Spin catalysis: dynamics of three-spin systems

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The kinetic theory of a new phenomenon, spin catalysis, has been developed. This phenomenon takes place in three-spin systems, when the third radical (or a paramagnetic ion) induces spin conversion in the pair, removes spin forbiddance, and thus changes the reactivity of the first two radicals. Kinetic equations for yields of spin catalyzed reactions have been derived. Conditions for spin catalysis, values of the catalytic effect, and the kinetic behavior are discussed. A new kind of quantum beats in chemical reactions is predicted.

Key words: catalysis, spin effects, kinetics; radical reactions, quantum beats.

Spin selectivity of interaction between particles and unpaired electrons (radicals, paramagnetic ions, or triplet molecules) is the reason for all magnetic and spin effects in chemical reactions.[1,2] A combined action of the law of conservation of angular moments and the Pauli principle does not allow triplet radical pairs (RP) to recombine to form diamagnetic molecules until their triplet spin state is transformed to a singlet state. It is known that the spin conversion in RP is induced by hyperfine, Zeeman, and spin-orbit interactions in radicals, while the exchange interaction between them tends to stabilize RP in singlet or triplet states. The theory based on analysis of spin dynamics of RP explains the majority of experimental data obtained in studying both traditional spin properties and secondary generation spin effects, which are induced by radio-frequency fields.[2,3]

A new phenomenon called spin catalysis has been discovered recently. It has been shown for photolysis of D,L-2,4-diphenylpentane-3-one in benzene that the probability of recombination of the triplet RP ($PhCH(Me)CO^{\cdot}$ $^{\cdot}CH(Me)Ph$) can be triply increased, when the concentration of the nitroxyl radical, tetramethylpiperidinoxyl (TEMPO), which is known to be a strong acceptor of alkyl radicals, increases from 0 to 0.15 mol L^{-1}. This result not only indicates the spin-catalytic effect in radical reactions, but also demonstrates that the catalytic function of nitroxyls dominates over their traditional function as radical acceptors.[4]

Another kinetic evidence of the spin-catalytic effect has been found in studying the recombination between alkyl radicals and nitroxyl biradicals.[5] It has been shown that the rate constant of the first recombination between the alkyl radical and one of paramagnetic centers of the biradical is 10—50 % higher than that for the rest monoradical moiety. This effect can be explained by the spin catalysis of the first recombination by the second paramagnetic center of the biradical.[5]

It is unambiguous that three radicals are involved in the chemical process (recombination) in each of these systems, and the spin evolution induced by three-spin interactions determines the chemical dynamics. Phenomena similar to chemical spin catalysis were also observed in such processes as paramagnetic quenching of a positronium in condensed media,[6] internal rotation around a double bond (*cis—trans* isomerization of molecules[7]), and recombination of spin-polarized hydrogen atoms due to triple encounters.[8] Polarization spin effects in ensembles of three radical ions formed in bacterial photosynthetic systems with a preliminarily reduced secondary acceptor were described in several works.[9,10]

Experimental observation of spin catalysis in chemical reactions stimulates the theoretical analysis of spin and chemical dynamics in multispin systems. The first stage is studying the system containing three particles with unpaired electrons, *i.e.*, the radical triad, whose properties have been described previously.[11—13] For spin catalysis, a radical triad serves as the simplest model object as a hydrogen molecule in quantum chemistry and RP in analysis of spin effects. The task of the theory is complete description of spin and chemical dynamics and the properties of radical triads, assuming prediction and experimental testing of them.

Three-spin model

A radical triad (R^1, R^2, R^3) is a system consisting of three radicals with a spin $S = 1/2$, in which one of them

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(R^3) is a spin catalyst, and the other two radicals (R^1 and R^2) are formed as RP either in singlet or in triplet states. It is the initial spin correlation in one of the pair moieties that distinguishes the radical triad from the system of three radicals randomly encountered in solution. It is assumed that partners of the triad can move in solution but at such distances that they can interact with one another. As usual, we will assume that the reaction product in the triad is formed only from singlet RP. This rule, which was multiply confirmed by experiments, is valid for any RP (R^1, R^2), (R^1, R^3), or (R^2, R^3); however, we will calculate only the probability of formation of a chosen R^1R^2 molecule.

There is a principle difference in spin dynamics between RP entering the triad and the isolated pair. The latter undergoes the spin conversion only under the action of magnetic interactions. The RP in the triad is prone to spin evolution even in the absence of magnetic interactions; nonmagnetic exchange interactions in the triad described by the Hamiltonian are enough for this

$$\hbar H = -\hbar J_{12}(1/2 + 2S_1S_2) - \hbar J_{13}(1/2 + 2S_1S_3) - \\ - \hbar J_{23}(1/2 + 2S_2S_3), \qquad (1)$$

where J_{ij} are exchange energies of spin pairs R^i and R^j, S_i are spin operators of unpaired electrons in radicals.

