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# Magnetic Isotope Effects on the Decay Kinetics of Micellized Triplet Ketyl–Phenoxy Radical Pairs. Role of Hyperfine, Exchange, and Dipole–Dipole Interactions

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The geminate recombination kinetics of ketyl–phenoxy radical pairs (RP) produced by quenching of triplet benzophenone by 4-phenylphenol and in corresponding perdeuterated system in micellar solutions of sodium octyl (SOS) or dodecyl sulfates (SDS) in D<sub>2</sub>O have been examined by using the laser flash technique under an external magnetic field up to 0.43 T. The recombination rate and magnetic isotope effect (MIE) in zero magnetic field increase as the micellar size is decreased. Application of a very small magnetic field (0.01 mT) results in the pronounced retardation of deuterated RP geminate recombination and MIE enhancement in SDS while the corresponding magnetic field effects in SOS are small. Under a strong magnetic field MIE becomes negligible. The magnetic field dependences and attendant regularities are discussed in terms of a simple kinetic scheme, which includes the singlet–triplet transitions in the separated and contact states of RP. The relative contributions of hyperfine coupling, exchange, and dipole–dipole interactions as well as the spin–orbit coupling may be revealed by the comparison of MIE magnetic field dependences in micelles of different size.

## Introduction

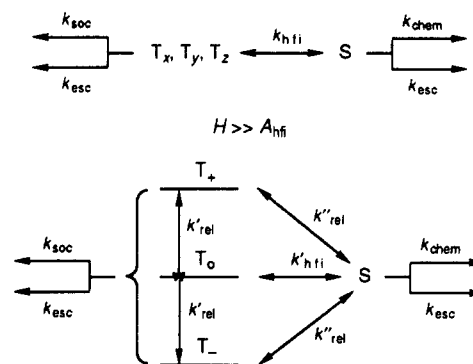
The behavior of geminate triplet-derived radical pairs (RP) in micellar solutions has been extensively investigated particularly due to the outstanding magnetic field effect and accompanying magnetic isotope effect (MIE).<sup>1,2</sup> Relatively few time-resolved studies of MIE in decay kinetics of a number of micellized RPs from ketone photocleavage<sup>3</sup> or benzophenone photoreduction<sup>4,5</sup> reveal some regularities. The deuteration or <sup>13</sup>C isotopic substitution of ketyl radical of the RP in benzophenone–hydrogen donor systems results in a MIE for decay rate constant in zero magnetic field, which does not exceed 20% and it is even less in high magnetic field.<sup>4–6</sup> In the case of RPs of C-centered radicals from ketone photocleavage the deuteration of aliphatic groups in positions with high hyperfine interaction (hfi) leads to a 10% MIE in zero magnetic field as well; however, the MIE increases up to 50% with increase of magnetic field to 10 mT and it is independent of magnetic field in the range 10–50 mT.<sup>3b</sup>

The magnetic field dependences of the MIE have been explained in terms of the interplay of the hfi induced spin evolution and diffusional process of the intramicellar encounters.<sup>3b</sup> If the rate of triplet–singlet (T–S) transitions due to the hfi ( $k_{hfi}$ ) is bigger than the frequency of reencounters ( $k_{dif}$ ) then diffusion is the rate-determining step, and no MIE would be observed. For most of the commonly used micelles the value of  $k_{dif}$  seems to be smaller than that of  $k_{hfi}$  in zero magnetic field,<sup>7,8</sup> and a small MIE is expected. These speculations suggest that in zero field the isotopic substitution should have kinetic consequences in smaller micelles. Recently the corresponding dependence of a zero-field MIE on micellar size has been reported.<sup>9</sup>

In the presence of small magnetic fields (magnetic field strength  $H \approx A_{hfi}$ , where  $A_{hfi}$  is the effective constant of the hfi), the hfi induced T<sub>±</sub>–S transitions may become the rate-limiting step of RP decay, and that is the reason for the rapid increase of MIE in the field range 0–10 mT.<sup>3b</sup> The behavior of MIE in the intermediate field region 10–500 mT has been explained in terms of spin relaxation, which depends upon the anisotropy of the hfi.<sup>3b</sup>

Further increase of magnetic field results in decrease of the kinetic MIE, which becomes negligible at  $H > 0.1$  T.<sup>3b,6</sup> This finding evidences the importance of a recombination pathway, which is insensitive to isotopic substitution. Many regularities of RP behavior in a high magnetic field are consistent with intersystem recombination–intersystem crossing from triplet RP to the singlet diamagnetic products induced by the intermolecular spin–orbit coupling (soc) in contact states of RP.<sup>6,7c,8</sup> The intersystem recombination may become the basic and the only pathway for the recombination of RP in T<sub>±</sub> states in a strong magnetic field, when hfi and relaxation routes of T<sub>±</sub>–T<sub>0</sub>, S transitions in RP are suppressed.

