

# Metalloporphyrin – Organic Polymer Photosensitive Compositions: Experimental Studies and Computer Simulation of Photoprocesses

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A high-performance photochromogenic destruction reaction of Zn tetra (4-tert-butylbenzo) porphine molecules in polyvinylbutyral polymer matrix at room temperature is reported. The dependence of porphyrin photobleaching vs. excitation power density has been found to be linear and points to a one-photon reaction type. The influence of pyridine and ethyl iodide additions and of molecular oxygen on the pigment decomposition rate has been investigated. It is assumed that most probably the destruction process is due to the reaction of porphyrin molecules in the excited triplet state  $T_1$  with light-generated free radicals, which has been confirmed by the results of computer simulations of the photoprocesses studied. Photosensitivity of the composition has been estimated to be  $S = 0.4 \cdot 10^3 \text{ cm}^2/\text{J}$ . The medium is proposed for using as a photosensitive substance.

**Keywords:** porphyrin metallocomplex, photodestruction, free radical, photosensitive substance, optical data recording.

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## 1. INTRODUCTION

The choice of an appropriate photosensitive material with definite characteristics is a key problem of optical data recording. Many modern optical data recording methods, e.g., wavelength-selected hole burning [1, 2], holographic recording [3], CD-R data recording, etc., use photosensitive media containing an organic dye as a main component. This is why searching for ways of increasing phototransformation efficiency for various dyes as well as using them in new high-performance photoreactions is seen to be important.

Until recently, free base porphyrins were considered the most promising compounds of the porphyrinic pigment variety for the purposes of optical recording. The commonly known reason is the efficient photoinduced NH rearrangement in the macrocycle center [4], resulting in noticeable spectral changes of newly produced NH isomers, that is favorable for using the phenomenon in optical data recording [2]. As far as metalloporphyrins are concerned, the use of metallophthalocyanines and metallonaphthalocyanines as IR irradiation-sensitive ablation recording layers is known [5]. Photochemical reaction with the participation of metalloporphyrins, e.g., a Zn tetrabenzporphyrin (ZnTBP) derivative and Zn tetraphenylporphyrin (ZnTPP), as tetrapyrrolic electron donors in polymer matrices containing halomethanes, aromatic cyanides and some other additives as specific electron acceptors were investigated [6-11]. In the reactions, electron transfer takes place from the  $T_n$  state of the donor populated via two-photon excitation to the acceptor. As a result, a porphyrin monocation not absorbing the exciting light is formed that leads to the appearance of a spectral hole in the 0-0 band of  $S_1 \leftarrow S_0$  transition. Irreversible photochemical reactions of porphyrin metallocomplexes in halomethanes solutions are reported in [12,13]. In the system, an electron is transferred from the  $S_1$  state of the porphyrin to the  $\text{CCl}_4$  molecule, that results in the radical-cation pigment formation and, consequently, to significant spectral changes. In addition, the

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interaction of the metalloporphyrin with reactive products of halomethane photodissociation takes place followed by destruction of the former. A photochromic thermal reversible reaction of a ZnTBP derivative in polymethylmethacrylate containing a small amount of acceptor molecules has been reported in [14]. Though a similar kind of electron transfer followed by ZnTBP radical-cation formation takes place, the photoreaction is asserted to be of the one-photon type, in contrast to findings reported in [6-11]. In summary, all of the findings reported above prove the diversity of pathways of photochemical reactions which metalloporphyrins are involved in. Therefore, the search for new conditions which provide higher rates of photochemical reactions seems to be of considerable importance.

In this paper, investigations of phototransformations of ZnTBP and Zn tetra(4-*tert*-butylbenzo)porphyrin (ZnTBP<sup>tBu</sup>) in a polyvinylbutyral (PVB) polymer matrix at room and liquid nitrogen temperatures are considered. In addition, computer simulations have been implemented to strengthen the interpretation of experimental findings. Based on model data, a verification of working hypotheses concerning the reaction mechanism has been made. Although the systems explored are specific, the suggested phototransformation mechanism is believed to bear certain universal features, i.e., it can be extended to some other porphyrin - organic host combinations. Also, the aim of the study has included exploration of the possibility of utilizing a ZnTBP<sup>tBu</sup> - PVB composition as a photosensitive medium for optical data recording. Some results were reported briefly in [15,16].

