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Kinetics of fast reactions of triplet states and radicals under photolysis of 4,4´-dimethylbenzophenone in the presence of 4-halophenols in micellar solutions of sodium dodecyl sulfate in magnetic field

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Quenching kinetics of the 4,4´-dimethylbenzophenone triplet state with *para*-substituted phenol derivatives RC_6H_4OH (R = H, F, Cl, Br, I) was studied by nanosecond laser photolysis in aqueous micellar solutions of sodium dodecyl sulfate. The kinetic data were processed in the framework of a model with the Poisson distribution of phenols between micelles. The partition constants of RC_6H_4OH between the aqueous and micellar phases and the rate constants of their escape from a micelle and quenching of the 4,4´-dimethylbenzophenone triplet state with phenols in micelles were obtained. The quenching proceeds with high rate constants through hydrogen atom transfer to form the ketyl and phenoxyl radicals (no radicals are formed in the case of 4-iodophenol), which then recombine in a micelle or escape into the outer aqueous volume. The application of an external magnetic field retards radical pair recombination in a micelle and increases the fraction of radicals escaped into the aqueous phase. The quantum yield of radical pairs decreases 2.5-fold, and the rate of their recombination in micelles increases 2.5-fold on going from 4-chloro- to 4-bromophenol. This is caused by the acceleration of triplet radical pair recombination in the solvent cage.

Key words: 4,4´-dimethylbenzophenone, 4-halophenol, laser photolysis, triplet states, hydrogen atom transfer, radical recombination, heavy atom effect, magnetic effect.

Researchers are interested in the kinetics of fast photoinduced reactions in systems containing carbonyl and phenol compounds in micellar solutions due to pronounced magnetic and spin effects for the recombination of triplet radical pairs (RPs) formed in these reactions.[1—15] Hydrophobic substituted phenols almost completely localized in the micellar phase were predominantly used in earlier studied systems. Neither the kinetics of primary processes of quenching of triplet states of carbonyl compound with phenols and RP formation, nor the kinetic behavior of RPs at different phenol concentrations in micellar solutions were studied. Several kinetic regularities observed for RP recombination in micelles, in particular, internal heavy atom effect, assume that the corresponding effect can appear during the primary step.[3,5—10] The effect of a heavy atom on the primary step of radical formation in carbonyl—phenol systems was repeatedly observed in homogeneous solutions. This effect depends on the parameters of the medium.[16—18] It is of interest to study the kinetics of all the processes of radical formation and recombination during photosensitized oxidation of phenols in micellar solutions. A study of the quenching kinetics of the triplet state of a photosensitizer localized in the micellar phase by molecules of hydrophilic phenols, which are distributed between the aqueous and micellar phases, also provides information on the partition constants.[19] The kinetics of fast processes during photooxidation of water-soluble halosubstituted phenols is also worthy of attention because of the problem of industrial sewage decontamination.

In this work, nanosecond laser photolysis was used to study the kinetics of quenching of the triplet state of 4,4´-dimethylbenzophenone (DB) with *para*-substituted phenols RC_6H_4OH (R = H, F, Cl, Br, I) in aqueous micellar solutions of sodium dodecyl sulfate (SDS). The kinetic data were processed by the global analysis method in the framework of a model with the Poisson distribution of RC_6H_4OH between micelles. The partition constants of RC_6H_4OH between the aqueous micellar phases and the rate constants of RC_6H_4OH escape from a micelle and quenching of the triplet state ^{3}DB by phenols in micelles were determined. The decay kinetics of RPs formed due to quenching and the external magnetic field effect were obtained. The quantum yields of radical recombina-

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tion and the rate constants of RP recombination in micelles and radical escape from a micelle were measured. The heavy atom effect on the kinetics of RP recombination in micelles was found and compared with a similar influence on their quantum yield.

