t, kt), \tag{11.5}$$

and for the x and t variables

$$\widetilde{E}(x, t) = E_0 \exp\bigl[-q_1(E_0, t)x\bigr], \tag{11.6}$$

$$\widetilde{A}(x, t) = A_0 \exp\bigl[-\varphi \widetilde{E}(x, t)t\bigr], \tag{11.7}$$

$$\widetilde{B}(x, t) = \frac{\varphi \widetilde{E}(x, t) A_0}{k - \varphi \widetilde{E}(x, t)} V_1\bigl(\varphi t \widetilde{E}(x, t), kt\bigr), \tag{11.8}$$

$$\widetilde{C}(x, t) = A_0 - \widetilde{A}(x, t) - \widetilde{B}(x, t). \tag{11.9}$$

In the case of reaction 4 one can write down for the E and t variables

$$A(E, t) = A_0 \exp(-\varphi_1 E t), \tag{12.1}$$

$$B(E, t) = \frac{\varphi_1 A_0}{\varphi_2 - \varphi_1} V_1(\varphi_1 E t, \varphi_2 E t), \tag{12.2}$$

$$C(E, t) = A_0 - A(E, t) - B(E, t), \tag{12.3}$$

$$\widetilde{x}(E, t) = \frac{1}{q_1(E_0, t)} \ln \frac{E_0}{E}, \tag{12.4}$$

where

$$q_1(E_0,t) = a_C A_0 + A_0(a_A - a_C)\exp(-\varphi E_0 t) + \frac{\varphi_1 A_0(a_B - a_C)}{\varphi_2 - \varphi_1} V_1(\varphi_1 E_0 t, \varphi_2 E_0 t), \tag{12.5}$$

and for the x and t variables

$$\widetilde{E}(x,t) = E_0 \exp\bigl[-q_1(E_0,t)x\bigr], \tag{12.6}$$

$$\widetilde{A}(x,t) = A_0 \exp\bigl[-\varphi_1 \widetilde{E}(x,t)t\bigr], \tag{12.7}$$

$$\widetilde{B}(x,t) = \frac{\varphi_1 A_0}{\varphi_1 - \varphi_2} V_1\bigl(\varphi_1 \widetilde{E}(x,t)t, \varphi_2 \widetilde{E}(x,t)t\bigr), \tag{12.8}$$

$$\widetilde{C}(x,t) = A_0 - \widetilde{A}(x,t) - \widetilde{B}(x,t). \tag{12.9}$$

3. Solving the PDE systems with iterative methods

Let us find solutions of the first and the second type systems by the method of successive iterations. For the first type system the nth step solutions, $A^{[n]}$, $B^{[n]}$ and $E^{[n]}$, are related to the $(n-1)$th step solutions, $A^{[n-1]}$, $B^{[n-1]}$ and $E^{[n-1]}$, with the following expressions:

$$\begin{cases} \dfrac{\mathrm{d}A^{[n]}}{\mathrm{d}t} + \bigl(\alpha_2 + \alpha_3 E^{[n-1]}\bigr)A^{[n]} = \alpha_1, & (13.1)\\ B^{[n]} = A_0 + B_0 - A^{[n]}, & (13.2)\\ \dfrac{\mathrm{d}E^{[n]}}{\mathrm{d}x} = -E^{[n]}\bigl(\varepsilon_1 + \varepsilon_2 A^{[n-1]}\bigr). & (13.3) \end{cases}$$

Here, the boundary and initial conditions, $A^{[n]}(x,0) = A_0$, $B^{[n]}(x,0) = B_0$, $E^{[n]}(0,t) = E_0$, are to be fulfilled. In the case of the second type system one can write down the nth step solutions, $A^{[n]}$, $B^{[n]}$, $C^{[n]}$ and $E^{[n]}$, as

$$\begin{cases} \dfrac{\mathrm{d}A^{[n]}}{\mathrm{d}t} + \alpha_3 A^{[n]}E^{[n-1]} = 0, & (14.1)\\ \dfrac{\mathrm{d}B^{[n]}}{\mathrm{d}t} + \bigl(\beta_2 + \beta_3 E^{[n-1]}\bigr)B^{[n]} = \beta_1 E^{[n-1]}A^{[n-1]}, & (14.2)\\ C^{[n]} = A_0 - A^{[n]} - B^{[n]}, & (14.3)\\ \dfrac{\mathrm{d}E^{[n]}}{\mathrm{d}x} = -E^{[n]}\bigl(\varepsilon_1 + \varepsilon_2 A^{[n-1]} + \varepsilon_3 B^{[n-1]}\bigr), & (14.4) \end{cases}$$

where

$$A^{[n]}(x,0) = A_0, \qquad B^{[n]}(x,0) = B_0, \qquad C^{[n]}(x,0) = 0, \qquad E^{[n]}(0,t) = E_0,$$
$$0 \leqslant n \leqslant \infty.$$