## 2. EXPERIMENTAL

Porphyrin zinc complexes, ZnTBP and ZnTBP<sup>tBu</sup>, were synthesized according to [17,18], respectively. The structure of ZnTBP is shown in Fig. 1. Polymer films were prepared by mixing ethanol solutions of PVB monodisperse powder and metalloporphyrin and pouring the mixed solution onto a glass or quartz substrate surface, followed by drying of a 1mm-thick layer for 24 hours at 20°C. Optical density of the prepared films did not exceed 0.2 for the S<sub>1</sub>←S<sub>0</sub> absorption band.

Evidence of photoinduced transformations in porphyrin-polymer systems was obtained through a time-dependent fluorescence intensity decrease measured at 630 nm upon photoexcitation of a specific power density and wavelength range. A 500-W mercury lamp was used as a light source. The 350-450 and 570-640 nm spectral ranges to excite the Soret- and S<sub>1</sub>←S<sub>0</sub>-bands, respectively, were selected by a combination of color and neutral filters providing excitation power density control within 0-1.6 mW/cm<sup>2</sup>.

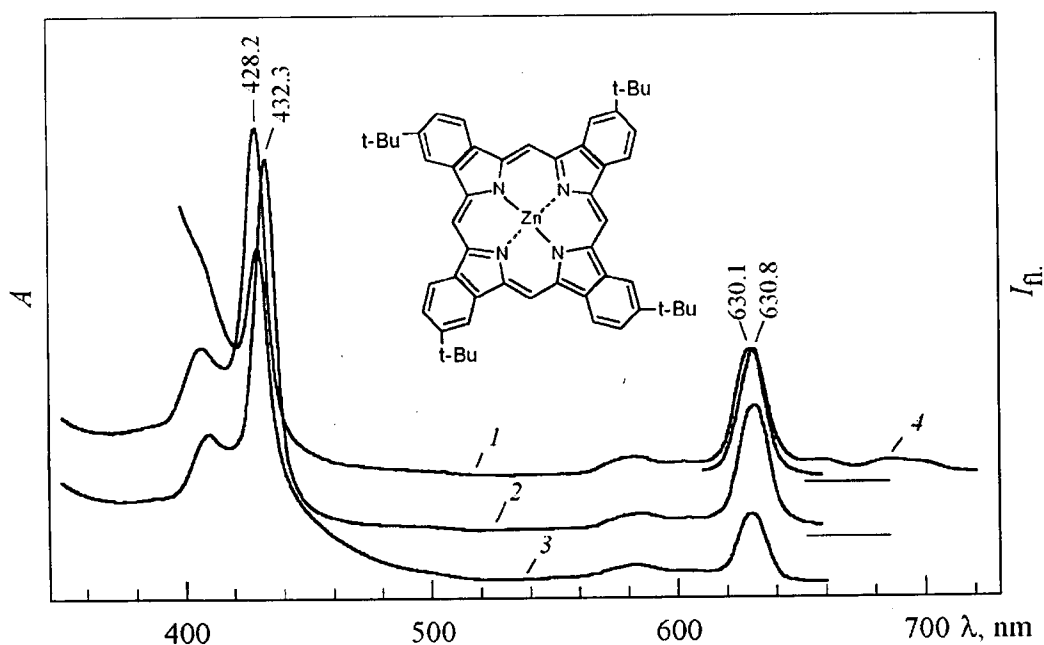


Fig. 1. ZnTBP<sup>tBu</sup>: absorption spectra in PVB (1), PVB+Pyr (2), PVB+C<sub>2</sub>H<sub>5</sub>I (3) films and fluorescence spectrum in PVB film (4) at 300 K. Structure of ZnTBP<sup>tBu</sup>.

