

Laser-induced reduction of a dye characterised by a high triplet-state yield and dissolved in a polymer

A G Sizykh, E A Tarakanova, L L Tatarinova

Abstract. An investigation was made of the photoreduction kinetics of a dye in a solid polymer solution under the influence of laser radiation corresponding to the band of the first singlet–singlet transition. Participation of higher triplet states was considered in a model of the photoreduction of a dye characterised by a high intersystem crossing yield. An analytic solution was obtained for a system of kinetic equations. This solution takes into account the difference between the photoprocess rates. It is shown that a linear dependence of the effective dye-photoreduction rate on the laser radiation intensity can serve as a test of the participation of higher triplet states in the reaction. A comparison of the theoretical and experimental results obtained in the present study is used to determine the ratio of the photoreduction and deactivation rate constants of the higher triplet state of eosin K.

1. Introduction

Investigations of the mechanisms of photochromic conversion in solid polymer solutions of dyes [1] are of considerable relevance in tackling the topical task of developing optical data storage systems. Some of the studies of the oxidation–reduction photochromism, carried out mainly on liquid solutions of xanthene dyes with various luminescence capabilities, have shown that there is a great variety of photoreactions resulting from flash photolysis and involving triplet excitations [2, 3]. Excitation in the UV part of the spectrum increases the photobleaching quantum yield by five orders of magnitude compared with excitation in the visible range. In the case of multistage excitation by laser pulses, the photoreaction is of two-photon nature and involves higher singlet and triplet states [5, 6]. Moreover, an important role should be played by nonradiative energy transfer from these states to solvent molecules [7]. The photochromism of dyes is still a topical subject for research [8, 9].

Identification of the photoconversion mechanisms requires the use of unique experimental equipment and methods (laser chronoscopy, kinetic spectroscopy, etc.), as well as a theoretical kinetic analysis which (considered within the framework of a general mathematical model) may prove

either impossible or may fail to give clear analytic results. Consequently, the search for and the adoption of reasonable simplifications in the case of such complex systems assumes practical importance.

We report here an investigation of laser-induced chemical reduction of a dye in thin polymer films, taking as the example a solid solution of eosin K in gelatin. The interest in this composite arises from the fact that the dye occupies an intermediate position in respect of the energy balance of its radiative and nonradiative transitions, whereas gelatin is a biopolymer widely used in industry. The approach based on taking account of the difference (contrast) between the photoprocess rates leads to a clear analytic result which makes it possible to test the characteristic features of the mechanism of laser reduction by relatively simple experimental procedures.

2. Principal photophysical and photochemical processes

We shall consider the combination of photophysical and photochemical processes that develop in the investigated system as a result of continuous photoexcitation and we shall consider the kinetic characteristics necessary in theoretical estimates.

The excitation of a dye molecule in the band of the first S_0-S_1 singlet–singlet transition is characterised by a rate constant $I\varepsilon$, where I is the quantum intensity of the radiation and ε is the molar extinction coefficient of the dye. For eosin K in a solid gelatin matrix this coefficient is $\varepsilon \approx 10^5$ litre $\text{mol}^{-1} \text{cm}^{-1}$ when exposed to argon laser radiation of the wavelength $\lambda = 514.5$ nm. The population of the S_1 level decreases mainly as a result of the S_1-T_1 intersystem crossing with the singlet–triplet quantum yield $\varphi_{st} = 0.71$, and also as a result of fluorescence ($\varphi_f = 0.19$) [2] and a number of nonradiative processes (S_1-S_0).

These data were used to calculate the rate constants $k_{st} = 7.61 \times 10^8 \text{ s}^{-1}$ and $k_f = 3.57 \times 10^8 \text{ s}^{-1}$, where k_f is understood to be the effective rate constant considered taking into account the S_1-S_0 nonradiative transitions. The reverse T_1-S_1 transition is unlikely since the T_1 level lies approximately 40 kJ mol^{-1} below the S_1 level. Room-temperature T_1-S_0 phosphorescence in rigid matrices is not very efficient. However, as shown in Ref. [2], this process cannot be ignored. The triplet–triplet absorption at the $\lambda = 514.5$ nm wavelength remains highly efficient since the molar extinction coefficient of the triplet–triplet transition is an order of magnitude less than the corresponding coefficient for the singlet–singlet transition [10]. The rate constant of the deactivation of the upper triplet state is estimated taking into account the

A G Sizykh, E A Tarakanova, L L Tatarinova Quantum Electronics Division, Krasnoyarsk State University, Svobodnyĭ prospekt 79, 660041 Krasnoyarsk, Russia
fax: (3912) 44-86-25, e-mail: grad@krasu.ru, tel.: (3912) 44-54-69

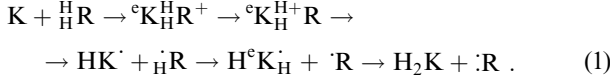
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fact that it can exceed the rate constant of an allowed radiative transition.

