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Effect of nitroxide radicals on chemically induced dynamic electron polarization of spin-correlated radical pairs in aqueous micellar solutions of sodium dodecyl sulfate

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The multispin systems consisting of spin-correlated radical pairs (SCRPs) and stable nitroxide radicals, localized in micelles of sodium dodecyl sulfate (SDS), were studied by ESR and pulse laser photolysis techniques. In all the systems studied, the stable nitroxide radicals exert no effect on the shape of the ESR spectra of the SCRPs (in particular, on the shape of their antiphase structure) and on the decay kinetics of the ESR signal of the SCRPs. In the SDS micelles, the electron spin polarization transfer from the nonequilibrium electron spin states of the molecular triplets (SCRP precursors) is the most efficient mechanism of generation of the electron spin polarization in nitroxide radicals. The experimental data also show that the nitroxide radicals and SCRP radicals are most probably distributed uniformly in the micellar phase.

Key words: electron spin resonance, chemically induced dynamic electron polarization, micelles, micellized radical pairs, spin-correlated radical pairs, electron spin polarization transfer.

Micelles represent an example of nonuniform supramolecular media widely used in the applied and scientific areas.[1] The micellar phase is inhomogeneous,[1—4] which provides various models for solubility[1—3,5] of organic molecules in micelles. According to the most popular model, hydrophilic compounds are localized in the Stern layer, whereas hydrophobic compounds are predominantly localized in the micelle core. Of course, the assertion about a certain localization of molecules in the micellar phase is idealization, because any molecule incorporated into the micellar phase diffuses. An opposite case of idealization is an assumption that the diffusion coefficient of a dissolved molecule is independent of its position in the micellar phase.[6] ESR spectroscopy of stable nitroxide radicals is widely used to study the local molecular mobility of various media,[7] including micellar media.[8] The interpretation of ESR spectra[8—10] depends substantially on the accepted model of paramagnetic probe distribution in the nonuniform micellar phase.

The microreactor model proposed[11,12] for the description of spin selective processes in micellized spin-correlated radical pairs (SCRPs) assumes the uniform diffusion of radicals over the whole micelle volume. A comparison of the temperature dependences[13] of the translational diffusion coefficients obtained by the numerical simulation of the ESR spectra of the SCRPs with analogous dependences of the correlation time of rotational diffusion of various paramagnetic probes shows that the both dependences are identical, *i.e.*, the assumption on the uniform diffusion of radicals does not contradict the experimental data. However, in this case, the rotational correlation times are an averaged characteristic of the whole micellar phase rather than, *e.g.*, of the Stern layer in which the paramagnetic probe is localized.[8] In addition, it can be assumed in the microreactor theory that the SCRP radicals diffuse in certain concentric layers of micelles, for instance, in the Stern layer or in the palisade layer. If the hydrophilicities of the probe and SCRP partners are approximately equal, the coincidence of the above-mentioned results is quite expected and cannot be interpreted in favor of this or another point of view.

In the present work, we suggest another approach to the problem of investigation of the localization of organic molecules and radicals in the micellar phase. Populations of the electron spin states of excited molecular triplets are known to be primarily nonequilibrium. When colliding with nitroxide radicals, spin-polarized triplets can transfer their electron spin polarization to the radi-

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cals. This mechanism of chemically induced dynamic electron polarization (CIDEP) is named the electron spin polarization transfer (ESPT).[14] The absence of polarization transfer in systems for which the latter is efficient in uniform solvents could indicate the specific localization of organic molecules (triplets) and radicals in the micellar phase, which prevents collisions of the triplet-excited molecules with the radicals.

The electron spin polarization transfer in the micellar phase was first observed in Ref. 15. It was speculated that the polarization of the nitroxide radicals appears due to the spin polarization transfer from the net polarized radicals formed upon the photodissociation of 1-hydroxycyclohexyl phenyl ketone.

Another purpose of the presented study was the following. If the micelle containing the SCRPs includes the nitroxide radical, then the relatively long-lived three-spin system is formed. Such three-spin systems are very interesting from the viewpoint of spin communication, and one of its variants has earlier been discussed in detail.[16] Moreover, these systems correspond to the criteria of applicability of Purtov´s theory[17] for the spin dynamics of three-spin systems to a considerably greater extent than the systems organized by radical pairs (RPs) and the nitroxide radical in usual homogeneous organic solvents. It is important that the increase in the probability of recombination of triplet RPs in the zero magnetic field induced by the nitroxide radicals was observed[18] just in the latter systems. Later this phenomenon was named spin catalysis.[19] It would be very informative to observe the effect of nitroxide radicals on ESR spectra of SCRPs from the viewpoint of both the applicability and testing conditions for the existing theories of spin catalysis and the formulation of experimental conditions that are most adequate to these theories.

Main characteristics of ESR spectra of SCRPs. Time-resolved ESR spectroscopy (TR ESR) of SCRPs was not practically discussed in the Russian scientific literature. Therefore, we will briefly present the main characteristics of the TR ESR spectra of the SCRPs detected in the time interval from several tens of nanoseconds to several tens of microseconds.

In liquid low-viscosity solvents generation of CIDEP is mainly dictated by the electron exchange interaction, whereas the dipole spin-spin interaction is usually neglected. The energy levels of the RPs calculated in the high-field approximation with the spin-spin exchange interaction between the radicals exponentially decaying with an increase in the *r* distance between them for an arbitrary configuration of the magnetic nuclear spins χ ($\chi = \chi_\mathbf{A}\chi_\mathbf{B}$, where $\chi_\mathbf{A}$ and $\chi_\mathbf{B}$ are the nuclear spin configurations of radicals **A** and **B** of the pair) are shown in Fig. 1. The Boltzmann differences in the populations of the RP spin states are not usually detected, because the magnetic field modulation cannot be used and, as a consequence, the sensitivity of the method is insufficient. Detected differences due to CIDEP are typically of the two types. The first variant takes place when the spin states $|\alpha\beta;\chi>$ and $|\beta\alpha;\chi>$ of the pair (see Fig. 1) are populated equally, while the populations of the spin states $|\alpha\alpha;\chi>$ and $|\beta\beta;\chi>$ are different. This situation appears when CIDEP in the SCRPs is determined by the triplet mechanism.[20,21] In this case, all the spectral lines in the TR ESR spectrum are polarized equally, regardless of the configuration of magnetic spins of the pair. If the populations of the levels $|\alpha\alpha;\chi>$ and $|\beta\beta;\chi>$ are the same and the populations of the levels $|\alpha\beta;\chi>$ and $|\beta\alpha;\chi>$ are different, the SCRPs are polarized *via* the radical-pair ST_0 mechanism.[21] In this case, the sign of polarization of the low-field parts of the ESR spectrum is opposite to that of the high-field parts.