Computer simulation of porphyrin photodestruction kinetics was carried out on an IBM PC compatible machine by numerical integration of an ordinary differential equation system (ODE), i.e., rate equations, describing electronic level population of reactive compounds. The backward method of LSODE solver [19] was used. Absolute and relative accuracies were controlled to be typically  $10^{-9}$  and  $10^{-7}$ , respectively. The choice of appropriate solutions was based on the maximum likelihood between experimental and simulated curve manifolds. Such an approach was successfully applied by the authors in [20, 21], assisting in a deeper understanding of the processes investigated.

### 3. RESULTS AND DISCUSSION

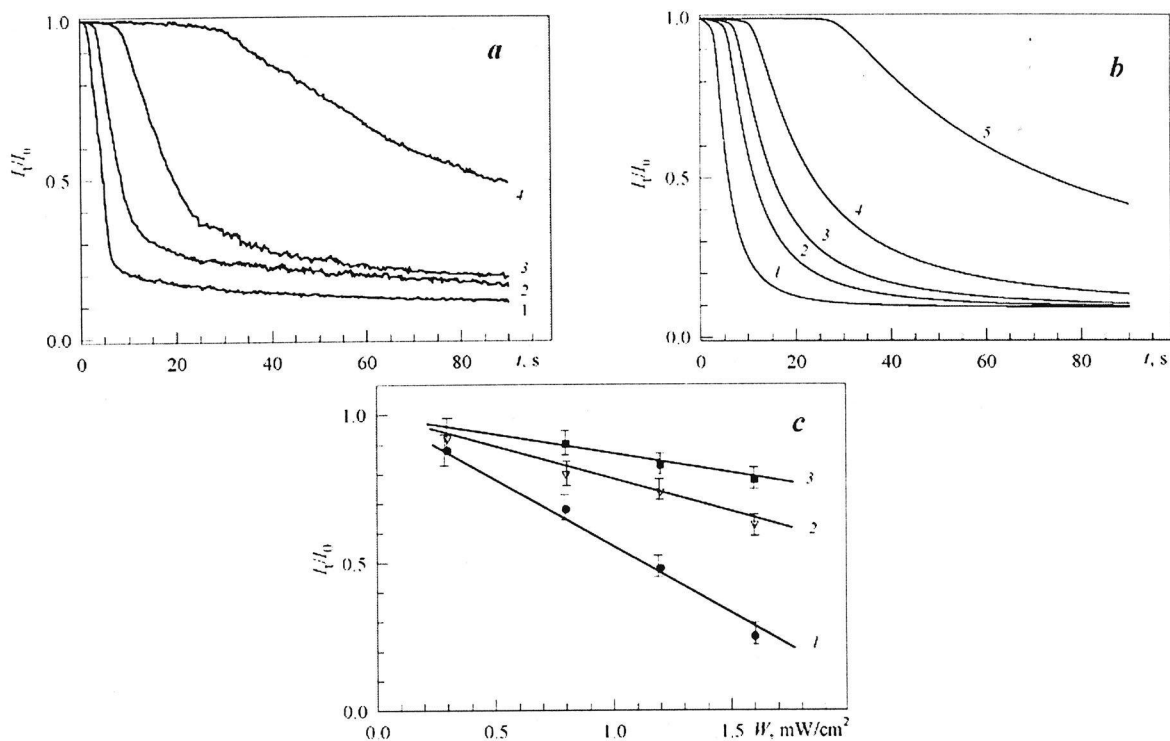
The investigated systems have typical absorption and fluorescence spectra presented in Fig. 1. Photochromogenic (irreversible) transformations in metalloporphyrin spectra were observed with UV excitation. Similar effects were seen with excitation in the red (570–640 nm) region, but the efficiency was lower by two orders of magnitude than in the UV. The presence of a small amount of pyridine (Pyr) in the initial mixture ZnTBP/PVB speeded up the photochromogenic reaction, whereas the ethyl iodide ( $C_2H_5I$ ) admixture inhibited the reaction rate significantly. It was noticed also that addition of bulky butyl groups to the ZnTBP molecule increased the rate. As an example, relative fluorescence intensities of ZnTBP<sup>BU</sup>/PVB + Pyr at 630 nm vs. the time at which the 350–450 nm excitation of variable power density was applied are shown in Fig. 2a. Almost all the curves explicitly exhibit three parts. In the first one, a negligible photodegradation of the sample is seen. Subsequently, the fluorescence drops drastically, as is reflected in the second part, after which tailing down of emission to a steady state is observed.

