

A kinetic description of monomolecular photochemical reaction with the use of polychromatic irradiation

O. Machalický^{a,*}, L. Lichý^a, J. Bad'ura^a, R. Hrdina^a, T.M. Miranda^{a,b}

^a University of Pardubice, Faculty of Chemical Technology, Studentská 95, 532 10, Pardubice, Czech Republic

^b Departamento de Engenharia Têxtil, Universidade do Minho, Guimarães, Portugal

Received 28 July 2004; received in revised form 15 June 2005; accepted 14 September 2005

Available online 17 October 2005

Abstract

Any kinetic description of a (photo)chemical reaction primarily involves a mathematical analysis showing how the concentration of the (photo)reactant depends on time. The desired dependence, namely the time dependence of concentration of (photo)reactant, is obtained by integration of differential rate equation. The simplest case of (photo)reaction is a (pseudo)monomolecular one. Unlike the kinetic model of (pseudo)monomolecular chemical reaction, the general analytical solution of mathematical model of photochemical reaction is, depending on experimental conditions, much more complicated or even impossible. In the present study, an approximation of the integral kinetic description of (pseudo)monomolecular photolysis has been developed, using high conversion and polychromatic irradiation. It was found that the reaction rate of photolysis of the model compound used can be described by a simple exponential asymptotical equation with two parameters, a linear and an exponential one. The former parameter means the maximum reaction rate and also characterises an overlap of absorption spectrum of starting photo-reactant and the spectrum of incident light. The physical meaning of the latter one is, unfortunately, more complex. Unlike the linear parameter, the value of exponential parameter has to be optimised on basis of the measured dependence of concentration of photo-reactant on time. Integration of the empirical rate equation proposed gave a simple relationship between concentration and reaction time. Potassium ferrioxalate was used as a model photo-reactant. Its photolysis was carried out both in a differential through-flow and an annular integral reactor. Medium pressure Hg arc lamps were used as polychromatic light sources in both cases. The maximum conversion of ferrioxalate was about 90%. It is supposed that the model can be extended to account for any (pseudo)monomolecular irreversible photochemical reaction.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Monomolecular photochemical reaction; Kinetic model; Polychromatic light; Potassium ferrioxalate; Tubular through-flow photochemical reactor; Annular reactor

1. Introduction

The kinetics of monomolecular photochemical reaction $R \xrightarrow{h\nu} P$ is described by simple rate Eq. (1), where r is the reaction rate, dc_R the infinitesimal change of concentration of photo-reactant R , φ is, generally, the quantum efficiency of process and P_a is the irradiation absorbed per time unit (excitation rate) [1,2]:

$$r = \frac{-dc_R}{dt} = \varphi P_a \quad (1)$$

The quantum efficiency $\varphi = r/P_a$ [1] is one of the most useful and fundamental quantities in the study of photochemical

reactions, and its determination is strongly recommended for every basic photochemical study. From the direct relationship of its definition with an energy yield, the overall quantum yield (quantum efficiency) φ also has a very important practical (economical) implication [3]. In order to determine the quantum efficiency mentioned, we have to know, beside the reaction rate, also the excitation rate P_a . In a very simple case, if only monochromatic irradiation is applied (then φ converges to quantum yield Φ) and no light absorption of the reaction product (P) is assumed, the rate equation converges to Eq. (2):

$$r = \Phi P_0 (1 - 10^{-\varepsilon_R L c_R}) \quad (2)$$

Φ is the quantum yield, P_0 the total incident photon flux, ε_R the absorption coefficient, L the width of the irradiated layer and c_R is the actual concentration of the photo-reactant (R). This simple rate equation can be solved mathematically [1,2]. Unfortunately,

* Corresponding author. Tel.: +420 466038001; fax: +420 466038004.
E-mail address: oldrich.machalicky@seznam.cz (O. Machalický).

the theoretical kinetic curve thus obtained has limited practical importance since the condition of monochromatic irradiation is very difficult to fulfil in preparative photochemistry.

Generally, the monomolecular photo-process (carried out with the use of monochromatic light) by which a species R is converted into P can be described by non-linear differential Eq. (3) for which simple analytical solution does not exist [4,5]:

$$r_{\lambda} = \varphi P_{\text{a}\lambda} = \varphi P_{\lambda 0} (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} \quad (3)$$

In this equation, $P_{\lambda 0}$ is the incident molar photonic flux at wavelength λ per unit volume and time (incident photon rate), $A_{\lambda R}$ is the absorbance of photo-reactant (R) and $\sum_i A_{\lambda i}$ is the total absorbance of an irradiated solution which contains both the photo-reactant (R) and photo-product and other absorbing substances present in the real reaction system (e.g. filter or buffer). The reaction rate depends not only on the actual concentration of the starting photo-reactant but on the concentration of the photo-product(s) as well.

Eq. (3) becomes much more complex when polychromatic irradiation is assumed. There we have to consider the variations of the incident photon flux and absorption coefficients of the photo-reactant and products formed over the whole incident light spectrum.

1.1. Excitation rate as a function of absorbance and emission spectrum

Let the derivation of the Eq. (3) yield an infinitesimal change of the reaction rate with the incident molar photonic flux $dP_{\lambda 0}$ (Eq. (4)):

$$dr_{\lambda} = \varphi (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} dP_{\lambda 0} \quad (4)$$

The molar photonic flux dP_{λ} is given by the incident fraction of photons $d(N_{\lambda}/t)$ at wavelength λ per time (t) and volume (V) (Eq. (5)):

$$dP_{\lambda} = \frac{d(N_{\lambda}/t)}{N_A V} = \frac{d\dot{N}_{\lambda}}{N_A V}, \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad (5)$$

The photon fraction $d\dot{N}_{\lambda}$ defined in Eq. (5) is connected with the emission spectrum ($S_{\lambda} = f(\lambda)$) of the light source. In terms of photometry (radiometry), an emission spectrum is measured with the help of a suitable photomultiplier (bolometer) as a dependence of the flux of energy $d(Q/t)/d\lambda$ (monochromatic radiation) [1] on the emission wavelength. This energy is proportional to $d\dot{N}_{\lambda}$. If the relative response $S_{\lambda r}$ of the radiometer (in dependence on wavelength λ) is proportional to $d(N_{\lambda}/t)/d\lambda$, then the total number of photons \dot{N}_T emitted per time unit is proportional to the total area $\int_0^{\infty} S_{\lambda r} d\lambda$ under the emission spectrum. The photon fraction $d\dot{N}_{\lambda}$ of wavelength “almost λ ”, emitted per unit time, can be expressed by Eq. (6):

$$d\dot{N}_{\lambda} = \dot{N}_T \frac{1}{\int_0^{\infty} S_{\lambda r} d\lambda} S_{\lambda r} d\lambda \quad (6)$$

