Peculiarities of Magnetic and Spin Effects in a Biradical/Stable Radical Complex (Three-Spin System). Theory and Comparison with Experiment

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Received: March 4, 2005; In Final Form: May 17, 2005

The field dependencies of biradical recombination probability in the presence of paramagnetic species with spins $S_3 = 1$ and $S_3 = {}^1/_2$ have been calculated in the framework of the density matrix formalism. To describe the effect of the "third" spin on the spin evolution in biradical, we have also considered the spin exchange interaction between the added spin and one of the paramagnetic biradical centers. A characteristic feature of the calculated field dependencies is the existence of several extrema with positions and magnitudes depending on the signs and values of the exchange integrals in the system. The method proposed can be used to describe the effect of spin catalysis. It is shown that for the system with the third spin $S_3 = 1$ spin catalysis manifests itself stronger than in the case of spin $S_3 = {}^1/_2$. The dependence of spin catalysis efficiency on the exchange interaction with the third spin has an extremum with position independent of the value of the spin added.

Introduction

At present, the study of magnetic and spin effects in multispin systems is one of the most interesting problems of spin chemistry. In 1994, an increase in the cage effect in solution was observed experimentally for triplet radical pairs in the presence of a stable radical, that is, the phenomenon of spin catalysis.[1] In addition, the effects of an added (so-called "third") spin on magnetic-field effects in radical ion pairs (RIP)[2,3] and of stable radicals on CIDNP formation in a radical pair (RP)[4] were discovered. These effects indicate that paramagnetic species can efficiently influence the processes of spin evolution in RP and RIP. In literature, several examples are available that demonstrate the effect of the third spin on the field dependencies of magnetic-field effects (MFE) in biradicals.[3,5] Thus, the existence of an additional paramagnetic species in a multispin system (a radical triad or tetrade) can not only lead to the well-known relaxation effects (mainly due to dipole−dipole interaction)[2] but could also affect spin dynamics directly.

The classical version of the existing radical pairs theory[6] neglects the interaction with other paramagnetic centers of the macrosystem. The analysis of spin and magnetic-field effects in multispin systems requires the improvement of the approaches to take into account the interaction of all electrons during the entire lifetime of the radical triad or tetrade. Such an approach was used by Berdinsky and Buchachenko to describe spin catalysis.[7] However, their results do not describe magnetic-field effects and their field dependencies. A model suggested by Molin and Lukzen[8] describes the magnetic field effect, but only concerns the case in which paramagnetic species are generated by radiolysis, which allows one to neglect molecular dynamics. The latter does not allow one to use this model for analyzing magnetic field effects in the case of thermal or photochemical generation of paramagnetic species.

In ref 9, we proposed the approach for calculating the probability of recombination in a three-spin system biradical/paramagnetic species in which a paramagnetic species is rigidly bound near one of the biradical centers. The approach was applied for calculating the probability of the recombination of a complex biradical/paramagnetic species with spin $S_3 = 1$. In the present paper, we have extended this approach to the system with an additional paramagnetic species with spin $S_3 = {}^1/_2$ to reveal the similarities and differences of these two cases.

Theoretical Basis

The approach developed[9] allows us to describe the main peculiarities of magnetic-field effects that appeared (as assumed in ref 5) in complexes of silicon-centered biradicals with molecular oxygen formed by the photolysis of 7-silanorbornadiene in solution. In this process, the influence of the 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy stable radical (4-OH-TEMPO) on the quenching rate of triplet dimethylsilylene (precursor of the aforementioned biradicals) was also found.[10] Therefore, our description of magnetic and spin effects in a three-spin system consisting of biradical and a third paramagnetic species with spin $S_3 = {}^1/_2$ is aimed to account for the effects observed.

The system under study is a bound radical triad consisting of two radical centers, R_1 and R_2, which form a covalent bond and yield the product, and R_3, which is rigidly bound to R_1. Between the R_1, R_2 and R_1, R_3 centers there are exchange interactions J_1 and J_2, respectively. In radical center R_1, electron spin has a hyperfine coupling constant (HFC) with a magnetic nucleus. Thus, the Hamiltonian of the system is of the form

$$\hat{\mathrm{H}} = g_1\beta H\hat{S}_{1z} + g_2\beta H\hat{S}_{2z} + g_3\beta H\hat{S}_{3z} + J_1\hat{S}_1\hat{S}_2 + J_2\hat{S}_1\hat{S}_3 + a\hat{S}_1\hat{I} \quad (1)$$

where g_1, g_2, and g_3, are the g factors of the electrons of the corresponding radical centers, $\hat{S}_1$, $\hat{S}_2$, and $\hat{S}_3$ are the electron spin operators of the corresponding radical centers, a is HFC value, β is the Bohr magneton, and H is the external magnetic field strength.