Solving systems (13) and (14) as the first-order ODEs having variable coefficients and variable right-hand parts, one obtains general solutions for the first type system

$$\begin{aligned} A^{[n]}(x,t) = A_0 \exp\left\{-\left[\alpha_2 t + \alpha_3 \int_0^t E^{[n-1]}(x,\tau)\,\mathrm{d}\tau\right]\right\} \\ + \alpha_1 \int_0^t \exp\left\{-\left[\alpha_2(t-\tau) + \alpha_3 \int_\tau^t E^{[n-1]}(x,\xi)\,\mathrm{d}\xi\right]\right\}\mathrm{d}\tau, \end{aligned} \tag{15.1}$$

$$B^{[n]}(x,t) = A_0 + B_0 - A^{[n]}(x,t), \tag{15.2}$$

$$E^{[n]}(x,t) = E_0 \exp\left\{-\left[\varepsilon_1 x + \varepsilon_2 \int_0^x A^{[n-1]}(\eta,t)\,\mathrm{d}\eta\right]\right\}, \tag{15.3}$$

and for the second type one:

$$A^{[n]}(x,t) = A_0 \exp\left\{-\left[\alpha_2 t + \alpha_3 \int_0^t E^{[n-1]}(x,\tau)\,\mathrm{d}\tau\right]\right\}, \tag{16.1}$$

$$\begin{aligned} B^{[n]}(x,t) = \beta_1 \int_0^t A^{[n-1]}(x,\tau) E^{[n-1]}(x,\tau) \\ \times \exp\left\{-\left[\beta_2(t-\tau) + \beta_3 \int_\tau^t E^{[n-1]}(x,\xi)\,\mathrm{d}\xi\right]\right\}\mathrm{d}\tau, \end{aligned} \tag{16.2}$$

$$C^{[n]}(x,t) = A_0 - A^{[n]}(x,t) - B^{[n]}(x,t), \tag{16.3}$$

$$E^{[n]}(x,t) = E_0 \exp\left\{-\left[\varepsilon_1 x + \varepsilon_2 \int_0^x A^{[n-1]}(\eta,t)\,\mathrm{d}\eta + \varepsilon_3 \int_0^x B^{[n-1]}(\eta,t)\,d\eta\right]\right\}. \tag{16.4}$$

Let us consider the first type system. The zeroth approximation can be written as

$$A^{[0]}(x,t) = A_0, \qquad B^{[0]}(x,t) = B_0, \qquad E^{[0]}(x,t) = E_0. \tag{15.4}$$

Substitution of $A^{[0]}(x,t)$ and $E^{[0]}(x,t)$ into equations (15.1) and (15.3) gives the first-order approximation

$$A^{[1]}(x,t) = a_1 + b_1 \exp(-p_1 t), \tag{17.1}$$

$$B^{[1]}(x,t) = A_0 + B_0 - A^{[1]}(x,t), \tag{17.2}$$

$$E^{[1]}(x,t) = E_0 \exp(-qx), \tag{17.3}$$

where

$$p_1 = \alpha_2 + \alpha_3 E_0, \qquad a_1 = \frac{\alpha_1}{p_1}, \qquad b_1 = A_0 - a_1, \qquad q = \varepsilon_1 + A_0\varepsilon_2. \tag{17.4}$$

Substitution of $A^{[1]}(x,t)$ and $E^{[1]}(x,t)$ into the right-hand part of the general solutions given by equations (15.1) and (15.3) permits one to obtain the second-order approximations

$$A^{[2]}(x,t)=a_1(x)+b_1(x)\exp\bigl(-tp_1(x)\bigr), \tag{18.1}$$

$$B^{[2]}(x,t)=A_0+B_0-A^{[2]}(x,t), \tag{18.2}$$

$$E^{[2]}(x,t)=E_0\exp\bigl[-xq_1(t)\bigr], \tag{18.3}$$

where

$$\begin{aligned} p_1(x)&=\alpha_2+a_3E_0\exp(-qx), \qquad & a_1(x)&=\frac{\alpha_1}{p_1(x)},\\ q_1(t)&=\varepsilon_1+\varepsilon_2\bigl[a_1+b_1\exp(-tp_1)\bigr], \qquad & b_1(x)&=A_0-a_1(x). \end{aligned} \tag{18.4}$$