SCHEME I: Dynamic Behavior of a Radical Pair in a Micelle at Zero Magnetic Field ( $H \ll A_{hfi}$ ) and at a High Field ( $H \gg A_{hfi}$ )<sup>a</sup>



<sup>a</sup> Here  $k_{hfi}$  is the rate constant of T–S and T<sub>±</sub>–T<sub>0</sub> transitions due to isotropic hfi;  $k'_{hfi} = k_{hfi} + k_g$  ( $k_g$  depends on the difference of isotopic  $g$  factors of the radicals in RP);  $k'_{rel}$  and  $k''_{rel}$  are the rate constants of the corresponding transitions due to relaxation;  $k_{soc}$  is the effective rate constant of recombination of the RP in the triplet state;  $k_{chem}$  is the rate constant of RP recombination in the singlet state;  $k_{esc}$  is the sum of the rate constants of the escape of the radicals from the micelle.

In general, the decay kinetics of the triplet-derived RP in micelles may be determined by the contributions of several processes: intramicellar diffusion, T–S evolution due to the isotropic hfi or paramagnetic spin relaxation, and intersystem recombination. The effects of the spin exchange interaction should be taken into account as well.<sup>3b,9,10</sup> By application of an external magnetic field or by change in the internal one by means of isotopic substitution, the relative contributions of the processes of different nature can be varied. The kinetic investigations of the magnetic field dependences of the MIE in micelles of different sizes would provide evidences for the importance of the different mechanism, the interplay of which is not still fully understood. In order to carry out detailed kinetic studies in micelles, it is desirable to generate the RP in a short time and to restrict considerably the escape. The systems of the type like benzophenone together with a hydrophobic phenolic compound as a good hydrogen donor in aqueous micellar solutions are very suitable.<sup>6,8</sup>

The present paper deals with the recombination kinetics of model RPs formed in the reaction of hydrogen abstraction by the triplet excited state of benzophenone (<sup>3</sup>B<sub>h</sub>) from 4-phenylphenol (POD<sub>h</sub>) and in corresponding perdeuterated system (<sup>3</sup>B<sub>d</sub>–POD<sub>d</sub>) in micellar solutions of sodium octyl (SOS) or dodecyl sulfates (SDS) in D<sub>2</sub>O under an external magnetic field up to 0.43 T. The experimental results are discussed in terms of kinetic Scheme I of first-order processes,<sup>6</sup> using the exact solution of the corre-

**TABLE I: Contributions of Escape Process, Rate Constants (in  $10^6 \text{ s}^{-1}$ ), and Relaxation Parameters (Correlation Times in  $10^{-11} \text{ s}$  and Energies of Coupling in mT) for the Recombination of the Micellized Radical Pairs<sup>a</sup>**

system	$\varphi(0)$	$\varphi(0.43)$	$k^0$	$k^{\text{T}\pm}$	$k^{\text{T}0}$	$\phi^{\text{T}0}$	$k_{\text{hfi}}$	$k_g$	$k_{\text{chem}}$	$k_{\text{soc}}$	$k_{\text{esc}}$	$\tau_c$	$V$	$V_{\text{dd}}$	$V_{\text{hfi}}$
B <sub>d</sub> -POD <sub>d</sub> -SOS	0.28	0.35	3.9	2.5	6.0	0.24	1.8	2	51	1.2	1.1	7	0.60	0.60	0.07
B <sub>h</sub> -POD <sub>h</sub> -SOS	0.11	0.32	9.8	2.5	15	0.27	16	3	51	1.2	1.1	7	0.66	0.60	0.28
B <sub>d</sub> -POD <sub>d</sub> -SDS	0.07	0.21	2.9	0.75	5.5	0.32	4.0	4	17	0.52	0.21	11	0.28	0.27	0.08
B <sub>h</sub> -POD <sub>h</sub> -SDS	0.05	0.19	4.1	0.75	7.3	0.31	16	4	17	0.52	0.21	11	0.42	0.27	0.32

<sup>a</sup> The error in determination of  $\varphi(0.43)$ ,  $k^0$ , and  $k^{\text{T}\pm}$  does not exceed 5% and that of  $k^{\text{T}0}$  and  $\phi^{\text{T}0}$ , 20%. The errors in determination of kinetic and relaxational parameters extracted from the experimental data in terms of Scheme I and eqs 6 and 8 in most cases do not exceed 20% (see text).

sponding systems of rate equations. Besides the T-S transitions in separated RP due to the isotropic hfi ( $k_{\text{hfi}}$ ), the  $\Delta g$  mechanism ( $k_g$ ), or spin relaxation ( $k_{\text{rel}} = k'_{\text{rel}} + k''_{\text{rel}}$ , Scheme I includes the intersystem recombination ( $k_{\text{soc}}$ ).

### Experimental Section

The absorption spectra and decay kinetics of the intermediates were recorded by laser photolysis using a PRA LN-1000 nitrogen laser as an excitation source.<sup>6,8</sup> The kinetic spectrophotometer (10-ns resolution) included an averaging system consisting of a Biomation 6500 waveform recorder coupled to an Apple IIe microcomputer. Kinetic curves were averaged over 128 laser pulses. The photochemical reactions were sufficiently reversible to allow measuring without a flow system. In the magnetic field experiments, the quartz cell ( $8 \times 8 \text{ mm}$  cross section) was placed between the two pole pieces of a permanent magnet. The distance between the pole pieces can be varied and at the closest position (16 mm)  $H = 0.43 \text{ T}$ .