The calculations were performed in the framework of the density matrix formalism by solving Liouville stochastic equa-

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10.1021/jp051115y CCC: $30.25

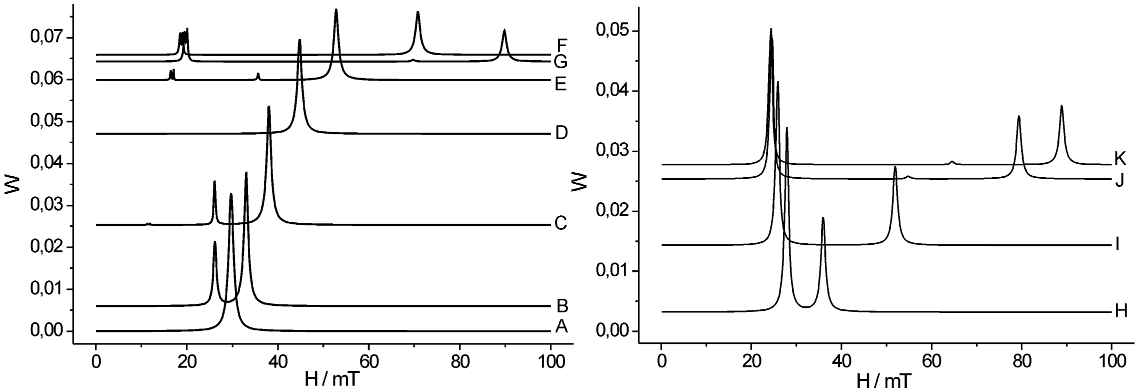

Figure 1. Field dependencies of the recombination probability for the triad biradical/radical ($S_3 = {}^1/_2$) for various J_2 (mT): (A) 0, (B) 10, (C) 20, (D) 30, (E) 40, (F) 60, (G) 80, (H) −10, (I) −30, (J) −60, (K) −70. The other parameters for calculations are the following: $J_1 = 30$ mT, $g_1 = 2.0035$, $g_2 = 2.0040$, $g_3 = 2.0045$, $U_0\tau_c = 5$, $n = 100$.

tions. The Hamiltonian (eq 1) commutates with the projection of the total spin on the direction of the external magnetic field. Therefore, the ensemble of the wave functions of the triad can be divided into a number of subensembles with defined projections of total spin *F*. The calculations were carried out for each subensemble and the total recombination probability was a sum of the results with their statistic weights. Let the reactive state be singlet. Then for the singlet and triplet initial state of the biradical, the recombination probabilities, respectively, are

$$W^{\mathrm{S}} = \frac{U_0\tau}{1 + U_0\tau}$$

$$W^{\mathrm{T}} = \frac{1}{3}\frac{U_0(\tau_p - \tau)}{1 + U_0\tau} \qquad (2)$$

here, τ_p is the total time of direct contacts between the active biradical centers, τ is the lifetime of the system in the reactive state, that is, when both of the active biradical centers are in the zone of direct contact and their electron spins form a singlet state if the spin evolution starts from the same singlet state. $\tau = \mathrm{Re}((\hat{g})_{\mathrm{SS,SS}})$, where $\hat{g}(s)$ is the result of the Laplace transform of the spin evolution operator convolved with a function characterizing spatial motion and averaged over the reaction zone. All elements of the matrix $\hat{g}(s)$ are expressed by means of function $g(s)$, which depends on mutual motion of the unpaired electrons in pair.

The two-position exponential model[11] is the most appropriate for the description of motion of the bond triad. On one hand, this model is mathematically simple. On the other hand, it provides a satisfactory description of the main point of cage effect.

In the frame of the model, two states of system are available. One is the state of direct contact; the radicals are located in the reaction zone. An escape of a RP from this state is described as a monomolecular decay with the characteristic time τ_1. The other is the state where the radicals are in the cage, but out of the reaction zone. This state is characterized by two parameters: τ_2 is the time of return of the system into the reaction zone and τ_c is the time of RP decay.

The trivial solution yields the following expression:

$$g(s) = \frac{\left(s + \dfrac{1}{\tau_2} + \dfrac{1}{\tau_c}\right)}{s\left(s + \dfrac{1}{\tau_2} + \dfrac{1}{\tau_c}\right) + \dfrac{1}{\tau_1}\left(s + \dfrac{1}{\tau_c}\right)} \qquad (3)$$

In the frame of the model we have[9]

$$\tau = \tau_p\left(\sum_i Q_{1i}{}^4 + 2\sum_{i>j}\frac{Q_{1i}{}^2Q_{1j}{}^2}{n+1}\left(1 + \frac{n}{1 + ((E_i - E_j)\tau_c)^2}\right)\right) \qquad (4)$$

In this case, Q_{1i} is the expansion coefficient of the singlet state in the basis of eigenfunctions of the system, E_i are the energies of the eigenfunctions, and $n = \tau_c/\tau_2$ is the number of reencounters in RP.