The efficiency of photochemical transformations was estimated for the second part of the kinetic curves using the tangent slope method [22]. In so doing, for each curve the relative fluorescence intensity of ZnTBP<sup>BU</sup> after irradiating the sample for  $\Delta t = 5$  s was determined, and thereby the dependence was obtained of the ZnTBP<sup>BU</sup> transformation rate on power density for samples differing in chemical composition. The plots are shown in Fig. 2c to be quite linear. According to [23], a linear dependence of photodestruction rate vs. photoexcitation power density indicates that molecules of the medium are involved in the process.

Since no new absorption bands, in particular, of radical-cations or -anions, in the visible and near UV region were detected after the process, one may state that irreversible destruction of the porphyrin to its colorless and reactionless photoproducts takes place. For example, as was shown in [7], in a medium favorable for *meso*-substituted Mg TBP ionic species formation, an optical density decrease of the  $S_1 \leftarrow S_0$  absorption band by  $\Delta D \approx 0.3$  gives rise to the appearance of the absorption band of the pigment radical-cation ( $D \approx 0.1-0.15$  at  $\lambda \approx 440$  nm).

Our experimental data allow us to conclude that ZnTBP<sup>BU</sup> molecules are transformed under the influence of the matrix radicals  $R^\bullet$ . One of free radical sources in the system may be the polymer matrix molecules themselves or polymerization initiator vestiges undergoing photolysis upon UV illumination. In addition, the presence of ethanol increases the number of  $R^\bullet$  since it is effectively involved in the chain of subsequent radical reactions. Due to local diffusion processes and/or chain reactions, the radicals can interact with the porphyrin by means of formation of labile porphyrin-radical pairs, thus destroying the porphyrin molecules. Indirect proof of the radical mechanism of ZnTBP<sup>BU</sup> photodestruction is variation of the reaction rate on incorporation of Pyr or  $C_2H_5I$  into the matrix. Addition of Pyr to the polymerization mixture leads to extra coordination of the Zn atom, clearly seen from Fig. 1 (curve 2) as a bathochromic shift of the absorption band. Most likely, the pyridine extra ligands, being in the vicinity of their porphyrin counterparts and being involved concurrently in radical reaction chains, promote the destruction (see Fig. 2c, curve 1). As was shown in [24], upon photoexcitation of ZnTPP coordinated with Pyr, the formation of a ZnTPP<sup>+</sup>-Pyr<sup>-</sup> complex of increased reaction ability takes place presumably via the  $T_1$  level. As regards  $C_2H_5I$ , its molecules are photolytically unstable and can generate mobile radicals  $I^\bullet$ , which can react with the initial polymer mixture radicals. Reacting with the polymer radicals, the radicals  $I^\bullet$  interrupt the radical reaction chains, thus inhibiting the photodestruction of the porphyrin (Fig. 2c, curve 3). At 77 K, when all local translational motions in the matrix are frozen, the photodestruction of the porphyrin stops, regardless of the presence of Pyr or  $C_2H_5I$ .