For the second type systems one can start from

$$A^{[0]}(x,t)=A_0, \qquad B^{[0]}(x,t)=0, \qquad C^{[0]}(x,t)=0, \qquad E^{[0]}(x,t)=E_0. \tag{18.1}$$

Substitution of $A^{[0]}(x,t)$ and $E^{[0]}(x,t)$ into the right-hand part of equations (15.1) and (15.3) gives the first-order approximation

$$A^{[1]}(x,t)=A_0\exp(-p_1t), \tag{19.1}$$

$$B^{[1]}(x,t)=a_2\bigl[1-\exp(-p_2t)\bigr], \tag{19.2}$$

$$C^{[1]}(x,t)=A_0-A^{[1]}(x,t)-B^{[1]}(x,t), \tag{19.3}$$

$$E^{[1]}(x,t)=E_0\exp(-qx), \tag{19.4}$$

where

$$p_1=\alpha_3E_0, \tag{19.5}$$

$$p_2=\beta_2+\beta_3E_0, \tag{19.6}$$

$$\alpha_2=\frac{\beta_1A_0E_0}{p_2}, \tag{19.7}$$

$$q=\varepsilon_1+\varepsilon_2A_0. \tag{19.8}$$

The second-order approximation can be written as

$$A^{[2]}(x,t)=A_0\exp\bigl[-p_1(x)t\bigr], \tag{20.1}$$

$$B^{[2]}(x,t)=b_2\bigl\{\exp(-p_1t)-\exp\bigl[-p_2(x)t\bigr]\bigr\}, \tag{20.2}$$

$$C^{[2]}(x,t)=A_0-A^{[2]}(x,t)-B^{[2]}(x,t), \tag{20.3}$$

$$E^{[2]}(x,t)=E_0\exp\bigl[-q_1(t)x\bigr], \tag{20.4}$$

where

$$p_1(x)=\alpha_3E_0\exp(-qx), \tag{20.5}$$

$$p_2(x)=\beta_2+\beta_3E_0\exp(-qx), \tag{20.6}$$

$$b_2(x)=\frac{\beta_1A_0E_0\exp(-qx)}{p_2(x)-p_1}, \tag{20.7}$$

$$q_1(t)=\varepsilon_1+\varepsilon_2a_2+\varepsilon_2A_0\exp(-p_1t)-\varepsilon_2a_2\exp(-p_2t). \tag{20.8}$$

Comparing the two methods described, it should be noted that both methods give the similar results when one keeps in expressions (8.5) and (8.6) the main term only in the method of the new coordinate system introduction or the second-order results of the method in successive iterations.

4. Conclusion

We proposed four mathematical models describing photochemical kinetics in the systems with absence of reagent mobility. The method was developed giving an opportunity to obtain the exact solutions of the mathematical models and two methods of obtaining the approximate solutions. Although transforming from the (x, t) independent variables to the (E, t) ones gives us the possibility to obtain the exact solutions, this method is connected with difficulties arising during integrals evaluating. The method of successive iterations has more wide area of applications, but it is more time consuming and gives very complicated formulas. However, both methods give the similar results and may be used in applications. The expressions for dependence of intensity of UV light passed through a film with photochemical reactions having place against the irradiation time give a basis for easy and exact determination of the kinetic parameters for the reactions involved.

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Appendix. Estimates of errors arising from abolishing all terms but main ones in $q_1(E, t)$ and $q_2(E, t)$

The absolute errors of the approximations for the reactions 1 and 2 may be estimated as

$$\Delta x_{1,2} = \left| \int_E^{E_0} \left[\frac{1}{q_1(u, t)} - \frac{1}{q_1(E_0, t)} \right] \frac{\mathrm{d}u}{u} \right|. \tag{A.1}$$

Taking into account the definition of $q_1(E, t)$ one may transform the expression (A.1) to

$$\Delta x_{1,2} = \left| \frac{\varepsilon_2}{q_1(E_0, t)} \int_E^{E_0} \frac{A(E_0, t) - A(u, t)}{q_1(u, t)} \frac{\mathrm{d}u}{u} \right|. \tag{A.2}$$