Each decay curve was recorded at 1024 points with 2, 5, 10, 20, and 50 ns per point. A total of  $\geq 800$  points in the time interval covering nearly 100% of the decay was used for the analysis of the experimental kinetic curves by the sum of several exponentials. The fitting procedure was a nonlinear least-square method using the Marquardt algorithm. The quality of the fitting was judged by the residuals and autocorrelation as well as by the standard deviation and the statistical parameter Durbin Watson. The data presented are the average of the results based on calculations performed on at least five kinetic curves obtained for a given system.

Commercially available perdeuterated benzophenone (>98%) was purified by sublimation. Perdeuterated 4-phenylphenol was prepared by an isotope-exchange reaction in the presence of Adams' catalyst. 4-Phenylphenol, 0.4 g, and 0.025 g of PtO<sub>2</sub> were heated in 10 mL of 1 N DCl ( $D = 99.8\%$ ) at 175–180 °C for 30 h. The crude product was isolated and the heating was continued with a fresh catalyst and acid for 100 h. The solids were collected and recrystallized from C<sub>2</sub>H<sub>5</sub>OD/D<sub>2</sub>O (3:7,  $D = 99.7\%$ ), yielding white needles or perdeuterated 4-phenylphenol. The degree of deuteration (>95%) was controlled by <sup>1</sup>H NMR (Bruker AM-400) in CDCl<sub>3</sub>.

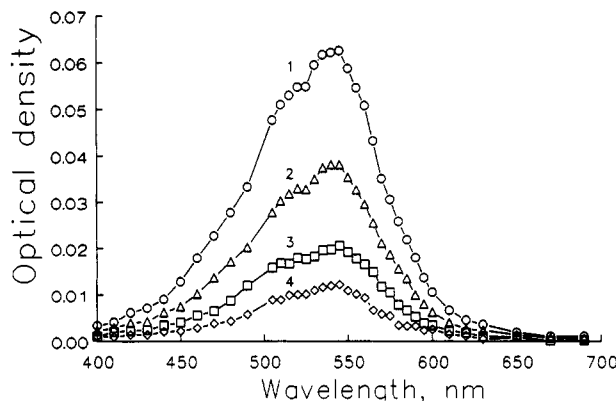
All other compounds were purified by sublimation and/or by recrystallization from EtOD-D<sub>2</sub>O mixture. The concentration of sodium alkyl sulfates in D<sub>2</sub>O was equal to 0.25 mol/L, which corresponds to a concentration of micelles of 0.002–0.004 mol/L.<sup>11</sup> The concentrations of B of the order of 0.005 mol/L and that of POD 0.01–0.02 mol/L were used. To avoid the formation of radical anions B<sup>•−</sup>, 0.01 mol/L HCl was added to the micellar solutions. Before the laser flash investigations, the solutions were flushed with Ar for 30 min. All measurements were conducted at 20 °C.

### Results

Photoexcitation of B in the presence of POD initiates the well-known processes<sup>8,12</sup>



where the brackets enclose the RP in a micelle. The solubility of the given hydrophobic reagents in water is very low. They are localized in a micellar phase, where the RPs are generated via reaction 1. At the present concentrations of POD ( $\approx 5$  molecules of a quencher per micelle), the lifetime of <sup>3</sup>B is shorter than the resolution time of the registering system. The superposition of



**Figure 1.** Absorption spectra of the intermediates formed from benzophenone in SDS solution in the presence of 4-phenylphenol in a magnetic field of 0.43 T under laser flash photolysis, recorded at 1–50 ns, 2–0.5  $\mu\text{s}$ , 3–2  $\mu\text{s}$ , and 4–9  $\mu\text{s}$  after the flash.

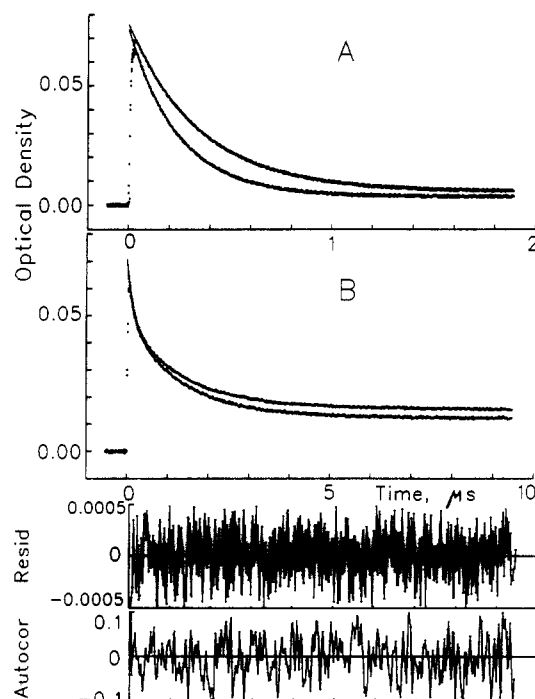
absorption of the ketyl radicals and that of PO<sup>•</sup> with maxima at 540 nm<sup>8,12</sup> is observed immediately after the laser pulse (Figure 1).