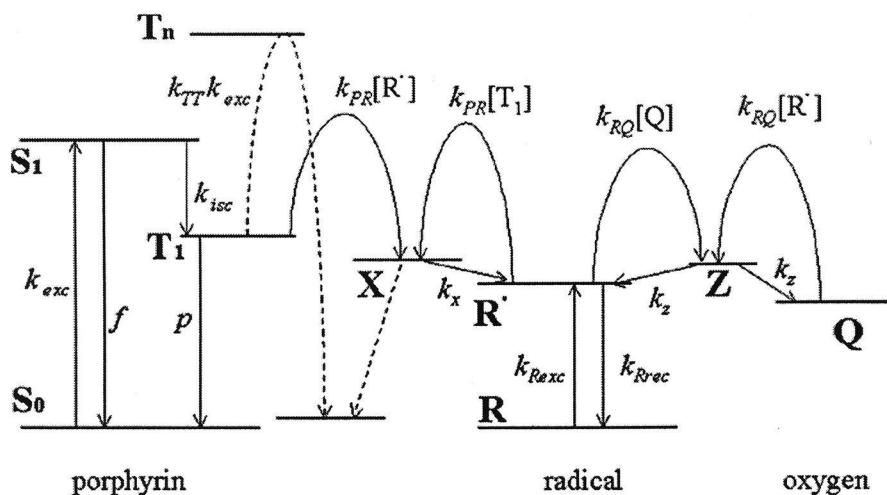
Investigation of the influence of molecular oxygen also gives evidence in favor of the radical mechanism of the porphyrin decomposition. The porphyrin photodestruction rate of the vacuum-dried and vacuum-kept ( $10^{-4}$  Torr) sample significantly exceeds that of the vacuum-dried sample kept in ambient air. This can be explained by the inhibiting effect of the interaction of the triplet (biradical) oxygen molecules with reactive radicals  $R^\bullet$ , leading either to regeneration of the latter or to ROO peroxide products formation. It is clear that, if the principal



**Fig. 2.** Photobleaching of ZnTBP<sup>IBu</sup> monitored via fluorescence intensity. a) Normalized experimental curves vs. time at excitation power densities  $W_{exc} = 1.6$  (1); 1.2 (2); 0.8 (3); 0.3 (4) mW/cm<sup>2</sup> in PVB+Pyr; b) normalized simulated curves vs. time at excitation power densities  $W_{sim} = 3.0$  (1); 1.6 (2); 1.2 (3); 0.8 (4); 0.3 (5) a.u.; c) at various excitation power densities after 5 second exposition time (see text) in PVB+Pyr (1), PVB (2), PVB+C<sub>2</sub>H<sub>5</sub>I (3) films.

mechanism of the photodestruction were connected with the porphyrin-oxygen interaction, the rates of samples kept in ambient air would be higher.

The fact that no porphyrin photodestruction was observed in radical-free medium, as the 5:5:2 (by volume) mixture of diethyl ether, petroleum ether and isopropyl alcohol both at room temperature and at 77 K: i) proves the suggested mechanism of the photodestruction, and ii) does not contradict the conclusion that molecular oxygen does not interact directly with the porphyrins in the reactions.



**Fig. 3.** Three-component (ZnTBP<sup>IBu</sup>, radical, oxygen) energy level scheme and proposed pathways of photochemical processes.

To verify the suggested mechanism of the photoprocesses, computer simulations of the fluorescence curves were carried out. The basic model, schematically shown in Fig. 3, included porphyrin, radical and oxygen electronic levels. In addition, pair static porphyrin–radical and radical–oxygen interactions were taken into account. The model was described by the following ODE set:

$$\left\{ \begin{array}{l} \frac{d[S_0]}{dt} + k_{exc} \cdot [S_0] - f \cdot [S_1] - p \cdot [T_1] = 0 \\ \frac{d[S_1]}{dt} - k_{exc} \cdot [S_0] + (f + k_{isc}) \cdot [S_1] = 0 \\ \frac{d[T_1]}{dt} - k_{isc} \cdot [S_1] + (p + k_{PR} \cdot [R^*]) \cdot [T_1] = 0 \\ \frac{d[R]}{dt} + k_{Rexc} \cdot [R] - k_{Rrec} \cdot [R^*] = 0 \\ \frac{d[R^*]}{dt} - k_{Rexc} \cdot [R] - k_X \cdot [X] - k_Z \cdot [Z] + (k_{PR} \cdot [T_1] + k_{RQ} \cdot [Q] + k_{Rrec}) \cdot [R^*] = 0 \\ \frac{d[X]}{dt} - k_{PR} \cdot [T_1] \cdot [R^*] + k_X \cdot [X] = 0 \\ \frac{d[Z_R]}{dt} - k_{RQ} \cdot [R^*] \cdot [Q] + k_Z \cdot [Z_R] = 0 \\ \frac{d[Q]}{dt} + k_{RQ} \cdot [R^*] \cdot [Q] - k_Z \cdot [Z] = 0 \\ \frac{d[Z_Q]}{dt} - k_{RQ} \cdot [R^*] \cdot [Q] + k_Z \cdot [Z_Q] = 0 \end{array} \right.$$

Initial conditions are as follows  $[S_0]_{t=0} = N_1$ ,  $[R]_{t=0} = N_2$ ,  $[Q]_{t=0} = N_3$  and  $[S_1]_{t=0} = [T_1]_{t=0} = [R^*]_{t=0} = [Z_R]_{t=0} = [Z_Q]_{t=0} = [X]_{t=0} = 0$ . In the system,  $S_0$ ,  $S_1$ ,  $T_1$  are the porphyrin's ground-, lowest singlet- and triplet levels, respectively; and  $k_{exc}$ ,  $f$ ,  $p$ ,  $k_{isc}$ ,  $k_{PR}$  are the rate constants of porphyrin photoexcitation, fluorescence, phosphorescence, intersystem crossing and porphyrin–radical interaction factor, respectively.  $R$  and  $R^*$  are the radical generator and radical reaction levels, respectively; and  $k_{Rexc}$ ,  $k_{Rrec}$ ,  $k_{RQ}$  are the rate constants of radical photoexcitation and recombination and the radical–oxygen interaction factor, respectively.  $Q$  and  $X$  are the oxygen and porphyrin–radical levels, respectively. The  $Z_R$  and  $Z_Q$  levels are components of the radical peroxide level  $Z$ . Finally,  $k_Z$  and  $k_X$  are the rate constants of  $X$  and  $Z$  level decays, respectively.

The selection of the model was grounded in preliminary simulations, which showed that either two-component—i.e., porphyrin–radical—or single-component (porphyrin) systems could not explain the characteristic delay of the photodestruction at the process beginning (see Fig. 2a). As followed from the calculations, such a stepwise shape (hump) of the curves could be observed at a non-monotone (abrupt) behavior of the porphyrin–radical interaction rate constant and/or at avalanche-like populating of the  $T_1$  level of the porphyrin. Moreover, correlations were found between the model parameters and inflection of the curve.

The interaction rate constant behavior is believed to be the main reason. Thus, in the model, the porphyrin–radical interaction brings about the destruction effect, whereas the radical–oxygen interaction modulates it. According to the proposed scheme, the metalloporphyrin—being in the  $T_1$  state—interacts with  $R^*$  followed by the porphyrin–radical pair formation (depicted as the  $X$  level) resulting in the decomposition of the former. Concurrently,  $R^*$  interacts with oxygen, generating metastable peroxide ROO ( $Z$  level). At the early stage of the process, which corresponds to the first part of the curves in Fig. 2a, the second type of interaction dominates in the system, thus inhibiting the decomposition. When oxygen is exhausted, the destruction process is launched. Although the model does not explicitly describe the diffusion process in the matrix, it takes it into account generally via the  $k_{PR}$  and  $k_{RQ}$  factors. The influence of activating and inhibiting additives like Pyr and  $C_2H_5I$  can also be controlled by these factors. Thus, they are generalized and, therefore, rather arbitrary parameters.