For the first reaction

$$\Delta x_1 = \left|\frac{\varepsilon_2}{q_1(E_0,t)} A_0 \int_E^{E_0} \frac{\exp(-\varphi E_0 t) - \exp(-\varphi u t)}{q_1(u,t)} \frac{\mathrm{d}u}{u}\right|.$$

It is obvious that the maximum of the expression in the integral is achieved at $u = E$ when $E \leqslant u \leqslant E_0$. This gives us an opportunity to write

$$\Delta x_1 \leqslant \left|\frac{a_A - a_B}{q_1(E_0,t)} A_0 V_1(\varphi E_0 t), (\varphi E t)\right| \int_E^{E_0} \frac{\mathrm{d}u}{u q_1(u,t)}. \tag{A.3}$$

Using equation (A.3) the relative error for x is to be determined as

$$\delta x_1 \leqslant A_0 \left|\frac{a_A - a_B}{q_1(E_0,t)} V_1(\varphi E_0 t, \varphi E t)\right|. \tag{A.4}$$

For the second reaction under study one may write

$$\begin{aligned}\Delta x_2 = \Bigg|\frac{\varepsilon_2}{q_1(E_0,t)} \int_E^{E_0} \Bigg\{ & \frac{k(A_0+B_0)\varphi(u-E_0)}{(k+\varphi E_0)(k+\varphi u)} + A_0\big\{\exp\big[-t(k+\varphi u)\big] \\ & + k(A_0+B_0)V_2(k+\varphi E_0, k+\varphi u, t)\big\}\Bigg\}\frac{\mathrm{d}u}{u}\Bigg|.\end{aligned} \tag{A.5}$$

Let us introduce a new function $\rho_1(u)$ as

$$\begin{aligned}\rho_1(u) = {} & \frac{\varphi k(A_0+B_0)(u-E_0)}{(k+\varphi E_0)(k+\varphi u)} + A_0 V_1\big(t(k+\varphi E_0), t(k+\varphi u)\big) \\ & + k(A_0+B_0)V_2(k+\varphi E_0, k+\varphi u, t),\end{aligned}$$

where

$$V_2(x,y,t) = \left\{\frac{\exp(-tx)}{x} - \frac{\exp(-ty)}{y}\right\}.$$

Taking into account that $\rho_1'(u) > 0$ for $E \leqslant u \leqslant E_0$, $|\rho_1(u)|$ takes its maximum at $u = E$. From this we can obtain an estimate for δx_2

$$\delta x_2 \leqslant \left|\frac{(a_A - a_B)(k+\varphi E_0)}{(A_0+B_0)(k a_A + \varphi E_0 a_B) + (\varphi E_0 A_0 - k B_0)\exp[-t(\varphi + k E_0)]} \rho_1(E)\right|. \tag{A.6}$$

Absolute error of the approximation in the case of the third and fourth type reactions can be found due to

$$\Delta x_{3,4} = \left|\int_E^{E_0} \left[\frac{1}{q_2(u,t)} - \frac{1}{q_2(E_0,t)}\right]\frac{\mathrm{d}u}{u}\right|. \tag{A.7}$$

Taking into account definition of $q_2(E,t)$, one can transform expression (A.7) to

$$\begin{aligned}\Delta x_{3,4} = \Bigg| & \frac{\varepsilon_2}{q_2(E_0,t)} \int_E^{E_0} \frac{A(E_0,t)-A(u,t)}{q_2(u,t)} \frac{\mathrm{d}u}{u} \\ & + \frac{\varepsilon_3}{q_2(E_0,t)} \int_E^{E_0} \frac{B(E_0,t)-B(u,t)}{q_2(u,t)} \frac{\mathrm{d}u}{u} \Bigg|.\end{aligned} \tag{A.8}$$

For the third reaction

$$\begin{aligned}\Delta x_3 = \Bigg| & \frac{\varepsilon_2 A_0}{q_2(E_0,t)} \int_E^{E_0} \frac{V_1(t\varphi E_0, t\varphi u)\,\mathrm{d}u}{u q_2(u,t)} \\ & + \frac{\varepsilon_3 A_0 \varphi}{q_2(E_0,t)} \int_E^{E_0} \left\{ \frac{E_0}{k-\varphi E_0} V_1(\varphi E_0 t, kt) - \frac{u}{k-\varphi u} V_1(\varphi u t, kt) \right\} \frac{\mathrm{d}u}{u q_2(u,t)} \Bigg|.\end{aligned} \tag{A.9}$$

