Russian Chemical Bulletin, International Edition, Vol. 54, No. 5, pp. 1131—1138, May, 2005

Modeling of recombination kinetics of radical pairs in magnetic field. Comparison with experimental dependences on the frequency of encounters in biradicals

V. F. Tarasov[a] and P. P. Levin[b]★

[a]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 119991 Moscow, Russian Federation
[b]*N. M. Emanuel' Institute of Biochemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 4101. E-mail: levinp@sky1.chph.ras.ru

The recombination kinetics of spin-correlated radical pairs (RPs) with three nonequivalent magnetic nuclei were calculated under conditions of enforced encounters between radicals at time-independent frequency n_{dif}. The simplest two-position model of a RP was used, which includes two states (contact state and distance-separated state) of the RP, differing in magnitude of isotropic spin-spin exchange interaction between radicals. The calculated kinetic curves were treated in terms of a three-exponential model. The dependences of corresponding rate constants (k_{rec}) on n_{dif}, external magnetic field strength (B_0), and intensity, A_{eff}, of isotropic hyperfine coupling (HFC) were obtained. The k_{rec}-*vs.*-n_{dif} or k_{rec}-*vs.*-viscosity (n_{dif} varies simultaneously with the inverse lifetime of the contact state) plots pass through maxima whose positions are shifted from the n_{dif} region near the A_{eff} value at $B_0 = 0.5$ G toward high n_{dif} values with an increase in B_0. At $n_{dif} \gg A_{eff}$, the k_{rec}-*vs.*-B_0 plots pass through maxima in the region $B_0 = A_{eff}$. The calculated dependences are compared with experimental data on recombination of biradicals. The results of calculations show that the experimentally observed maxima on the k_{rec}-*vs.*-B_0 or k_{rec}-*vs.*-n_{dif} plots can be due to peculiar features of the spin dynamics induced by the hyperfine coupling rather than the exchange interaction effects, as is commonly accepted.

Key words: radical pair, biradical, magnetic effect, hyperfine interaction, recombination kinetics, Liouville equation.

The magnetic field and spin effects in the physicochemical processes involving radical pairs (RPs) are due to specific features of the behaviour of correlated electron spins.[1,2] One of best examples is provided by spin-selective recombination of RPs. This process is controlled by the triplet-singlet (T—S) transitions in RPs, because it is the singlet RPs that most efficiently recombine when radicals collide. Usually, the T—S transitions in RPs are due to the electron-nuclear hyperfine coupling (HFC) in radicals and/or to the Zeeman energy difference between the unpaired electrons in external magnetic field. The Zeeman splitting of the triplet sublevels in external magnetic field slows down the HFC-induced $T_{\pm}$—S transitions, thus affecting the rate of the corresponding chemical process.

Often, the magnitude of the magnetic field effects appreciably increases if RPs are produced under the conditions when radicals are enforced to enter numerous re-encounters, as is the case for structure-organized systems, *e.g.*, micellar solutions or biradicals where the radical centers are chemically bonded by flexible polymethylene chains.[3—7] It was experimentally established that the strongest magnetic field effect on the recombination kinetics of RPs in structurally organized systems occurs at some optimum ratio of the molecular dynamics-to-spin dynamics parameters. For instance, plotting the magnetic field effect magnitude and the rate constant, k_{rec}, for recombination of triplet RPs (*i.e.*, RPs produced in the triplet state) *vs.* the frequency of re-encounters (ν_{dif}) in micelles and biradicals revealed maxima in the corresponding curves.[5,8—12] This was also observed when k_{rec} were plotted *vs.* the micelle size,[8,9] the length of spacer in biradical,[10—12] the medium viscosity,[12—14] and the temperature.[15] The dependences of the magnetic isotope effects on the viscosity and temperature also pass through maxima.[9,16]

This unexpected, from the viewpoint of the classical chemical kinetics, behaviour is usually explained by the effect of the average exchange interaction in RPs.[17,18] This hypothesis is substantiated by the facts that anomalous behaviour is usually characteristic of the systems with relatively short mean distances between radicals in RPs and the k_{rec}-*vs.*-magnetic field plots exhibit extrema

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1103—1110, May, 2005.

in the region of weak fields. Then the nonmonotonic behaviour of the magnetic field dependences could be explained by crossing of the corresponding spin sublevels of RPs.[1—7,13,14,19—24]

At the same time the appearance of maxima in the magnetic field dependences at weak fields can be due to removal of forbiddenness of the T—S transitions, imposed by permutation symmetry of the spin states of RPs.[25,26] Theoretical analysis of the recombination kinetics of RPs containing one magnetic nucleus in microreactors in zero magnetic field showed that the k_{rec}-*vs.*-ν_{dif} plot has a bell shape, *i.e.*, an increase in ν_{dif} in the region where ν_{dif} exceeds the HFC constant is accompanied by a decrease in k_{rec} owing to specific features of modulation of coherent hyperfine interaction in the stochastic process of transition between contact and separated RPs.[8,9]

In this work we calculated the recombination kinetics of spin-correlated RPs with three nonequivalent magnetic nuclei, which were generated in initial triplet state under the conditions, when radicals are enforced to reencounter at a time-independent frequency ν_{dif}. The molecular dynamics is simulated in the framework of a two-position model, which considers two states of a RP (a contact state and a distance-separated state) with different intensity, J, of the isotropic spin-spin exchange interaction between radicals. The spin dynamics is governed by the Zeeman interaction of electron spins with the external magnetic field and by the isotropic HFC and exchange interaction. In this study we will consider only the effects of the HFC and external magnetic field. Therefore, all kinetic curves presented here were calculated at zero J for the distance-separated state of RPs and at zero rates of the longitudinal and transverse relaxations of the electron and nuclear spins in RPs. The calculated kinetic curves were treated in the framework of an exponential model, which made it possible to obtain the dependences of k_{rec} on ν_{dif}, external magnetic field strength (B_0), and the HFC intensity. The results of calculations are compared with the experimental dependences of the rate constants for recombination of biradicals on the linker chain length, viscosity, magnetic field, and isotopic substitution.