Experimental

Absorption spectra and the kinetics of decay and formation of intermediates were recorded with a nanosecond laser technique.[1,18] A PRA LN 1000 nitrogen laser was used as the excitation source (pulse duration 1 ns, radiation wavelength 337 nm) operating in a frequency mode of 10 Hz. Kinetic curves were scanned and averaged over 16—128 laser pulses using a Biomation 6500 high-performance analog-to-digital converter (USA) connected with a personal computer based on a Pentium processor (100 MHz). Each kinetic curve contained 1024 points, the average distance between which ranged from 2 to 100 ns, depending on the process duration. The data presented in the work are averaged values obtained by processing of at least ten kinetic curves under the indicated conditions. Dissolved oxygen was removed by purging with argon for 20 min. All measurements were carried out in a quartz cell with an optical path length of 8 mm at 20 °C. In experiments with magnetic field, the cell was placed between the poles of a permanent magnet (magnetic field intensity $B = 0.2$ T).

Phenols (Aldrich) were purified by sublimation *in vacuo*; DB and SDS were recrystallized from ethanol. Distilled water was used as solvent.

Results and Discussion

Decay kinetics of intermediates of photolysis of 4,4´-dimethylbenzophenone in aqueous micellar solutions of SDS in the absence of phenols. Pulse photolysis of aqueous solutions of DB (0.002 mol L^{-1}) in the presence of SDS (0.2 mol L^{-1}) produces (during a laser pulse) a ^{3}DB state characterized by the known absorption spectrum with a maximum at ~535 nm (Fig. 1, curve *1*).[9,20] After ^{3}DB disappeared ~4 μs after laser pulse, the absorption with a maximum at ~555 nm (see Fig. 1, curve *4*) of a longer-lived intermediate product, ketyl radical DBH$^•$, is observed.[9,20] The absorbance (*i.e.*, observed amount of relatively long-lived radicals DBH$^•$) increases substantially when an external magnetic field is applied (*cf.* intensities of absorbance at 530 nm detected 4 μs after laser pulse in the absence and presence of the external magnetic field in kinetic curves *2* and *1*, respectively (Fig. 2)). The triplet states of benzophenone and its derivatives are known[21—24] to react with SDS molecules in micelles to form triplet RPs, including the ketyl radical and detergent radical. Then (due to a high local concentration), the radicals recombine rapidly in micelles or escape into the outer volume of the aqueous phase, where their recombination is much slower. The external magnetic field application retards recombination and increases the concentration of relatively long-lived ketyl radicals, which escaped into the volume. The introduction of oxygen into solutions accelerates the decay of ^{3}DB and DBH$^•$ (see Fig. 2). The decay kinetics of intermediates in air-saturated solutions is described, regardless of the observation wavelength, by a monoexponential law with a rate constant of $1.5 \cdot 10^6$ s^{-1}. In deaerated solutions, the monoexponential decay of the induced absorbance is observed only at $\lambda \geq 630$ nm, where virtually only ^{3}DB absorbs (see Fig. 1). The decay rate constant of the ^{3}DB state in micellar solutions of SDS is ~$8 \cdot 10^5$ s^{-1}, which is much lower than a similar value for unsubstituted benzophenone ($3.5 \cdot 10^6$ s^{-1}).[23,24] This difference is a consequence, most likely, of a less pronounced

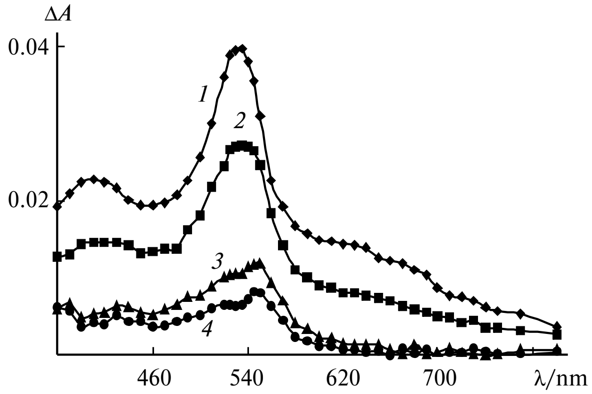

Fig. 1. Differential absorption spectra of intermediates obtained upon laser photolysis of deaerated aqueous solutions of DB (0.002 mol L^{-1}) in the presence of SDS (0.2 mol L^{-1}) 0.1 (*1*), 0.7 (*2*), 2.5 (*3*), and 4 μs (*4*) after laser pulse in a magnetic field with $B = 0.2$ T.

