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Spin-Selective Reaction with a Third Radical Destroys Spin Correlation in the Surviving Radical Pairs

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ABSTRACT: The goal of this work is to reveal the effect that an irreversible spin-selective reaction of a partner of the spin-correlated radical pair (SCRP) with a third paramagnetic particle has on the spin state of the surviving SCRPs in the absence of spin exchange interaction. As studied SCRPs, we used the geminate (excess electron/radical cation) pairs generated by ionizing irradiation of tetramethyl-*para*-phenylenediamine solutions in *n*-dodecane. As a spin-selective reaction, the scavenging of electrons by nitroxide radicals from the bulk of the solution was used. Both the electron scavenging reaction and the spin correlation in the surviving SCRPs were monitored by measuring the recombination fluorescence decays of the irradiated solutions under the same experimental conditions. It was found that the spin-selective electron scavenging results in the acceleration of spin correlation decay in the remaining unreacted SCRPs. In accordance with the suggested theoretical model, the rate of this additional spin correlation decay is revealed to be equal to the scavenging rate.
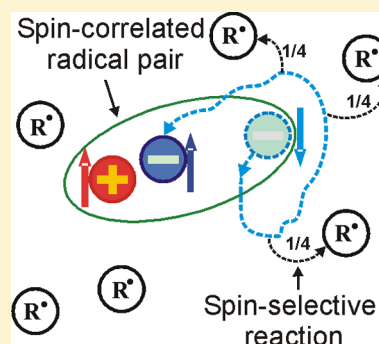
INTRODUCTION

Spin-correlated radical pair (SCRP) is an example of a quantum mechanical system in which dynamical transitions between spin levels interplay with irreversible processes involving nonspin degrees of freedom. For example, partners in a SCRP can recombine with formation of covalent bonds, with the recombination rate depending on the total electron spin of the radical pair.[1,2] In general, the reaction changes the spin state of the surviving SCRP subensemble. However, consistent description of the spin evolution of such subensemble is still a challenging problem. In particular, various approaches to account for the spin-sensitive recombination of the SCRP partners are actively debated.[3−7]

The effect of spin-sensitive chemical reactions of SCRP's partners with a third paramagnetic particle on the spin state of surviving SCRPs, without any contribution of the spin exchange interaction, has not yet been explored. There are a number of experimental studies[8,9] of organic radicals' reactions, where this effect potentially could be detected. However, in such experiments, spin transitions in the SCRP driven by the spin exchange with the third radical dominates,[8,10] thus precluding the detection of the effect under discussion. In a broader context, fundamentally the same effect of spin-selective interaction could also be searched for in the spin-dependent tunneling from two-electron quantum dots (see, e.g., ref 11), as well as in the exciton−polaron interaction phenomena in semiconductors.[12,13]

The present work focuses on the effect of a spin-selective reaction of one of the SCRP partners with a third radical on the spin state of surviving pairs. The ensemble of SCRPs was created by pulsed ionizing irradiation of dodecane solution of tetramethyl-*p*-phenylenediamine (TMPD), and it consisted of excess electrons, e^-, and radical cations, $TMPD^{+\bullet}$, created via scavenging of primary solvent holes by TMPD molecules. In these conditions, the recombination of $e^-/TMPD^{+\bullet}$ pair produces a fluorescing state of luminophore, $^1TMPD^*$, if the SCRP is in the singlet spin state at the moment of recombination:

$$e^- + TMPD^{+\bullet} \rightarrow\ ^1 TMPD^* \rightarrow\ ^1 TMPD + h\nu \qquad (1)$$
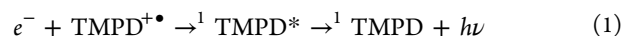
As the spin-selective reaction, the scavenging

$$e^- + R^\bullet \rightarrow R^- \qquad (2)$$

of electron partners in $e^-/TMPD^{+\bullet}$ SCRPs by nitroxide radicals $R^\bullet$ was used. In order to minimize the spin exchange contribution to spin transitions in the SCRPs, we have studied long-distance electron transfer to 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) as well as to 2,2,3,4,5,5-hexamethyl-imidazolidin-1-oxyl (HMI) in *n*-dodecane. As our previous studies showed,[14,15] reaction 2 proceeds in these cases only if the spin state of $e^-/R^\bullet$ encounter pair is singlet, with the typical reaction distances of about 1.5 nm. Rates of all the processes involved, i.e., recombination of the SCRPs, spin evolution of SCRPs, and the reaction of excess electrons scavenging, have been monitored using recombination fluorescence decays from the irradiated TMPD solutions.