Computational Procedure

Calculations were carried out for radicals with isotropic g-factors and HFC. The RPs model used in this work included the Heisenberg isotropic spin-spin interaction as the only magnetic interaction between radicals. The dipole-dipole interaction between electron spins of radicals was included as a contribution to the relaxation matrix (see below). The model spin Hamiltonian had the form

$$H_{\mathrm{RP}} = H_{\mathrm{a}} + H_{\mathrm{b}} + H_{\mathrm{ex}}, \tag{1a}$$

$$H_{\mathrm{a}} = \omega_{\mathrm{a}} S_{\mathrm{a}z} + \sum_i A_{\mathrm{a}i}\mathbf{S}_{\mathrm{a}}\mathbf{I}_{\mathrm{a}i}, \tag{1b}$$

$$H_{\mathrm{b}} = \omega_{\mathrm{b}} S_{\mathrm{b}z} + \sum_i A_{\mathrm{b}i}\mathbf{S}_{\mathrm{b}}\mathbf{I}_{\mathrm{b}i}, \tag{1c}$$

$$H_{\mathrm{ex}} = -J(r)\cdot(0.5 + 2\mathbf{S}_{\mathrm{a}} + \mathbf{S}_{\mathrm{b}}), \tag{1d}$$

where $\mathbf{S}_{\mathrm{a}}$ and $\mathbf{S}_{\mathrm{b}}$ are the electron spins of the radicals a and b, respectively; $\mathbf{I}_{\mathrm{a}}$ and $\mathbf{I}_{\mathrm{b}}$ are the nuclear spins of the radicals a and b, respectively; $\omega_i = g_i\beta B_0$ (i = a, b); g_i are the g-factors of the radicals; β is Bohr magneton, and $A_{i,j}$ are the HFC constants (i is the number of radical and j is the number of nucleus in the radical).

In spin chemistry the dependence of the exchange interaction intensity, $J(r)$, on the distance r between radicals is described by an exponential function

$$J(r) = J_0\exp[-(r - R)/\lambda], \tag{2}$$

where J_0 is the intensity of the Heisenberg exchange interaction at the shortest distance between radicals ($r = R$) and the parameter λ characterizes the rate of decrease in the exchange interaction with an increase in r. In our calculations expression (2) was replaced by corresponding theta-function:

$$J(r) = \begin{cases} J_{\mathrm{c}}, & r \le R + \lambda \\ 0, & r > R + \lambda \end{cases}, \tag{3}$$

where J_{c} is the intensity of exchange interaction in the contact state. In spite of apparent roughness of this approximation, it quite correctly reproduces specific features of internal spin relaxation in RPs due to simulation of exchange interaction.[27]

Details of the diffusion motion of radicals in RPs in structurally organized media are usually unknown. However, in many cases radicals are mainly at distances at which $|J(r)| \ll |A_{\mathrm{eff}}|$ (A_{eff} is the effective HFC constant). At such distances, details of the molecular motion become insignificant. Therefore, it seems reasonable to use the effective radical encounter frequency, ν_{dif}, which is independent of both time and coordinates, as a first approximation. We thus introduce an additional parameter, but it can be determined accurately provided known details of radical diffusion in the system under study. Besides, in many cases (in particular, in micellar systems and dyads with flexible linkers) the ν_{dif} value can be quite satisfactorily estimated using independent experimental data obtained from, *e.g.*, fluorescence kinetics measurements.

From the standpoint of the chemical kinetics soundness of this approximation is ensured by the fact that, as time passes, the species involved in spatially organized diffusion reach a steady state in which the probability density of a particle to arrive at a given point of the accessible volume is independent of both time and coordinates of this point. The time taken to reach the steady state depends on the geometric and viscosity parameters of a given organized medium. For instance, for a homogeneous spherical volume V this time can be estimated at $[3V/(4\pi)]^{1/3}[r_{\mathrm{a}}/(\pi D_{\mathrm{a}})]$, where r_{a} ($r_{\mathrm{a}} \ll V^{1/3}$) and D_{a} are the radius and the diffusion coefficient of the species, respectively.[28] For a sphere 2 nm in diameter at $r_{\mathrm{a}} = 0.3$ nm and $D_{\mathrm{a}} = 1\cdot10^{-6}$ cm^2 s^{-1} the time taken to reach the steady state is 2 ns, which is much shorter than the characteristic lifetimes of triplet biradicals and RPs in micellar solutions. Therefore, the decay of real triplet RPs in many organized systems occurs under steady-state conditions and the kinetic features are not due to the process of attainment of the steady state.

The definition of $J(r)$ using function (3) means that a RP can be in one out of two states, a "contact" state and a "distance-separated" state characterized by the lifetimes k_c^{-1} and ν_{dif}^{-1}, respectively. The spin density matrix is composed of the density matrices (vectors in the Liouville space) of RPs in the contact state ($\rho_c(t)$) and in the distance-separated state ($\rho_s(t)$) and of the state vectors of the RPs lost as a result of spin-nonselective decay ($\rho_e(t)$) with the rate constant k_e. The corresponding Liouville stochastic equation for the state vector of a system in the Liouville spin space can be written as follows:

$$\begin{pmatrix} \dot{\rho}_c(t) \\ \dot{\rho}_s(t) \\ \dot{\rho}_e(t) \end{pmatrix} = \begin{pmatrix} L_c - \tau_c^{-1} - k_e & Z & 0 \\ \tau_c^{-1} & L_s - Z - k_e & 0 \\ k_e & k_e & L_s \end{pmatrix} \cdot \begin{pmatrix} \rho_c(t) \\ \rho_s(t) \\ \rho_e(t) \end{pmatrix}, \quad (4)$$

where L_c and L_s are the Liouville superoperators of the contact and distance-separated pairs, respectively. The Liouville superoperators are defined as follows

$$L_c = -iH^{\times}(J = J_0) - 0.5k_s P_s^{\times} + W, \quad (5a)$$

$$L_s = L_c\,(J = 0;\ k_s = 0), \quad (5b)$$

where $H^{\times} = [H_{ab},...]_-$ and $P_s^{\times} = [P_s,...]_+$ are the superoperators (commutator and anticommutator, respectively); P_s is the projection superoperator onto a subset of singlet electron spin states, and k_s is the rate constant for recombination of the contact RPs of this subset.