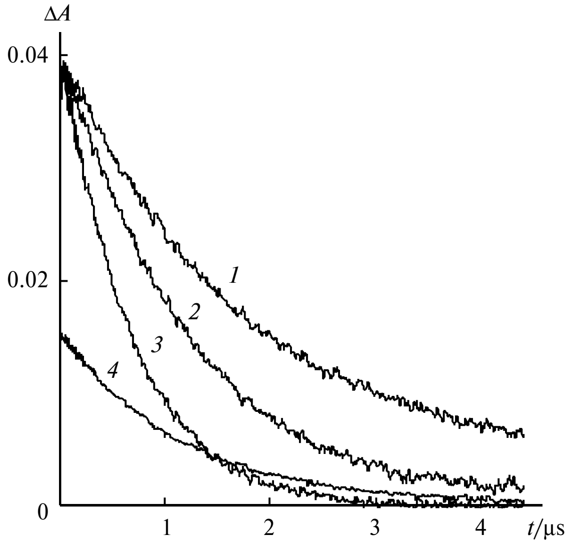

Fig. 2. Decay kinetics of intermediates absorbing at λ = 530 (*1*—*3*) and 630 nm (*4*) obtained upon laser photolysis of aqueous solutions of DB (0.002 mol L^{-1}) containing SDS (0.2 mol L^{-1}) in the absence (*1*, *2*, *4*) and presence of air (*3*) without magnetic field (*2*, *3*) and in a magnetic field with $B = 0.2$ T (*1*, *4*).

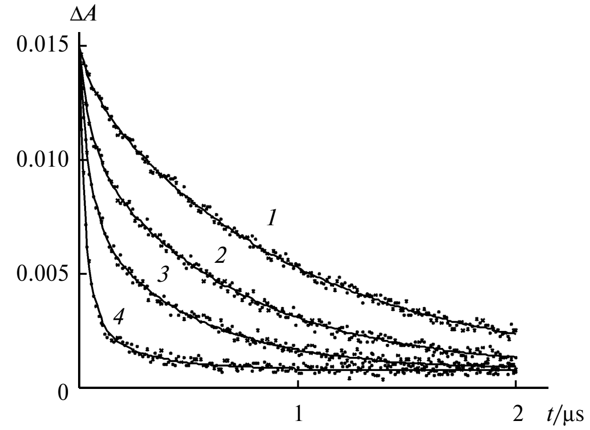

Fig. 3. Decay kinetics of intermediates absorbing at λ = 630 nm obtained upon laser photolysis of deaerated aqueous solutions of DB (0.002 mol L^{-1}) in the presence of SDS (0.2 mol L^{-1}) and 4-chlorophenol (0.0003 (*1*), 0.001 (*2*), 0.002 (*3*), and 0.005 mol L^{-1} (*4*)). Lines are the result of approximation using Eq. (1).

nπ*-nature of the triplet state of DB compared to that of unsubstituted benzophenone.

Quenching of the triplet state of 4,4´-dimethylbenzophenone with phenols in aqueous micellar solutions of SDS. A successive increase in the phenol concentration in micellar solutions accelerates the ^{3}DB decay and increases the yield of comparatively long-lived radicals DBH$^\bullet$ (exceptions are 4-bromo- and 4-iodophenols), and the kinetics of ^{3}DB decay gains a pronounced non-exponential character (Fig. 3). This shape of kinetic curves is observed for quenching of triplet states in micellar solutions and caused by the distribution of quencher molecules in a microheterogeneous system.[25,26]

For the random distribution of a quencher between micelles, which is usually fulfilled at its rather low concentration, the Poisson formula is used

$$P_{\langle N\rangle N} = \langle N\rangle^N/N!\exp(-\langle N\rangle),$$

where $P_{\langle N\rangle N}$ is the probability that N molecules of a quencher are localized in a particular micelle of the sample, and $\langle N\rangle$ is the average number of quencher molecules per micelle. In this case, the concentration of triplet states ([T]) as a function of time is described by the equation[27,28]

$$[\mathrm{T}]/[\mathrm{T}]_0 = \exp\{-A_1t - A_2[1 - \exp(-A_3t)]\}, \qquad (1)$$

where $[\mathrm{T}]_0$ is the initial concentration of triplets,

$$A_1 = k_0 + k_\mathrm{q}k_-\langle N\rangle/(k_\mathrm{q} + k_-), \qquad (2)$$

$$A_2 = k_\mathrm{q}{}^2\langle N\rangle/(k_\mathrm{q} + k_-)^2, \qquad (3)$$

$$A_3 = k_\mathrm{q} + k_-, \qquad (4)$$

where k_0, k_q, and k_- are the first-order rate constants of triplet decay in the absence of a quencher, quenching in the case when one quencher molecule is localized in a micelle, and quencher escape from a micelle, respectively.