■ EXPERIMENTAL SECTION

The recombination fluorescence of deoxygenated n-dodecane solutions of TMPD was excited by X-ray pulses with quantum energy of about 20 keV and detected in the single photon counting mode at 293 K. The delayed fluorescence intensity decay $I_B(Q,t)$ was recorded with time resolution of about 3 ns at different concentrations Q of nitroxide radicals and magnetic fields strength, B, varied within the range from zero ($< 5 \times 10^{-6}$ T) to 1 T. The experimental setup was described elsewhere.[16]

The rate of electron scavenging by radicals has been determined using the method of prerecombinational quenching.[17,18] Namely, time dependences of the ratio $I_0(Q,t)/I_0(0,t)$ for various values of Q were approximated with an exponential dependence to estimate the rate kQ of electron scavenging using the expression

$$\frac{I_0(Q,\,t)}{I_0(0,\,t)} \approx e^{-kQt} \qquad (3)$$

where k is the scavenging rate constant. The approximation was performed in the time range of 50 to 100 ns. In TMPD solutions, there are deviations at times shorter than 50 ns that are caused by the finite lifetime of the excited TMPD molecules and the energy transfer from excited solvent molecules.[19]

Since the generation of radical ion pairs by high energy ionization is a vertical, spin-conserving process, SCRPs are preferentially formed in the spin singlet state. The subsequent evolution of the singlet state population depends on the external magnetic field (see Figure 1).[1,2,20] Time-resolved
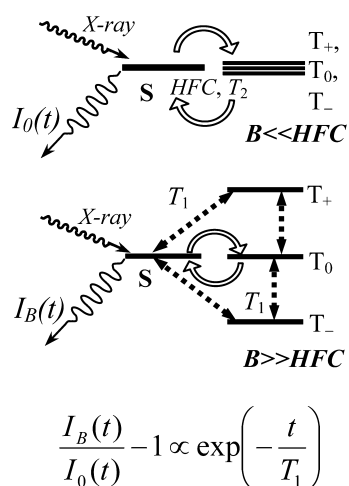
Figure 1. Spin-state energy diagram for a radical pair in zero magnetic field ($B \ll HFC$) and in a strong one ($B \gg HFC$). Straight dotted arrows show relaxation transitions between the states. Formula shows the asymptotic behavior for the ratio of recombination fluorescence decay curves at some initial excess of singlet states as created by the solvent ionization.

magnetic field effect (TR MFE) curve was determined as the ratio $I_B(Q,t)/I_0(Q,t)$ of the fluorescence decays registered in strong, $B = 1$ T, and zero magnetic fields. In this work, to estimate the rate of SCRP singlet state depopulation, we have measured the rate of spin−lattice relaxation at a comparatively long time, where TR MFE curve can, typically, be approximated by a single exponent[20]

$$\frac{I_B(Q,\,t)}{I_0(Q,\,t)} - 1 \approx \theta \cdot \exp\left(-\frac{t}{T_1}\right) \qquad (4)$$

Here $1/T_1$ is the sum of the spin−lattice relaxation rates of radicals composing the SCRP in strong magnetic field. The parameter $\theta \approx 0.25$ for the solutions studied is introduced to take into account that only a part of recombining radical ion pairs arises as singlet-correlated ones. Its value is actually of no significance for using eq 4 to obtain T_1. The approximation of TR MFE curves with eq 4 has been performed within the time range of 60−100 ns.

n-Dodecane (99%, Aldrich) was treated with sulfuric acid, washed repeatedly with water, and dried over $CaCl_2$. Then it was passed two times through a column with activated alumina. Tetramethyl-$para$-phenylenediamine (TMPD, 98%, Aldrich) was sublimated under vacuum several times before use. 1,2-Dibromoethane (97%, Aldrich) was used as received. Nitroxide radicals, 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO), 2,2,3,4,5,5-hexamethyl-imidazolidin-1-oxyl (HMI), and 2,2,6,6-tetramethyl-4-piperidinone-1-oxyl (TEMPON) were received from N. N. Vorozhtsov Institute of Organic Chemistry.