Combination of Eqs. (5) and (6) leads to expression (7):

$$dP_{\lambda} = \dot{N}_T \frac{1}{N_A V \int_0^{\infty} S_{\lambda r} d\lambda} S_{\lambda r} d\lambda \quad (7)$$

The substitution of Eq. (7) into Eq. (4) gives an infinitesimal variation dr_{λ} of the reaction rate in the wavelength range $\lambda + d\lambda$ (Eq. (8)):

$$dr_{\lambda} = \varphi \frac{\dot{N}_{T0}}{N_A V} (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} \frac{S_{\lambda r}}{\int_0^{\infty} S_{\lambda r} d\lambda} d\lambda \quad (8)$$

The integration of differential Eq. (8) gives the overall reaction rate r under irradiation of photo-reactant with continuous polychromatic radiation (Eq. (9)):

$$r = \varphi \frac{\dot{N}_{T0}}{N_A V} \int_0^{\infty} (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} \frac{S_{\lambda r}}{\int_0^{\infty} S_{\lambda r} d\lambda} d\lambda \quad (9)$$

Hence, Eq. (9) can also be written in the implicit form (Eq. (10)):

$$r = \varphi P_0 F_A = \beta F_A \quad (10)$$

The terms P_0 and F_A represent the total number of incident moles of photons (per volume, and time unit) and the so-called absorption fraction [6], respectively.

$$P_0 = \frac{\dot{N}_{T0}}{N_A V} \quad (11)$$

$$F_A = \int_0^{\infty} (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} \frac{S_{\lambda r}}{\int_0^{\infty} S_{\lambda r} d\lambda} d\lambda \quad (12)$$

From definition Eq. (12) it is reasonable that absorption fraction F_A characterises an overlap of absorption spectrum of photo-reactant and the spectrum of an incident light. Its value can vary between zero and unity ($0 < F_A < 1$). In fact, F_A will depend not only on the shape of absorption and the incident light spectrum of photo-reactant and light source but also on concentration c_R of photo-reactant. It is also evident that the integral (12) must converge asymptotically to some limit value if concentration (absorption) of photo-reactant increases to maximum. If total overlap of absorption spectrum of photo-reactant and an incident light and the condition $c_R \rightarrow \text{max}$, then it is $F_A = F_{\infty} \rightarrow 1$.

If polychromatic light and higher photo-conversion are assumed, then from comparison of Eqs. (1) and (10) we can see that the determination of quantum efficiency generally needs the knowledge of absorption fraction (12).

An evaluation of proportionality constant β in Eq. (10), based on experimental values of r and F_A measured during photolysis of a convenient photo-reactant (actinometer) of known quantum efficiency, allows the determination of the molar photonic flux P_0 entering a photo-reactor. This knowledge then allows the determination of both the absolute scale of ordinate in the spectrum of incident light and also the quantum efficiency of some other (pseudo)monomolecular photoreaction studied.

The integral–differential Eq. (9), of course, cannot be analytically solved and, therefore, we cannot exactly express the time dependence of concentration of the starting photo-reactant.

Of course, some articles dealing with problem of mathematical description of monomolecular photo-reaction were published in the past. For example, a detailed theoretical analysis of Eq. (3) is performed in Ref. [4]. Using theoretical approach, the authors showed the dependence of reaction rate on conversion of starting photo-reactant in three possible limit situations. These variants differed in ratio ($\varepsilon_P/\varepsilon_R$) of absorptivities of product (P) and starting substance (R) at irradiation wavelength. It was shown [4] that this ratio is a key parameter determining the shape of kinetic curve of the photo-reaction given. If the ratio $\varepsilon_P/\varepsilon_R$ discussed here is lower than, equal to, or higher than 1, then the curve of dependence of reaction rate on conversion is concave, straight-line or convex one, respectively.

On the basis of our practical experience we suppose that the first case (i.e. $\varepsilon_P/\varepsilon_R < 1$) represents a much more common case of photo-reactions. The second case practically means monochromatic irradiation strictly in an isosbestic point. Such conditions (irradiation) are, from practical point of view, rather rare and a kinetic description of such monomolecular photo-process is relatively easy. The last choice, where $\varepsilon_P/\varepsilon_R > 1$, means that the reaction product will inhibit the photo-process desired, and the reaction will be (more or less rapidly) stopped. Such conditions are not convenient for usual photo-reactions requiring some photolyte to be obtained.

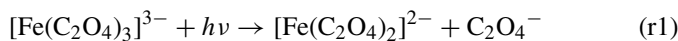
A sophisticated analytical solution of Eq. (3) based on a series expansion was suggested in Ref. [5]. However, the result of the integration has limited use in analysis of photochemical schemes. Another article [7] deals with monochromatic irradiation of excimer 308 nm lamp. The authors used the method of numerical integration of formula (3) to evaluate their experimental data. Paper [8] deals with determination of incident light as a function of wavenumber using absorption filters, actinometer and polychromatic light of Hg lamp. Article [9] only states problem of polychromatic irradiation of photo-reactant, and indicating the complexity of solution it does not submit any practical result. An earlier work [10] concerns only method of numerical integration of Eq. (3).

On the basis of literature research it can be concluded that many articles concerning the measurement of quantum efficiency of photoreactions determine only the starting reaction rate r_0 (computed from the slope value of the straight line). This r_0 value depends, more or less, on the number of the experimental points counted (or, as the case may be, on the conversion of such reaction), and the deviation of r_0 is significant.

The aim of our work was to develop an integral kinetic description of photolysis (for example, photolysis of dyes) with polychromatic irradiation in a photochemical reactor. In our opinion, this description represents a mathematical tool allowing (irrespective of the high values of conversion of photo-reaction) the evaluation of experimental constants of different (mono)molecular irreversible photochemical reactions.

Our model proposed here was tested by means of photolysis of potassium ferrioxalate both in differential through-flow reactor and annular integral reactor, using different Hg arc lamps. Potassium ferrioxalate was chosen as a convenient water-soluble photo-reactant R, its photo-reduction being described by reac-

tion (r1) [11]:



Both the starting substance (Fe(III)) and the reaction product (Fe(II)) involved in (r1) are light absorbing species in the active wavelength range, and the molar absorptivity of the starting ferrioxalate is higher than that of its photolyte. In the mentioned (active) wavelength range, the absorption coefficients of Fe(II) product are equal to about 10% of those of the Fe(III) substrate [12]. The (monochromatic) quantum yield of photo-reduction is approximately $\Phi_\lambda \approx 1.2$ in the wavelength range of 250–450 nm [1,13]. Hence, we assume (in accordance with the definition of quantum efficiency φ [1]) that $\Phi_\lambda \approx \varphi$; the standard deviation based on literature data [1] is $s_\varphi = \pm 0.1$ in the wavelength interval of 250–450 nm.