If the quencher molecules are soluble in both micellar and aqueous phases, the following equilibrium should be taken into account:

$$\mathrm{RC_6H_4OH_W} + \mathrm{M} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{RC_6H_4OH_M}, \qquad (5)$$

where $\mathrm{RC_6H_4OH_W}$ is the quencher in the aqueous phase, M is the micelle, $\mathrm{RC_6H_4OH_M}$ is the quencher in the micellar phase, and k_+ is the rate constant of association of a quencher and micelle. Then, the $\langle N\rangle$ value can be determined from the equation

$$\langle N\rangle = k_+[\mathrm{RC_6H_4OH}]/(k_+[\mathrm{M}] + k_-), \qquad (6)$$

where $[\mathrm{RC_6H_4OH}]$ is the quencher concentration in a micellar solution, and [M] is the concentration of micelles. At a rather high detergent concentration (much higher than the critical micelle concentration), the [M] value can be estimated as $[\mathrm{SDS}]/N_\mathrm{A}$, where N_A is the aggregation number. Under the conditions used in this work ([SDS] = 0.2 mol L^{-1}, 20 °C), N_A was accepted to be 100.[29,30]

Equation (1) describes well the kinetic curves of ^{3}DB decay in the presence of different amounts of $\mathrm{RC_6H_4OH}$ in micellar solutions of SDS (see Fig. 3). The k_q and k_- rate constants obtained using Eq. (1) by the simultaneous approximation of a series of the corresponding kinetic curves measured at different $[\mathrm{RC_6H_4OH}]$ are given in Table 1. In this case, the k_q and k_- values were varied, and k_+ for all phenols was accepted equal to a typical value of $5 \cdot 10^9$ L mol^{-1} s^{-1}.[19]

The resulting k_q values, as well as in several organic solvents or in water,[16—18] are only insignificantly lower

Table 1. Rate constants of quenching of the triplet state of 4,4´-dimethylbenzophenone with phenols 4-$\mathrm{RC_6H_4OH}$ (k_q), escape of phenols and phenoxyl radicals from micelles (k_- and k_e, respectively), and radical recombination in micelles (k_r) in the zero magnetic field and at B = 0.2 T, the quantum yields of radicals (φ_R), and the partition constants of phenols between the micellar and aqueous phases (P_MW)*

R	k_q	k_-	k_e**	P_MW	φ_R	$k_\mathrm{r} \cdot 10^{-6}$ **/s^{-1}	
	$\cdot 10^{-6}$ s^{-1}					B = 0	B = 0.2 T
H	15	30	30	6.7	1.0	5.0	—
F	9.5	10	18	20	1.0	5.8	—
Cl	8.3	2.0	5.1	100	0.95	5.6	2.6
Br	9.1	1.0	4.9	210	0.39	14	13
I	12	0.42	—	480	≤0.02	—	—

* Relative errors of determination of rate constants and quantum yields are ±10%, and those for P_MW are 20%.

** Determined at $[\mathrm{RC_6H_4OH}]$ = 0.05 mol L^{-1}.

than the diffusion limit (typical collision frequencies for a pair of aromatic reactants in SDS micelles are ν_d = (2—5) • 10^7 s^{-1}).[9,10,21] The k_q value somewhat decreases when electron-withdrawing substituents (halogen atoms) are introduced into a phenol molecule but increases substantially with an increase in the atomic weight of a halogen atom (see Table 1, transition from 4-chloro- to 4-bromo- and 4-iodophenols), indicating the appearance of a new channel of ^{3}DB quenching.[16—18] In an encounter complex of ^{3}DB and RC_6H_4OH containing a heavy atom, intersystem crossing is accelerated (external heavy atom effect) in addition to the chemical reaction. A comparison of k_q for 4-chloro- and 4-iodophenols shows that the expected quenching rate constant with 4-iodophenol due to heavy atom is ~4 • 10^6 s^{-1}.