Simulation has assisted in investigation of the relationship between the rate constants and the shape of the curves. Since variation of the whole parameter set would be a rather time-consuming procedure and, thus, quite problematic, the following solution based on parsimony principle has been chosen. Known from the literature [25], porphyrin parameters such as the triplet formation quantum yield and values for  $f$  and  $p$  have been fixed to

be 0.9,  $10^8$  and  $10^3$  s<sup>-1</sup>, respectively. Some constants like  $k_{exc}$  and  $k_{Rexc}$  have been assumed to be in a certain relationship, for example,  $k_{exc}/k_{Rexc} \approx 30-100$ . Constraints like  $p \gg k_{exc} > k_{Rexc}$  and  $k_X > 10^{-2}$  s<sup>-1</sup> have been imposed. In addition, the initial concentration of porphyrin  $[S_0]$  has been fixed and the  $k_2$  values have been set to be equal and zero. The following parameters have been varied: i) initial concentration of [R] and [Q], ii)  $k_{exc}$  and  $k_{Rexc}$ , iii)  $k_R$  and  $k_{RQ}$ , and iv)  $k_X$  and  $k_{Rrec}$ .

The maximum likelihood of the juxtaposed experimental and simulated curves has been reached at  $[S_0] < [R]$  and  $[Q] \leq [R]$ . Typically, radical and oxygen concentrations should have exceeded those of the porphyrin up to 1.5–5 and 1–3 times, respectively. It has turned out that simulated curves have been more sensitive to variation of the concentrations rather than to that of the interaction factors. The factors have controlled the curves' smoothness. Increase of the rate constant  $p$ , which would simulate the triplet quenching in the presence of C<sub>2</sub>H<sub>5</sub>I, has shortened the duration of the first part of the curves. At the same time, according to the calculations, the effect of C<sub>2</sub>H<sub>5</sub>I presence cannot be totally explained by its quenching of the porphyrin triplets. The initial and second parts of the curves have been determined, in the first turn, by the concentration ratios. Yet, the steepness of their second parts has been controlled by the saturation factor  $k_{Rexc}/k_{Rrec}$ . Finally, the tailing of the third part has been solely determined by the porphyrin–radical pair decomposition rate constant  $k_X$ . The successful simulated curves have been obtained at the following parameters:  $k_{exc} \approx 30-100 \cdot k_{Rexc}$ ,  $k_{exc}/p \approx 0.01-0.1$ ,  $k_{PR} \approx k_{RQ} \approx 10^{-6}-10^{-3}$  s<sup>-1</sup>,  $k_{Rrec} \approx 10^{-1}-10^{-2}$  s<sup>-1</sup>,  $k_X \geq 10^{-3}$  s<sup>-1</sup>.

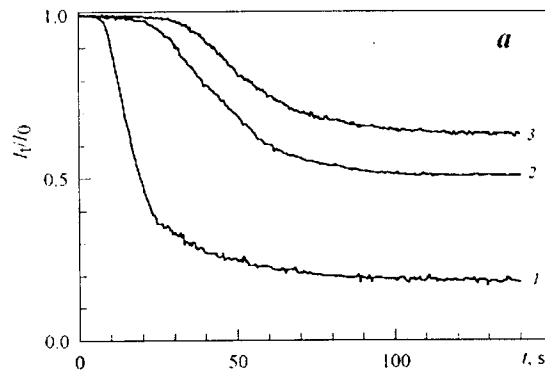
The simulated curves manifest at various excitation power densities, shown in Fig. 2b, demonstrate a good similitude with those depicted in Fig. 2a. An analogous likeness is seen between the curves shown in Figs. 4a (effect of drying on the fluorescence intensity) and 4b. The latter result has been obtained by mere variation of [R] concentration. Such a similarity points to a quite adequate simulation of the real processes by the proposed model. It has to be emphasized that the simulations can consistently explain all three parts of the observed curves.