The dependencies of the recombination probability of the system on the external magnetic field strength were calculated for the initial biradical state being triplet.

Results and Discussion

Figure 1 shows the calculated field dependencies of the recombination probability for fixed J_1 and variable J_2. The general character of the field dependencies, that is, the existence of several extrema of the recombination probability, is similar to that for $S_3 = 1$.[9] However, there are some qualitative and quantitative distinctions.

When $J_2 \lesssim J_1$, the main extremum is located in a lower field as compared to that of $S_3 = 1$. The number of extrema also decreases, probably due to a simpler structure of terms because of the smaller total spin, *F*, of the system.

The extrema in the field dependence of the recombination probability arise in the fields of anticrossings of the system terms (Figure 2).

Let us consider the term structures of the two systems in two extreme cases: $J_2 \ll J_1$ and $J_2 \gg J_1$ to understand the origin of the differences between these two cases and predict the positions of extrema. The field dependencies of the recombination probability for both cases are shown in Figure 3.

Figure 4 shows the terms of the biradical/paramagnetic species system with spins $S_3 = {}^1/_2$ and $S_3 = 1$ for the cases of high and low J_2. The wave functions are represented by a linear combination of singlet and triplet states of the biradical interacting with the third species (Table 1). Expressions for the wave functions were derived from a numerical solution of equations for the eigenvalues and eigenvectors of the Hamiltonian in the singlet−triplet basis of the biradical and the third species. Transitions arising in the region of anticrossing (Table 2) can be due to the flip of the spin of biradical S_1 induced by hyperfine interaction. Let us consider the biradical/radical system. In the case of a weak interaction (Figure 4a), the singlet state of the biradical converts into the doublet state, D_1, the

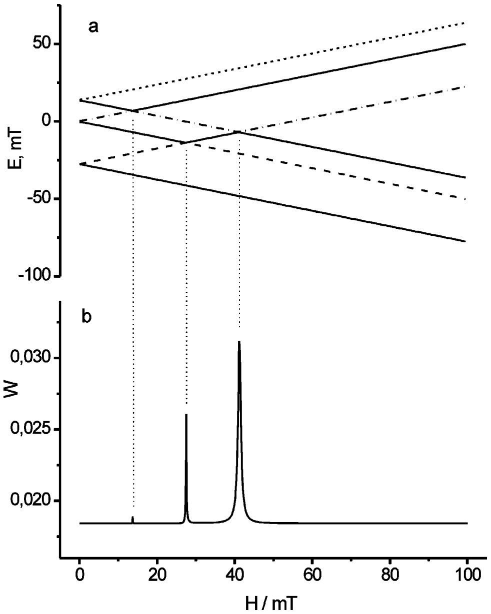

Figure 2. (a) Dependence of the energy levels of the triad biradical/radical ($S_3 = {}^1/_2$) on the external magnetic field for the subensemble with the total spin projection $F_z = 0$ and (b) the contribution of the subensemble to the recombination probability. J_1= 30 mT, and J_2 = 25 mT. The other parameters are similar to those in Figure 1.

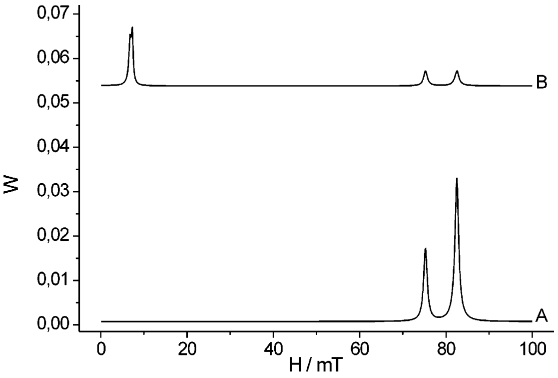

Figure 3. Magnetic field dependencies of the recombination probability for the triad biradical/radical ($S_3 = {}^1/_2$). (A) J_1 = 80, J_2= 10; (B) J_1= 10, J_2= 80, all values are in mT. The other parameters are similar to those in Figure 1.

triplet states mix up and split into the quartet, Q, and doublet, D_2, states shifting in energy by $J_2/4$ and $-J_2/2$, respectively. The system can get into the reactive state at a field of anticrossing of two terms, provided that one of the terms includes the reactive singlet state of the biradical. In Figure 4, such terms are denoted by a bold line. When $J_2 \ll J_1$, the transitions in the system occur at the anticrossing of the Q and D_2 levels with D_1 in the fields $J_1 + J_2/4$ and $J_1 - J_2/2$. By analyzing the composition of multiplicative functions composing the terms (Table 1), we conclude that the extrema in the field dependencies of the recombination probability cause $S{-}T_-$ transitions.