The traces of the radical absorption decay were independent of the wavelength of observation in the time range 0–50  $\mu\text{s}$  (Figure 1). They contain the fast component ( $t \leq 5 \mu\text{s}$ ), which corresponds to the micellized RP recombination and the slow component ( $t \gg 50 \mu\text{s}$ ), reflecting the decay of the radicals that have escaped to the aqueous phase and the lone micellized radicals (Figure 2). The transient absorption disappears up to zero at long times. The formation of any colored products was not observed. The ratios of the absorption due to the escaped and lone radicals to that of initial RP ( $\varphi = \text{OD}_\infty/\text{OD}_0$ ) correspond to the contributions of the escape process to the RP decay. Table I presents values of  $\varphi$  measured at  $H = 0$  ( $\varphi(0)$ ) and 0.43 T ( $\varphi(0.43)$ ).

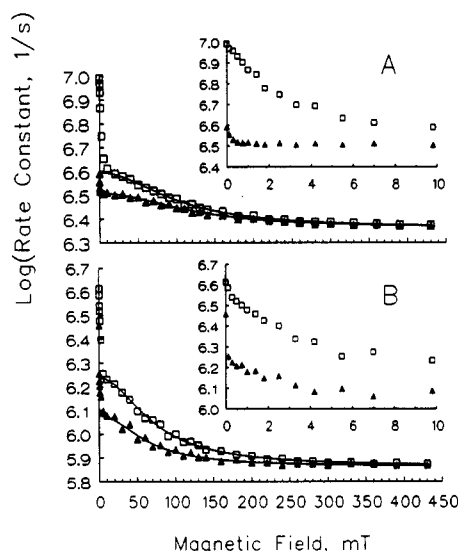
At  $H = 0$ , only one exponential ( $k^0$  at  $H = 0 \text{ T}$ , see Table I) is necessary to fit the fast component adequately (Figure 2A). Imposition of a magnetic field leads to an increase in the value of  $\varphi$  and the inhibition of geminate recombination (Figures 2 and 3, Table I). A monoexponential law is unable to describe the fast component any more, but two exponentials can appropriately fit whole decay with low values of the standard deviation and Durbin Watson values in the range 1.6–2.0 and a good autocorrelation function (Figure 2B). The using of three exponentials does not lead to noticeable improvement of the fittings and its gives a third exponential with very low contribution and very small rate constant. The parameters recovered from two exponential fittings of the different experimental curves for the same system have a fair reproducibility  $\leq 5\%$  for a slow exponential but may have scattering, which may exceed 30% for a fast one.

At high  $H$ , the contribution of fast exponential ( $\phi^{\text{T}0}$  at  $H = 0.43 \text{ T}$ , Table I) is near one-third and the corresponding value of rate constant ( $k^{\text{T}0}$  at  $H = 0.43 \text{ T}$ ) is larger than that of  $k^0$ . The fast exponential seems to describe the geminate recombination of RPs produced in the T<sub>0</sub> state. The first-order rate constants of the second slow exponential ( $k^{\text{T}\pm}$  at  $H = 0.43 \text{ T}$ , see Table I and Figure 3) should represent the decay of RPs produced in the T<sub>±</sub> states at high magnetic fields.<sup>13</sup> The values of  $k_{\text{esc}}$  (Table I) were obtained from the values of  $\varphi$  at  $H = 0.43 \text{ T}$  according to the expression<sup>6,8</sup>  $\varphi = 2k_{\text{esc}}/3k^{\text{T}\pm} + k_{\text{esc}}/3k^{\text{T}0}$ .

Figure 3 shows the magnetic field dependences of  $k^{\text{T}\pm}$ , which exhibit a very "sharp" initial part (on going from  $H = 0$ –10 mT,



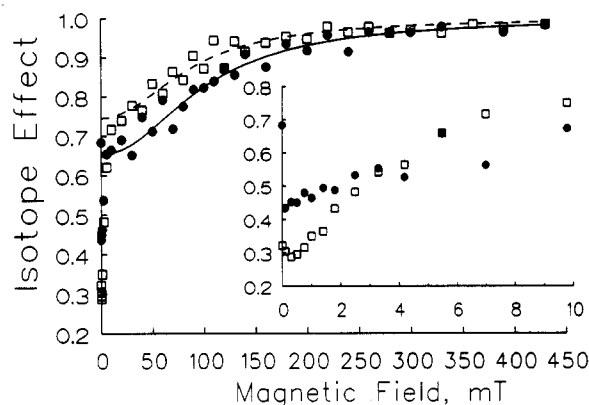
**Figure 2.** Variation of the optical density at 540 nm in SDS solution following a laser flash under a zero magnetic field (A) and  $H = 0.43$  T (B) for protonated (lower curves) and perdeuterated (upper curves) benzophenone-4-phenylphenol systems. Solid lines, approximation by the mono- (A) and biexponential (B) laws; the respective parameters are given in Table I. Residual and autocorrelation functions for the biexponential approximation of curve B.



**Figure 3.** Rate constants of a slow part of the decay of triplet ketyl-phenoxyl radical pairs as a function of magnetic field strength and isotopic substitution: (A) in SOS; (B) in SDS; protonated ( $\square$ ) and perdeuterated ( $\Delta$ ) benzophenone-4-phenylphenol system. Solid lines, approximation by expression 5 using expression 6 and parameters from Table I.