The long lifetime of the triplet state T_1 is 4.2 ms in the case of eosin [10] and it increases the photochemical reaction probability. The reduction of eosin K in its excited state by a hydrogen-bearing compound H_2R can be represented formally as follows [2]:



The role of a proton donor in the photoreduction of the dye in the gelatin matrix may be played by amino acids of the polypeptide chain of gelatin. Since these components are present in excess, the reaction can be regarded as quasimonomolecular. The effective photoreduction rate constant determined experimentally ($\sim 10^{-3} \text{ s}^{-1}$ [11]) represents the slowest of the photoprocesses occurring in the investigated system.

Another channel of the formation of the photoreduced form of KH_2 is the dismutation reaction. However, this channel does not play a significant role because of the low mobility of the molecules in the solid solution. If the dye photoreduction occurs in the presence of oxygen, partial regeneration of the leuco form to the coloured form takes place [2]. Nevertheless, in practice the low permeability of the gelatin matrix to atmospheric oxygen ensures irreversibility of the photochemical reaction and prevents oxygen from quenching the triplet molecules [10].

The dye photoreduction process becomes possible if hydrogen detachment sensitised by the excited dye occurs in the gelatin matrix. The hydrogen detachment energy lies in the range 380–540 kJ mol^{-1} for the C–H and N–H bonds [12]. Since the excitation energy of the first triplet state (about 190 kJ mol^{-1}) is insufficient for the detachment of hydrogen, it is reasonable to assume that the higher triplet states may be the initial participants of the chemical reaction. Filling of the higher triplet states as a result of the T_1 – T_n transition can occur effectively in dyes with a high intersystem crossing yield and long lifetimes of the triplet states. This is facilitated by a high steady-state population of the T_1 level, comparable with the population of the ground state [13], during continuous pumping. Filling of the higher singlet states in a two-stage transition by excitation of radiation from a cw argon laser is not very effective because of the low population of the S_1 state.

3. Kinetic model of the dye photoreduction process

We shall describe the laser-induced processes in the dye by a four-level (S_0 , S_1 , T_1 , T_n) scheme which includes the singlet–singlet and triplet–triplet absorption events (S_0 – S_1 , T_1 – T_n), fluorescence and nonradiative processes (S_1 – S_0), the intersystem transition (S_1 – T_1), phosphorescence (T_1 – S_0), a number of radiative and nonradiative transitions (T_n – T_1), such as fluorescence and internal conversion, and also deactivation of the triplet states T_1 and T_n in the course of the chemical reaction.

The system of the material balance equations is of the form

$$\frac{d[S_0]}{dt} = -I\varepsilon_1[S_0] + k_f[S_1] + k_{\text{ph}}[T_1] , \quad (2)$$

$$\frac{d[S_1]}{dt} = I\varepsilon_1[S_0] - (k_f + k_{\text{st}})[S_1] , \quad (3)$$

$$\frac{d[T_1]}{dt} = k_{\text{st}}[S_1] - (k_{\text{ph}} + I\varepsilon_2)[T_1] + k_q[T_n] - k_{\text{ch1}}[T_1] , \quad (4)$$

$$\frac{d[T_n]}{dt} = -(k_q + k_{\text{ch2}})[T_n] + I\varepsilon_2[T_1] . \quad (5)$$

Here $[S_0]$, $[S_1]$, $[T_1]$, $[T_n]$ are the normalised (to the initial dye concentration) populations of the ground, singlet, and triplet excited states; ε_1 and ε_2 are the molar extinction coefficients for the S_0 – S_1 and T_1 – T_n transitions at a fixed wavelength; k_{ph} , k_q , k_{ch1} , k_{ch2} are, respectively, the phosphorescence rate constant, the effective T_n – T_1 transition rate constant, and the photoreduction rate constants for molecules in the first and higher triplet states, respectively.