The k_- value decreases sharply with a decrease in the solubility of RC_6H_4OH in water (see Table 1). The distribution of dissolved substances between different phases in micellar solutions is usually characterized by a dimensionless magnitude of the ratio of concentrations of a reactant in the micellar and aqueous phases (partition coefficient P_{MW}). When neglecting the micellar phase volume (5% at [SDS] = 0.2 mol L^{-1}), then $P_{MW} = k_+/k_-vN_A$, where v = 0.2456 L mol^{-1} is the partial molar volume of SDS.[31] Thus calculated P_{MW} values (see Table 1) are substantially lower than the values for buffer solutions of SDS known from literature (for example, P_{MW} = 30 and 250 for phenol and 4-chlorophenol, respectively, in a borate—phosphate buffer at pH 7).[31,32] The transition to such a buffer solution of SDS in experiments on ^{3}DB quenching with phenol is accompanied by 1.5-fold increase in k_q and 3-fold decrease in k_-. The resulting value P_{MW} = 20 agrees satisfactorily with published data.

Radical formation for quenching of the triplet state of 4,4´dimethylbenzophenone with phenols in aqueous micellar solutions of SDS. Quenching of the ^{3}DB triplet state with phenol or 4-fluoro- and 4-chlorophenols in micellar solutions of SDS increases the yield of ketyl radicals $DBH^•$. This also produces the corresponding phenoxyl radicals $RC_6H_4O^•$, whose absorption spectra contain characteristic bands at λ = 400 nm (phenoxyl and 4-fluorophenoxyl radicals) and 410 nm (4-chlorophenoxyl radicals; Fig. 4).[16—18] The position of absorption band maxima of the $RC_6H_4O^•$ radicals indicates that these radicals are formed in the organic phase. The transition of $RC_6H_4O^•$ into the aqueous phase due to escape from micelles (see further) is accompanied by the red shift of the absorption band at 400 nm (for instance, the absorption band maximum of 4-chlorophenoxyl radical shifts to the long-wave region from 410 to 415 nm with an elongation of the time delay of detection after laser pulse; see Fig. 4). As in organic solvents, the primary product of ^{3}DB quenching with phenols (in the nanosecond time scale) is represented by ketyl radicals, while in water radical anions of benzophenones are formed first.[16—18]

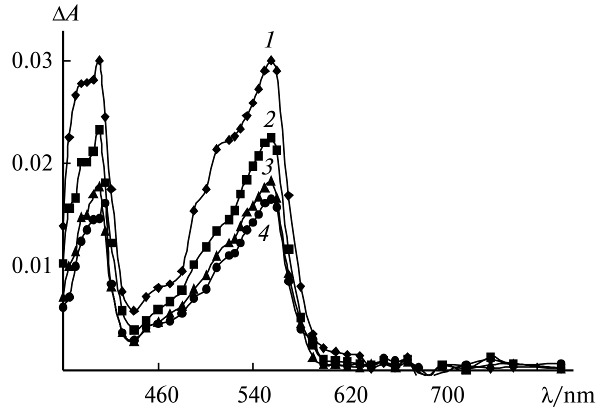

Fig. 4. Differential absorption spectra of intermediates obtained upon laser photolysis of deaerated aqueous solutions of DB (0.002 mol L^{-1}) in the presence of SDS (0.2 mol L^{-1}) and 4-chlorophenol (0.05 mol L^{-1}) 0.03 (*1*), 0.3 (*2*), 0.7 (*3*), and 4 μs (*4*) after laser pulse in a magnetic field with B = 0.2 T.