In the opposite case, $J_2 \gg J_1$ (Figure 4b), terms D_1 and D_2 change their components. D_1 consists mainly of the triplet states with a small addition of the singlet one. D_2 includes mainly singlet states (Table 1). As a result, the $S{-}T_-$ transitions occur between D_1 and D_2, Q and D_1, and Q and D_2 in the fields ${}^3/_4J_1$, $J_2 + J_1/4$, and $J_2 - J_1/2$, respectively (Table 2). The greatest efficiency of the transitions in the approximation of long-lived pairs should be observed for the greatest difference in the singlet-state component in anticrossing terms. Thus, far from anticrossing of terms, the fractions of the singlet state in D_1, D_2, and Q are ${}^1/_4$, ${}^3/_4$, and 0, respectively (Table 2). Therefore, in the case $J_2 \gg J_1$ the main extremum is observed upon the anticrossing of D_2 and Q states in lower fields.

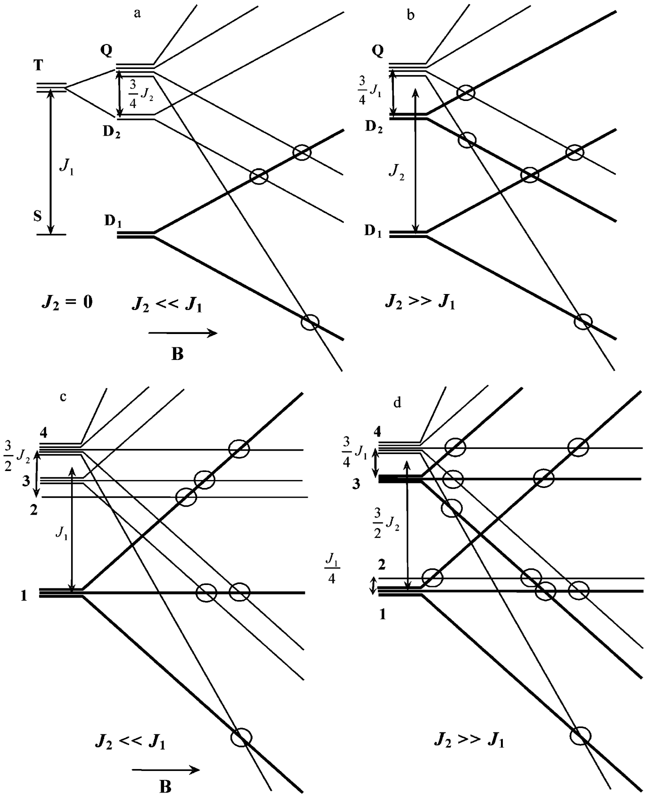

Figure 4. Dependence of the energy levels of the triad biradical/paramagnetic species on the external magnetic field for two different ratios of J_1 and J_2. (a and b) $S_3 = {}^1/_2$; (c and d) $S_3 = 1$. The other parameters are similar to those in Figure 1.

For $S_3 = 1$ in the limit $J_2 \ll J_1$ (Figure 4c), the triplet functions of the biradical are distributed between two multiplets, 3 and 4 and a single term, 2, which differ in energy by J_2 and $J_2/2$ and are J_1 apart from the multiplet of the singlet states of the biradical (1). Thus, the anticrossings involving the reactive states of 1 that give the extrema of recombination probability occur in the fields close to J_1: $J_1 - J_2$, $J_1 \pm J_2/2$. When $J_2 \gg J_1$ (Figure 4d), as for $S_3 = {}^1/_2$, multiplets 1 and 3 change their composition and 1 consists mainly of triplet states with a small admixture of the singlet state, and 3 is mainly the triplet state. As a result, the field dependence shows two groups of extrema, that is, the major one is observed in the lower field at $J_1/4$ and ${}^3/_4J_1$ and the minor one at ${}^3/_2J_2 \pm J_1/4$ and ${}^3/_2J_2 - J_1/2$ (Table 2). In the intermediate case, $J_1 \approx J_2$, the extremum at ${}^3/_2J_2 - J_1/2$ manifests itself as a separate one and is strong enough.

When $J_2 = J_1$, the field dependence is simplified. For $S_3 = 1$ we observe a few small extrema and only one large extremum at ${}^3/_2J_1$. For $S_3 = {}^1/_2$ the extremum at ${}^3/_2J_1$ is the only one.

Thus, in both systems, the main extremum shifts to a higher field with increasing J_2. When $J_1 \approx J_2$, the low-field extrema rise, and with $J_2 \gg J_1$ the main extrema are in low field.