1.2. Mathematical description of through-flow reactor with total reflux

The through-flow photo-reactor used in our study (see Fig. 1a) consists of two main parts: quartz phototube and a retention tank. Therefore, it is possible to monitor two reaction rates in such reactor system. The first one is inside the photo-tube and the second is inside the retention tank. While the former means the real reaction rate the latter is an apparent reaction rate.

Unless photochemical reaction takes place, the input concentrations of reactant c_a (see Fig. 1a, in the notation of previous text c_{R_a}) and output concentration c_p (c_{R_p}) are equal and constant in time. When the photo-process is started, the concentration difference $\Delta c = c_p - c_a$ appears along the photo-tube (Fig. 1a). This difference Δc causes a decrease in the concentration c_a in the retention tank (denoted with letter A in Fig. 1a). The reaction rate $r_a = -dc_a/dt$ observed in the retention tank A depends on the reaction rate $r = -\Delta c/\Delta t$ in the photo-reactor P. In order to evaluate photochemical processes in this complex system, the relationship between both rates ($r = f(r_a)$) must be known. The steady-state material balance of both the through-flow tubular photo-reactor and the well-stirred container gives the desired relationship.

The material balance of through-flow tubular photo-reactor is described by the differential Eq. (13), where r is the reaction rate, dV the element of volume and \dot{V} the flux and dc is the concentration increment. Integration of Eq. (13) gives the concentration difference Δc (Eq. (14)):

$$r dV = -\dot{V} dc \quad (13)$$

$$-\int_{c_a}^{c_p} dc = \frac{r}{\dot{V}} \int_0^{V_p} dV = -\Delta c = r \frac{V_p}{\dot{V}} \quad (14)$$

The observed reaction rate r_a in the well-stirred container A depends on this difference Δc , flux \dot{V} , and on the container volume V_a (Eq. (15)):

$$r_a = -(c_p - c_a) \frac{\dot{V}}{V_a} = -\Delta c \frac{\dot{V}}{V_a} \quad (15)$$

Combination of Eqs. (14) and (15) leads to the proportional dependence between reaction rate r and observed reaction rate

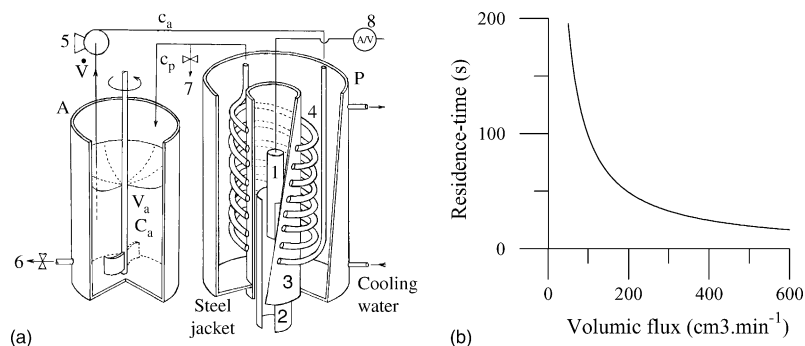


Fig. 1. Through-flow tubular reactor. (a) 1: medium-pressure Hg arc lamp TESLA RVC 125 ($U = 45 \pm 3$ V, $I = 1.17$ A); 2: optical stop (shutter, black paper tube); 3: protective quartz cylinder equipped with “cut-off” absorption filter (absorption edge 260 nm, transmitted light $\lambda \geq 260$ nm); 4: spiral quartz tube (the inside diameter 0.5 cm, the length 8.3 m, diameter of spiral eye 9.5 cm, cross-section of the quartz tube was $S_p = 1.96 \times 10^{-5}$ m²); 5: circulating pump; 6, 7: sample outlet; 8: A/V meter. (b) Residence-time Δt as the function of volumic flux \dot{V} .

r_a (Eq. (16)):

$$r = \frac{r_a V_a}{V_p} = \alpha r_a \quad (16)$$

The ratio of the container volume V_a and the volume V_p of the photo-reactor (the volume of quartz tube) at steady-state is the constant α . In the differential reactor with total recycle (the volume of samples that were taken is negligible), the concentration varies along the reactor (quartz) tube.

2. Experimental

2.1. The through-flow tubular reactor with total reflux

The scheme of photochemical reactor used is shown in Fig. 1a. The reactor vessel was constructed at the Research Institute of Organic Syntheses in Pardubice, Czech Republic (denoted with letter P in Fig. 1a).

The apparatus consists of a well-stirred retention tank A (working volume $V_a = 450$ cm³), a circulating pump (volumic flux $\dot{V} = 500$ cm³ min⁻¹) and a through-flow tubular reactor P equipped with a spiral quartz tube (irradiated volume $V_p = 160$ cm³). The inner diameter of the quartz tube was negligible as compared to its length, and it was possible to consider the reactor to work as a differential one. The flow $\dot{V} = 500$ cm³ min⁻¹ of the solution through the quartz tube meant that a differential volume unit was irradiated for a period of approximately 20 s (the residence-time Δt). The relation between the flux and the residence-time is shown in Fig. 1b. It can be seen (Fig. 1b) that the slope $-d\Delta t/d\dot{V}$ is small, and the residence-time in the phototube is well stabilized when the flux is higher than 300 cm³ min⁻¹.

In order to carry out the reaction, the apparatus was filled with 610 cm³ reaction mixture, whereupon the circulation pump, cooling water, and the lamp were switched on. The consumption of the lamp was checked with V- and A-meters. After ca. 40 min of warming up (the steady-state regime of the lamp was monitored by the V-meter) the optical stop was removed. Samples (concentrations c_a , and c_p , volume 2 cm³) of irradiated solution were withdrawn at regular time intervals.

The Fe(III) concentration in the diluted samples was determined by VIS spectroscopy (standard method [13], the red complex of Fe(II) ion with 1,10-phenanthroline has $\varepsilon_{510} = 11060$ dm³ mol⁻¹ cm⁻¹ at 510 nm).