The relaxation shifts of the resonance frequencies[22] (Δ_S and Δ_T, see Fig. 1) appear due to the stochastic modulation of the spin-spin exchange interaction in the SCRPs induced by radical diffusion. Let us call this relaxation type the internal relaxation. The shift of the resonance frequencies results in the situation when no compensation (for example, transitions $|\alpha\alpha;\chi> \leftrightarrow |\beta\alpha;\chi>$ and $|\alpha\beta;\chi> \leftrightarrow |\beta\beta;\chi>$ in radical **A**) occurs even if the spin states

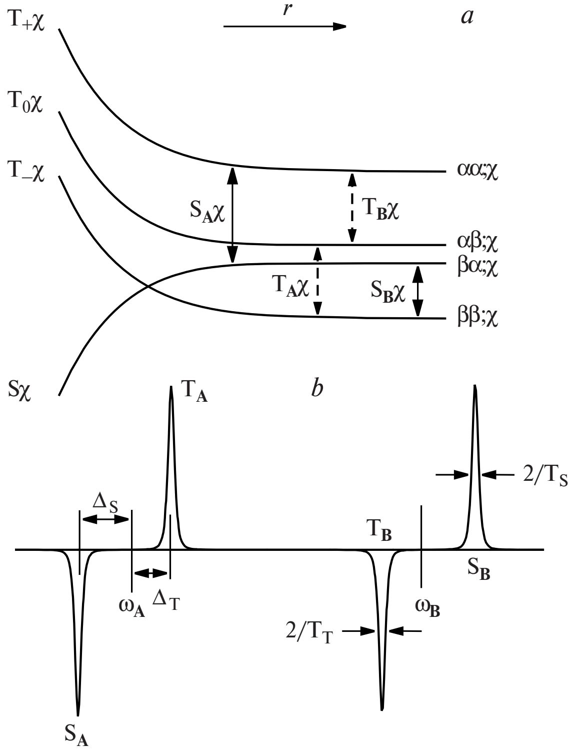


Fig. 1. Diagram of the energy states of the SCRPs at different distances *r* between the pair radicals **A** and **B** (*a*) and the idealized TR ESR spectrum of the SCRPs at the spin-adiabatic occupation of the SCRPs and the equilibrium triplet state of the precursor (*b*); Δ_S and Δ_T are the spectral shifts of the S and T components of the APS, respectively; $2/T_S$ and $2/T_T$ are their widths.

$|\alpha\alpha;\chi>$, $|\beta\beta;\chi>$ and $|\alpha\beta;\chi>$, $|\beta\alpha;\chi>$ are occupied equally in pairs. The appearance of shifts is due to the spin-correlated state of the pair, *i.e.*, to the fact that at any moment the spin state of the SCRP is the coherent superposition of the basis spin states. In the absence of net polarization, the superposition of two spectral lines for the case of slow exchange results in the signal, whose shape coincides with that of the signal of the first derivative of the absorption signal. This shape of the resonance signal is named the antiphase structure (APS).[23] Spectral shifts can substantially exceed the linewidths within the fast exchange when the resonance lines are exchange-narrowed (precisely this limit was used for the numerical simulation of the ESR spectrum of the SCRPs in Fig. 1). The latter case is often observed for the spin-correlated biradicals.[24]

At the positive (negative) difference in the energies of the spin states $|\alpha\beta;\chi>$ and $|\beta\alpha;\chi>$, these states correlate[22] with the triplet $|T_0>$ (singlet $|S>$) and singlet $|S>$ (triplet $|T_0>$) states of the contact pair, respectively. If the first case takes place, the component of the APS $|\alpha\alpha;\chi> \leftrightarrow |\beta\alpha;\chi>$ is named singlet (S) and the $|\beta\beta;\chi> \leftrightarrow |\alpha\beta;\chi>$ — component is named triplet (T). Just this case is presented in Fig. 1 (Δ_S and Δ_T are the resonance shifts of the singlet and triplet components, respectively). For the slow exchange (the resonance shifts of the components are smaller than their widths $2/T_S$ and $2/T_T$), the assignment of the ESR signals to an individual radical still has the physical sense. For instance, the S component $|\alpha\alpha;\chi> \leftrightarrow |\beta\alpha;\chi>$ belongs to radical **A**.

In the cases when the difference between the resonance frequencies is high, the high-field approximation can be invalid and the difference in the populations of the RP spin states depends substantially on the nuclear configuration. This mechanism is named the radical-pair $ST_\pm$ mechanism.[21] The ESR spectra of the micellar SCRPs in which the ST_- mechanism is efficient have been analyzed[25] in detail.

Experimental

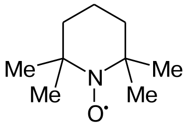
In all cases, we used 0.1 *M* aqueous micellar solutions of sodium dodecyl sulfate (SDS). The micelle concentration was $\sim10^{-3}$ mol L^{-1}. Some uncertainty in the micelle concentration is related to the dependence of the aggregation number on the solubilizate concentration.

Stable nitroxide radicals, *viz.*, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), 3,4-dimethyl-2,2,5,5-tetraethylimidazolin-1-oxyl (TENIO), ammonium *N*,*N*,*N*-trimethyl(2,2,6,6-tetramethyl-1-oxypiperidin-4-yl) iodide, and ammonium *N*,*N*,*N*-trimethyl(2,2,6,6-tetramethyl-1-oxypiperidin-4-yl)methyl sulfate (NTR_1 and NTR_2, respectively) were used.

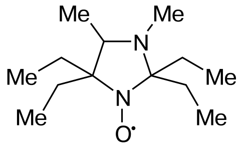
Aqueous micellar solutions of the ketones under study were irradiated in the presence and absence of the nitroxide radicals directly in the ESR cavity with the light of an Nd-YAG laser (λ = 355 nm). ESR spectra were acquired at the outlet of a preamplifier (12 MHz) using a LeCray digital oscillograph.

Results and Discussion

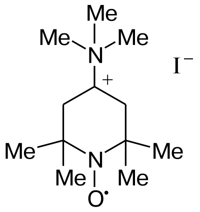
Based on the model "similar-in-similar," we can assert that TEMPO should be localized near the Stern layer with the NO group "immersed" into this layer.[8–10] According to the concepts of localization, the TENIO radical should be situated closer to the center of the micelles, perhaps, in the palisade layer due to the hydrophobic character of four ethyl groups. The NTR_1 and NTR_2 nitroxide radicals are the hydrophilic positively charged radical ions. Therefore, they should be localized in the aqueous layer that is directly adjacent to the Stern layer.



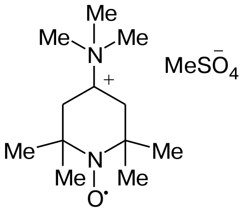
TEMPO



TENIO



NTR_1

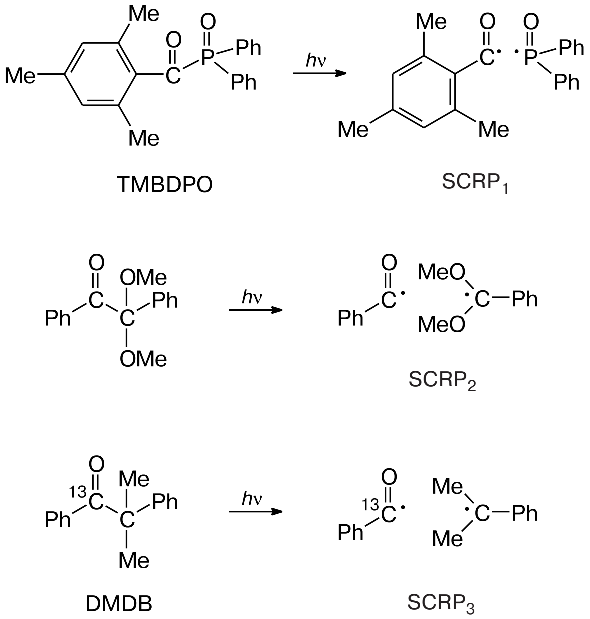


NTR_2

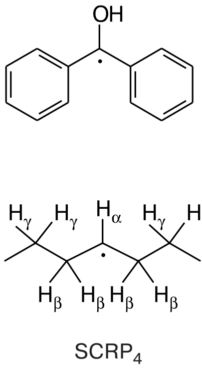
(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TMBDPO), 2,2-dimethoxy-2-phenylacetophenone (Irgakur 651), [^{13}CO]-α,α´-dimethyldeoxybenzoin (DMDB), 2-methyl-1,4-naphthoquinone (MNQ), benzophenone, xanthone, and benzyl are localized in the micellar phase, which follows from the optical absorption spectra. Ketones TMBDPO,[26] Irgakur 651,[27] and DMDB (see Ref. 28) photodissociate in the triplet excited state to form the triplet SCRPs (Scheme 1) consisting of 2,4,6-trimethylbenzoyl and phosphinoyl radicals ($SCRP_1$), benzoyl and α,α´-dimethoxybenzyl radicals ($SCRP_2$), and benzoyl and cumyl radicals ($SCRP_3$), respectively.