A comparison of the absorbance of ^{3}DB in the absence of phenol and the initial absorbance of radicals measured at rather high concentrations of RC_6H_4OH (when the lifetime of ^{3}DB is shorter than the resolution time of the detection system), taking into account the known molar absorption coefficients of $RC_6H_4O^•$ and assuming that the molar absorption coefficients of ^{3}DB and $DBH^•$ are close to similar characteristics of the unsubstituted analogs, shows that the $RC_6H_4O^•$ and $DBH^•$ radicals are formed in equimolar amounts in the yield φ_R ~100% (see Table 1).[16—18]

The yield of $DBH^•$ changes insignificantly during ^{3}DB quenching by 4-bromophenol but an absorption band of the corresponding $RC_6H_4O^•$ with a maximum at ~420 nm appears. No radicals are formed in the case of 4-iodophenol. Thus, as in homogeneous solutions,[16—18] the introduction of heavy atoms into a phenol molecule is accompanied by a decrease in the radical yield (see Table 1), and the heavy atom effect substantially exceeds the value expected from the heavy atom effect on the quenching rate of ^{3}DB. This inconsistency is caused by an additional internal heavy atom effect in the primary triplet RP in a solvent cage. This additional effect appears as an acceleration of RP recombination when the radicals contain heavy atoms.[3—9,18] The probability of this recombination (W_l) calculated from the radical yield in the case of 4-bromo- and 4-iodophenols taking into account the external heavy atom effect ($W_l = 1 - k_q\varphi_R/k_q{}^0\varphi_R{}^0$, where $k_q{}^0$ and $\varphi_R{}^0$ is the quenching rate constant and yield of $DBH^•$ radicals for ^{3}DB quenching by 4-chlorophenol[18]) is 0.6 and ≥0.95, respectively. It was assumed that for 4-chlorophenol W_l = 0, because the yields of radicals in this system almost coincide with similar values in systems without heavy atoms (see Table 1). The heavy atom effect in micellar solutions is much stronger than in water or low-viscosity organic solvents. This is caused by an elongation of the lifetime of the RP in the cage due to an increase in the viscosity of the medium.[3–9,16–18]

Kinetics of recombination of ketyl—phenoxyl triplet radical pairs in SDS micelles: external magnetic field effect. The kinetic curves of decay of the $RC_6H_4O^\bullet$ and $DBH^\bullet$ radicals at rather high RC_6H_4OH concentrations (when the lifetime of ^3DB is shorter than the time resolution of the detection system) contain the fast and slow components (Fig. 5, *a* and *b*). The fast component is caused by RP recombination in a micelle, and the slow component corresponds to the decay of the radicals that have left micelles or remained in a micelle without a partner.[3–10] The application of an external magnetic field retards the recombination of the spin-correlated RP in a micelle, which increases the contribution of the slow component. The kinetics of RP decay in micellar solutions is satisfactorily described by a biexponential law: the RP recombines in a micelle with the rate constant k_r and separates due to the escape of a radical from a micelle with the rate constant k_e, and the first-order rate constant k_s, acting as a fitting parameter, corresponds to the initial region of the slow component.[3–12]