2.2. The annular reactor

A Laboratory UV Annular Reactor System 2, Heraeus Noblelight (Departamento de Quimica, Universidade do Minho, Portugal) was equipped with a medium-pressure Hg arc lamp Heraeus TQ 150 (power input ca. 160 W). The actual electric current and voltage were measured using A/V meter ($U = 90$ V, $I = 1.8$ A). The volume of reaction mixture (the maximum working volume) was 800 cm³. The beam pathway was ca. 2.5 cm. The reactor bottle was completely wrapped with Al-foil to prevent light scattering. Reaction mixture was vigorously stirred with magnetic stirrer (Fig. 2).

This type of reactor is not equipped with an optical stop, which is why the reactor bottle was filled at first with 750 cm³ “actinometric” solution (mixture of oxalic acid and potassium hydroxide) without addition of iron(III) sulphate. The lamp and cooling water circulation were switched on. The aliquot of iron(III) in 50 cm³ aqueous solution was added into reaction mixture in one portion after the lamp was ready (warmed up). The first sample (1 cm³) of reaction mixture (time = 0) was withdrawn as soon as possible (after ca. 30 s). Then the other samples were withdrawn at regular time intervals. The iron(III) concentration was evaluated in the same way as described above (tubular through-flow reactor).

2.3. Preparation of modified potassium ferrioxalate solution

The solution of 0.01 mol dm⁻³ potassium ferrioxalate with excess oxalic acid was prepared by dissolving (COOH)₂·2H₂O (67.04 g, 0.530 mol), KOH (1.68 g, 0.030 mol) and Fe₂(SO₄)₃·9H₂O (2.81 g, 0.005 mol) in water (total volume 1 dm³). The solution prepared was used immediately in the photochemical experiments.

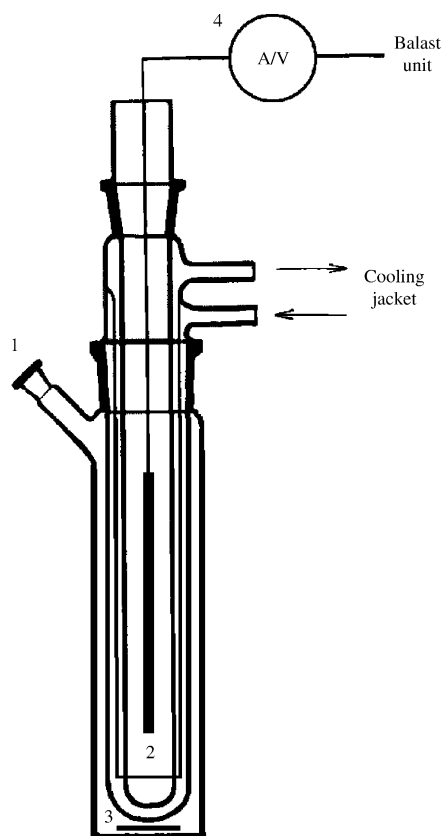


Fig. 2. Laboratory UV Reactor System 2, Heraeus Noblelight. 1: filling inlet/sample port; 2: medium-pressure Hg arc lamp Heraeus TQ 150; 3: stirrer bar; 4: A/V meter.

2.4. Other equipment

The emission spectra (radiation of the medium-pressure Hg arc lamp passed through quartz cylinder and cut-off filter of the photo-reactor) were measured with a Perkin-Elmer LS-5 fluorescence spectrophotometer (this was also the lamp used in tubular through-flow reactor; Department of Organic Technology, University of Pardubice; Fig. 3a) and/or Spex Fluorolog II fluorescence spectrophotometer (the lamp used in annular integral reactor; Departamento de Física, Universidade do Minho; Fig. 3b). The emission spectra obtained were numerically cor-

rected for detection channel (monochromator and photomultiplier) sensitivity dependence [14] and expressed in $\text{Es m}^{-2} \text{s}^{-1}$.

The UV/vis spectra were measured with a UV/vis Perkin-Elmer absorption spectrophotometer Lambda 35 and/or UV/vis Shimadzu absorption spectrophotometer UV-2501PC.

2.5. Calculations

The linear regressions of measured data were calculated by means of commercial software (Microsoft Excel 97 SR-1).

The absorption fraction F_A and reaction rates were calculated using a special program assembled by the authors (in Turbo Pascal 6.0). The input data consisted of the constant α , the absorption spectrum of potassium ferrioxalate, the spectrum of incident light and the spectra of reaction mixture samples at defined reaction times.

3. Results and discussion

The corrected spectra [14] of the incident light of both RVC 125 and TQ 150 Hg arc lamps are presented in Fig. 3a–b. The absolute ordinate scales were determined using results of ferrioxalate actinometry (incident light P_0).

The absorption spectrum of an aqueous solution of potassium ferrioxalate is shown in Fig. 4. By comparing with spectra in Fig. 3a it can be seen that the incident light of RVC 125 between 500 and 600 nm is out of the range of absorption of photo-reactant (for its spectrum, see Fig. 4, curves 2 and 4). Given that the light efficiency of RVC 125 in the interval of 500–600 nm represents approximately 55% of its total output, the overlap integral (Eq. (12)) for $c_R \rightarrow \max$ cannot probably exceed the maximum value of $F_A \leq 0.45$ at the beginning of the reaction.

Similar situation ($F_A \leq 0.4$) arises in the case of TQ 150 lamp (compare Fig. 3b with Fig. 4). In order to find the maximum value of F_A more precisely, we calculated integral (12) for different increasing (starting) concentrations of the photo-reactant (potassium ferrioxalate) assuming $A_{\lambda R} / \sum_i A_{\lambda i} = 1$. The asymptote of this dependence ($F_A = f(c_R)$) for $c_R \rightarrow \max$ means a limit value of $F_A \rightarrow F_\infty$.

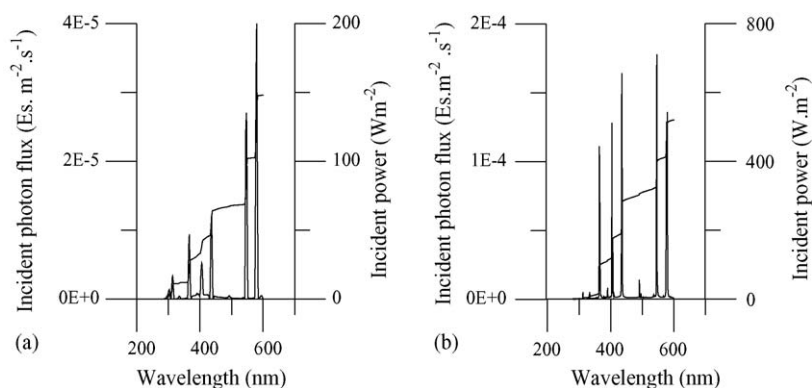


Fig. 3. Spectra of incident photon flux (solid line) and incident energy (dashed line) entering the reaction solution. (a) Tubular through-flow reactor ($P_0 = 12.4 \times 10^{-5} \text{ Es dm}^{-3} \text{ s}^{-1}$) and (b) annular integral reactor ($P_0 = 8.3 \times 10^{-5} \text{ Es dm}^{-3} \text{ s}^{-1}$).