Benzophenone[29] and MNQ[30] are photoreduced in SDS micelles to form the $SCRP_4$ and $SCRP_5$ of the corresponding ketyl radical and alkyl radical of the detergent. As follows from the studies of benzophenone photoreduction in homogeneous solutions of dodecyl alcohol[31] in acetonitrile and in SDS micelles,[32] hydrogen atom abstraction from different CH_2 fragments of the hydrocarbon chain of both the alcohol and detergent occurs with approximately the same efficiency, except for the $—CH_2—OSO_3^-$ fragment, which is stable to photooxidation. This indirectly indicates in favor of the uniform distribution of benzophenone over the whole micellar

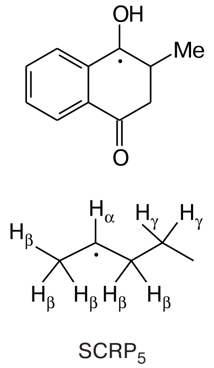
Scheme 1



phase. No similar detailed experimental studies were carried out for MNQ; however, there is no evidence to believe that the photooxidation of the detergent molecules by this quinone is more stereospecific.



SCRP$_4$



SCRP$_5$

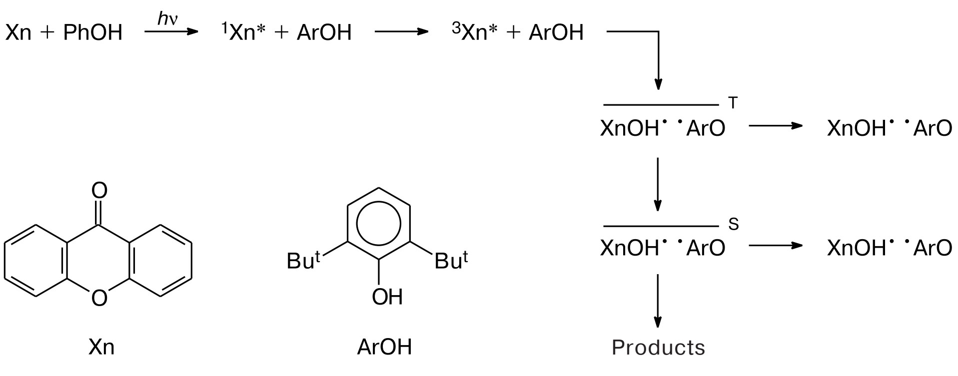
Di-*tert*-butylphenol dissolved in the micellar phase was used for xanthone as a hydrogen atom donor. In this case,[33] the SCRP$_6$ consists of the ketyl radical of xanthone and the phenoxy radical of di-*tert*-butylphenol (Scheme 2).

TR ESR of the SCRPs in micelles in the absence of stable nitroxide radicals. The TR ESR spectrum of the SCRP$_1$ (Fig. 2) is formed by two signals.[25] The doublet with a splitting of 36.5 mT and g = 2.0036 belongs to the phosphinoyl radical (see Scheme 1). The central signal is assigned to the 2,4,6-trimethylbenzoyl radical (g = 2.0007).

Initially (see Fig. 2, *a*) the both components of the doublet and the central signal are positively polarized. Since none of the APS components is emission, the populations of the "internal" spin states $|\alpha\beta;\chi\rangle$ and $|\beta\alpha;\chi\rangle$ are lower than that of the spin state $|\beta\beta;\chi\rangle$ and higher than that of the $|\alpha\alpha;\chi\rangle$ state. In the considered case, the intense polarization of the radicals *via* the triplet mechanism is a consequence of high anisotropy of occupation of the spin states[34] and the high dissociation rate[35] of the triplet.

As the observation time t_{obs} increases, the intensity of the low-field component ($m_Z(^{31}\text{P}) = +1/2$) of the doublet signal decreases substantially more rapidly than the intensity of the high-field component ($m_Z(^{31}\text{P}) = -1/2$). This occurs because the internal relaxation rate in the subsystem with the overall spin $F_z = -1/2$ (two electron spins plus the ^{31}P nuclear spin) is much higher[21,25] than that in the subsystem with $F_z = +1/2$. As a result, at $t_{\text{obs}} > 250$ ns the emission-polarized S component of the APS appears in the low-field and central signals (see Fig. 2, *b*). The T component of the APS of the high-field signal becomes negative considerably later (see Fig. 2, *c*) at $t_{\text{obs}} > 500$ ns. To this time, the emissive S component of APS predominates in the low-field signal, because to this moment the total population of the subsystem $F_z = -1/2$ becomes less than the population of the $|\alpha\alpha;\alpha\rangle$ spin state. This evolution of the spectral shape is possible only in the case when the internal relaxation rate exceeds the rate of external one.

Scheme 2



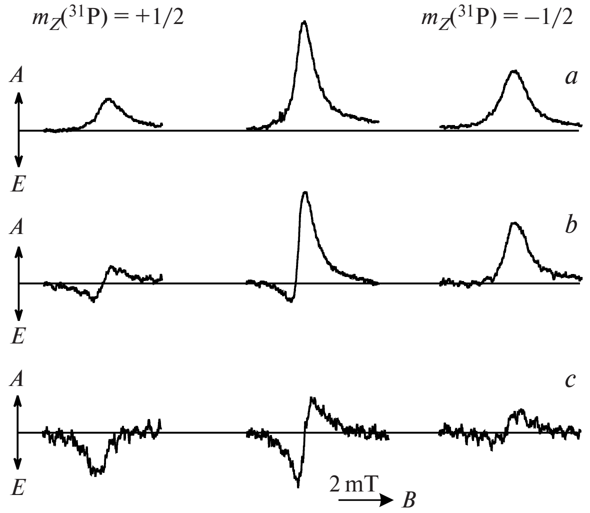


Fig. 2. The TR ESR spectra of the $SCRP_1$ observed upon the photodissociation of TMBDPO in SDS micelles at t_{obs} = 120 (*a*), 290 (*b*), and 480 ns (*c*). The intensities of the spectra are amplified by 3 (*b*) and 12 times (*c*); *A* is adsorption (absorption, positive ESR signal), and *E* is emission (radiation, negative ESR signal).

The evolution of the shape of the low-field APS is shown in Fig. 3. For the short observation time, the T component prevails (see Fig. 3, *a*), whereas the S component of the APS predominates at the long observation time (see Fig. 3, *b*). It is well seen that the APS components have different resonance frequencies, *i.e.*, the observation of the APS is due, in fact, to the spectral shifts caused by the internal spin relaxation because of the electron spin Heisenberg exchange between unpaired electrons of the radicals.