It is worth noting that for both systems the widths of the extrema are quite different. Thus, if the high-field extrema exhibit the expected width, close to HFC, the low-field ones are more narrow by a factor of up to 2. However, in all of the cases, we observed either the $S{-}T_-$ or $S{-}T_+$ transitions caused by hyperfine interaction.

TABLE 1: Expansion Coefficients of the Eigenfunctions of Biradical/Radical ($S_3 = {}^1/_2$) Triad Spin States for Various Ratios of J_1 and J_2 (1−4)[a]

spin state	1: $J_2 \ll J_1$	2: $J_2 = 2J_1$	3: $J_2 \gg J_1$	4: $\lvert J_2\rvert \gg J_1$, $J_2 < 0$
D_1	$\lvert S\alpha\rangle$	$\sqrt{1/2}\,\lvert S\alpha\rangle - \sqrt{1/2}\Phi_1^+$	$\sqrt{1/4}\,\lvert S\alpha\rangle - \sqrt{3/4}\Phi_1^+$	$\sqrt{3/4}\,\lvert S\alpha\rangle + \sqrt{1/2}\Phi_1^+$
	$\lvert S\beta\rangle$	$\sqrt{1/2}\,\lvert S\beta\rangle + \sqrt{1/2}\Phi_1^-$	$\sqrt{1/4}\,\lvert S\beta\rangle + \sqrt{3/4}\Phi_1^-$	$\sqrt{3/4}\,\lvert S\beta\rangle - \sqrt{1/2}\Phi_1^-$
D_2	Φ_1^+	$\sqrt{1/2}\,\lvert S\alpha\rangle + \sqrt{1/2}\Phi_1^+$	$\sqrt{3/4}\,\lvert S\alpha\rangle + \sqrt{1/4}\Phi_1^+$	$\sqrt{1/4}\,\lvert S\alpha\rangle - \sqrt{3/4}\Phi_1^+$
	$\Phi_1{}^-$	$\sqrt{1/2}\,\lvert S\beta\rangle - \sqrt{1/2}\Phi_1^-$	$\sqrt{3/4}\,\lvert S\beta\rangle - \sqrt{1/4}\Phi_1^-$	$\sqrt{1/4}\,\lvert S\beta\rangle + \sqrt{3/4}\Phi_1^-$
Q			$\lvert T_+\alpha\rangle$	
			Φ_2^+	
			Φ_2^-	
			$\lvert T_-\beta\rangle$	

[a] Where $\Phi_1^+ = \sqrt{1/3}\,|T_0\alpha\rangle - \sqrt{2/3}\,|T_+\beta\rangle$; $\Phi_1^- = \sqrt{1/3}\,|T_0\beta\rangle + \sqrt{2/3}\,|T_-\alpha\rangle$, $\Phi_2^+ = \sqrt{2/3}\,|T_0\alpha\rangle - \sqrt{1/3}\,|T_+\beta\rangle$; $\Phi_2^- = \sqrt{2/3}\,|T_0\beta\rangle + \sqrt{1/3}\,|T_-\alpha\rangle$ and $|S\rangle$ and $|T\rangle$ are the states of a biradical and $|\alpha\rangle$ and $|\beta\rangle$ are the states of S_3.

TABLE 2: Magnetic Fields of the Triad ($S_3 = {}^1/_2$ and $S_3 = 1$) Recombination Probability Extrema Locations for the Case of Weak and Strong J_2 Interactions

S_3	$J_2 \ll J_1$	$J_2 \gg J_1$
$^1/_2$	$J_1 + J_2/4$, $J_1 - J_2/2$	$^3/_4J_1$, $J_2 + J_1/4$, $J_2 - J_1/2$
1	$J_1 - J_2$, $J_1 \pm J_2/2$	$J_1/4$, $^3/_4J_1$, $^3/_2J_2 \pm J_1/4$, $^3/_2J_2 - J_1/2$

As was shown earlier[9] for the $S_3 = 1$ case, the recombination probability at a field far from the recombination probability extrema depends on the J_2 value (the effect of spin catalysis). This effect can also be obtained for a system with added spin $S_3 = {}^1/_2$. Figure 5 demonstrates the dependence of the biradical recombination probability in zero field (the efficiency of the spin catalysis) on the exchange interaction with the added spin. As one can see from Figure 5, for the $S_3 = {}^1/_2$ case the spin catalytic effect is less effective. Transitions corresponding to spin catalysis are caused by exchange interaction with the third species.[7,9] As follows from Table 1, for the $S_3 = {}^1/_2$ case the transitions in terms D_1 and D_2 corresponding to spin catalysis occur in the subensembles $\{|S\alpha\rangle, |T_0\alpha\rangle, |T_+\beta\rangle\}$ and $\{|S\beta\rangle, |T_0\beta\rangle, |T_-\alpha\rangle\}$. The J_2 interaction occurs between all multiplicative functions included in the subensembles. It is concluded then that, unlike the extrema of the field dependence of recombination probability, spin catalysis is caused by the $S-T_0$, $S-T_-$, and $S-T_+$ transitions. Consideration of the $S_3 = 1$ case leads to a similar result.