As concluding remarks to the two-position model including the contact and distance-separated RPs, mention may be made of the so-called ST_-mechanism in the RP theory. This mechanism is often used for quantitative interpretation of the integrated nuclear and electron spin polarization. The mechanism involves electron-nuclear spin transitions in a narrow nonadiabatic region $r_{ST\_} \approx R + \lambda\ln(2|J_0|/\omega_0)$. At first glance, the two-position model is basically inconsistent with the existence of the nonadiabatic region. At the same time, correspondence between exact numerical calculations and calculations in the framework of the two-position model can be successfully attained by varying the intensity, J_c, of the exchange interaction. Therefore, J_c is in some sense an arbitrary parameter, which requires additional interpretation. But this problem goes beyond the scope of this study.

The W superoperator in Eq. (5a) describes the spin relaxation. Modulation of exchange interaction and spin-selective reaction also induce the spin relaxation in RPs. It should be noted that the equilibrium states, which are due to relaxation processes W and exchange interaction, can be different.

Ignoring the Boltzmann polarization, the relaxation matrix for an individual spin 1/2 in the Liouville space can be written using the Bloch superoperator

$$W_i = \begin{pmatrix} w_{1i} & 0 & 0 & -w_{1i} \\ 0 & w_{2i} & 0 & 0 \\ 0 & 0 & w_{2i} & 0 \\ -w_{1i} & 0 & 0 & w_{1i} \end{pmatrix}, \quad (6)$$

where w_{1i} and w_{2i} (i = a, b) are the rates of the longitudinal and transverse spin relaxation, respectively. For a multispin system the relaxation superoperator is constructed from the corresponding operators (6). One must take into account that the direct product of the state vectors is not isomorphic to the direct product of superoperators in the Liouville space.

Radical pairs can be generated in both contact and distance-separated states, being correlated, stochastic, polarized, or equlibrium. In this work calculations were carried out assuming that at $t = 0$ the RP is in the triplet contact state with equally populated electron spin states T_+, T_-, and T_0, except for prescribed cases. Therefore, the initial state vector of the RP is as follows

$$\rho_c(t = 0) = 0.75 + S_a S_b, \quad (7a)$$

$$\rho_s(t = 0) = 0. \quad (7b)$$

Thus, numerical solution of Eq. (4) is reduced to calculating the matrix exponent. This can be done using the MATLAB package. However, it should be noted that a FORTRAN implementation of the Padé method[29] gives a considerable gain in the computing time.

Calculations of the recombination kinetics were carried out for a RP in which one radical contained three nonequivalent nuclear spins 1/2 with HFC constants of 14, 7, and 4 G, which corresponded to $A_{eff} = (0.75\Sigma A_i^2)^{1/2} = 14$ G; the HFC for the second radical was considered negligible; and the g-factors of both radicals were equal to 2. Limitation of the number of nuclear spins was governed by the time taken to calculate the kinetic curves. At the same time, three nuclear spins are sufficient for quite a detailed description of experimental systems. The A_{eff} values mentioned above are characteristics of biradicals comprised of porphyrin—viologen[6] or benzophenone—phenol[20,21,30] dyads.

In simulating deuterated biradicals comprising benzophenone—phenol dyads the A_i values were reduced by a factor of four. Calculations using isotropic HFC and exchange interaction were carried out for two states of RPs, namely, the distance-separated state ($J = 0$) and contact state ($J = 2\pi \cdot 10^9$ rad s^{-1}), except for prescribed cases. Transition from the distance-separated state to the contact state of the RP occurs at the ν_{dif} frequency while separation of the contact state of the RP is characterized by the rate constant k_c. In the contact state the triplet RPs do not recombine, but the singlet RPs recombine with the rate constant $k_s = 10k_c$. Calculations were carried out at $k_e = 0$ and zero rates of the longitudinal and transversal electron and nuclear spin relaxation in RPs. Interplay between the parameters of the two-position model and the parameters of the diffusion motion of radicals in various microreactors will be considered separately.

Results and Discussion

The recombination kinetics of real polynuclear RPs with relevant structural organization (*e.g.*, biradicals or RPs in micelles) in weak magnetic field are correctly described by a single-exponential law. In strong magnetic field, it is often necessary to use a two-exponential approximation owing to the existence of the fast component with a statistical weight of about 1/3. The fast component can be attributed to the recombination of the RPs produced in the T_0 electron spin state.[3,4,6,10,11,20,27] The kinetic curves of recombination of the RPs with three nonequivalent magnetic nuclei calculated using the two-position model usually exhibit a nonexponential behavior both in weak and in strong magnetic fields.

Ignoring the spin relaxation, only 3/4 of the spin configurations of the model RP can recombine in zero magnetic field. To understand the origin of this effect, one can take into account that both the total spin moment $\mathbf{F} = \mathbf{S} + \mathbf{N}$ and its projection F_z are conserved in zero magnetic field. The states of two electron spins can be conveniently classified using their total momenta $S = S_a + S_b$; *i.e.*, they form one triplet state and one singlet state. Three nuclear spins 1/2 ($N = I_1 + I_2 + I_3$) form one quartet (Q) and two doublet (D) states. Eventually, the spin system of a model RP can be represented by one sextet, four quartet, and five doublet states. The sextet state includes the triplet state of the total electron spin. Therefore, these six spin states can not change their electron spin multiplicity. In other words, six out of twenty-four triplet electron spin states are unreactive, or at most 3/4 of non-polarized triplet RPs can recombine in zero magnetic field in the time interval governed by spin relaxation.

Application of a weak magnetic field (even so weak as, *e.g.*, 0.5 G, which corresponds to terrestrial magnetic field) removes the limitations related to the total spin conservation. In this case only two states, characterized by the maximum and minimum F_z values, can not change their multiplicities. Thus, in weak magnetic field at most 11/12 of nonpolarized triplet RPs can recombine while 1/12 of the total number of RPs with $F_z = 5/2$ and $-5/2$ is unreactive. This approach is valid for the case of non-equivalent nuclear spins.