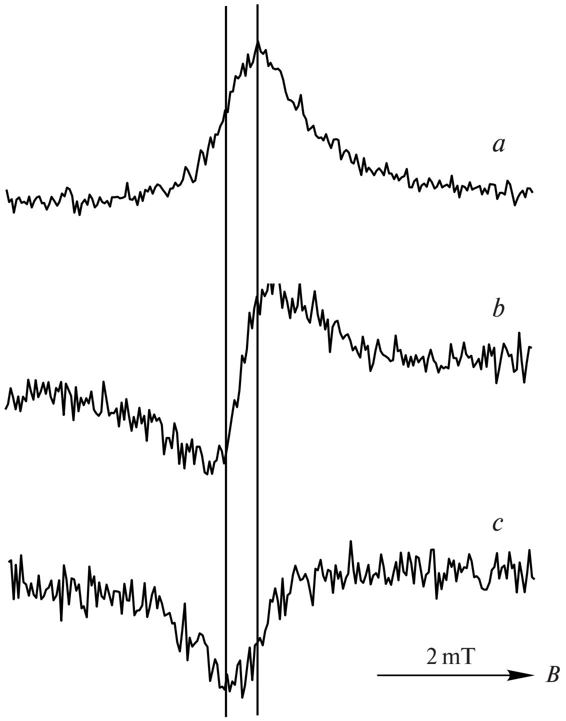


Fig. 3. The low-field component ($m_Z(^{31}P) = +1/2$) in the ESR spectrum of the phosphinoyl radical at t_{obs} = 136 (*a*), 312 (*b*), and 500 ns (*c*). The triplet (*a*) and singlet (*c*) components of the APS have different resonance frequencies.

Since the HFC constant on the carbonyl carbon atom ($A(^{13}C{=}O)$ = 12.5 mT) in the benzoyl radical substantially exceeds the collision frequencies of the $SCRP_3$ radicals in SDS micelles,[28] the spectral lines of the $SCRP_3$, by analogy to the $SCRP_1$, can be attributed to individual radicals. The ESR spectrum of this pair is shown in Fig. 4. The doublet signal (g = 2.0006), each component of which is antiphase-split, is assigned to the benzoyl radical (see Scheme 1). The multiplet signal (g = 2.0026) in the center of the spectrum belongs to the cumyl radical. Since the dissociation rate of DMDB in the triplet-excited state is lower than the spin relaxation rate, the contribution of the triplet mechanism to the electron polarization of the $SCRP_3$ radicals is small. In this case, the initial population of the "internal" spin states $|\alpha\beta,\chi>$ and $|\beta\alpha,\chi>$ (see Fig. 1) is twofold lower than the populations of the "external" spin states $|\alpha\alpha,\chi>$ and $|\beta\beta,\chi>$. The high difference between the populations and rather large spectral shifts of the S and T components of the APS provide the high APS intensity in the TR ESR spectra of the $SCRP_3$ due to the high HFC constant. In spite of the high HFC constant in the benzoyl radical, the contribution of the radical-pair ST_- mechanism proportional to the squared HFC constant (*i.e.*, by an order of magnitude lower than that in the case of the $SCRP_1$) is small in the magnetic field of the spectrometer. As a result, the APS shape is time-independent. At long t_{obs}, the signal of the benzoyl radical is a superposition of the APS and the signal of the free (escaped from the SCRP) radical (the doublet of the poorly resolved triplets). It is important that the ESR linewidth of the free radical

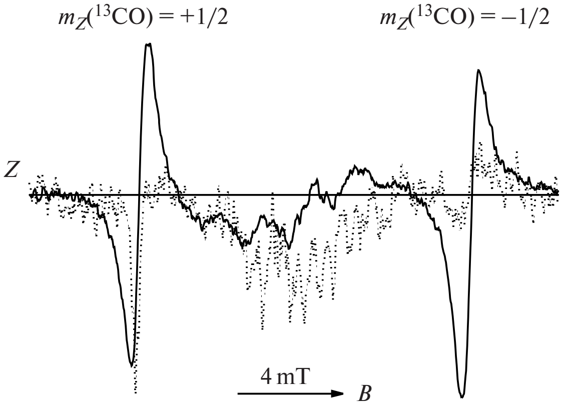


Fig. 4. The ESR spectra of the $SCRP_3$ observed upon the photolysis of DMDB in SDS micelles at t_{obs} = 500 ns (solid line) and 1.6 μs (dotted line, the intensity of the spectrum is amplified by 1.8 times).

(see Fig. 4, dotted line) is much narrower than the APS components of the same radical in the SCRP$_3$ composition. The same is observed for the SCRP$_1$. In this case, both the free radicals and SCRP radicals are localized in the micellar phase. Thus, in the SCRP$_1$ and SCRP$_3$ the rate of external relaxation induced by the anisotropic HFC is much lower than the internal relaxation rate induced by the exchange interaction. Thus, the division of the total width of the APS into additive contributions is not quite valid, because Redfield´s theory of external relaxation is applicable for the SCRP case only within the slow and weak exchange.

In the case of the SCRP$_2$ (Fig. 5), the HFC constants in the benzoyl and α,α´-dimethoxybenzyl radicals are low and do not exceed 0.6 mT. That is why, the electron spin exchange in the SCRP$_2$ is fast for the majority of nuclear configurations. Therefore, it is impossible to assign the ESR signals to any individual radical of the pair. However, the times of external transverse relaxation in the SCRP$_2$ radicals lie in the microsecond range. This results in a monotonic change in the spectral linewidths, depending on the observation time, which impedes an analysis and interpretation of the ESR spectrum of the SCRP$_2$. The radical pairs are negatively polarized according to the triplet mechanism, *i.e.*, the populations of the triplet levels $|\alpha\alpha;\chi>$ exceed those of the $|\beta\beta;\chi>$ levels. Because of the weak intensity of the HFC, the spectral shifts of different APS components are low and the rates of the processes that proceed *via* the radical-pair ST_ mechanism are negligible. Due to this, the external relaxation rate is faster than the rate of equalization of the populations of the "internal" spin states of the SCRP$_2$. As a result, the SCRP$_2$ have no APS, whose components possess opposite signs of polarization.

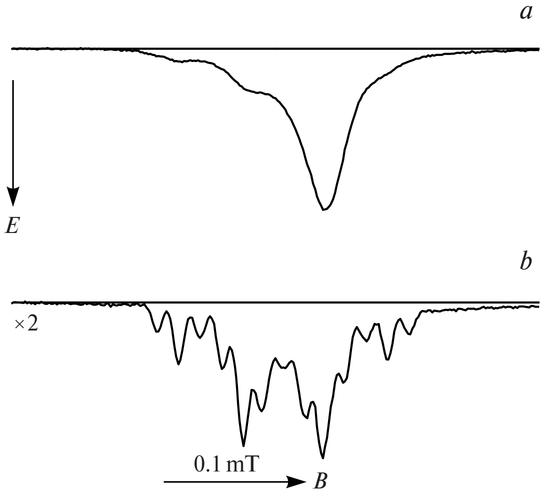


Fig. 5. The TR ESR spectra of the SCRP$_2$ observed upon the photolysis of 2,2-dimethoxy-2-phenylacetophenone in SDS micelles at t_{obs} = 260 ns (*a*) and 1.12 μs (*b*).

In the case of the SCRP$_4$ and SCRP$_5$ formed upon the photoreduction of benzophenone and MNQ, the ESR spectra (Fig. 6, *a* and *b*) are approximately the same, representing a superposition of the antiphase-split ESR spectra of the alkyl radicals (products of SDS photooxidation) and the ESR spectra of the corresponding ketyl radicals of benzophenone and MNQ. For the both SCRPs, the exchange is slow for the external components of the spectrum of the alkyl radicals (the corresponding differences in the resonance frequencies exceed the collision frequencies of the radicals) and fast for the central part.[22]

Since the photoreduction rate in the micellar phase is rather low (~10^7 s^{-1} for benzophenone), the contribution of the triplet polarization mechanism to the ESR spectra of these pairs is small. Therefore, the pairs have the distinctly pronounced APS (see Fig. 6, dashed lines). At long time delays (more than 2 μs), the signals of the free alkyl radicals polarized *via* the radical-pair ST$_0$ mechanism predominate in the spectrum.