It should be noted that in both cases ($S_3 = 1$, $^1/_2$), the dependence of the spin catalysis efficiency on J_2 has an extremum that corresponds to $J_2 = 2J_1$ (see Figure 5). The origin of the extremum can be elucidated by considering the system of terms. Figure 6 shows the energy diagram of spin system for $S_3 = {}^1/_2$. Table 1 summarizes the terms in the singlet−triplet basis. The J_2 interaction between S and Φ_1 mixes and separates them. At $J_2 = 2J_1$, where the S state is distributed equally among the terms (Table 1), the $T-S$ transitions in the system are most efficient. For any triad spin state, the recombination probability should be proportional to the probability of finding the spin state of the biradical in the reactive singlet state, C_S^2. However, because the initial state of the system was the triplet one, the population of the term is proportional to $\sum C_T^2$. Thus, summing up the populations of the terms, we can estimate the recombination probability as $W_{T-S} = \sum(C_S^2 \sum C_T^2) = \sum C_S^2(1 - C_S^2)$. Thus, for $C_S^2 = 0.5$ we observe the maximum recombination probability. Table 1 shows that these conditions are satisfied for $J_2 = 2J_1$. The form of the estimated dependence, W_{T-S} (Figure 6), is also similar to the form of the calculated W^T(eq 2) (Figure 5). It is worth noting that in contrast to the field dependence of recombination probability, in this case the interaction between the terms, which is the exchange integral, is a variable parameter. Therefore, the extremum in W^T and W_{T-S} corresponds not to the position of the anticrossing of the D_2 and D_1 terms where they are most close to each other, but to the position in which the parameter of mixing, that is, the exchange integral to term separation ratio $J_2/\Delta E$ has a maximum.

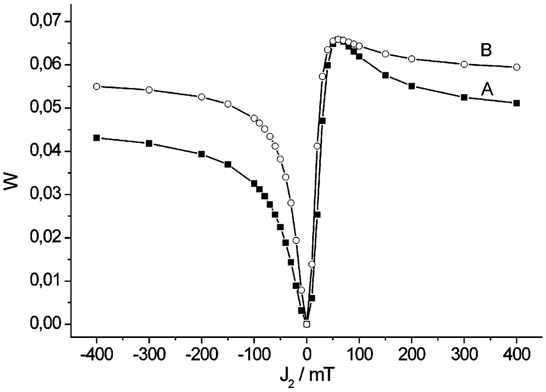

Figure 5. Dependence of the triad recombination probability in zero magnetic field on J_2 for (A) $S_3 = {}^1/_2$, (B) $S_3 = 1$. The other parameters are the same as those in Figure 1.

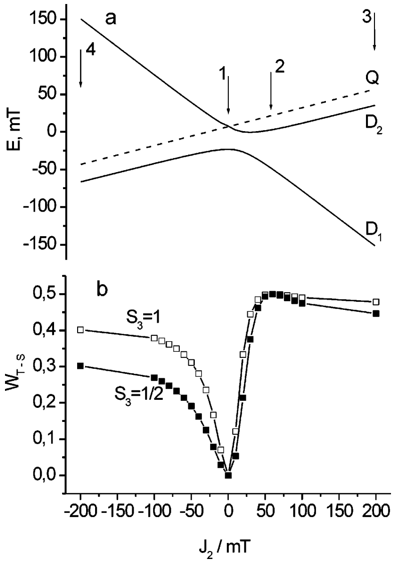

Figure 6. Dependence on J_2 of (a) the energy-level splitting of the triad ($S_3 = {}^1/_2$) and (b) recombination probability estimation in zero magnetic field for $S_3 = {}^1/_2$ and $S_3 = 1$. The marks (1−4) correspond to the states described in Table 1. The other parameters are similar to those in Figure 1.

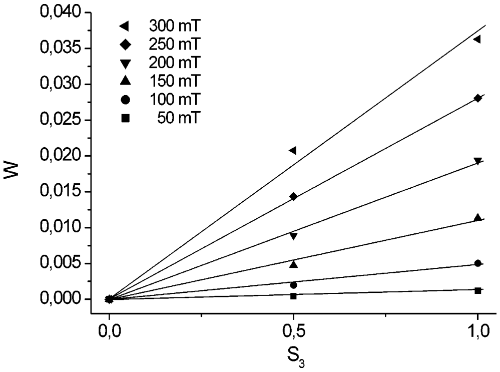

Figure 7. Dependence of the spin catalysis efficiency (recombination probability in zero field) on added spins value for various values of J_2. $J_1 = 50$ mT. The other parameters are similar to those in Figure 1.