In most cases the decay kinetics of the triplet RPs with non-polarized electron and nuclear spins in external magnetic field can be quite correctly described by a three-exponential law with a constant term equal to 1/12:

$$[\mathrm{RP}] = (1/3)\exp(-k_{\mathrm{rec}}{}^{\mathrm{f}}t) + (5/12)\exp(-k_{\mathrm{rec}}{}^{\mathrm{m}}t) + \\ + (1/6)\exp(-k_{\mathrm{rec}}{}^{\mathrm{s}}t) + 1/12, \tag{8}$$

where t is the time and $k_{\mathrm{rec}}{}^{\mathrm{f}}$, $k_{\mathrm{rec}}{}^{\mathrm{m}}$ and $k_{\mathrm{rec}}{}^{\mathrm{s}}$ are the rate constants (superscripts "f", "m", and "s" denote the fast, medium, and slow components, respectively; $k_{\mathrm{rec}}{}^{\mathrm{f}} \geq k_{\mathrm{rec}}{}^{\mathrm{m}} \geq k_{\mathrm{rec}}{}^{\mathrm{s}}$). It is accepted that the initial concentration of RPs is equal to unity. The proportion of the fast component was chosen to be 1/3 owing to the fact that in a strong magnetic field ($B_0 \gg A_{\mathrm{eff}}$) the RPs born in the T_0 state undergo fast recombination. The slow component with a weight of 1/6 is due to the four sextet (with respect to the total spin) states. These states are kinetically nonequivalent to the remaining eighteen triplet (with respect to electron spin) states. The second component with a weight of 5/12 is in essence a fitting parameter. Division of the full kinetics into components according to the transition types (in the doublet, quartet, and sextet spin subspaces) would seem to be more convenient, but separation of the T_0-component is more physically substantiated.

Ignoring the exchange interaction, the spin evolution in the contact and distance-separated RPs should obey an identical pattern, *i.e.*, the two-position model could be automatically reduced to one-position model. However, this is not the case. According to the model, spin-selective recombination occurs in the contact RPs only. But the assumption of spin selectivity means not only selection of the singlet spin states but also a strong influence on the spin evolution. In order to qualitatively demonstrate the effect of spin-selective decay on the spin evolution of RPs, let us assume that radical "a" has an electron in the spin state $|\alpha\rangle$ and radical "b" has an electron in the spin state $|\beta\rangle$. Therefore, the RP is in the spin state $|\alpha\beta;\chi\rangle$, where χ is the nuclear spin configuration. The $|\alpha\beta;\chi\rangle$ state can be represented as a superposition of the $|S;\chi\rangle$ and $|T_0;\chi\rangle$ spin states. Due to spin-selective decay the population of the $|S;\chi\rangle$ spin state will tend to zero faster than the population of the $|T_0;\chi\rangle$ spin state. Therefore, the population of the $|T_0;\chi\rangle$ state is a superposition of the $|\alpha\beta;\chi\rangle$ and $|\beta\alpha;\chi\rangle$ spin states, which in turn means the appearance of RPs in which the electron spin of the radical "a" will be in the $|\beta\rangle$ state. Thus, spin-selective recombination causes changes in the spin states of radicals. Relaxation of the electron spin states due to spin-selective recombination strongly depends on the ratio between the radical encounter frequencies ν_{dif} and the HFC intensity in the radicals.

In weak magnetic field and in the slow encounter regime ($\nu_{\mathrm{dif}} \ll A_{\mathrm{HFC}}$) the RP decay kinetics are similar to one-exponential kinetics and $k_{\mathrm{rec}}{}^{\mathrm{f}} = k_{\mathrm{rec}}{}^{\mathrm{m}} = k_{\mathrm{rec}}{}^{\mathrm{s}} = \nu_{\mathrm{dif}}/4$, because the hyperfine interaction has sufficient time to mix different spin states during the time interval between encounters. An increase in ν_{dif} in weak fields leads to the appearance of a fast component with a contribution of about 1/3 and the rate constant $k_{\mathrm{rec}}{}^{\mathrm{f}} \approx A_{\mathrm{eff}}$. Such a fast component cannot be ascribed, as is possible in strong magnetic field, to disappearance of RPs generated in a particular spin state. The kinetic curves of the decay of the RPs produced in the T_0, and $T_\pm$ states include practically the same fast component with a statistical weight of about 1/3.

Consider some examples of the calculated kinetic curves of RP recombination at different magnetic field strength and two ν_{dif} values, one of them being smaller and another being much larger than A_{eff} (Fig. 1). In the former case an increase in B_0 from 0.5 to 10 G leads to retardation while in the latter case to acceleration of RP recombination. This acceleration is a consequence of three main factors, namely, electron spin relaxation induced by spin-selective character of the RP recombination, changes in the number of the spin states involved into the

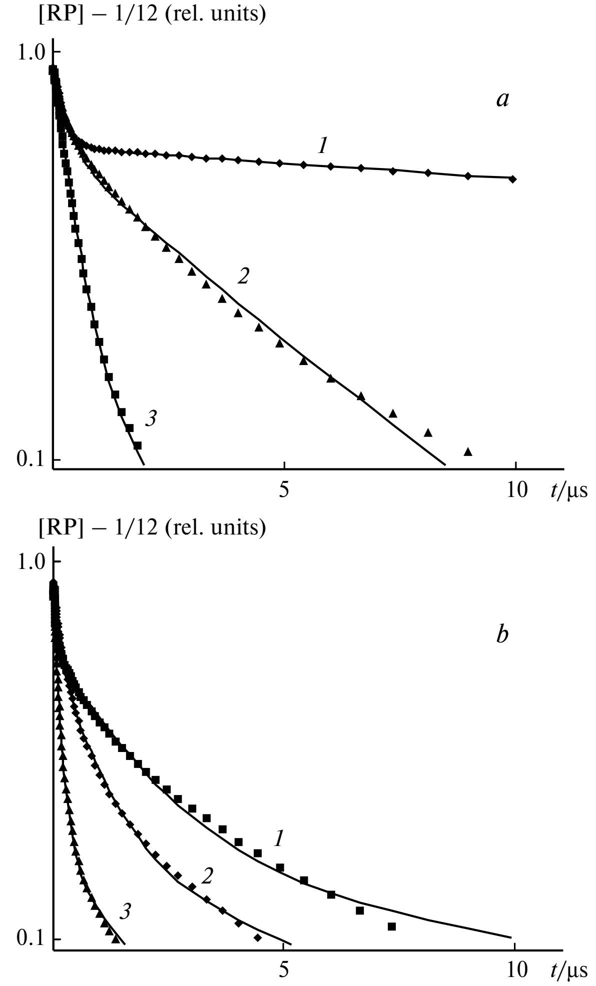

Fig. 1. Kinetic curves of RP recombination calculated at k_c = 10 ns^{-1}: *a*. $\nu_{\rm dif}$ = 10 μs^{-1}, B_0 = 50 (*1*), 10 (*2*), and 0.5 G (*3*); *b*. $\nu_{\rm dif}$ = 1 ns^{-1}, B_0 = 0.5 (*1*), 50 (*2*), and 10 G (*3*). Lines denote approximations using relation (8).