The TR ESR spectra of the SCRP$_6$ formed upon the photooxidation of di-*tert*-butylphenol with xanthone in SDS micelles are presented in Fig. 7, *a*. The spectra were obtained at t_{obs} = 560 ns and represent a superposition of the unresolved ESR signals distributed in a narrow interval of resonance fields. Due to this, the spin exchange is

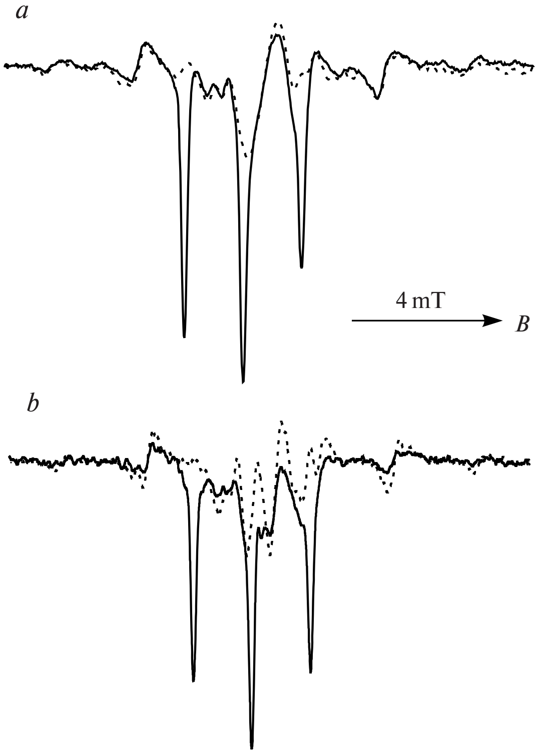


Fig. 6. The TR ESR spectra of the SCRP$_4$ (*a*) and SCRP$_5$ (*b*) at C_{TEMPO} = 1 (*a*) and 2 mmol L^{-1} (*b*). Dashed lines show the spectra of the SCRP$_4$ and SCRP$_5$ in the absence of TEMPO; t_{obs} = 320 ns.

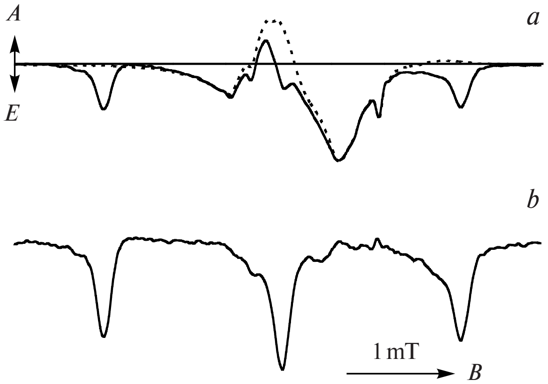


Fig. 7. *a*. The TR ESR spectrum observed upon the photolysis of xanthone (2 mmol L^{-1}) in aqueous micellar solutions of SDS and di-*tert*-butylphenol (2 mmol L^{-1}) in the presence of TEMPO (2 mmol L^{-1}) (solid line) and absence of TEMPO (dashed line). *b*. Difference in the TR ESR spectra in the presence and absence of TEMPO.

fast. The presence of the APS is proved exclusively by the numerical simulation of the spectra. Since the rate of 2-butylphenol photooxidation is much higher than that of the photooxidation of the detergent molecules with benzophenone or MNQ, the contribution of the net polarization *via* the triplet mechanism to the CIDEP of the SCRP$_6$ is noticeably higher than that for the SCRP$_4$ and SCRP$_5$.

The emissive and poor TR ESR spectrum observed for the laser photolysis of benzyl in SDS micelles is shown in Fig. 8 (curve *1*). The spectrum contains no characteristic signals of the alkyl radicals of SDS. Presently we cannot identify the observed signal. Probably, it belongs to the triplet of benzyl but, perhaps, to the radical products of photooxidation of unknown admixtures. Further we will neglect this weak signal and believe that the photolysis of benzyl in SDS micelles is not accompanied by SCRP formation.

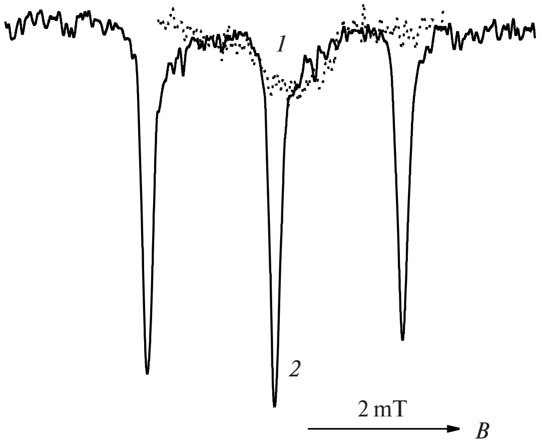


Fig. 8. The TR ESR spectrum observed upon the laser photolysis of benzyl (2 mmol L^{-1}) in aqueous SDS micelles in the absence (*1*) and presence of TEMPO (1 mmol L^{-1}) (*2*).

Effect of the stable nitroxide radicals on the CIDEP of the SCRPs in micelles. The addition of stable nitroxide radicals to aqueous micellar SDS solutions of the considered ketones provides two main effects: CIDEP generation in the stable nitroxide radicals and a decrease in the intensity of the TR ESR signals of the SCRPs (or in other words, CIDEP quenching in the SCRP radicals). It is important to underline several factors.

1. We found indications to the specificity of localization of the ketones and radicals, including the stable nitroxide radicals, in none of the experimental examples. In all experimental systems, CIDEP generation in the nitroxide radicals occurs with approximately the same efficiency.

2. The TEMPO radical is chemically active during the photolysis of all ketones under study. This is expressed in the fact that TEMPO is consumed either in the reactions with triplet-excited ketone or with radicals of the corresponding SCRPs.

3. The shape of the TR ESR spectra of the SCRPs is independent of the presence of TEMPO. This is valid for both the SCRPs in which no APS is observed (Fig. 9, *a* (SCRP$_1$ at short observation times) and Fig. 10 (SCRP$_2$)) and the SCRPs in which the APS predominates in the spectrum (see Fig. 9, *b* (the low-field component of the TR ESR spectrum of the SCRP$_1$ at intermediate t_{obs} values), Fig. 11 (SCRP$_3$ at $t_{obs} < 1$ μs), Fig. 6, *a* and *b* (SCRP$_4$ and SCRP$_5$, respectively)). In the case of the SCRP$_6$, the shape of the complicated ESR signal also remains unchanged, because the observed signal (see Fig. 7) is a superposition of the ESR signals of the SCRP$_6$ and TEMPO.

4. A comparison of the linewidths of the polarized TEMPO radical at low concentrations, when the occupation of micelle is less than unity, shows that the linewidth of the polarized radical is equal to that of the thermolyzed TEMPO. In other words, no additional broadening of the resonance lines occurs for the TEMPO. At high TEMPO concentrations, the ESR linewidths of the spin-polarized nitroxide radicals increase with an increase in the TEMPO concentration in micellar SDS solutions substantially more slowly than the linewidths of the equilibrium radicals, which is caused, most likely, by a decrease in the TEMPO concentration during photolysis.

5. The kinetics of the TR ESR intensities of the SCRP$_1$ normalized to the maximal intensity is shown in Fig. 12. The normalized decay kinetics of the TR ESR signals (CIDEP quenching kinetics) is independent of the presence of TEMPO (see Fig. 12). This is valid for other studied SCRPs. The listed conclusions also concern the systems consisting of the SCRP$_1$ and stable radicals TENIO, NTR$_1$, and NTR$_2$.