We shall solve the system of equations (2)–(5) in the quasi-steady-state approximation in accordance with the time resolution capability of our experimental setup (described below). We shall introduce a variable which has the meaning of the total concentration of all the states of the initial form of the dye:

$$B = [S_0] + [S_1] + [T_1] + [T_n] . \quad (6)$$

The rate of change of this quantity is determined by summing the left- and right-hand parts of Eqns (2)–(5):

$$\frac{dB}{dt} = -k_{\text{ch1}}[T_1] - k_{\text{ch2}}[T_2] . \quad (7)$$

Since the effective rate constant of the dye photoreduction process is considerably less than the rates of the other photoprocesses occurring in the system, the variable B can be regarded as weakly time-dependent. We shall assume that the fast photophysical processes ensure that the distribution of the populations of the levels S_0 , S_1 , T_1 , T_n during the measurement time reaches a quasi-steady state, described by the system of equations

$$-I\varepsilon_1[S_0] + k_f[S_1] + k_{\text{ph}}[T_1] = 0 , \quad (8)$$

$$I\varepsilon_1[S_0] - (k_f + k_{\text{st}})[S_1] = 0 , \quad (9)$$

$$k_{\text{st}}[S_1] - (k_{\text{ph}} + I\varepsilon_2)[T_1] + k_q[T_n] = 0 , \quad (10)$$

$$-k_q[T_n] + I\varepsilon_2[T_1] = 0 . \quad (11)$$

It is assumed above that $k_{\text{ch2}} \ll k_q$, $k_{\text{ch1}} \ll I\varepsilon_2 + k_{\text{ph}}$. The system of equations (6), (8)–(11) makes it possible to express the variables $[S_0]$, $[S_1]$, $[T_1]$, $[T_n]$ in terms of the function B :

$$[S_0] = \frac{k_{\text{ph}}k_q(k_f + k_{\text{st}})}{(k_{\text{ph}} + k_{\text{st}})k_qI\varepsilon_1 + k_qk_{\text{ph}}(k_f + k_{\text{st}}) + I^2\varepsilon_1\varepsilon_2k_{\text{st}}} B , \quad (12)$$

$$[S_1] = \frac{k_{\text{ph}}k_qI\varepsilon_1}{(k_{\text{ph}} + k_{\text{st}})k_qI\varepsilon_1 + k_qk_{\text{ph}}(k_f + k_{\text{st}}) + I^2\varepsilon_1\varepsilon_2k_{\text{st}}} B , \quad (13)$$

$$[T_1] = \frac{k_qk_{\text{st}}I\varepsilon_1}{(k_{\text{ph}} + k_{\text{st}})k_qI\varepsilon_1 + k_qk_{\text{ph}}(k_f + k_{\text{st}}) + I^2\varepsilon_1\varepsilon_2k_{\text{st}}} B , \quad (14)$$

$$[T_n] = \frac{k_{\text{st}}I^2\varepsilon_1\varepsilon_2}{(k_{\text{ph}} + k_{\text{st}})k_qI\varepsilon_1 + k_qk_{\text{ph}}(k_f + k_{\text{st}}) + I^2\varepsilon_1\varepsilon_2k_{\text{st}}} B . \quad (15)$$

Eqn (7) has the following solution:

$$B = \exp \left[- \frac{\alpha(k_{\text{ch1}}k_{\text{q}} + k_{\text{ch2}}I\varepsilon_2)}{\alpha I\varepsilon_2 + k_{\text{q}}} (t + t') \right], \quad (16)$$

where t' is the time in which a quasi-steady state is established in the system;

$$\alpha = \left[1 + \frac{k_{\text{ph}}(I\varepsilon_1 + k_{\text{f}} + k_{\text{st}})}{k_{\text{st}}I\varepsilon_1} \right]^{-1}. \quad (17)$$

In estimating the error resulting from the use of the quasi-steady-state approximation, we shall use the residual vector [14] with the components:

$$\Delta_i = \frac{\partial f_i}{\partial B} \frac{dB}{dt} - \frac{df_i}{dt}, \quad (18)$$

where f_i is understood to represent the variables $[S_0]$, $[S_1]$, $[T_1]$, $[T_n]$, and the expressions df_i/dt and dB/dt are determined by the right-hand parts of Eqns (2)–(5) and (7) calculated at the point t' .

4. Experimental investigation of the photoreduction of eosin K in gelatin

The results of our modelling were utilised in an analysis of the experimental data on laser-induced reduction of eosin K in a gelatin matrix. The following reagents were used: photographic grade-A gelatin with pH = 5.5–6.8 and eosin K of the analytic grade. Samples, prepared by slow drying of an aqueous solution of the dye in gelatin on a glass substrate, were films 1–5 μm thick. The dye concentration in a film and the film thickness were selected to ensure readily detectable gradations of the minimum optical density, which changed during photolysis. When these conditions were obeyed, the necessary optimal dye concentration did not exceed 1%.