S—T-spin evolution, and changes in the efficiencies of the flip-flop transitions in the subsets of states with equal total F_z values.

The magnetic field dependences of the rate constants $k_{\rm rec}{}^{\rm f}$ and $k_{\rm rec}{}^{\rm m}$ in the fast and slow encounter regimes are shown in Fig. 2. The $k_{\rm rec}{}^{\rm f}$ value relatively slightly depends on B_0, as should be expected for the RPs generated in the T_0 state, because the Zeeman splitting does not change the energy of this state. In the slow encounter regime the $k_{\rm rec}{}^{\rm f}$ value in strong magnetic field approaches a statistically averaged value of $\nu_{\rm dif}/2$. At fast encounters, the $k_{\rm rec}{}^{\rm f}$ value is somewhat smaller than $A_{\rm eff}$; *e.g.*, at $\nu_{\rm dif}$ =1 ns^{-1}, the $k_{\rm rec}{}^{\rm f}$ value in weak fields is about $A_{\rm eff}/2$ and nonmonotonically decreases as B_0 increases.

In the slow encounter regime the $k_{\rm rec}{}^{\rm m}$ value monotonically decreases with an increase in B at $B_0 \geq 0.5$ G, whereas in the fast encounter regime an analogous dependence passes through a maximum in the region $B_0 = A_{\rm eff}$.

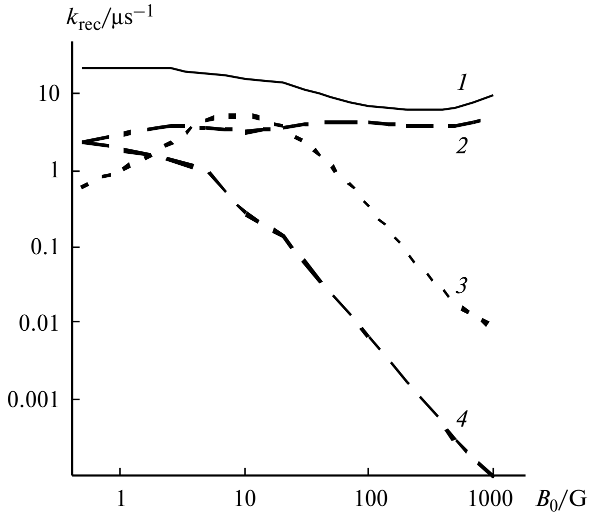

Fig. 2. Dependences of $k_{\rm rec}{}^{\rm f}$ (*1*, *2*) and $k_{\rm rec}{}^{\rm m}$ (*3*, *4*) on B_0 obtained by approximating the kinetic curves of RP recombination calculated at k_c = 10 ns^{-1}, $\nu_{\rm dif}$ = 10 μs^{-1} (*2*, *4*) and 1 ns^{-1} (*1*, *3*) using relation (8). The axes are given in logarithmic scale.

Thus, calculations showed that maxima in the magnetic field dependences of the rate constants for RP recombination, which were repeatedly observed in the experiments, can be due to coherent character of the HFC-induced spin dynamics. Position of the maximum allows one to determine the $A_{\rm HFC}$ value. A decrease in $\nu_{\rm dif}$ in any way (by, *e.g.*, increasing the viscosity of the medium) can be accompanied by increasing $k_{\rm rec}$ in weak fields, narrowing of the magnetic field dependences, and disappearance of maximum, as was often observed experimentally.[6,12—14]

According to calculations, a pronounced maximum in the magnetic field dependences can appear if in the contact state the J_c value is comparable with $A_{\rm eff}$ and, besides, the RP exists the most part of time in this state. The strongest effects also were observed at high $\nu_{\rm dif}$; however, an increase in the viscosity (simultaneous decrease in $\nu_{\rm dif}$ and k_c), which is responsible for the decrease in the maximum $k_{\rm rec}$ values, does not lead to disappearance of maximum in the magnetic field dependences at $B_0 = A_{\rm eff}$ and is not accompanied by narrowing of the magnetic field dependences, as was observed in the experiments for biradicals comprised of porphyrin—viologen dyads.[6,12—14]

In strong magnetic field ($B_0 \gg A_{\rm eff}$) the $k_{\rm rec}{}^{\rm m}$ value is proportional to $1/B_0{}^2$ and the magnetic field dependence can be described by approximate relation

$$k_{\rm rec}{}^{\rm m} = \nu_{\rm dif}/[4(1 + 3B_0/A_{\rm eff})^2] = p\nu_{\rm dif}, \qquad (9)$$

where p is the $\nu_{\rm dif}$-independent probability of formation of a singlet contact RP in an encounter between radicals. The $k_{\rm rec}{}^{\rm m}$-*vs.*-$\nu_{\rm dif}$ and p-*vs.*-$\nu_{\rm dif}$ plots presented in Fig. 3 show that $k_{\rm rec}{}^{\rm m}$ is proportional to $\nu_{\rm dif}$ in strong magnetic field. Therefore, under particular conditions (slow para-