$k^{\pm}$  decreases by a factor of more than 2). In the case of the  $B_d$ -POD<sub>d</sub> system in SDS even  $H = 0.1$  mT is sufficient for a pronounced decrease in the RP recombination rate.

The magnetic field dependences of the isotope effect are presented in Figure 4. As a measure of the isotope effect the relation between values of  $(k^0 - k_{\text{esc}})$  at  $H = 0$  or  $(k^{\pm} - k_{\text{esc}})$  at  $H > 0$  for deuterated RP and those for nondeuterated one has been used. These dependences in SOS and SDS show quantitatively different behavior. But in both micelles the isotope effect increases with the increase of  $H$  and reaches the maximum value in the range 0.1–0.5 mT (Figure 4). A further increase of the magnetic field strength results in the decrease of the isotopic



**Figure 4.** Magnetic field effect on the  $(k^{\pm} - k_{\text{esc}})$  ratio for perdeuterated and protonated ketyl-phenoxyl radical pairs of the benzophenone-4-phenylphenol system in SOS ( $\square$ ) and SDS ( $\bullet$ ). Solid and dashed lines, approximation by the corresponding ratio calculated by using expressions 5 and 6 with parameters from Table I.

substitution effect, which becomes negligible at  $H > 0.1$ – $0.2$  T. The kinetic isotope effect at small  $H$  is stronger in a smaller micelles, but at high  $H$  the reversed situation is observed.

## Discussion

**The Kinetic Scheme of RP Recombination in Micelles.** The validity of utilization of the simple Scheme I, described by a system of four first-order equations, is based on a notion that the interference of nuclear spin states in many nuclear systems simplifies the overall RP spin dynamics.<sup>13–15</sup> Although it is not possible to use first-order rate constants for an adequate description of the effects of nuclear and electron polarizations, the time dependence of the overall probability to find the many nuclear RPs in a singlet or triplet spin state may be approximated probably by the exponential functions<sup>13–15</sup> for the description of RP recombination kinetics in some cases. Numerous observations of the simple monoexponential form of the RP decay kinetics in micellar solutions at  $H = 0$  and a biexponential one at an external magnetic field lends support to the validity of this exponential approach to the micellized RP kinetics.<sup>6,8,13</sup>

The solution of the system of rate equations for Scheme I at  $H = 0$  gives two exponentials with rate constants

$$2k_{\text{hfi}} + \frac{1}{2}(k_{\text{chem}} + k_{\text{esc}}) + k_{\text{esc}} \pm A^{1/2} \quad (2)$$

where  $A = 3k_{\text{hfi}}^2 + [k_{\text{hfi}} + \frac{1}{2}(k_{\text{chem}} - k_{\text{esc}})]^2$ . Under the condition of T-precursor the contribution of fast exponential is negative with absolute value less than 10%. Thus the RP decay should be very close to monoexponential with the value of experimentally observed rate constant  $k^0$  being close to the smallest one from expression 2. The comparison of  $k^0$  values in terms of expression 2 for  $B_h$ -POD<sub>h</sub> and  $B_d$ -POD<sub>d</sub> systems gives an opportunity to calculate values of  $k_{\text{chem}}$  and  $k_{\text{hfi}}$  by using the known values of  $k_{\text{esc}}$  and  $k_{\text{esc}}$  (see below) and the ratio between the values of  $k_{\text{hfi}}$  for nondeuterated and deuterated RPs. This ratio was taken to be equal to 0.25, which is expected for the corresponding ratio between  $A_{\text{hfi}}$  being estimated as<sup>14</sup>  $(\sum a_i^2 I_i(I_i + 1))^{1/2}$  (here  $a_i$  and  $I_i$  are hfi constants and spin quantum numbers of magnetic nuclei in RP). The  $a_i$  constants for  $^2\text{H}$  nuclei are 15.35% of the corresponding proton values available in refs 10 and 16 for  $\text{BH}^\bullet$  and  $\text{PO}^\bullet$ .

The calculation of  $k_{\text{chem}}$  and  $k_{\text{hfi}}$  from  $k^0$  according to the described procedure gives very reasonable values in SDS, represented in Table I. However, it results in senseless values in SOS implying the much more pronounced decrease in  $k_{\text{hfi}}$  after the deuteration. Table I presents the value of  $k_{\text{chem}}$  for SOS, which was calculated from expression 2 and  $k^0$  for nondeuterated RP in SOS, with  $k_{\text{hfi}}$  being equal to that in SDS. Then the value of  $k_{\text{hfi}}$  in Table I for deuterated RP in SOS was calculated by assuming the independence of  $k_{\text{chem}}$  on the isotopic substitution. This  $k_{\text{hfi}}$  value is two times smaller than the corresponding one of  $k_{\text{hfi}}$  in SDS for deuterated RP, illustrating the pronounced retardation of hfi induced T-S transitions in small SOS micelles.