Since the photoreduced form of the dye did not absorb at the argon laser wavelength, the concentration of the initial form of the dye was monitored by measuring the transmission of the samples taking account of the Bouguer–Lambert–Beer law, known from experiments to be obeyed in our case.

Measurements of the transmission of our samples in the course of photoreduction were made by using the setup shown in Fig. 1. Radiation from an LGN-503 argon laser (1) was resolved by an Abbé prism (2) into a spectrum. An aperture (3) was used to separate a beam with the 514.5 nm wavelength from the spectrum. A beam-splitting plate (4) made it possible to employ a two-channel measuring system.

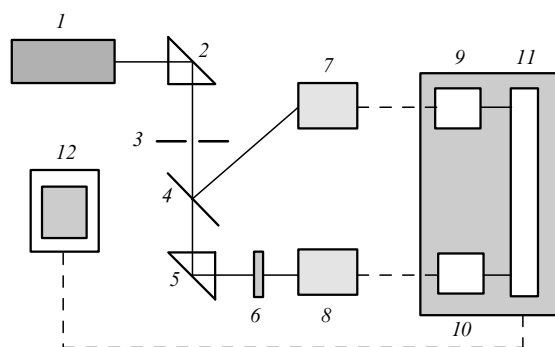


Figure 1. Schematic diagram of the experimental setup.

The working channel included a rotatable prism (5), a sample (6), a photodiode (8), and an analogue–digital converter (10), whereas the comparison channel contained a photodiode (7) and an analogue–digital converter (9). A controller unit (11) switched alternately between the channels and the information obtained from them was analysed on a computer (12). This setup made it possible to carry out measurements with a discretisation time 1 ms, followed by averaging of the results over 500 points.

The laser generated the transverse TEM_{00} mode with a distribution not more than 1.5 mm wide. The power of the laser radiation incident on the sample was varied in the range 3–200 mW by a set of neutral optical filters. The measurements were carried out at room temperature.

5. Comparison of the results of the model calculation with experimental data

It follows from formulas (12)–(15) that the concentrations $[S_0]$, $[S_1]$, $[T_1]$, $[T_n]$ were in the ratio $1 : 10^{-6} : 1 : 10^{-8}$, and the time t' was governed by the duration of the slowest photophysical process (phosphorescence) and was approximately 10^{-3} s. Therefore, the main part of the initial form of the dye exposed to the laser radiation field was in the ground singlet and first triplet states. It then follows from formulas (12), (14), and (16) that the time dependence of the optical density measured at the laser wavelength is a simple function:

$$D = \text{const} \exp(-kt). \quad (19)$$

The coefficient k is the effective rate constant of the loss of the initial form of the dye, dependent on the rates of the photophysical processes resulting in a redistribution of the populations between the excited states. When the triplet–triplet absorption is ignored ($\varepsilon_2 = 0$), the constant k in the argument of the exponential function in formula (16) becomes $k_{\text{ch1}}\alpha$ and the investigated scheme reduces to a three-level configuration.

An analysis of formula (16) predicts a complex functional dependence of the slope k of the straight line $\ln D(t)$ on the radiation intensity. If the molecules in the T_1 state participate in the chemical reaction, the saturation power is approximately 15 mW, determined by equating to unity the second term in the denominator of formula (17) [$I\varepsilon_1 \approx k_{\text{ph}}(1 + k_{\text{f}}/k_{\text{st}})$]. If the chemically active state of the dye is T_n , the saturation power increases by six orders of magnitude ($I\varepsilon_2 \approx k_{\text{q}}$). It follows that in the range of the output powers obtainable from the cw argon laser the dependence $k(P)$ is linear.

The functional dependences describing the effective rate of photoreduction of the dye molecules on the laser radiation power are quite different for the first and higher triplet states. This was used by us as the basis of a method for determination of the role of the various excited triplet states participating in the photochemical reaction.

The results of a calculation of the dependence of the argument k of the exponential function on the laser radiation power are presented in Fig. 2. We can see that in the four-level scheme the functional dependence of k on the laser power is linear in the range going beyond the limit typical of saturation in a three-level scheme. We can show that the slope of this dependence is governed by the ratio $k_{\text{ch2}}/k_{\text{q}}$.