Most of the experimental data presented have been obtained with 10 mM 2,4,4-trimethylpent-2-ene (98%, Aldrich) added to n-dodecane solutions. The purpose of the addition was to scavenge primary positive charge carriers in irradiated n-dodecane for the period before encounter with TMPD molecule. The only effect of this unsaturated compound was the increase in the amplitude of TR MFE due to accelerating singlet−triplet transitions in the geminate (electron/radical cation) pairs. No effects on both the solvated electron mobility as measured by the method of time-resolved electric field effect[21] and the TMPD radical cation formation rate have been detected.

■ RESULTS

Figure 2 demonstrates the effects of quencher additions and magnetic field on the delayed fluorescence decay from the TMPD solution. As shown in Figure 2a, the addition of nitroxide radicals $R^\bullet$ to the solution accelerates the fluorescence decay. At the quencher concentration used ($Q \approx 0.1$ mM), the time between binary encounters for molecular species is longer than 1 μs. Therefore, the only possible process affecting the yield of the excited states of the luminophore is reaction 2 since the mobility of electron in dodecane is about 2 orders of magnitude higher than that of molecular species.[18] The relative change of the decays agrees well with eq 3 within the range of 50−100 ns. The upper time limit is due to the fact that, at high $R^\bullet$ concentration, the intensity of recombination fluorescence decreases to such extent that channels of ^{1}TMPD* formation unrelated to ion recombination become relevant.

This allows estimating the rate of this scavenging reaction at different values of Q. Note that the addition of TEMPON or 1,2-dibromoethane at a concentration of 0.03 mM leads to virtually the same effect as does the addition of TEMPO at four times greater concentration. The reason of 4-fold more effective scavenging by the TEMPON radical is its spin independence since the formation of the triplet state of anion diradical is energetically allowed.[14] We emphasize that if the electron transfer to nitroxide radicals in our experimental conditions occurs then the typical electron−radical distance is about 1.5 nm, but for TEMPO, only one-quarter of the encounters results in the scavenging due to spin statistical factor 1/4.
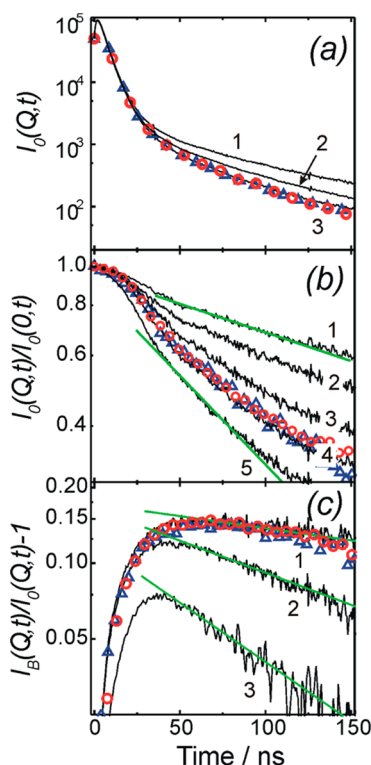
Figure 2. Fluorescence intensity decays $I_0(Q,t)$ and the decay curve ratios for *n*-dodecane solutions of 1 mM TMPD + 30 mM 2,4,4-trimethylpentene-2 + quenchers (see experimental section). Curves obtained at $[Q] = 0.03$ mM of either 1,2-dibromoethane or TEMPON are shown by circles and triangles, respectively. (a) Intensity decays $I_0(Q,t)$ without quenchers (curve 1) and at $[$TEMPO$] = 0.07$ mM (2) and 0.13 mM (3). (b) Ratios $I_0(Q,t)/I_0(0,t)$ at $[$TEMPO$] = 0.05$ mM (1), 0.07 mM (2), 0.1 mM (3), 0.13 mM (4), and 0.15 mM (5). $I_0(0,t)$ is the curve 1 from plot a; straight lines show an exponential approximation within the range of 50−100 ns. (c) Ratios $I_B(Q,t)/I_0(Q,t)$ for $B = 1$ T, at $[$TEMPO$] = 0$ mM (1), 0.1 mM (2), and 0.15 mM (3); straight lines show an exponential approximation within the range of 60−100 ns.

Figure 2c shows the TR MFE curves, rising parts of which are determined primarily by the rates of the singlet−triplet mixing between the nearly degenerate singlet and triplet states of the radical pairs driven by hyperfine couplings (HFC) in the TMPD$^{+\bullet}$ radical cation and its precursors, as well as by phase relaxation as schematically illustrated in Figure 1. As mentioned above, the decay of the TR MFE curves at long times proceed due to the depopulation of the singlet state in strong magnetic field that occurs usually due to spin−lattice relaxation.[20]

Experiment shows that the decay rate of the TR MFE curves increases with TEMPO concentration. Such a faster decay cannot be attributed to the recombination fluorescence quenching effect giving way to any magnetically insensitive channels of TMPD fluorescing states formation. Indeed, the addition of dibromoethane or TEMPON also leads to strong quenching (Figure 2b) but leaves the magnetic field effect curves almost unaffected (Figure 2c).