In the limit of very high  $H$ , when  $k_{\text{rel}}, k_{\text{hfi}} \ll k_{\text{soc}}$ , the ensemble of RPs falls into two independent groups. The RPs that were produced in  $T_{\pm}$  states disappear with a rate constant

$$k^{\infty} = k_{\text{soc}} + k_{\text{esc}} \quad (3)$$

Table I represents the values of  $k_{\text{soc}}$  calculated according to expression 3 from the experimental values of  $k^{T_{\pm}}$  extrapolated to  $H \rightarrow \infty$ . The differences in  $k^{\infty}$  and  $k^{T_{\pm}}$  at  $H = 0.43$  T were taken to be equal to the values that give the best linear approximation of the dependences of  $1/k_{\text{rel}}$  on  $H^2$  obtained from the corresponding treatment of field dependences (see below).

The RPs that were produced in  $T_0$  disappear according to two-exponential law with a rate constant in exponential with the most important contribution (>80%)

$$k'_{\text{hfi}} + \frac{1}{2}(k_{\text{chem}} + k_{\text{soc}}) + k_{\text{esc}} - [k'_{\text{hfi}}{}^2 + \frac{1}{2}(k_{\text{chem}} - k_{\text{soc}})^2]^{1/2} \quad (4)$$

The experimentally observed value  $k^{T_0}$  should be close to this value. Expression 4 may be suitable for estimation of  $k'_{\text{hfi}}$  and  $k_g$  from experimental values of  $k^{T_0}$  using values of  $k_{\text{chem}}, k_{\text{soc}}$ , and  $k_{\text{hfi}}$  obtained earlier. Table I presents corresponding  $k_g$  values.<sup>17</sup> It should be mentioned that these  $k_g$  values seems to be only rough estimations because of relatively large scatter in measurements of  $k^{T_0}$ . The uncertainty in extraction of other kinetic parameters in terms of Scheme I is much smaller due to relatively small experimental errors in determination of  $k^0$ ,  $k^{T_{\pm}}$ , and  $\varphi$ .

In the intermediate case when  $k_{\text{rel}} \approx k_{\text{soc}}$  and  $H \gg A_{\text{hfi}}$ , the kinetics of RP geminate combination obeys a three-exponential law with relatively complicated expressions for the rate constants. However, a simple expression for the smallest rate constant of the exponential with the most important contribution close to two-thirds is valid

$$k^{T_{\pm}} = k^0 + k_{\text{rel}} - [k_{\text{rel}}^2 + (k^0 - k^{\infty})^2]^{1/2} \quad (5)$$

The dependence of calculated values of  $1/k_{\text{rel}}$  vs  $H^2$  at  $H \geq 10$  mT is close to the linear one in accordance with the relaxation theory in terms of the perturbation with exponential correlation function,<sup>13</sup> if the energy of coupling ( $V$ ) is independent of  $H$ :

$$k_{\text{rel}} = 2\tau_c V^2 / \hbar^2 (1 + \omega^2 \tau_c^2) \quad (6)$$

Here  $\tau_c$  is the rotational correlation time; the frequency  $\omega = g\beta H / \hbar$  ( $g$  is the mean value of the isotropic  $g$  factors of the radicals in RP). The values of  $\tau_c$  and  $V$  obtained from the slopes and the intercepts of the linear fits of  $1/k_{\text{rel}}$  vs  $H^2$  dependences in the range  $20 < H < 100$  mT are presented in Table I. It should be mentioned that some uncertainty ( $\leq 10\%$ ) in estimation of  $k^{\infty}$  has only minor influence on the values of  $k_{\text{rel}}, \tau_c$ , and  $V$  extracted according to the procedure described above. The calculated field dependences of  $k^{T_{\pm}}$  and of MIE in terms of eq 5 based on corresponding values of  $k_{\text{rel}}$  are plotted in Figures 3 and 4.

**Role of Diffusion, Hyperfine, and Exchange Interactions in Zero Magnetic Field.** It has already been assumed<sup>6,8</sup> that the values of  $k_{\text{chem}}$  (Table I) for SDS solutions seem to be close to that of the first-order rate constant of the intramolecular encounters ( $k_{\text{dif}}$ ). Values of the rate constants for the diffusion-controlled intramolecular process of pyrene excimer formation in SDS equal to  $2 \times 10^7$  and  $2.6 \times 10^7$  s<sup>-1</sup> have been reported.<sup>18</sup> However, for a similar RP of small radicals in SDS a higher value of  $5 \times 10^7$  s<sup>-1</sup> has been measured.<sup>19</sup> The value of  $k_{\text{dif}}$  may also be estimated by the equation<sup>20</sup>

$$k_{\text{dif}} = 6Dr / (R_m - r)^3 \quad (7)$$

Here  $D$  is the coefficient of the mutual diffusion of the radicals,  $r$  is the radius of a radical ( $r$  for both radicals was taken to be  $0.35$  nm<sup>21</sup>), and  $R_m$  is the radius of a micelle. At  $R_m = 2.2$  or  $1.6$  nm<sup>11</sup> and  $D = 1.6 \times 10^{-6}$  or  $3.6$  cm<sup>2</sup>/s<sup>9</sup> for SDS or SOS micelles, respectively, expression 7 leads to  $k_{\text{dif}} = 5.3 \times 10^7$  or  $3.8 \times 10^8$  s<sup>-1</sup>, which is three and eight times higher<sup>22</sup> than the values of  $k_{\text{chem}}$  calculated from the experimental data obtained for the SDS or SOS solutions, respectively (Table I). The difference is  $k_{\text{chem}}$  and  $k_{\text{dif}}$  increases with decrease of micellar size. At the same time the observed three times increase of  $k_{\text{chem}}$  on