To explain CIDEP generation in the nitroxide radicals in micellar solutions during the photolysis of alkyl-

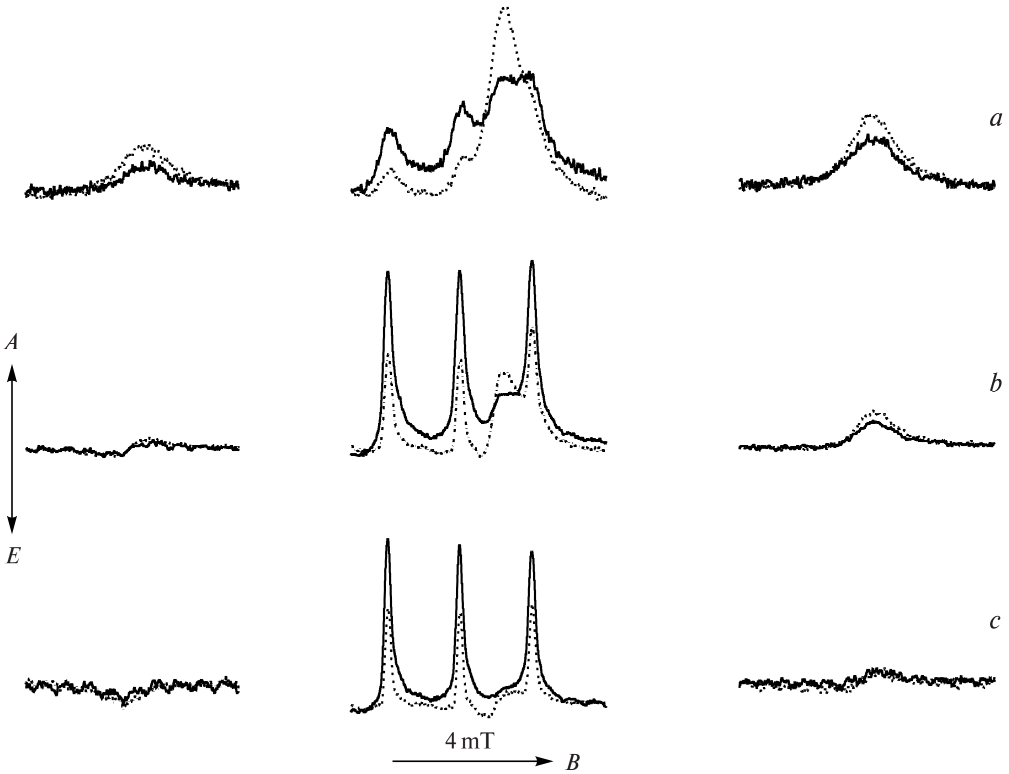


Fig. 9. The CIDEP of TEMPO upon the photolysis of TMBDPO (6 mmol L^{-1}) in SDS micelles at C_{TEMPO} = 1.5 (solid line) and 6 mmol L^{-1} (dotted line) and t_{obs} = 120 (*a*), 290 (*b*), and 490 ns (*c*).

aromatic ketones, it was suggested[15] that the nonequilibrium magnetization is transferred from the SCRP radicals to the nitroxide radicals due to the spin-spin exchange interaction between the radicals of the pair and the nitroxide radical. However, this explanation is not general as minimum, because the CIDEP of the nitroxide radicals is also observed when no RPs are formed in the micelles. In fact, the laser photolysis of benzyl in SDS micelles produces the broad and low-intensity ESR signal (see Fig. 8, curve *1*) with g = 2.0045 at the intensity maximum, which possibly belongs to triplet-excited benzyl. At the same time, the addition of TEMPO to micellar solutions of benzyl results in the easily detected signal of the negatively polarized TEMPO radicals (see Fig. 8, curve *2*). Analogously, the strong emissive net polarization of TEMPO was observed[36] for the photolysis of

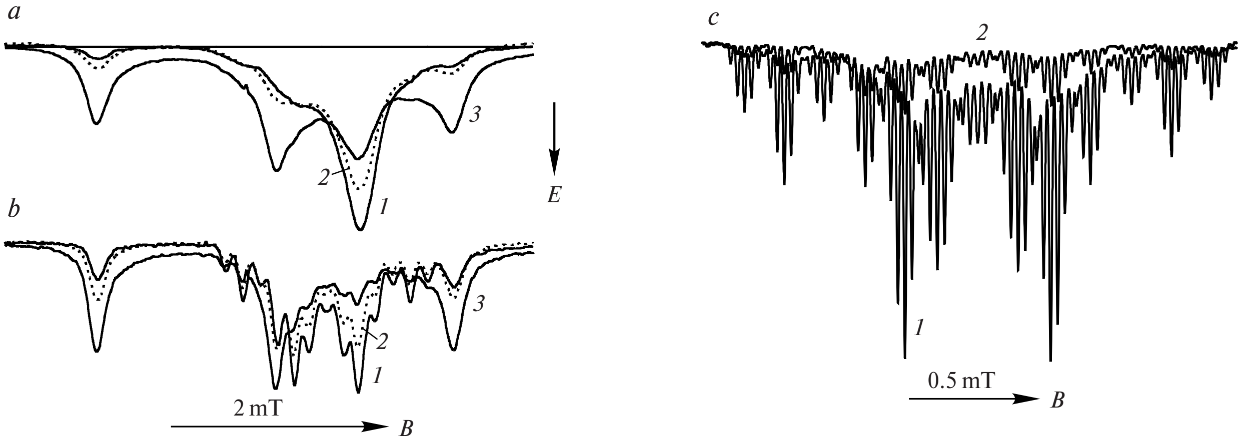


Fig. 10. The CIDEP of TEMPO upon the photolysis of 2,2-dimethoxy-2-phenylacetophenone (6 mmol L^{-1}) in SDS micelles at C_{TEMPO} = 2 (*1*), 4 (*2*), and 6 mmol L^{-1} (*3*) and t_{obs} = 260 ns (*a*) and 1.12 μs (*b*). *c*. Fragments of the TR ESR spectra observed at t_{obs} = 3.6 μs in the absence (*1*) and presence (*2*) of TEMPO (4 mmol L^{-1}).

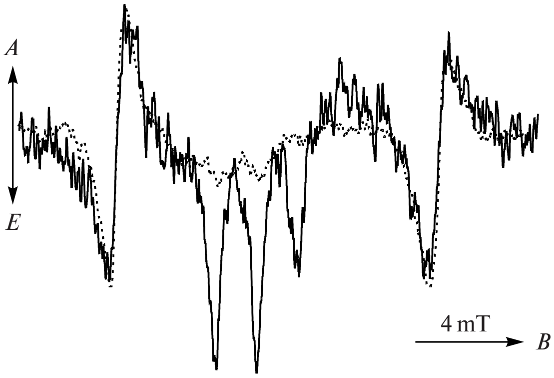


Fig. 11. The CIDEP of TEMPO (2 mmol L^{-1}) upon the photolysis of DMDB (2.4 mmol L^{-1}) in SDS micelles at t_{obs} = 500 ns. Dotted line is the TR ESR spectrum observed under the same conditions but in the absence of TEMPO. The intensity of the spectrum in the presence of TEMPO is amplified by 4.6 times.

xanthone and bromopyrene in SDS micellar solutions, which also form no RPs.