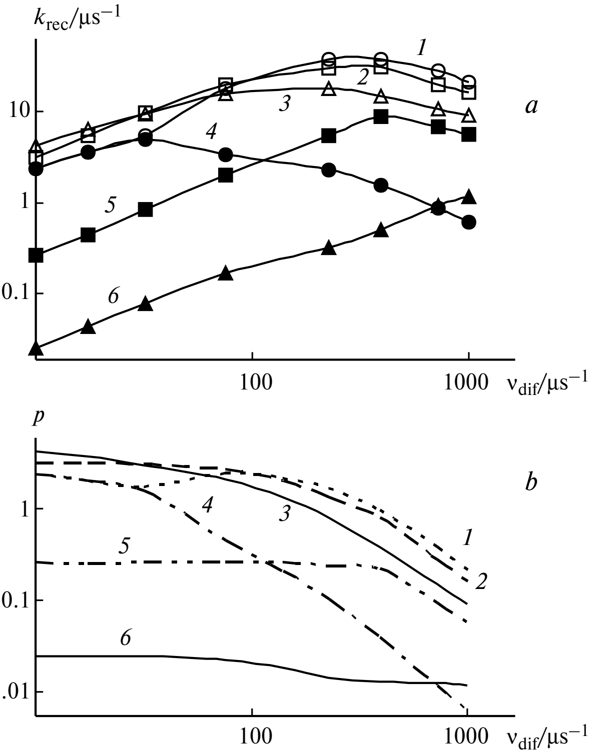

Fig. 3. Dependences of $k_{rec}{}^{f}$ (*1—3*) and $k_{rec}{}^{m}$ (*4—6*) (*a*), and corresponding *p* values (*b*) on v_{dif} at B_0 = 0.5 (*1*, *4*), 10 (*2*, *5*), and 50 G (*3*, *6*) obtained by approximating the kinetic curves of RP recombination calculated at k_c = 10 ns^{-1} using relation (8). The axes are given in logarithmic scale.

magnetic relaxation) the RP recombination in strong magnetic field is a slow diffusion-controlled process, which can be treated as an example of the so-called pseudodiffusion-controlled reactions.[31] Low *p* values characteristic of the earlier known pseudodiffusion-controlled radical recombination reactions are due to steric hindrances while in the case of recombination of spin-correlated RPs in strong magnetic fields they are due to the spin effects.

The ratios of the $k_{rec} = pv_{dif}$ type are also widely used in the interpretation of experimental kinetic data on RP recombination in weak magnetic field.[4] The results of calculations show that this approach is valid only in the slow re-encounter regime ($v_{dif} \ll A_{eff}$). As mentioned above, in this case *p* takes a statistically averaged value of 1/4 for RP recombination in weak magnetic field or 1/2 for the RPs generated in T_0 state in strong magnetic field (see Fig. 3, *b*). The increase in v_{dif} in the region of fast re-encounters leads to retardation of RP recombination in weak magnetic field and to retardation of RP recombination produced in the T_0 state in strong magnetic field rather than acceleration. The dependences of $k_{rec}{}^{m}$ and $k_{rec}{}^{f}$ on v_{dif} pass through maxima in the regions A_{eff} and $2\pi A_{eff}$, respectively (see Fig. 3, *b*). This result is a consequence of a coherent character of the HFC-induced spin dynamics and can not be predicted in the framework of formal kinetics, which assumes that the change in the limiting stage (diffusion or spin evolution) is accompanied by a monotonic change in k_{rec} and that k_{rec} is independent of v_{dif} in the fast re-encounter regime.

Figure 4 presents the calculated dependences of $k_{rec}{}^{m}$ and $k_{rec}{}^{f}$ on v_{dif} and the experimental values of the rate constant for recombination of biradicals formed upon transfer of an electron from viologen to the triplet porphyrin in porphyrin—viologen dyads linked by a $(CH_2)_n$-type flexible linker. In the experiments the v_{dif} value was varied by changing the *n* value from 4 to 138 in a non-viscous solvent (see Fig. 4, *a*) or by changing the medium viscosity (for the dyad with *n* = 6, see Fig. 4, *b*). In both cases the experimental plots and the dependences calculated at the same v_{dif} and k_c values have a bell shape. Quantitative correspondence between the experimental and calculated values of the kinetic parameters can be obtained by using, *e.g.*, the average rate constant obtained in the two-expo-

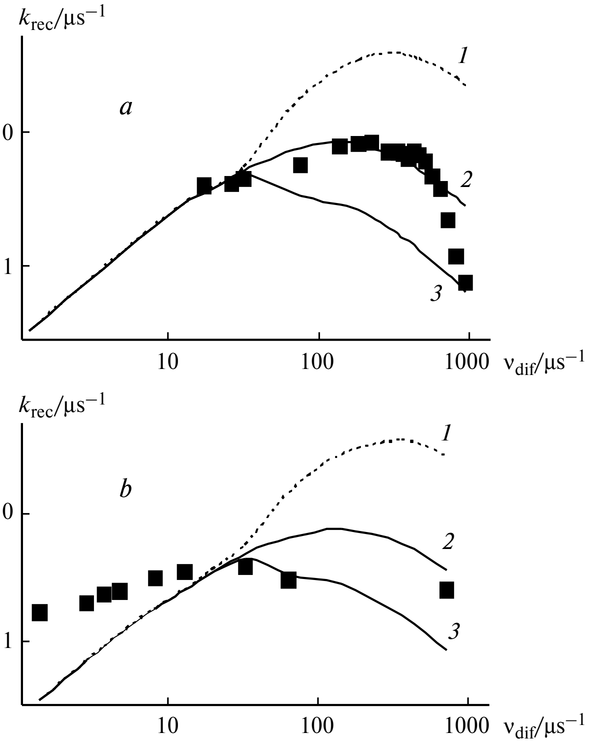

Fig. 4. Dependences of $k_{rec}{}^{f}$ (*1*), $k_{rec}{}^{a}$ (*2*), and $k_{rec}{}^{m}$ (*3*) on v_{dif}, obtained by approximating the kinetic curves of RP recombination calculated at B_0 = 0.5 G, k_c = 10 ns^{-1} (*a*) and $14v_{dif}$ (*b*) using relation (8) (curves *1* and *3*) and (10) (curve *2*). Points denote experimental values for recombination, in terrestrial magnetic field, of biradicals comprised of porphyrine-viologen dyads with differemt length of flexible linker chain (4 to 138 carbon atoms) in methanol and with a chain of six carbon atoms in methanol—glycerine mixtures (*b*). The experimental data were taken from Refs 10—14. The axes are given in logarithmic scale.

nential approximation of the calculated kinetic curves (see Fig. 4):

$$[\mathrm{RP}] = (3/4)\exp(-k_{\mathrm{rec}}{}^{\mathrm{a}}t) + (1/6)\exp(-k_{\mathrm{rec}}{}^{\mathrm{s}}t) + 1/12, \quad (10)$$

where $k_{\mathrm{rec}}{}^{\mathrm{a}}$ is the averaged rate constant.