Fig. 3 gives the experimental dependences of the optical density of our film samples on the duration of illumination with laser radiation of various powers. Throughout the inves-

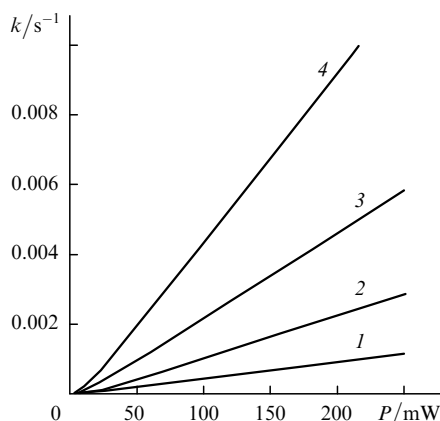


Figure 2. Dependences of the effective dye-photoreduction rate on the radiation power, calculated for $k_{\text{ch2}}/k_q = 2 \times 10^{-6}$ (1), 5×10^{-6} (2), 10^{-5} (3), and 5×10^{-5} (4).

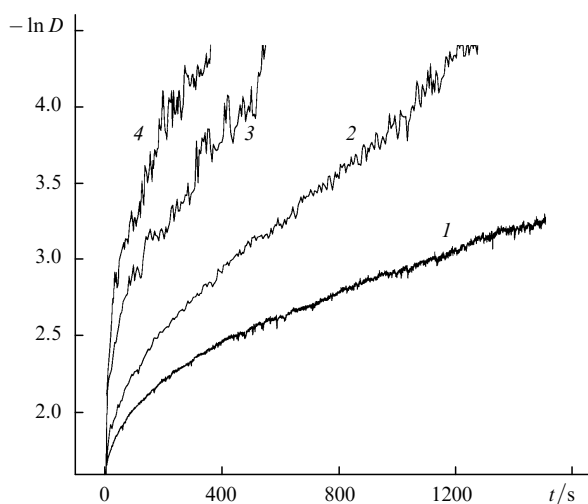


Figure 3. Experimental dependences of the optical density on the duration of illumination of eosin K films in gelatin, obtained for radiation powers 3.5 mW (1), 12 mW (2), 55 mW (3), and 130 mW (4).

tigated time interval (except for the initial part) the observed linear dependence, $-\ln D(t)$, is in agreement with our theoretical calculations. It follows from formula (16) that the exponential time dependence of the total relative concentration of the unmodified form B of the dye applies if the intensity remains constant with depth in a sample. A more complex functional form of the initial part of the $-\ln D(t)$ curve can result from changes in the intensity with depth because the condition of low optical density of the samples is not satisfied and also because of the influence of the intensity distribution in the transverse laser radiation mode.

Fig. 4 shows how the effective rate constant depends on the laser radiation power, as deduced from the experimental data (Fig. 3). A comparison of the experimental and theoretical results (Fig. 2) demonstrates that the linear nature of the dependence $k(P)$, observed at powers outside the range of saturation of the first triplet state, is a proof of the participation of higher triplet states in the photochemical reaction. The experimental results for eosin indicate that $k_{\text{ch2}}/k_q = (1.31 \pm 0.10) \times 10^{-6}$. According to formula (18), the modulus of the residual vector, which governs the error

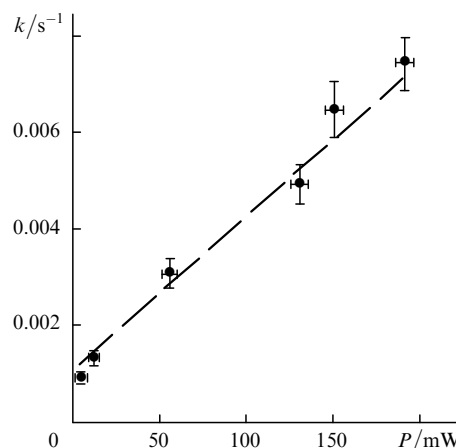


Figure 4. Dependence of the observed dye-photoreduction rate on the radiation power.

resulting from the use of the quasi-steady-state approximation, is no more than 10^{-6} s^{-1} or about 0.1%.

An estimate of the photoreduction rate constant of xanthene dyes in the specific case of erythrosin, considered in the quasi-monomolecular reaction approximation, is 10^5 s^{-1} [2]. Since, in the course of deactivation of the excited T_n states, the internal crossing predominates over the inter-system crossing ($T_n - S_n$) and over the fluorescence, its rate constant lies in the range $10^{10} - 10^{12} \text{ s}^{-1}$ [15]. Consequently, the range of the values of the ratio k_{ch2}/k_q is $10^{-5} - 10^{-7} \text{ s}^{-1}$, which is not in conflict with the experimental results.

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