All the systems under study are qualitatively identical in the sense than the CIDEP in the stable radicals appears with approximately the same efficiency, regardless of the structure of both the radicals and ketones and corresponding SCRPs. This observation makes it possible to neglect the specificity of solubilizate localization in the micellar phase, *i.e.*, to advocate that the compounds dissolved in the micellar phase experience pair collisions with the frequency (Z) determined by the equation

$$Z = 3RD\eta_{fil}/V_F,$$

where R is the collision radius, D is the mutual diffusion coefficient, V_F is the free volume of the micellar phase, and η_{fil} is the number of micelle filling with the collision partner. For the SCRP radicals, $\eta_{fil} = 1$. For the nitroxide radicals, η_{fil} is usually identified with the mean value obtained by the Poisson distribution. Thus, one can accept $Z = 6 \cdot 10^7\eta_{fil}$ s^{-1} as the standard characteristic. Note that V_F is determined by the geometry of the micelle and radicals and also by the hydrophobic properties of the solubilizate because of the equilibrium of the diffusion flows directly at the interface of two phases (aqueous and micellar) and the dependence of the region of diffusion roving of the solubilizate on its hydrophilic properties. The polar radicals can diffuse to the regions with the increased water content, and the region of nonpolar radical diffusion is restricted by the more hydrophobic (smaller in geometric sizes) part of the micellar phase. This, particularly, results in the dependence of the HFC constants in the nitroxide radicals on their polarity[8] rather than their specific localization.

Several different physicochemical spin selective processes involving the stable nitroxide radicals can occur in the considered systems. First, the nitroxide radicals are quenchers of both the triplet and singlet photoexcited electronic states.[37] The CIDEP can be generated in the nitroxide radicals according to the radical-triplet pair mechanism (RTPM).[38] If the polarization on the nitroxide radicals in all the SCRPs under study was negative, the predomination of the RTPM in CIDEP generation could be assumed; the more so, the viscosity of the micellar SDS phase is relatively high. However, in the case of TMBDPO, the polarization of the nitroxide radicals is positive (see Fig. 9). Therefore, it is improbable that the RTPM is the predominant mechanism in the generation of nitroxide radical polarization in micellar solutions. The positive polarization could appear due to the quenching of the excited singlet state of TMBDPO, as it occurs for coronene quenching in benzene.[39] However, this assumption contradicts the emission polarization of TEMPO during the photolysis of other ketones.

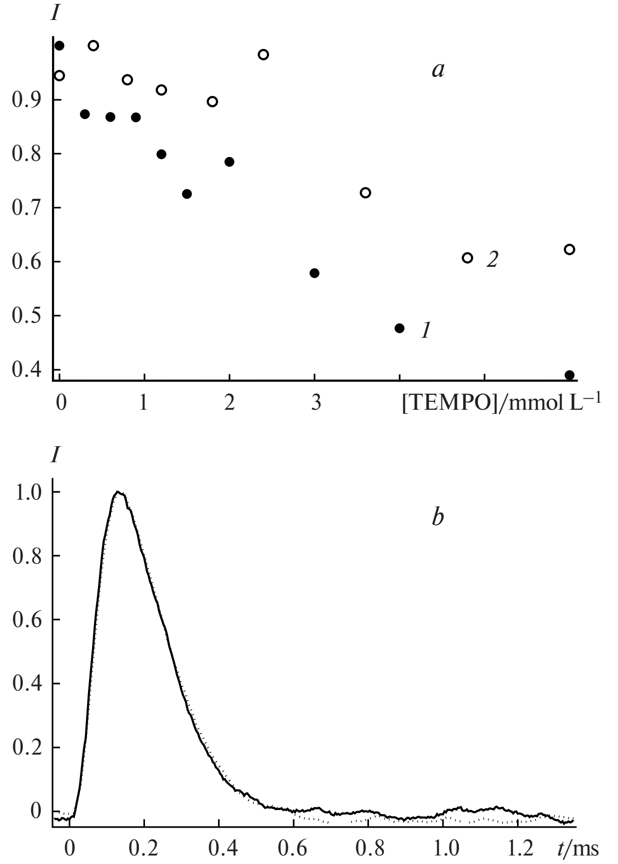


Fig. 12. *a*. Relative net TR ESR intensities (I) of the high-field signal (*1*) and optical absorption at the maximum (*2*) of the phosphinoyl radical upon the photolysis of TMBDPO (6 mmol L^{-1}) in SDS micelles at different TEMPO concentrations. *b*. Kinetics of the high-field ESR signal normalized to the maximum intensity value for the phosphinoyl radical upon the photolysis of TMBDPO (6 mmol L^{-1}) in SDS micelles in the absence (solid line) and presence (dotted line) of TEMPO (4 mmol L^{-1}).

Collisions of the radicals with the spin-polarized molecular triplets can result in polarization generation in the stable radicals *via* the ESPT mechanism.**[14]** It is conventional but useful to distinguish the ESPT and RTPM mechanisms, because the time of CIDEP generation *via* the ESPT mechanism is restricted by a substantially shorter interval than that in the RTPM, *viz.*, the relaxation time of the electron spin states of the molecular triplet. In the case of the ESPT mechanism, the signs of polarization on the nitroxide radical and RP radicals polarized *via* the triplet mechanism should coincide, *i.e.*, this mechanism qualitatively agrees with the experimental data. Quantitatively it also does not contradict the experimental results. In fact, the relaxation rate of populations of the isotropically rotating triplet with the zero-field splitting parameters, which satisfy the inequality $|D_{\mathrm{ZFS}}| >> |E_{\mathrm{ZFS}}|$, is the following**[20]**:

$$1/T_1 = (2/15)D^2{}_{\mathrm{ZFS}} \cdot [4\tau_c/(1 + 4\omega_0{}^2\tau_c{}^2) + \\ + \tau_c/(1 + \omega_0{}^2\tau_c{}^2)],$$

where τ_c is the correlation time, and ω_0 is the frequency of the ESR spectrometer in the X-range.

For the case**[34]** of TMBDPO, $|D_{\mathrm{ZFS}}| = 0.185$ cm^{-1}. Accepting $\tau_c \approx 100$ ps as an approximate estimate for TMBDPO in SDS micelles, for $\omega_0 = 6 \cdot 10^{11}$ s^{-1} we obtain that the longitudinal relaxation time in the electron-excited triplet of TMBDPO is approximately $1/T_1 = 3 \cdot 10^8$ s^{-1}. For a nitroxide radical concentration of $6 \cdot 10^{-3}$ mol L^{-1}, the average micelle filling is $\eta_{\mathrm{fil}} = 4$. Using these estimates, we have that the fraction of depolarized triplets due to collisions with the nitroxide radical is $(Z\eta_{\mathrm{fil}}\eta_{\mathrm{pol}}T_1)/(1 + Z\eta_{\mathrm{fil}}\eta_{\mathrm{pol}}T_1)$, where η_{pol} is the polarization coefficient equal to ~0.4 for the diffusionally controlled quenching of the triplet. This value is well consistent with the experimental data (see Fig. 12, *a*).

The relative absorbance values of the phosphinoyl radical at the wavelength $\lambda = 355$ nm (at the maximum of the optical absorption spectrum) measured at the kinetic curve maximum (immediately after a laser pulse) and the relative net intensities of the TR ESR high-field component of the SCRP$_1$ at the maximum of its kinetic curve are shown in Fig. 12. In the both cases, the values were obtained relative to the corresponding signals in the absence of TEMPO. The almost coincidence of the results of different experiments and the agreement with the theoretical estimate indicate that the ESPT mechanism is predominant for CIDEP generation in the nitroxide radicals, if assuming the simultaneous polarization transfer and triplet state quenching.