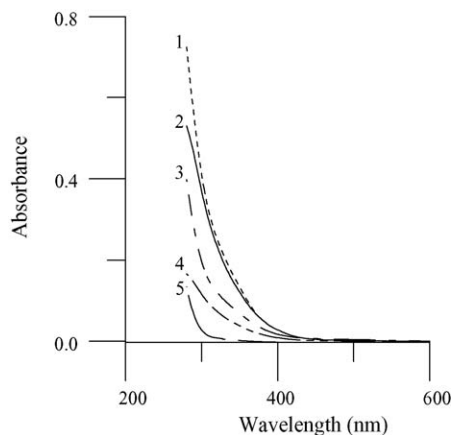


Fig. 4. Absorption spectra of photo-reactant and reaction mixtures (the starting concentration of potassium ferrioxalate in the reaction mixture was $0.005 \text{ mol dm}^{-3}$). The spectra depicted correspond to 50 times diluted solutions. Curve 1: the starting reaction mixture; 2: the starting potassium ferrioxalate; 3: the final reaction mixture; 4: ferrioxalate remaining in the final reaction mixture; 5: the excess of oxalic acid present.

The results of such calculations are shown in Fig. 5a and b for both RVC 125 and TQ 150 lamps. The asymptotes in Fig. 5a and b are $F_{\infty} = 0.355$ and 0.502 , respectively. From Fig. 5a it can also be seen that the ferrioxalate concentration higher than 0.02 mol dm^{-3} is relatively close to asymptotic F_A , and a “linear” dependence $r = f(t)$ of reaction rate r on time t can be expected using RVC 125 lamp. Similarly (Fig. 5b), the ferrioxalate concentration of 0.04 mol dm^{-3} is sufficiently close to asymptotic F_A in the case of TQ 150 light source, hence a “constant” reaction rate should be expected here.

The first experiments were performed using pure potassium ferrioxalate in aqueous solutions ($c_{a0} = 0.005\text{--}0.15 \text{ mol dm}^{-3}$) and tubular reactor (Fig. 1a). The kinetic data obtained are presented in Fig. 6a, where it can be seen that the conversion of ferrioxalate varied in the interval of 20–0% (in relation to the starting concentration). However, the calculated rate data exhibited a significant deviation (Fig. 6b).

The second set of irradiations was performed with excess oxalic acid (0.5 mol dm^{-3}). This addition of oxalic acid to the

ferrioxalate solution led to an increase in reaction rates, but the dispersion of data was always relatively high. Some solid precipitate (containing Fe^{2+} ions) was found to be formed during photolysis. If the amount of KOH used for the preparation of ferrioxalate solution was one half of the stoichiometric amount (see Section 2.3), then this modified solution gave the best results (Fig. 6c) without forming any precipitate. In this case, the conversion of the reactant varied in the interval of 30–80% (see final data in Fig. 8a). The absorption spectra of pure photo-reactant and those of the reaction mixtures at the beginning and at the end of the irradiation are presented in Fig. 4. The starting concentration of potassium ferrioxalate in the reaction mixture (Fig. 4) was $0.005 \text{ mol dm}^{-3}$. The absorption spectrum (Fig. 4, curve 1) of reaction mixture (defined in Eq. (3) as $\sum_i A_{\lambda i}$) practically corresponds to the starting ferrioxalate solution at the beginning of irradiation (Fig. 4, curve 2). A slight difference at 300 nm is caused by the excess oxalic acid (curve 5 in Fig. 4). As the concentration of ferrioxalate in reaction mixture decreases, the absorption of the irradiated solution decreases too. When the photolysis is stopped, the final absorption $\sum_i A_{\lambda i}$ (Fig. 4, curve 3) is higher than that of the remaining ferrioxalate (Fig. 4, curve 4). The rate data r versus r_a (Fig. 6c) exhibited linear correlation (correlation coefficient 0.996) and, therefore, the constant $\alpha = 2.75$ (S.D. = ± 0.04) was evaluated by linear regression (Fig. 6c).

From Fig. 6b and c it can be seen that the reaction rate of photochemical decomposition of pure ferrioxalate in water is generally lower than that with excess oxalic acid. Presumably, the simple (thermodynamic) dissociation of photo-active $[\text{Fe}(\text{C}_2\text{O}_2)_3]^{3-}$ ion decreases its actual concentration (reaction scheme (r2)), which is why equilibrium (r2) can be shifted in favour of the starting compound by the addition of oxalic acid. Thus, in the next discussion, only the data obtained from the photolysis of a modified potassium ferrioxalate solution were considered:



The relationship between reaction rate and absorption fraction F_A is shown in Fig. 7a. Since this function should be linear

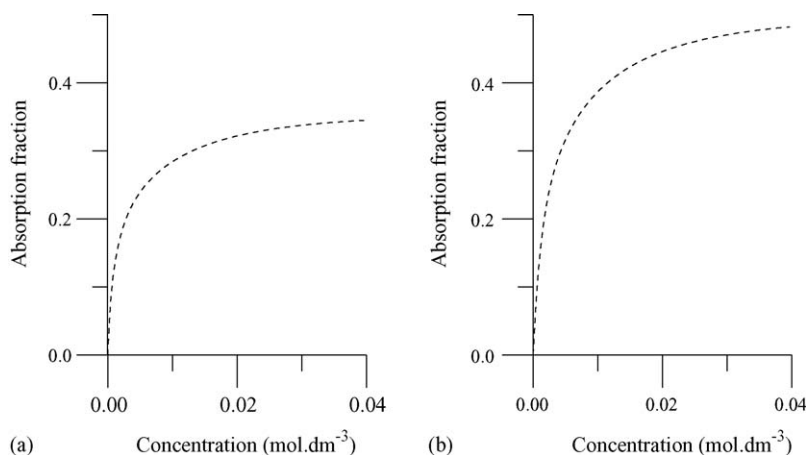


Fig. 5. The theoretical dependence of absorption fraction F_A on starting concentration c_R of potassium ferrioxalate in accordance with Eq. (12): (a) ferrioxalate irradiated with RVC 125 type lamp and (b) ferrioxalate irradiated with TQ 150 type lamp.