going from SDS to SOS corresponds to the decrease of micellar volume. That is in agreement with the chemical nature of the rate determining step for singlet RP recombination. However, it should be mentioned that the  $k_{\text{chem}}$  value in SOS was calculated by using the  $k_{\text{hfi}}$  value equal to that in SDS. This may result in low  $k_{\text{chem}}$  because the valid value of  $k_{\text{hfi}}$  may be smaller due to the exchange interaction in SOS micelles (see below).<sup>9</sup>

The value of  $k_{\text{hfi}}$  in SDS is in a very good agreement with the effective  $A_{\text{hfi}}$  ( $k_{\text{hfi}} = A_{\text{hfi}}/2\hbar$ ). Such a good coincidence apparently testifies the minor role of the exchange interaction ( $J$ ) in T-S transitions in SDS micelles. At the same time in small SOS micelles the magnitude of the exchange interaction ( $J$ ) becomes comparable with small  $A_{\text{hfi}}$  for the deuterated RP (0.3 mT) and results in at least two times the retardation of T-S transitions in the deuterated RP.<sup>23</sup> The very pronounced MIE in SOS at  $H = 0$  is due not only to the importance of hfi induced T-S transitions as a rate-limiting step of RP recombination but to the noticeable exchange interaction as well.

**Small Field Region ( $0 < H < 10$  mT).** The presence of the exchange interaction in SOS determines the behavior of magnetic field dependences in the range  $0 < H < 1$  mT (Figures 3 and 4). The recombination rates and MIEs in SOS are not very sensitive to the presence of a small magnetic field  $H \leq 1$  mT. In the case of deuterated RP with a small exchange interaction in SDS micelles, a small hfi can be switched off by a very small magnetic field, and very "sharp" initial parts of corresponding field dependences are observed (Figures 3 and 4). The finding that on one hand a very small magnetic field  $H = 0.1$  mT smaller than  $A_{\text{hfi}}$  (0.29 mT) results in pronounced changes in rate constant for deuterated RP in SDS but on the other hand a similar change for the nondeuterated RP takes place at  $H \approx 2$  mT higher than  $A_{\text{hfi}}$  (1.16 mT) should be the subject of a special discussion. Such an unusual behavior of deuterated RP seems to be the result of the interplay of a small hfi with a very small exchange interaction available in SDS micelles.<sup>24</sup>

The further increase of magnetic field in the range  $1 < H < 10$  mT results in a decrease of the MIE due to the retardation of hfi induced T-S transitions in nondeuterated RP and a corresponding decrease in the RP recombination rate while hfi in deuterated RP has already been switched off (Figures 3 and 4).

**Paramagnetic Relaxation Parameters in the Intermediate Field Region ( $10 < H < 200$  mT).** The comparison of  $|V|$  values obtained for deuterated and nondeuterated RP permits one to analyze the contribution of the mechanisms of relaxation due to the dipole-dipole interaction  $V_{\text{dd}}$  and to hfi anisotropy  $V_{\text{hfi}}$ .<sup>13,25</sup>

$$V^2 = V_{\text{dd}}^2 + V_{\text{hfi}}^2 \quad (8)$$

Table I presents these values, which have been calculated from  $V$  values assuming that  $V_{\text{dd}}$  is independent on isotopic substitution and the ratio of  $V_{\text{hfi}}$  for deuterated RP to that for nondeuterated one is equal to 0.25 to SDS as well as in SOS micelles. These calculations reveal the 2-fold increase in  $V_{\text{dd}}$  on going from SDS to SOS. For  $T_{\pm}$ - $T_0$  transitions due to the dipole-dipole interaction between the unpaired electrons

$$V_{\text{dd}} = (3/20)^{1/2} g^2 \beta^2 / R^3 \quad (9)$$

Here  $R$  is the effective distance between the unpaired electrons of radicals in the RP.<sup>13</sup> The  $V_{\text{dd}}$ s obtained correspond to  $R = 1.4$  and  $1.1$  nm for RP in SDS and SOS, respectively, which is in a good agreement with the effective distance between the radicals in the micelle. This distance for a three-dimensional diffusion within the spherical boundary may be estimated<sup>7c</sup> as  $(2R_m r)^{1/2} = 1.24$  and  $1.06$  nm for SDS and SOS, respectively. For a two-dimensional model of diffusion on a spherical interface<sup>7c</sup>  $R = 2(2R_m^2 r^4)^{1/6} = 14.5$  and  $13$  nm for SDS and SOS micelles. The comparison of experimental and theoretical  $R$  values leads to a conclusion that the effect of preferential localization of the radicals in the interface in the vicinity of the Stern layer occurs in SDS micelles and its does not in SOS micelles. However, it should be noted that the estimation of the  $V$  values in terms of a given model with a single correlation time<sup>26</sup> may turn out to be a rough one<sup>7c</sup> and results in some deviations of the calculated parameters from

those that might be obtained from the more accurate consideration.<sup>27</sup> Nevertheless the simplest approach reveals the increase of the contribution of dipole-dipole relaxation in small micelles and very reasonable  $R$  values have been obtained. The rate of relaxation in small micelles becomes higher than that in large micelles due to the enhancement of the effective dipole-dipole interaction.