Figure 3 shows the result of the comparison between the rates of the spin-selective scavenging of electrons by TEMPO or HMI and that of the spin−lattice relaxation in the surviving SCRPs. One can see a linear correlation between these values with the intersection corresponding to $T_1 = 480 \pm 60$ ns, and the slope, which equals 1 within experimental errors.
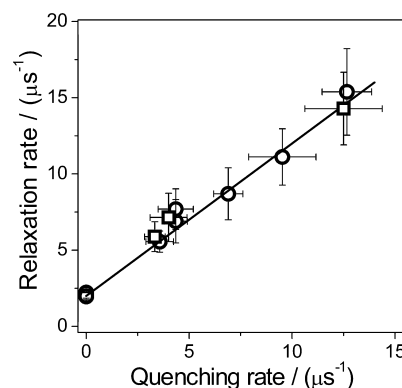
Figure 3. Rate of the TR MFE curve decay (relaxation rate) vs fluorescence quenching rate at different concentration of TEMPO (circles) and HMI (squares). The straight line corresponds to the slope of 1.

■ THEORETICAL MODEL

To evaluate theoretically the effect of the spin-selective reaction with radicals on the TR MFE, we employed an approach of projection operator, similar to that used in ref 22. To this end, we considered three spin 1/2 particles, including isolated SCRPs consisting of A ($A =$ TMPD$^{+\bullet}$) and B (e^-), in the presence of paramagnetic species C ($R^\bullet$) capable of reacting with B only provided that B and C are found in the singlet spin state (S-state) at the moment of their encounter. Since in our experiments the recombination kinetics of geminate radical ion pairs does not affect noticeably TR MFE curves,[20] there is no need to consider the geminate recombination of AB pairs in this model.

If only binary encounters of the B and C species are considered, the probability $W_{AB}(t)$ to find the AB pair in S-state can be expressed using density matrix $\hat{\rho}(t)$ of the ensemble of spin triads ABC in the following way:

$$W_{AB}(t) = \langle S_{AB}|Tr_C\hat{\rho}(t)|S_{AB}\rangle \qquad (5)$$

where Tr_C stands for the trace over the spin variables of species C, and $|S_{AB}\rangle$ is the vector of the S-state for pairs AB.

Let us neglect any interactions in the ABC triads except those that lead to the reaction of C with B. Let us also neglect recombination and spin−lattice relaxation in AB pairs. As an initial state of the ensemble of triads, let us consider the mixed state where spin C is in a random state, while among the AB pairs there is a fraction $(1 - \theta)$ of uncorrelated pairs, and a fraction θ equally shared between the S-state and the triplet state with zero projection of total spin (T_0-state). Such an initial state corresponds to the conditions of our experiment in strong magnetic field, where a fraction θ of all pairs were born singlet-correlated and the populations of the S- and T_0-states have equalized due to $S-T_0$ transitions driven by phase T_2-relaxation. Then

$$\hat{\rho}(0) = \frac{\hat{1}_C}{2}\left[\frac{\theta}{2}(\hat{P}^S_{AB} + \hat{P}^{T0}_{AB}) + \frac{\hat{1}_{AB}}{4}(1 - \theta)\right] \qquad (6)$$

where $\hat{1}_{AB}$ and $\hat{1}_C$ are unity operators in the space of spin variables of the AB pair and the C species, respectively; $\hat{P}^S_{AB}$ and $\hat{P}^{T0}_{AB}$ are projection operators on the S- and T_0-states of the AB pair, respectively. The sum of these projection operators is

$$\hat{P}_{AB}^{S} + \hat{P}_{AB}^{T0} = \frac{\hat{1}_{AB}}{2} - 2\hat{s}_{AZ}\hat{s}_{BZ} \qquad (7)$$

where $\hat{s}_{AZ}$ and $\hat{s}_{BZ}$ are projection operators of respective spins on the quantization axis. Substituting eq 7 into 6, we get for the initial state

$$\hat{\rho}(0) = \frac{\hat{1}_C}{2}\left(\frac{\hat{1}_{AB}}{4} - \theta \cdot \hat{s}_{AZ}\hat{s}_{BZ}\right) \qquad (8)$$

$$W_{AB}(0) = \langle S_{AB}|Tr_C\hat{\rho}(0)|S_{AB}\rangle = \frac{1}{4}(1 + \theta) \qquad (9)$$