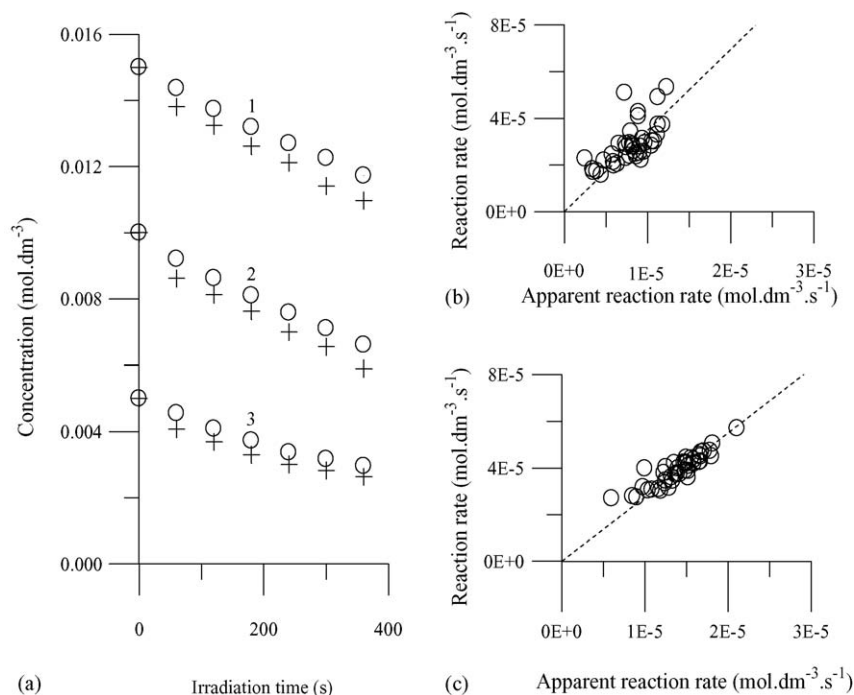


Fig. 6. Photolysis of aqueous solutions of potassium ferrioxalate: (a) sets of kinetic curves (1–3) of pure ferrioxalate solution (the sets 1, 2 and 3 are for $c_{a0} = 0.015$, 0.01 and 0.005 mol dm⁻³, respectively); (○) concentration c_a (sample port 6, Fig. 1a); (+) concentration c_p (sample port 7, Fig. 1a). (b) The relationship between the reaction rate r and the apparent reaction rate r_a for pure ferrioxalate solution. (c) The relationship between the reaction rate r and the apparent reaction rate r_a for modified ferrioxalate solution. The data were fitted with a straight line $r = \alpha r_a$, where $\alpha = 2.75$ (S.D. = ± 0.04).

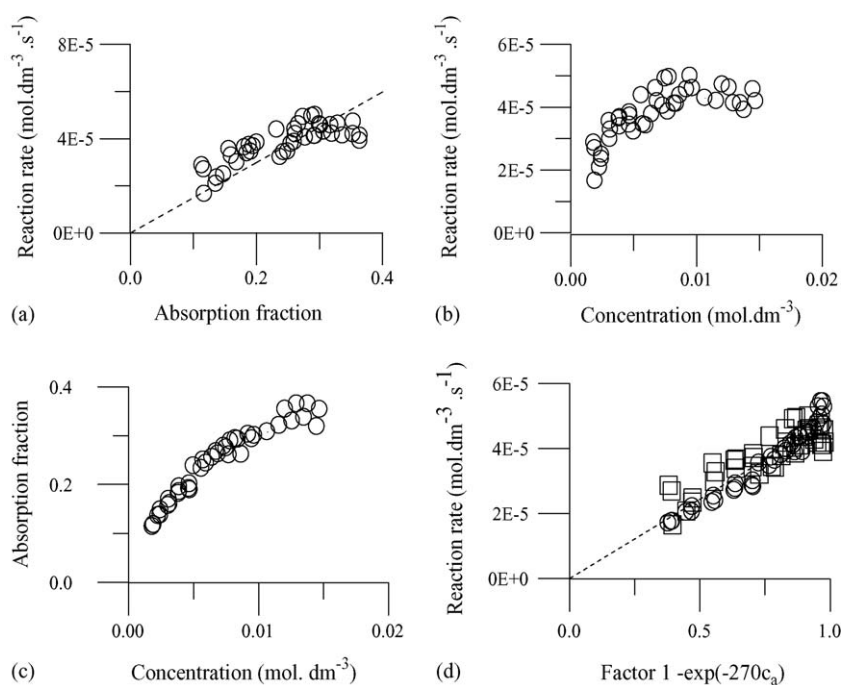


Fig. 7. Evaluation of kinetic measurements: (a) the relationship between the reaction rate r and the absorption fraction F_A . The data were fitted with a straight line $r = \beta F_A$. (b) The reaction rate r as a function of reactant concentration c_a . (c) The experimental absorption fraction F_A as a function of reactant concentration c_a . (d) Reaction rate r (□) and/or βF_A (○) as a function of an exponential factor $1 - e^{-270c_a}$.

(Eq. (10)), the data were fitted with a straight line, and the coefficient β was evaluated ($\beta = 14.9 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$, standard deviation $s_\beta = \pm 0.4 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$). Hence, the incident molar photonic flux was $P_0 = \beta/\varphi = 12.4 \times 10^{-5} \text{ Es dm}^{-3} \text{ s}^{-1}$ (standard deviation $s_P = \pm 1.1 \times 10^{-5} \text{ Es dm}^{-3} \text{ s}^{-1}$).

Note: The standard deviation of incident light was evaluated from the formula $s_P = \pm P_0 \sqrt{(s_\beta/\beta)^2 + (s_\varphi/\varphi)^2}$, where s_β and s_φ are standard deviations of the slope β in Fig. 7a and potassium ferrioxalate quantum efficiency, respectively.

The relation between the reaction rate r and the concentration of the reactant c_a is shown in Fig. 7b. Similarly, in Fig. 7c is shown the relationship between the F_A and the concentration c_a . It can be seen that both the reaction rate and the absorption fraction converge to an asymptote ($r \rightarrow r_\infty$, $F_A \rightarrow F_\infty$) at the highest concentrations of ferrioxalate (cf. Figs. 7c and 5a).