Calculations for the $S_3 = 1$ case has analogous results. One can see from Figure 5 that spin catalysis for the $S_3 = {}^1/_2$ case is less effective than for the $S_3 = 1$ case. However, the efficiency of spin catalysis in the point of extremum (state 2 on Table 1 and mark 2 in Figure 6) for both cases is the same. That is correct: for the $S_3 = {}^1/_2$ case one can see from Table 1 that in this state point only two (D_2) of six (D_2 and Q) triplet-containing terms mix up with the two singlet-containing (D_1) ones completely. Other triplet-containing terms (Q) remain nonreactive. The results for the $S_3 = 1$ case are similar: at $J_2 = 2J_1$, only one-third of the triplet-containing terms completely mix up with the singlet-containing ones. Consequently, at the highest reactivity of biradical, ${}^1/_3$ of all of the initial states containing triplets can recombine. Because the resulting recombination probability depends on both probability to find the system in the reactive singlet state of the biradical and the biradical reactivity, it should be less than its highest possible value (compare Figures 5 and 6). Outside the extremum, because of stronger interaction with the higher spin, there is a more effective S$-$T mixing in the $S_3 = 1$ case (see W_{T-S} in Figure 6).

Let us consider the agreement of our results with the experimental data available in the literature. Thus, in ref 12, the Ln^{3+} ions present in solution were established to substantially affect the distribution of the products of dibenzyl ketone (DBK) photolysis in micella. In ref 13, the dependence of the ratio of the recombination rate constants with and without the Ln^{3+} ion process versus Ln^{3+} ion spin value is given. This dependence is approximated well by a linear dependence. However, the studies on the ^{13}C CIDNP of DBK photolysis in micelles point out the existence of an exchange interaction between radicals in a pair observed in the micelle.[14] Thus, the effect of Ln^{3+} ions can be interpreted in terms of the formation of a radical triad. In this case, the diffusing Ln^{3+} ions approach the micelle that contains a radical pair. However, because the Ln^{3+} ions do not enter the micelle, the effective exchange interaction between the Ln^{3+} ions and the radicals in the micelle should be much smaller than that between the radicals in the micelle. In the framework of our model, this condition corresponds to the relation $J_2 \ll J_1$. For this case, the dependence of the efficiency of the calculated spin catalytic effect on the added spin is also close to the linear one (Figure 7). Thus, our model qualitatively describes the results reported in papers[12,13] well, in terms of the concept of spin triads.

The influence of spin triads on the magnetic-field-effect formation can be demonstrated using the photodecomposition of 7-silanonorbornadiene (SNBD).[5,10] Thus, it has been established that the process involves the primary photodecomposition of SNBD into tetraphenylnaphthalene (TPN) and dimethylsilylene ($SiMe_2$) in the triplet state. Further, $SiMe_2$ attacks the initial SNBD to form the 1,6-biradical by $SiMe_2$ inserting into the Si$-$C bond of SNBD. The product of its decay is TPN. When photolysis is performed the external magnetic field, the yield of TPN is magnetic-field-dependent. It has been established[5] that the S$-$T evolution in the 1,6-biradical is the magnetosensitive stage responsible for the MFE observed. In the absence of additional reagents, the field dependence of MFE exhibits an extremum in a field of about 25 mT. In the presence of oxygen, the MFE extremum shifts to a higher field and increases its scale substantially.[5] The addition of the stable radical 4-OH-TEMPO causes no shift in the field dependence extremum. However, as the 4-OH-TEMPO concentration increases, the MFE magnitude first decreases and then changes its sign.[10]

In ref 10, the effect of triplet oxygen was assigned to the formation of the 1,6-biradical/oxygen complex. Indeed, in ref 9 we have demonstrated that by considering this complex as a spin triad, at certain sets of parameters of the spin triad the calculation can describe both the shift of extremum to a higher field and the increase in the MFE value.

The absence of the shift of MFE extremum on the addition of 4-OH-TEMPO indicates that the latter does not form complexes with the 1,6-biradical in which there would be a considerable exchange interaction between 4-OH-TEMPO and the paramagnetic 1,6-biradical centers. At the same time, a decrease in MFE with the change of sign found in the presence of 4-OH-TEMPO,[9] which indicates a change in the predominant multiplicity of the 1,6-biradical, allows us to assume that $SiMe_2$ undergoes the T$-$S conversion before the reaction with initial SNBD. In the framework of this assumption, the influence of 4-OH-TEMPO is essentially its interaction with $SiMe_2$ (the precursor of the 1,6-biradical), which accelerates its conversion into the singlet state. This corresponds to those of the discussed results that concern spin catalysis.