Let us focus on subensembles of SCRPs in which by the moment t there have been $n = 0, 1, 2, \ldots$ pair encounters of radicals B with different species C. Let us calculate density matrixes $\hat{\rho}_n(t)$ for pairs AB that survived after n encounters. For $n = 0$

$$\hat{\rho}_0(t) = Tr_C\hat{\rho}(0) = \frac{\hat{1}_{AB}}{4} - \theta \cdot \hat{s}_{AZ}\hat{s}_{BZ} \qquad (10)$$

is identical to the initial density matrix of the AB pairs. For $n = 1$, projecting the initial density matrix on any of the T-states of B and C and taking trace over C, we get

$$\hat{\rho}_1(t) = Tr_C(\hat{1}_{BC} - \hat{P}_{BC}^S)\frac{\hat{1}_C}{2}\hat{\rho}_0(t)(\hat{1}_{BC} - \hat{P}_{BC}^S)$$

$$= \frac{3}{4}\left(\frac{\hat{1}_{AB}}{4} - \frac{2}{3}\theta \cdot \hat{s}_{AZ}\hat{s}_{BZ}\right) \qquad (11)$$

The result (eq 11) can be obtained using the known relationship for the operator of projection to S-state

$$\hat{P}_{BC}^S = \frac{\hat{1}_{BC}}{4} - \hat{\vec{s}}_B\hat{\vec{s}}_C \qquad (12)$$

Comparison of the eqs 10 and 11 shows that $\hat{\rho}_1(t)$ differs from $\hat{\rho}_0(t)$, first, by a factor 3/4 reflecting the reaction decay of 1/4 ABC triads that have zero total spin of B and C. Second, the fraction of correlated AB pairs, that was equal to θ before the encounter, after the encounter dropped to $2/3\theta$.

The calculation of the second encounter and further ones let us assume that species C, which is part of a particular triad ABC, after its first contact with B either reacts (if BC is in the S-state) or loses (if BC is in the triplet state) its capability to further react with the B species of this triad. This assumption can be substantiated by referring to the experimental situation studied in this work. Actually, excess electron mobility is very high, and the encounter time for BC, that is electron/radical, pair is short enough to prevent HFC induced singlet–triplet transitions within the pair. Therefore, the AB pairs of the subensemble described by the density matrix (eq 11) have a chance to react at the second encounter only with other species of the C type with a random spin state relative to these pairs. This gives us a recurrent relationship

$$\hat{\rho}_n(t) = Tr_C(\hat{1}_{BC} - \hat{P}_{BC}^S)\frac{\hat{1}_C}{2}\hat{\rho}_{n-1}(t)(\hat{1}_{BC} - \hat{P}_{BC}^S)$$

$$= \left(\frac{3}{4}\right)^n\left[\frac{\hat{1}_{AB}}{4} - \left(\frac{2}{3}\right)^n\theta \cdot \hat{s}_{AZ}\hat{s}_{BZ}\right] \qquad (13)$$

The statistics of encounters between B and C in time interval t follows the Poisson distribution, giving for the density matrix of the AB pairs that survive by the moment t

$$\hat{\rho}_{AB}(t) = \sum_{n=0}^{\infty} \frac{(\nu t)^n}{n!}e^{-\nu t}\hat{\rho}_n(t)$$

$$= e^{-1/4\nu t}\left(\frac{\hat{1}_{AB}}{4} - \theta \cdot e^{-1/4\nu t}\hat{s}_{AZ}\hat{s}_{BZ}\right) \qquad (14)$$

Here, ν is the average rate of the encounters of B and C.