These results (Fig. 7b and c) and the fact that the photoreaction products absorb approximately 10 times less than the starting photo-reactant [12] led us to the idea that the function describing the relationship between the reaction rate r and the actual concentration c_R of the reactant (at irradiation time t) could be written in an asymptotical exponential form (Eq. (17)), and the relationship between F_A and the actual concentration c_R could be expressed similarly (Eq. (18)):

$$r \approx r_\infty(1 - e^{-\gamma c_R}) \quad (17)$$

$$F_A \approx F_\infty(1 - e^{-\gamma c_R}) \quad (18)$$

The asymptotes r_∞ and F_∞ are the maximum reaction rate and the maximum absorption fraction, respectively, which can be achieved in such photochemical experiment (regarding the absorption spectrum of photo-reactant and the incident light of the lamp used). The coefficient γ is an experimental constant. The linear relationship between r and F_A (Eq. (10)) means that the coefficient γ has to be the same in both Eqs. (17) and (18).

Thus, differential Eq. (19) can be written in accordance with the above-expressed considerations:

$$-\frac{dc_R}{r} = dt \approx -\frac{dc_R}{r_\infty(1 - e^{-\gamma c_R})} = -\frac{dc_R}{\varphi P_0 F_\infty(1 - e^{-\gamma c_R})} \quad (19)$$

Relationship (20) between r_∞ and F_∞ follows from the comparison of the constant terms in denominators of Eq. (19):

$$r_\infty = \varphi P_0 F_\infty \quad (20)$$

It can also be seen that empirical Eq. (17) is formally similar to Eq. (2) [1,2] for monochromatic irradiation and non-absorbing products. The basic difference between that reported equation and our Eq. (17) lies in that the latter approximates a photoreaction with the use of polychromatic irradiation (continuous emission spectrum).

Eq. (19) can be integrated analytically to give the kinetic equation of the photolysis (21). The symbol c_{R0} is the starting concentration of the photo-reactant at irradiation time

$t = 0$:

$$-\gamma(c_R - c_{R0}) - \ln\left(\frac{1 - e^{-\gamma c_R}}{1 - e^{-\gamma c_{R0}}}\right) = \gamma r_\infty t$$

or $c_R = \frac{1}{\gamma} \ln[(e^{\gamma c_{R0}} - 1)e^{-\gamma r_\infty t} + 1]$ (21)

If $1 - \exp(-\gamma c_{R0})$ converges to 1 (a sufficiently concentrated solution), then the logarithmic argument in Eq. (21) is r/r_∞ . It can also be seen that at the beginning of photolysis of a sufficiently concentrated solution the actual reaction rate is practically the same as the asymptotical one, and the logarithmic term converges to zero; Eq. (21) converges to a linear dependence of concentration on time with slope r_∞ . This conclusion is in accordance with “zero-order” kinetics of photoreactions frequently observed (not only in the case of ferrioxalate actinometry) and mentioned [2].

The logarithmic term in Eq. (21) increases its importance during the photolysis, where the actual concentration c_R of reactant decreases sufficiently. Eq. (21) can be also rewritten as Eq. (22):

$$e^{\gamma c_R} = (e^{\gamma c_{R0}} - 1)e^{-\gamma r_\infty t} + 1 \quad (22)$$

From this expression, it follows that near the end of the reaction ($\gamma c_R \leq 10^{-2}$) Eq. (22) converges to the exponential form (23) corresponding to the “first-order” kinetics [2]:

$$c_R = \frac{e^{\gamma c_{R0}} - 1}{\gamma} e^{-\gamma r_\infty t} \quad (23)$$

Kinetic Eqs. (21) and (22) are exactly valid for a photoreaction carried out in a well-stirred integral reactor.

Some changes in kinetic description are needed if differential through-flow reactor (Fig. 1) is used. If the concentration gradient Δc between reactor output and input is relatively small (i.e. the flow rate of solution through the photochemical tube is sufficiently high), then it is possible to rewrite Eq. (19) into Eq. (24), where c_a is the actual concentration observed in the retention tank A:

$$-\frac{dc_a}{dt} = r_a \approx \frac{r_\infty}{\alpha}(1 - e^{-\gamma c_a}) \quad (24)$$

The ratio $-dc_a/dt$ is the observed apparent reaction rate r_a , and α is constant (Eq. (24)). The integration of Eq. (24) gives, in the end, the kinetic equation valid for the retention tank of our differential reactor:

$$-\gamma(c_a - c_{a0}) - \ln\left(\frac{1 - e^{-\gamma c_a}}{1 - e^{-\gamma c_{a0}}}\right) = \frac{\gamma r_\infty}{\alpha} t \quad (25)$$

This kinetic equation is formally similar to Eq. (21) and the same mathematical operations and considerations can be applied to it (i.e. the influence of logarithmic term, “zero-order” kinetics at the beginning and “first-order” kinetics at the end of irradiation).

Linearization of Eq. (17) and/or Eq. (18) (Fig. 7d) allowed simultaneous calculation of the constant $\gamma = 270 \text{ mol}^{-1} \text{ dm}^3$ and $r_\infty = 4.87 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ (S.D. = $\pm 0.06 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$). The asymptote $F_\infty = r_\infty/\beta = 0.33$ (S.D. = ± 0.01) was then calculated.

Table 1
Basic characteristics and optimised parameters of photo-reactors used and the form of optimised kinetic curves for photolysis of potassium ferrioxalate

	Type of reactor	
	Differential (University of Pardubice)	Integral (Universidade do Minho)
Lamp	TESLA RVC 125	TQ 150
Electric power P_E (W)	~50	~160
Irradiated volume V (L)	0.16	0.8
Incident light P_0 ($\text{Es L}^{-1} \text{s}^{-1}$)	12.4×10^{-5} (S.D. = $\pm 1.1 \times 10^{-5}$)	8.3×10^{-5} (S.D. = $\pm 0.9 \times 10^{-5}$)
Light output P_L (W)	~5	~10
Maximum reaction rate r_∞ (mol L^{-1})	4.87×10^{-5} (S.D. = $\pm 0.06 \times 10^{-5}$)	4.62×10^{-5} (S.D. = $\pm 0.07 \times 10^{-5}$)
Parameter γ (L mol^{-1})	270	100
Parameter F_∞	0.33	0.46
Kinetic curve	$c_a = \frac{\ln(56.4 e^{-0.0048t} + 1)}{270}$	$c = \frac{\ln(41.5 e^{-0.0046t} + 1)}{100}$