The $k_{\mathrm{rec}}{}^{\mathrm{a}}$ value can serve as an effective rate constant for the decay of various spin states in the RPs containing three magnetic nuclei in weak magnetic field. Probably, this value approaches the rate constant for the decay of real polynuclear RPs, whose recombination is quite correctly described by single-exponential law.[3,6,10–14,20,21,27]

When ν_{dif} is varied by changing of the linker chain length, the experimental k_{rec} values significantly differ from the $k_{\mathrm{rec}}{}^{\mathrm{a}}$ values in the high-ν_{dif} region for the biradicals with short linkers ($n = 4$, 5) and insignificantly differ from them for the biradical with $n = 6$ (see Fig. 4, *a*). The underestimated experimental k_{rec} values, compared with the $k_{\mathrm{rec}}{}^{\mathrm{a}}$ values for the biradicals with short linker chains, can be explained by effective exchange interaction in real systems, which slows down the T—S-transitions in RPs.[19] At the same time, both the experimental and calculated dependences exhibit maxima at much smaller ν_{dif} values corresponding to $n \approx 20$, which corresponds to weak effective exchange interaction. Thus, calculations showed that the bell shape of the experimental plots of the rate constant for recombination of triplet biradicals *vs.* the linker chain length is mainly due to the nature of the HFC-induced spin dynamics rather than effective exchange interaction.

When ν_{dif} was varied by changing the viscosity (in calculations, ν_{dif} varied simultaneously with k_{c} to keep $\nu_{\mathrm{dif}}/k_{\mathrm{c}}$ ratio constant), significant differences of the experimental k_{rec} values for the dyad with $n = 6$ from the calculated values are observed in the region of low ν_{dif}, *i.e.*, at high medium viscosity (see Fig. 4, *b*). In this case the relatively high experimental k_{rec} values for the dyad with $n = 6$ can be due to the possibility of RP recombination (electron back-transfer) immediately as a result of exchange interaction or spin-orbit coupling through a relatively short methylene linker, which does not require encounters of ion-radical centers. The k_{rec}-*vs.*-viscosity dependence obtained for biradicals with longer linkers (with, *e.g.*, $n = 10$) at low ν_{dif} corresponds to the calculated dependence.[12] Qualitative correspondence between the experimental and calculated kinetic parameters in the region of high ν_{dif} shows that the bell shape of the k_{rec}-*vs.*-viscosity plots can be due to specific features of the interplay between the molecular dynamics and HFC-induced spin dynamics rather than peculiarities of modulation of the exchange interaction, as was assumed earlier.[17,18]

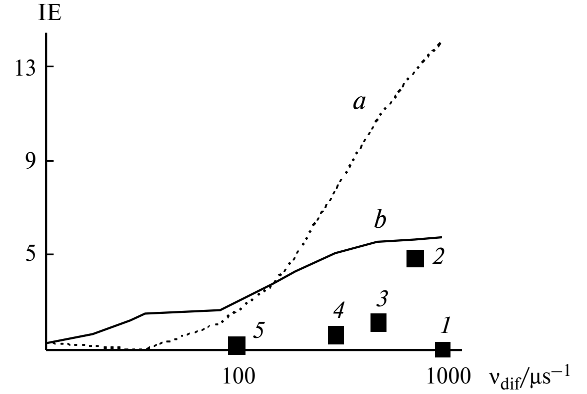

Fig. 5. Dependences of the kinetic magnetic isotope effect (the ratio of corresponding k_{rec} values at $A_{\mathrm{HFC}} = 40$ and 10 $\mu\mathrm{s}^{-1}$) on ν_{dif} for $k_{\mathrm{rec}}{}^{\mathrm{f}}$ (*a*) and $k_{\mathrm{rec}}{}^{\mathrm{m}}$ (*b*) obtained by approximation the kinetic curves of RP recombination calculated at $B_0 = 0.5$ G and $k_{\mathrm{c}} = 10$ ns^{-1} using relation (8). Points denote experimental values of the kinetic isotope effect for recombination of perdeuterated biradicals comprising benzophenone—phenol dyads with different length of flexible methylene linker containing 3 (*1*), 6 (*2*), 10 (*3*), 16 (*4*), and 42 (*5*) carbon atoms in terrestrial magnetic field in a mixture of deuterated methanol and deuterated chloroform. The experimental data were taken from Refs 12, 20, and 21.

Since, as mentioned above, the rate of RP recombination in weak magnetic fields is independent on A_{eff} at $\nu_{\mathrm{dif}} \ll A_{\mathrm{eff}}$, the corresponding calculated and experimental kinetic magnetic isotope effects (IE; the IE value is defined as the ratio of the k_{rec} values obtained for isotopically unsubstituted and isotopically substituted systems) observed, *e.g.*, upon deuteration of radicals in RPs are insignificant (Fig. 5). An increase in ν_{dif} is accompanied by a rather sharp increase in the IE, which can much exceed the ratio of the corresponding A_{eff} values at high ν_{dif}. In spite of poor quantitative agreement between the experimental and calculated data, good qualitative correspondence is observed. The absence of experimental IE for the dyad with $n = 3$ is due to the strong exchange interaction (RP is mainly in the contact state) in this system, which leads to suppression of the HFC-induced magnetic field effects, so that recombination of a given RPs is independent of external magnetic field and HFC, being governed by the spin-orbit coupling in the contact state of the RP.[12,20]f

Thus, calculations of the recombination kinetics of spin-correlated RPs with three magnetic nuclei in external magnetic field showed that many unusual (from the viewpoint of formal chemical kinetics) experimentally observed effects associated with the influence of the radical encounter frequency can be due to the coherent nature of the spin evolution due to the electron-nuclear hyperfine interaction. Calculations demonstrated that specific features of the HFC-induced spin dynamics are responsible for the appearance of extrema in the dependences of the kinetic parameters of triplet RP recombination on the size of microreactor, molecular mobility, and magnetic field.