Equation 14 makes it possible to obtain the decay kinetics of the singlet state population of the AB pairs:

$$W_{AB}(t) = \langle S_{AB}|\hat{\rho}_{AB}(t)|S_{AB}\rangle = e^{-1/4\nu t}\left(\frac{1}{4} + e^{-1/4\nu t}\frac{\theta}{4}\right) \qquad (15)$$

In eq 15, the multiplier $e^{-(1/4)\nu t}$ outside the parentheses is equal to the trace of the density matrix (eq 14) and accounts for the decay of AB pairs due to a spin-selective reaction with C species. Precisely the same multiplier inside the parentheses in eq 15 accounts for a decrease of the fraction of singlet-state pairs among the remaining SCRPs due to the same reaction. It can be easily shown that, in the case considered, the population of the T_0-state decreases to the same extent, which inevitably leads to an increase of the T_+ and T_- populations. This means that the occurrence of the reaction tends to equalize the spin states population. In our conditions, this is equivalent to an additional contribution to the spin–lattice paramagnetic relaxation in AB pairs. Therefore, eq 15 can be modified as the following:

$$W_{AB}(t) = \langle S_{AB}|\hat{\rho}_{AB}(t)|S_{AB}\rangle = e^{-1/4\nu t}\left(\frac{1}{4} + e^{-(\frac{\nu}{4}+\frac{1}{T_1})t}\frac{\theta}{4}\right) \qquad (16)$$

Here, T_1 is the spin–lattice relaxation time for AB pairs in the absence of the BC encounters.

Accounting for the exchange interaction of species C with the radicals of the SCRP would be a much more complicated problem, which is beyond the scope of this work. However, it is obvious that the introduction of the exchange interaction between B and C into the model cannot affect the rate of the irreversible reaction determined by the rate of encounters ν and the statistical factor 1/4.

■ DISCUSSION

Since in alkane solutions the recombination rate of geminate ion pairs does not depend on both pair's spin state and external magnetic field,[20] the magnitude of the TR MFE relates directly to the ratio of singlet populations in strong, $W_{AB}^H(t)$, and zero, $W_{AB}^0(t)$, magnetic field. Note that in zero magnetic field the singlet–triplet transitions driven by HFC and phase relaxation involve all triplet states (Figure 1) that quickly destroys the spin correlation in AB pairs. Thus, this case corresponds to $\theta = 0$ in eq 16 within the discussed model. Therefore, TR MFE curve for sufficiently long times t obeys

$$\frac{I_B(Q, t)}{I_0(Q, t)} \approx \frac{W_{AB}^H(t)}{W_{AB}^0(t)} = 1 + \theta \cdot e^{-(\frac{\nu}{4}+\frac{1}{T_1})t} \qquad (17)$$

The suggested model predicts that the spin-selective scavenging rate, which is equal to $kQ = \nu/4$, is equal to the rate of the additional spin correlation decay measured at the

same concentrations of quencher, which scavenge electrons spin-selectively. This prediction is in excellent agreement with the experimental result shown in Figure 3.

Note that our model is based on the assumption that each encounter with a third radical certainly results in the triplet state of surviving e^-/TEMPO pairs. This is equivalent of quantum measurement of the encounter pair spin state. This assumption is the same as that used in refs 3 and 4 to augment the equation of motion for the spin density matrix with recombination sink term. The relation of our results to other concurring approaches[5−7] taking the spin-selective reaction into account is to be the subject of further work.

It should be emphasized that in our model the loss of spin correlation in the pair occurs in the absence of exchange interaction with the third radical, though spin exchange could result in a similar effect. A similarity in the manifestation of spin exchange and recombination of SCRP was discussed earlier in refs 23 and 24. The negligible contribution of spin exchange in our experiment can be attributed to the considerable distance, ~1.5 nm, of electron transfer in reaction 2 and to the fact that the probability of electron transfer decays substantially slower with the distance between the reactants than exchange interaction does.[25] Additionally, the encounter time for e^-/$R^\bullet$ pairs is much shorter as compared to typical radical/radical encounters due to high electron mobility. Note that the magnitude of the spin exchange interaction can be significant for the triplet pairs $^3(e^-$/TEMPO) surviving after an encounter since the electron and the radical are able to approach each other. However, for these pairs the spin exchange interaction does not lead to additional singlet−triplet mixing in the geminate pairs e^-/TMPD$^{+\bullet}$.

CONCLUSIONS

In this work, by an example of distant electron transfer reaction in liquid solution, the rates of the two processes, (i) spin-selective reaction of a partner of a spin-correlated pair of spin 1/2 particles with a third paramagnetic species and (ii) decay of spin correlation in the pairs surviving after the reaction, were directly compared for the first time. In accordance with the suggested theoretical model, the spin-selective reaction modifies the spin state of the subensemble of surviving spin-correlated radical pairs. In the case under consideration, that is, the reaction occurring at the singlet spin state of reactants only, the effect of spin-selectivity appears as the additional contribution to spin−lattice relaxation with the rate equal to the rate of the reaction.

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Notes
The authors declare no competing financial interest.

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