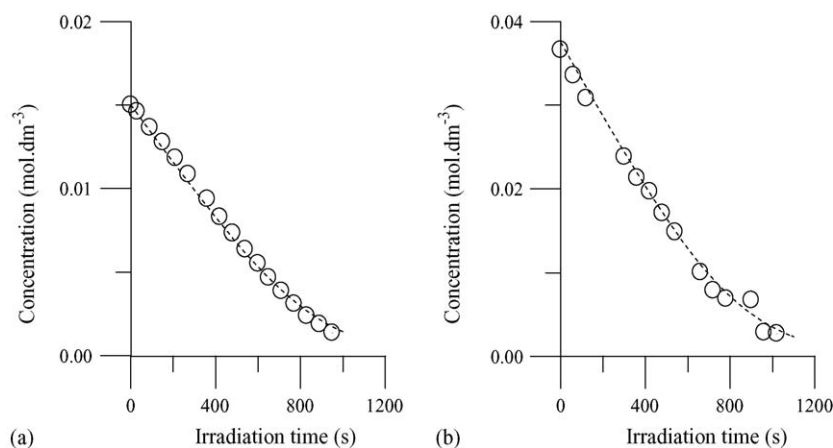


Fig. 8. The relationship between ferrioxalate concentration and irradiation time. The data are fitted with kinetic equation according to Table 1. (a) Time dependence of concentration measured in retention tank of differential photoreactor. (b) Time dependence of concentration detected in an integral photoreactor.

Similar results were obtained using annular integral reactor with TQ 150 Hg lamp (Universidade do Minho, Portugal). The results obtained for both differential and integral type of reactor are summarised in Table 1. It can be seen that the predicted F_∞ values (see asymptotes in Fig. 5a and b) are comparable with those optimised in Table 1. The obtained experimental constants α , γ and r_∞ allowed an approximation of the photo-kinetic data collected in accordance with both Eq. (25) (Fig. 8a) and Eq. (21) (Fig. 8b) for tubular differential and annular integral reactors, respectively.

Note: The experimental data in Fig. 8a represent average values of the data collected in three separate experiments using three different starting concentrations of photo-reactant (0.015, 0.01 and $0.005 \text{ mol dm}^{-3}$), each experiment being repeated several times.

The experimental data in Fig. 8b represent typical results of one of three experiments. The starting concentration was $c_{R0} = 0.375 \text{ mol dm}^{-3}$.

4. Conclusion

1. It can be concluded that the dependence of reaction rate r of (pseudo)monomolecular photolysis: $R \xrightarrow{h\nu} P$ on the absorp-

tion fraction F_A is linear. The quantum efficiency is calculated from the formula $\varphi = \frac{r}{P_0 F_A}$, where P_0 is incident light and $F_A = \int_{(\lambda)} (1 - 10^{-\sum_i A_{\lambda i}}) \frac{A_{\lambda R}}{\sum_i A_{\lambda i}} \frac{S_{\lambda r}}{S_{\lambda r}} d\lambda$.

2. If the condition $\varepsilon_R(\lambda)/\varepsilon_P(\lambda) > 10$ is approximately fulfilled in an overlap interval of the absorption spectrum of photo-reactant and incident light spectrum, then the reaction rate r of (pseudo)monomolecular photoreaction can be approximated as an asymptotical exponential function of the concentration c_R of the photo-reactant R: $r = \varphi P_0 F_A \approx \varphi P_0 F_\infty (1 - e^{-\gamma c_R}) = r_\infty (1 - e^{-\gamma c_R})$. The time dependence of concentration is then given by: $c_R \approx \frac{1}{\gamma} \ln[(e^{\gamma c_{R0}} - 1)e^{-\gamma r_\infty t} + 1]$. The second conclusion means that integral term F_A , which characterises an actual overlap of absorption spectrum of reaction mixture and incident light, converges to the simple term $F_A \rightarrow F_\infty (1 - e^{-\gamma c_R})$, where the linear parameter F_∞ is defined by the formula: $F_\infty = \int_{(\lambda)} (1 - 10^{-\sum_i A_{\infty \lambda i}}) \frac{A_{\infty \lambda R}}{\sum_i A_{\infty \lambda i}} \frac{S_{\lambda r}}{S_{\lambda r}} d\lambda$.

The terms $A_{\infty \lambda i}$ and $\sum_i A_{\infty \lambda i}$ mean absorption spectra of photo-reactant and reaction mixture at such concentration $c_R \rightarrow \max$, where the reaction rate is “time-independent”. The physical meaning of the complex exponential parameter γ cannot be interpreted on the basis of experiments carried out in this work.

3. From practical point of view, the results obtained here on photolysis of potassium ferrioxalate have also importance for the actinometry performed in photochemical reactors on preparative scale.

Acknowledgements

The authors wish to thank Professor Ana M. Oliveira-Campos of University of Minho, Portugal, who offered an integral photoreactor for this work, and also Dr. Mario Rui Pereira (Departamento de Física, Universidade do Minho), who measured the spectrum of incident light of TQ 150 lamp.

This work was financially supported by research grant CZ 351002, Ministry of Education, Youth and Sport of the Czech Republic.

References

- [1] A.M. Braun, M.-T. Maurette, E. Oliveros, Photochemical Technology, Wiley Ltd., Chichester, New York/Brisbane/Toronto, Singapore, 1991.
- [2] H.G.O. Becker, et al., Einführung in die Photochemie, VEB Deutscher Verlag der Wissenschaften, Berlin, 1975.
- [3] M.I. Cabrera, O.M. Alfano, A.E. Cassano, Ind. Eng. Chem. Res. 33 (12) (1994) 3031–3042.
- [4] B. Borderie, D. Lavabre, J.C. Micheau, J. Phys. Chem. 96 (1992) 2953–2961.
- [5] R.L. Jackson, D.G. Lishan, J. Phys. Chem. 88 (1986) 5986.
- [6] L. Sun, J. Bolton, J. Phys. Chem. 100 (1996) 4127.
- [7] J.-Y. Zhang, H. Esrom, Y.W. Boyd, Appl. Surf. Sci. 138–139 (1999) 315–319.
- [8] R. Hrdina, I. Čepčianský, H. Bittová, Collect. Czech. Chem. Commun. 56 (6) (1991) 1173.
- [9] R. Hrdina, I. Čepčianský, J. Poskočil, Collect. Czech. Chem. Commun. 50 (12) (1985) 2783.
- [10] H. Mauser, Z. Naturforsch. 34c (1979) 1295.
- [11] G.D. Cooper, B.A. DeGraff, J. Phys. Chem. 75 (19) (1971) 2897.
- [12] J.C. Crano, R.J. Guglielmetti (Eds.), Topic in Applied Chemistry, vol. 2, Kluwer Academic/Plenum Publishers, 1999, p. 173.
- [13] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley Ltd., New York/London/Sydney, 1966.
- [14] J.A. Gardecki, M. Maroncelli, Applied Spectroscopy 52 (9) (1998) 1179.