This work was finansially supported by the Russian Foundation for Basic Research (Project No. 05-03-32197), the Presidium of the Russian Academy of Sciences (in the framework of the Complex Program of Basic Research "Fundamental Problems of Physics and Chemistry of Nanoscale Systems and Nanomaterials", investigation line "Organic and Hybrid Organo-Inorganic Nanoscale Systems and Materials Based on Them for Information Technologies"), and the Chemistry and Materials Science Division of the Russian Academy of Sciences (in the framework of the Program «Theoretical and Experimental Research on the Nature of Chemical Bonding and Mechanisms of the Key Chemical Reactions and Processes").

References

1. A. L. Buchachenko, R. Z. Sagdeev, K. M. Salikhov, *Magnitnye i spinovye effekty v khimicheskikh reaktsiyakh* [*Magnetic and Spin Effects in Chemical Reactions*], Nauka, Novosibirsk, 1978, 296 pp. (in Russian).
2. A. L. Buchachenko, *Usp. Khim*,, 1993, **62**, 1139 [*Russ. Chem. Rev.*, 1993, **62**, 921 (Engl. Transl.)].
3. C. Doubleday, Jr., N. J. Turro, and J.-F. Wang, *Acc. Chem. Res.*, 1989, **22**, 199.
4. U. E. Steiner and T. Ulrich, *Chem. Rev.*, 1989, **89**, 51.
5. N. J. Turro, A. L. Buchachenko, and V. F. Tarasov, *Acc. Chem. Res.*, 1995, **28**, 69.
6. V. Ya. Shafirovich, E. E. Batova, and P. P. Levin, in *Photochemical Conversion and Storage of Solar Energy*, Eds E. Pelizzetti and M. Schiavello, Kluwer, Amsterdam (Netherlands), 1991, p. 47.
7. S. Nagakura, H. Hayashi, and T. Azumi, *Dynamic Spin Chemistry*, Kodansha—Wiley, Tokyo—New York, 1998, 300 pp.
8. V. F. Tarasov, N. D. Ghatlia, A. L. Buchchenko, and N. J. Turro, *J. Am. Chem. Soc.*, 1992, **114**, 9517.
9. V. F. Tarasov, N. D. Ghatlia, N. I. Avdievich, I. A. Shkrob, A. L. Buchchenko, and N. J. Turro, *J. Am. Chem. Soc.*, 1994, **116**, 2281.
10. V. Ya. Shafirovich and P. P. Levin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 574 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 599].
11. P. P. Levin and V. Ya. Shafirovich, *Mol. Phys.*, 2002, **100**, 1459.
12. P. P. Levin and V. Ya. Shafirovich, *RIKEN Rev.*, 2002, **44**, 59.
13. V. Ya. Shafirovich, E. E. Batova, and P. P. Levin, *J. Phys. Chem.*, 1993, **97**, 4877.
14. V. Ya. Shafirovich, E. E. Batova, and P. P. Levin, *Dokl. Akad. Nauk*, 1993, **328**, 355 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
15. Y. Tanimoto, N. Samejima, T. Tamura, M. Hayashi, A. Kita, and M. Itoh, *Chem. Phys. Lett.*, 1992, **188**, 446.
16. A. L. Buchachenko, *J. Phys. Chem. A*, 2001, **105**, 9995.
17. K. Schulten and R. Bittl, *J. Chem. Phys.*, 1986, **84**, 5155.
18. R. Bittl and K. Schulten, *J. Chem. Phys.*, 1989, **90**, 1794.
19. G. L. Closs, M. D. E. Forbes, and P. Piotrowiak, *J. Am. Chem. Soc.*, 1992, **114**, 3285.
20. P. P. Levin, V. Ya. Shafirovich, E. E. Batova, and V. A. Kuzmin, *Chem. Phys. Lett.*, 1994, **228**, 357.
21. E. E. Batova, P. P. Levin, V. Ya. Shafirovich, and V. A. Kuz´min, *Izv. Akad. Nauk*, *Ser. Khim.*, 1995, 442 [*Russ. Chem. Bull.*, 1995, **44**, 427 (Engl. Transl.)].
22. H. Cao, Y. Fujiwara, T. Haino, Y. Fukazawa, C.-H. Tung, and Y. Tanimoto, *Bull. Chem. Soc. Jpn*, 1996, **69**, 2801.
23. T. Ito, M. Naka, A. Miura, T. Ujiie, H. Nakamura, and T. Matsuo, *Bull. Chem. Soc. Jpn*, 2001, **74**, 657.
24. M. Wakasa and H. Hayashi, *J. Phys. Chem.*, 1995, **99**, 17074.
25. I. A. Shkrob, V. F. Tarasov, and E. G. Bagryanskaya, *Chem. Phys.*, 1991, **153**, 427.
26. S. N. Batchelor, C. W. M. Kay, K. A. McLauchlan, and I. A. Shkrob, *J. Phys. Chem.*, 1993, **97**, 13250.
27. V. F. Tarasov, S. D. Chemerisov, and A. D. Trifunac, *J. Phys. Chem. B*, 2003, **107**, 1293.
28. V. F. Tarasov and M. D. E. Forbes, *Spectrochim. Acta, Part A*, 2000, **56**, 245.
29. G. H. Golub and C. F. van Loan, *Matrix Computations*, The John Hopkins University Press, Amsterdam, 1983, 201 pp.
30. P. P. Levin, V. Ya. Shafirovich, and V. A. Kuzmin, *J. Phys. Chem.*, 1992, **96**, 10044.
31. I. V. Khudyakov, P. P. Levin, and V. A. Kuz´min, *Usp. Khim.*, 1980, **49**, 1991 [*Russ. Chem. Rev.*, 1980, **49**, 1121 (Engl. Transl.)].

Received November 4, 2004;
in revised form January 27, 2005