At the same time some minor disagreements have been revealed between experimental and model curves, pointing out that more complex photochemistry may occur in the investigated systems. Some reasons can be suggested. First, the photobleaching of the porphyrin can occur without participation of either radical or oxygen, i.e., owing to two-photon absorption via the T<sub>1</sub> state [6-11]. Such a situation has also been simulated by variation of the factor  $k_{TT}$ . The process is depicted by a dashed arc in Fig. 3. Second, the question of what excited electronic state the photodestruction take place in has not been finally answered. Moreover, draft simulations have displayed a possibility of the S<sub>1</sub> level being involved in the interaction. Third, the proposed scheme is obviously not unique. In principle, in the framework of the three-component system there can be other energy levels and pathways, which can result in successful simulations. In particular, the fact that the third part of the photodestruction curve (Fig. 2a) tends to the non-zero value can be explained by the heterogeneity of the system studied: a fraction of porphyrin molecules may be situated under conditions hindering their interaction with radicals. This fraction increases with drying time (see below).

Our findings can have a practical use in development of low-cost silver-free photosensitive materials [15, 16]. Photosensitivity of photochemically active dyes, including, for example, spiropyranes, in polymers and other media during primary photoprocesses is known to be only 10<sup>2</sup> cm<sup>2</sup>/J [26]. A greater sensitivity up to 10<sup>3</sup> cm<sup>2</sup>/J has been achieved for organic photoresists and photopolymerized layers [26]. However, they require additional chemical treatments of the composite material.

Photosensitivity  $S$  of the ZnTBP<sup>IBU</sup>/PVB + Pyr system has been estimated based on the experimental data. The criterion of photosensitivity has been the light exposition  $W \cdot t$  required to decrease optical density (in our case, luminescence intensity) by 20 percent, i.e.,  $S_{0.2} = 1/(W \cdot t_{0.2})$ . For the samples used, it meant the Soret band decrease on  $\Delta D \approx 0.1$  during the exposition time  $t_{0.2}$ , which has been quite enough for detection of the effect. The  $S_{0.2}$  value has been found to be (0.3–0.4) · 10<sup>3</sup> cm<sup>2</sup>/J for the curves shown in Fig. 2a and is approximately one order greater than those for organic dyes [26].

The effect of increasing drying time of pyridine-containing samples is shown in Fig. 4a. As the drying time increases, the signal-to-noise ratio and the destruction rate are decreased simultaneously with extension of the initial part of the curve that indicates the lowering of photosensitivity of the samples. Obviously, the tailing effect is due to evaporation of ethanol together with Pyr and C<sub>2</sub>H<sub>5</sub>I out of the films, along with the increase in matrix rigidity affecting local mobility of radicals. Fortunately, such aging effects worsening of recording ability are negligible for newly prepared samples. Thus the system may be used as irreversible material, for instance, for image recording and storage, requiring no subsequent chemical treatment except drying in the dark at room temperature in ambient air.



**Fig. 4.** Photobleaching of ZnTBP<sup>IBu</sup> in PVB+Pyr at 350–450 nm excitation ( $W_{\text{exc}} = 0.8 \text{ mW/cm}^2$ ) monitored via fluorescence intensity.

a) normalized experimental curves vs. time for 1- (1), 45- (2) and 90-days (3) drying time; b) normalized simulated curves vs. time at the radical concentration  $[R^{\cdot}]/[R^{\cdot}]_0$  ratios: 1.00 (1); 0.89 (2); 0.83 (3).

No photodestruction has been found at read-out when a couple of orders less intense white light was applied. At low pigment concentrations, when optical density of the Soret band is  $D < 0.1$ , recorded images are invisible, but due to the relatively high fluorescence quantum yield  $\phi_f \approx 0.1-0.2$  [27] they can be easily read-out via UV excitation. Spectral sensitivity of the material is determined by ZnTBP absorption and thus has a blue maximum. Owing to homogeneity of the composition, spatial resolution is limited by diffraction effects. It should be noted that the recorded information can be stored for years.

#### 4. CONCLUSION

A highly efficient photodestruction reaction of a ZnTBP derivative in PVB matrix, providing a basis for the development of a photosensitive medium, has been found and investigated. Computer simulations have proven the appropriateness of the three-component scheme for description of the photobleaching process. We believe that this photosensitive material may be utilized in image recording especially in silver-free photography and image visualization under UV excitation.

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