In the nitroxide radicals, CIDEP can also appear due to spin selective reactions of SCRP radical accepting by the nitroxide radicals. Let us assume that the radicals of the pair are positively polarized, *i.e.*, the number of radicals with the β-electron spin exceeds the number of radicals with the α-electron spin. Since no reaction occurs upon the collision of two radicals with the likely oriented spins, an excess of β-spins of the radicals of the pair will result in the situation when predominantly the nitroxide radicals with the α-electron spin would be involved in the accepting reaction, *i.e.*, the "reaction" polarization transfer will take place. This polarization mechanism is not less probable than the transfer of the nonequilibrium magnetization from an ensemble of the polarized radicals of the pair to an ensemble of the nitroxide radicals. However, in the case of the SCRP$_3$—SCRP$_5$ when the net polarization of the radicals is low, polarization generation due to this mechanism cannot be efficient. Nevertheless, the nitroxide radicals turned out to be spin-polarized.

Moreover, the accepting reaction of one of the partners by the SCRP should produce free radicals (partners by the SCRP of the accepted radical) polarized according to the radical-pair ST$_0$ mechanism. In the cases of the SCRP$_4$ and SCRP$_5$, it can be difficult to detect this effect, because the widths of the components of the APS and free radicals are comparable. In the cases of the SCRP$_1$ and SCRP$_3$, free radicals can easily be distinguished from the radicals in pair by substantially narrower resonance lines as well. However, no increase in the rate of formation of the free radicals polarized *via* the radical-pair ST$_0$ mechanism is observed in the presence of the nitroxide radicals in these systems. At the same time, accepting unambiguously takes place (see above). Therefore, the rate of this process is appreciably lower than the internal relaxation rate in the SCRPs, *i.e.*, the collision rate of the pair radicals in SDS micelles. Based on this, we may conclude that the radical-pair ST$_0$ mechanism can be neglected for random pairs formed by the nitroxide radical and one of the SCRP radicals; the more so, this mechanism occurs only at low concentrations of the nitroxide radicals.

The exchange electron spin-spin interactions of the pair radicals with the nitroxide radical can polarize the latter, if the pair radicals are net polarized. Indeed, among the eight spin states of the three-spin system for the fixed configuration χ of the nuclear spin subsystem in a strong magnetic field under the conditions when the external longitudinal paramagnetic relaxation can be neglected, the population of the two spin states $|\alpha\alpha\alpha;\chi>$ and $|\beta\beta\beta;\chi>$ remains unchanged. The other six states can be grouped according to the projection of the total electron spin: $|\alpha\beta\beta;\chi>$, $|\beta\alpha\beta;\chi>$, $|\beta\beta\alpha;\chi>$ ($M_z = -1/2$) and $|\alpha\alpha\beta;\chi>$, $|\alpha\beta\alpha;\chi>$, $|\beta\alpha\alpha;\chi>$ ($M_z = +1/2$). The pair exchange interactions between the pair radicals and the interactions of the pair radicals with the nitroxide radical ($J_{\mathbf{AB}}(r_{\mathbf{AB}})$, $J_{\mathbf{BC}}(r_{\mathbf{BC}})$, and $J_{\mathbf{CA}}(r_{\mathbf{CA}})$, respectively) equalize the populations of the states inside these groups but induce no "flip-flop" transitions of the electron spins between the spin states belonging to different groups. Let us assume that the pair is born from the molecular triplet polarized state, so that the population of the $|T_0\rangle$ spin state of the triplet is 1/3 and those of the spin states $|T_+\rangle$ and $|T_-\rangle$ are $1/3 - \eta$ and $1/3 + \eta$, respectively, where η is the net polarization *via* the triplet mechanism. If the spin exchange is efficient, the system reaches intermediate equilibrium within the time $2/Z \approx 30$ ns. It is easy to calculate the population of each group existing in the intermediate equilibrium state. If N nitroxide radicals are localized in a micelle, then the intensity of the ESR spectra of each SCRP radical is proportional to $2\eta/(2 + N)$ and the intensity of the ESR signal of the nitroxide radicals is proportional to $2\eta N/(2 + N)$. Using the standard approximation of the Poisson distribution of the solubilizate in micelles, we obtain that the intensities of the pair radicals ($I_\mathbf{A}$ and $I_\mathbf{B}$) and nitroxide radicals ($I_\mathbf{C}$) are proportional

$$I_\mathbf{A} \approx I_\mathbf{B} = \sum_N \frac{[N]^N \exp(-[N])}{N!} \cdot \frac{2\eta}{2+N},$$

$$I_\mathbf{C} = \sum_N \frac{[N]^N \exp(-[N])}{N!} \cdot \frac{2N\eta}{2+N}.$$

The time of establishing the quasi-equilibrium polarizations $I_\mathbf{A}$, $I_\mathbf{B}$, and $I_\mathbf{C}$ is determined by the collision frequency of the radicals in micelles, *i.e.*, lies in an interval of only several tens of nanoseconds. This time interval is much shorter than the characteristic time of exchange by the nitroxide radicals of micelles limited by bimolecular collisions of the micelles with each other or between the radicals and micelles. Due to this, the presence of the third spin in the micelle exerts no qualitative effect on the character of the ESR spectrum of the net polarized radicals, decreasing only its intensity. However, if this process is efficient, it should be accompanied by the additional exchange broadening of the spectral lines of both the SCRP radicals and the nitroxide radical. As shown by the analysis of the shape of the TR ESR spectra, no additional broadening is observed even for the very narrow resonance lines of the α,α′-dimethoxybenzyl radical (see Fig. 10, *c*, SCRP_2).

Thus, of the set of probable spin selective processes, namely, spin polarization transfer from the spin-polarized triplet states, spin polarization due to the RTPM, spin selective accepting, CIDEP due to the radical-pair ST_0 mechanism in random radical pairs, and exchange interaction with net polarized radicals, only the first one is completely consistent with the experimental results. The efficiency of other processes is substantially lower. In addition, these processes would contradict the experimental facts in several cases. Therefore, the observed increase in the probability of recombination of the SCRPs of the benzoyl and *sec*-phenetyl radicals[18] in the zero magnetic field contradicts our experimental observations and conclusions. Perhaps, the high concentration of the nitroxide radical induces the racemization of dimethyldeoxybenzoin already in the triplet state due to, *e.g.*, ketone enolization in the encounter complex. It is noteworthy that the lifetime of the triplet state of dimethyldeoxybenzoin is approximately two orders of magnitude longer than the lifetime of the SCRPs in benzene, *i.e.*, the quenching of the triplet state of the ketone by the nitroxide radical is a knowingly more probable event than the generation of the three-spin system.

Thus, among possible processes the electron spin polarization transfer from nonequilibrium molecular triplets to the nitroxide radical is most efficient. All other processes, including spin catalysis, which affect the decay kinetics of radicals to this or another extent, play a substantially smaller role in electron spin polarization generation of the nitroxide radicals in micellar multispin systems.

The lifetimes of the triplet excited states of the ketones under study lie in a rather wide interval: from 100 ps (TMBDPO) to microseconds (benzyl). In the cases of TMBDPO and 2,2-dimethoxy-2-phenylacetophenone, these lifetimes are shorter than the relaxation times of the nonequilibrium spin states of the corresponding triplets. Nevertheless, the numerical estimations show that the assumption on the uniform distribution of the radicals over the micelle volume is quite adequate to the experimental observations. Of course, this does not exclude a possibility of specific localization of the radicals in micelles, although it seems rather strange, because this localization was found for none of 13 radicals with different chemical structures. However, the experimental data obtained show that this specificity is unnecessary to assume.

The absence of any influence of the nitroxide radicals on the linewidths of the SCRP radicals and the width of the APS components even at relatively high concentrations of the nitroxide radicals suggests the following: either the exchange interaction between the nitroxide radicals and the pair radicals is low, which explains, particularly, the relatively low efficiency of accepting of the SCRP radicals, or the quenching of the excited triplet states of the considered ketones by the nitroxide radicals is so efficient that no three-spin systems are formed.

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