**High Magnetic Field  $H > 0.2$  T.** The absence of the MIE in the magnetic field range  $H > 0.2$  T (Figure 4) demonstrates the negligible role of the hfi in a very high magnetic field. This finding is in agreement with the conclusion about the intersystem nature of the rate-determining step of the reaction in high magnetic field, which is the intersystem crossing from the contact state of triplet RP to the energy surface of a recombination products or some diamagnetic intermediates due to a two-center soc.<sup>6,7c,8</sup> The values of  $k_{\text{soc}}$  are much lower than those of  $k_{\text{chem}}$  (Table I) and  $k_{\text{diff}}$ ; however, they are significantly larger than the values of  $k_{\text{rel}}$  predicted by eq 6 with parameters from Table I or than the values of  $1/T_1$  obtained for ketyl and phenoxyl radicals from ESR data in liquid solutions of corresponding viscosities.<sup>6,8e,21,28</sup> The dependence of  $k_{\text{soc}}$  on micellar volume is in satisfactory agreement with that one should expect for a slow bimolecular process, the rate of which does not depend on viscosity but it should be proportional to  $1/R_m^3$ . It is worthwhile to mention that for deuteriated RP in small SOS micelles  $k_{\text{soc}}$  is close to  $k_{\text{hfi}}$  (Table I). Thus the contribution of soc may be comparable to that of hfi even for RP without heavy atoms.

## Conclusion

In general, the consideration of geminate recombination kinetics of the radical pairs produced in the triplet state in the micelles as well as the attendant magnetic field and magnetic isotope effects in terms of a simple kinetic Scheme I of the first order processes gives an opportunity to distinguish reaction steps of different nature. The magnetic field dependence of kinetic MIEs follows the contribution of hfi induced steps of recombination. The MIE increases between 0 and 0.5 mT; however, this effect may be masked in small micelles by the exchange interaction. A further increase of magnetic field strength is followed by the decrease of MIE, which becomes negligible in the field region higher than 0.2 T, due to the intersystem recombination being the most important mechanism. The interplay of pathways and interactions of a different nature results in a regularity that MIE is higher in small micelles in a small magnetic field but the opposite situation is typical for a higher field region. The unusual very sharp magnetic field dependences may occur for RP with very small hfi. Those results underline the need for theoretical analysis of the field dependence of a spin evolution of RP under the conditions of small hfi and exchange interaction in a finite volume space.

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- (22) More precise calculations according to ref 20 give values of  $k_{\text{diff}}$  that are 25 and 60% higher than those from eq 7 for SDS and SOS micelles, respectively.<sup>9</sup>
- (23) A 2-fold decrease in the rate constant corresponds to effective  $J \approx -A_{\text{hfi}}/4 \approx -0.07 \text{ mT}$  for the deuteriated RP according to estimations in ref 9.
- (24) The behavior of magnetic field dependences at very small  $H$  is determined by the statistics of transitions, which depends on the degeneracy of the system and conservation of the total spin momentum. As the deuterium spin is two times larger than the proton spin, the deuteration may lead to a qualitative variation in the initial part of the field dependence.<sup>10</sup>
- (25) The contribution of the relaxation due to  $g$  anisotropy being estimated as  $\Delta g \beta H / 30^{1/2}$  ( $\Delta g$  characterizes the  $g$  anisotropy and should not exceed 0.002 for a given RP<sup>6b,20</sup>) is less than 10%.
- (26) The experimental errors do not permit analysis of the magnetic field dependences in the range  $H > 0.1 \text{ T}$  with an accuracy sufficient for use of a relaxation model with two correlation times.
- (27) It should be mentioned that the ST<sub>1</sub> mechanism can also contribute slightly to magnetic field dependences up to 0.1 T.<sup>10</sup>
- (28) The rigorous analysis of possible mechanisms of ketyl-phenoxyl RP recombination in  $T_{\pm}$  states in a high magnetic field in alkyl sulfate micelles has already led to a definite conclusion that neither  $g$  anisotropy nor spin-rotational coupling as well as other known mechanisms of paramagnetic relaxation can have any noticeable effect on the decay of the given RP in  $T_{\pm}$  states under a very strong magnetic field.<sup>6,8d,e</sup> A number of regularities of  $\text{BH}^{\bullet}\text{-PO}^{\bullet}$  recombination in a strong magnetic field in alkyl sulfate micelles reveal intersystem recombination as the most important pathway of the recombination of the given RP in  $T_{\pm}$  states in a strong magnetic field.<sup>6,8</sup> A pronounced internal heavy atom effect, which is observed in the RP geminate recombination kinetics in a strong magnetic field while it is not observed at  $H = 0$ , proves the soc nature of the process.<sup>6-8,21</sup>