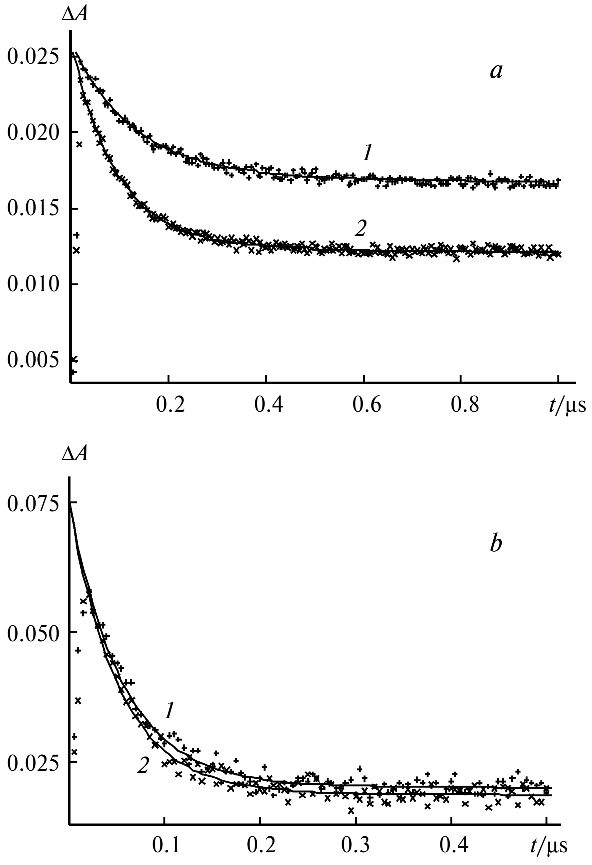

Fig. 5. Decay kinetics of intermediates absorbing at $\lambda = 555$ nm obtained upon laser photolysis of deaerated aqueous solutions of DB (0.002 mol L^{-1}) in the presence of SDS (0.2 mol L^{-1}) and 4-chlorophenol (*a*) or 4-bromophenol (*b*) (0.05 mol L^{-1}) in a magnetic field with $B = 0.2$ T (*1*) and without magnetic field (*2*). Lines are the result of approximation in the framework of the biexponential model.

The k_r and k_e rate constant values obtained by the approximation using the biexponential law of kinetic curves of RP decay in micellar solutions are presented in Table 1. Similarly to k_-, the k_e value decreases with a decrease in the phenol solubility in water. It should be mentioned that the $RC_6H_4O^\bullet$ radicals are more hydrophilic than $DBH^\bullet$, and the process of their escape from micelles contributes mainly to RP separation. A comparison of k_e and k_- shows that phenoxyl radicals are more hydrophobic than the starting phenols.

The main channel of the RPs decay including radicals $RC_6H_4O^\bullet$ with R = H and F is the escape of $RC_6H_4O^\bullet$ from a micelle. Nevertheless, a relatively insignificant magnetic effect is observed (the fraction of radicals escaped to the volume increases under the external magnetic field application). The value of this effect determined from the contribution of the slow component decreases from 25 to 5% with an increase in the RC_6H_4OH concentration from 0.001 to 0.05 mol L^{-1}. At rather high concentrations of phenols in micellar solutions of SDS, the structure of micelles changes. In particular, the aggregation number and partition coefficient decrease[33] along with a decrease, most likely, in the fraction of RPs recombining in a micelle, which decreases the observed magnetic effect.

The fraction of RPs recombining in a micelle is ~50% in the system with 4-chlorophenol. In this case, the magnetic field effect on the contribution of the slow component depends rather weakly on the phenol concentration (decreases from 60 to 50% with an increase in the RC_6H_4OH concentration from 0.001 to 0.05 mol L^{-1}).

In the systems without heavy atoms, the k_r values depend weakly on the substituent nature in the $RC_6H_4O^\bullet$ radical and are close in magnitude to $\nu_d/4$ (see Table 1), *i.e.*, the reaction is diffusion-controlled taking into account the spin-statistical factor (relaxation time of the spin state of RP is shorter than $1/\nu_d$), since only the radicals, which form singlet radical pairs upon collision, recombine.[8–10] The introduction of the Br atom as a substituent into the $RC_6H_4O^\bullet$ radical is accompanied by a substantial increase in the recombination rate constant and an almost complete disappearance of the magnetic effect (see Table 1 and Fig. 5, *b*). When the system contains heavy atoms, a new reaction channel appears: recombination of radicals that form a triplet RP upon collision. Therefore,

$$k_r = \nu_d(1 + 3W_2)/4,$$

where W_2 is the probability of recombination of triplet RPs formed upon collision of RP radicals in a micelle. The W_2 value calculated from the difference in the k_r values for RPs in the systems with 4-chloro- and 4-bromophenol, assuming that for 4-chlorophenol $W_2 = 0$, is ~0.5, which coincides with W_1 within experimental error.

Thus, as in homogeneous solutions, the heavy atom effects are close for the recombination of primary and secondary RPs in micelles.[18] It is of interest to compare the heavy atom effect on the geminal recombination of the primary contact RP in a solvent cage and the RP in a micelle, where radicals have time to separate spatially, due to the mechanism of heavy atom influence on magnetic effects in radical reactions.[7—9,34] In the kinetics of ketyl—phenoxyl RP recombination, the heavy atom effect is mainly manifested as the acceleration of intersystem transitions in the contact state rather than in the spatially separated state. The study of various heavy atom effects in all the reactions occurring during sensitized photooxidation of phenols in both homogeneous[18] and organized systems provides useful information on the mechanism and dynamics of processes involving excited states and radicals.

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