Indeed, $SiMe_2$ can be represented as a biradical in which both of the unpaired electrons are located at different orbitals of the same atom. The difference in the energies of the S and T states for a close analogue of $SiMe_2$, SiH_2, is known to be $\Delta E = 16.8$ kcal/mol $\cong$ 6500 T.[15] For GeH_2 and $GeMe_2$, these values are in the range between 19 and 29.4 kcal/mol[16] and between 13.7 and 28.6 kcal/mol,[17] respectively. It is expected then that for $SiMe_2$ ΔE also amounts to several thousand tesla. Thus, the interaction with the third species (4-OH-TEMPO) can cause a transition to the singlet state. The aforementioned theoretical calculations indicate that for $J_2 \ll J_1$ the extrema in the field dependence can manifest themselves in fields close to J_1 (Table 2). Thus, in the magnetic field range up to 100 mT, no dependence of MFE on the field should be observed. The spin catalysis in this system is sure to exist because it is independent of the magnetic field. The spin triad is a short-lived encounter complex in this case, which is not identical to the model under study. However, the model describes the processes in the system correctly.

Thus, the photolysis of SNBD in the presence of various paramagnetic additions has presented a unique opportunity to observe the two effects of the third spin considered in the present paper, that is, the influence of paramagnetic admixtures on the field dependence of the magnetic field effect and the spin catalysis effect.

In addition, this calculation method is in agreement with other calculations available in the literature. Thus, in the limiting case, for $J_1 = 0$ and the number of re-encounters $n = 1$, the system under study is similar to that studied by Lukzen and coauthors.[8] They theoretically considered a three-spin system that can be

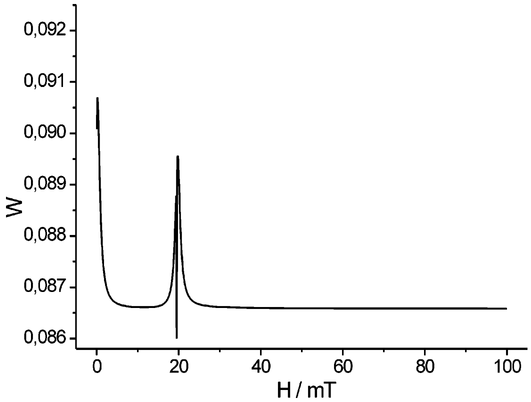

Figure 8. Field dependence of the recombination probability for the triad biradical/radical ($S_3 = {}^1/_2$). J_1= 0 mT, J_2= 20 mT. The other parameters are similar to those in Figure 1.

obtained experimentally under the irradiation of the spatially separated donor and acceptor and a spin label, calculated the spin dynamics of such a radical triad, and described the *J*-resonance effect, that is, the extremum of the recombination probability in the field close to the value of exchange interaction between the acceptor radical anion and the stable radical bound to it. Under the given conditions (Figure 8), the calculated field dependence of the recombination probability is of the form similar to that in ref 8. The field dependence exhibits both the main extremum of *J*-resonance and a narrow extremum with an opposite sign. This latter extremum is also described in ref 8 for the case where the donor radical cation (D^{+*}) has no substantial HFC and is assigned by the authors to the competition of spin evolution in both D^{+*} and the biradical anion.

Conclusions

Thus, in the present work, the method used earlier to calculate the recombination probability in a three-spin system biradical/paramagnetic species was extended to the case of the added paramagnetic species with spin $S_3 = {}^1/_2$. We analyzed the results from the calculations of the field dependencies of the recombination probability for systems with the electron spin of the added species $S_3 = 1$ and $S_3 = {}^1/_2$. In both cases, we observed similar behavior of field dependencies with varying values and signs of exchange interactions in the system. One of the most characteristic features of the calculated field dependencies is the existence of several extrema with positions and magnitude dependent on the signs and values of the exchange integrals in the system. By introducing an exchange interaction with the third species, we found a shift in the position of the main extremum. With $J_2 \approx J_1$ for the system with $S_3 = 1$, the main extremum was observed in a field stronger than that for $S_3 = {}^1/_2$. For $J_2 \gg J_1$ the main extremum for both of the systems is near ${}^3/_4 J_1$. In real systems, exchange integrals are not constants as assumed in calculations, which is sure to lead to a broadening of the extrema. As a result, with $J_2 \ll J_1$ and $J_2 \gg J_1$ we should experimentally observe one extremum and for $J_2 \approx J_1$ even two or three wide extrema for $S_3 = {}^1/_2$ and 1, respectively. It is also shown that the spin catalysis (the field-independent recombination probability) is also manifested with different efficiency in the systems studied. For the system with $S_3 = 1$, it is much stronger. In addition, the dependence of the spin catalysis efficiency on J_2 has an extremum at $J_2 = 2J_1$ independent of the values of the spin added.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (grant nos. 00-03-33048 and 04-03-32277).

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