Hence, one can write

$$\begin{aligned}\Delta x_3 \leqslant & \left| \frac{A_0 \varepsilon_2}{q_2(E_0,t)} V_1(\varphi E_0 t, \varphi E t) \right| \int_E^{E_0} \frac{\mathrm{d}u}{u q_2(u,t)} \\ & + \left| \frac{\varphi A_0 \varepsilon_3}{q_2(E_0,t)} \int_E^{E_0} \left[\frac{E_0}{k-\varphi E_0} V_1(\varphi E t, kt) - \frac{u}{k-\varphi u} V_1(\varphi u t, kt) \right] \frac{\mathrm{d}u}{u q_2(u,t)} \right|.\end{aligned} \tag{A.10}$$

Let us introduce another function $\rho_2(u)$:

$$\rho_2(u) = \frac{E_0}{k-\varphi E_0} V_1(\varphi E_0 t, kt) - \frac{u}{k-\varphi u} V_1(\varphi u t, kt).$$

When $k - \varphi u < 0$ then $\rho_2'(u) < 0$, and

$$\begin{aligned}\delta x_3 \leqslant & A_0 \left| \frac{\varepsilon_2}{q_2(E_0,t)} V_1(\varphi E_0 t, \varphi E t) \right| \\ & + \varphi A_0 \left| \frac{\varepsilon_2}{q_2(E_0,t)} \left\{ \frac{E_0}{k-\varphi E_0} V_1(\varphi E_0 t, kt) - \frac{E}{k-\varphi E} V_1(\varphi E t, kt) \right\} \right|.\end{aligned} \tag{A.11}$$

For the fourth type reaction

$$\begin{aligned}\Delta x_4 = \Bigg| & \frac{\varepsilon_2 A_0}{q_2(E_0,t)} \int_E^{E_0} V_1(\varphi_1 E_0 t, \varphi_1 E t) \frac{\mathrm{d}u}{u q_2(u,t)} \\ & + \frac{\varepsilon_3 A_0 \varphi_1}{q_2(E_0,t)} \frac{1}{\varphi_2 - \varphi_1} \int_E^{E_0} \big[V_1(\varphi_1 E_0 t, \varphi_2 E_0 t) - V_1(\varphi_1 u t, \varphi_2 u t) \big] \frac{\mathrm{d}u}{u q_2(u,t)} \Bigg|.\end{aligned} \tag{A.12}$$

Hence, one may obtain

$$\Delta x_4 \leqslant \left| \frac{\varepsilon_2 A_0}{q_2(E_0, t)} V_1(\varphi_1 E_0 t, \varphi_1 E t) \right| \int_E^{E_0} \frac{\mathrm{d}u}{u q_2(u, t)} + \left| \frac{\varepsilon_3 A_0 \varphi_1}{q_2(E_0, t)} \frac{1}{\varphi_2 - \varphi_1} \rho(u, t) \right| \int_E^{E_0} \frac{\mathrm{d}u}{u q_2(u, t)},$$

where

$$\rho(u, t) = V_1(\varphi_1 E_0 t, \varphi_2 E_0 t) - V_1(\varphi_1 u t, \varphi_2 u t).$$

Function $\rho(u, t)$ takes its maximum for $E \leqslant u \leqslant E_0$ when

$$u = \frac{1}{t(\varphi_1 - \varphi_2)} \ln \frac{\varphi_1}{\varphi_2},$$

and

$$\max \rho(u) = V_1(\varphi_1 E_0 t, \varphi_2 E_0 t) + \left(\frac{\varphi_2}{\varphi_1} \right)^{\varphi_1/(\varphi_1 - \varphi_2)} \left(1 - \frac{\varphi_1}{\varphi_2} \right).$$

But then

$$\delta x_4 \leqslant A_0 \left| \frac{\varepsilon_2}{q_2(E_0, t)} V_1(\varphi_1 E_0 t, \varphi_1 E t) \right| + A_0 \varphi_1 \left| \frac{\varepsilon_3}{q_2(E_0, t)(\varphi_2 - \varphi_1)} \left[V_1(\varphi_1 E_0 t, \varphi_2 E_0 t) + \left(\frac{\varphi_2}{\varphi_1} \right)^{\varphi_1/(\varphi_1 - \varphi_2)} \left(1 - \frac{\varphi_1}{\varphi_2} \right) \right] \right|. \tag{A.13}$$

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