The scheme of levels of Hamiltonian (1) is presented in Fig. 1. It is shown[9] that all quartet states of the radical triad with the spin $S = 3/2$ ($S_z = +3/2, +1/2, -1/2, -3/2$) not only are intrinsic stationary states of Hamiltonian (1), but, as all states of the higher multiplicity in multispin systems, are chemically inert toward any pair recombinations, because the state of an arbitrary pair of radicals R^i and R^j in them is a incoherent mixture of only symmetric triplet states. The only possible intratriad spin process is the doublet-doublet evolution between pairs of states with equal $S_z = +1/2$ and $S_z = -1/2$ separated by the energy gap $2\hbar\Omega$, and

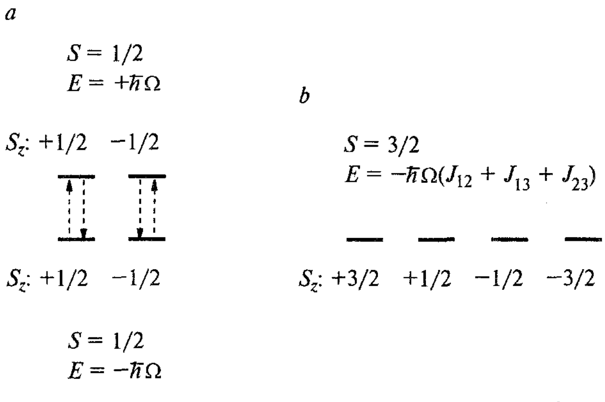

Fig. 1. Scheme of spin states of the radical triad (R^1, R^2, R^3) in a zero magnetic field: *a*, chemically active doublet states; *b*, chemically inert quartet states. Dotted lines indicate routes of the doublet-doublet evolution of the radical triad. In the RP (R^1, R^2), these routes correspond to the oscillating singlet-triplet conversion induced by the difference in exchange energies $\Delta J = J_{13} - J_{23}$.

$$\Omega = \left\{(1/2)\left[(J_{12} - J_{13})^2 + (J_{12} - J_{23})^2 + (J_{13} - J_{23})^2\right]\right\}^{1/2}, \qquad (2)$$

where $\hbar\Omega$ and $-\hbar\Omega$ are eigenvalues of Hamiltonian (1).

The spin dynamics of RP in the triad and the spin dynamics of triads are described by the time equation

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[H, \rho(t)], \qquad (3)$$

where $\rho(t)$ is the spin density matrix of triads, which allows one to determine the spin density matrix of RP

$$\rho^{12}(t) = Tr_3\rho(t) = \langle\alpha_3|\rho(t)|\alpha_3\rangle + \langle\beta_3|\rho(t)|\beta_3\rangle, \qquad (4)$$

where $Tr_3\rho(t)$ is the trace over spin variables $|\alpha_3\rangle$ and $|\beta_3\rangle$ of the R^3 radical. The probability $\rho_{ss}(t)$ of detecting the RP in the singlet state in the triad is equal to

$$\rho_{ss}(t) = \langle S^{12}|Tr_3\rho(t)|S^{12}\rangle = \\ = \langle S^{12}\alpha_3|\rho(t)|S^{12}\alpha_3\rangle + \langle S^{12}\beta_3|\rho(t)|S^{12}\beta_3\rangle. \qquad (5)$$

Initial states of the radical triad are determined by states of both its moieties (radical R^3 and RP (R^1, R^2)) and are described by the density matrix:

$$\rho_0 = \rho_3 \otimes \rho_{RP}(0), \qquad (6)$$

where ρ_3 is the spin density matrix of the R^3 radical and $\rho_{RP}(0)$ is the density matrix of the RP.

The R^3 radical is considered to be nonpolarized and corresponds to the density matrix ρ_3, which is proportional to the two-dimensional identity matrix. The initial state of the RP (R^1, R^2) is determined by the state of a decomposing molecule and can be a singlet state $|S^{12}\rangle$ or a mixture of triplet $|T_{0,\pm}{}^{12}\rangle$ states. Singlet RP form radical triads in doublet states with a probability $W = 1$. Triplet RP create triads in mixtures of quartet and doublet states. In these processes, 2/3 of the triads are in quartet states and can be involved only in extratriad reactions, and only 1/3 of these triads are in initial doublet states, in which spin catalysis and formation of products of geminate recombination are possible.

In the absence of pair recombinations in the radical triad with nonsymmetric spin exchange ($J_{13} \neq J_{23}$), the probability of the singlet state of the initially triplet RP ($\rho_{ss}{}^{T}(t)$) due to spin catalysis is equal to[13]

$$\rho_{ss}^{T}(t) = [\Delta J/(2\Omega)]^2\sin^2(\Omega t) = \delta^2\sin^2(\Omega t), \qquad (7)$$

where $\Delta J = (J_{13} - J_{23})$ is the difference between the exchange energies of each of the partners of the RP (R^1, R^2) and the radical-catalyst R^3; $\delta = \Delta J/(2\Omega)$. The value of the doublet-doublet splitting 2Ω in the radical pair determines the frequency of its doublet-doublet evolution, which causes the oscillating singlet-triplet conversion of the isolated RP (R^1, R^2) catalyzed by exchange interactions between the R^3 radical and the partners in RP R^1 and R^2. This oscillation corresponds to the migration ("overflowing") of pair spin correlations between all possible RP of the triad: (R^1, R^2), (R^1, R^3), and (R^2, R^3).

For the initially singlet RP (R^1, R^2), exchange interactions with R^3 in the triad force the RP to transit from a singlet state to a triplet state, and the probability of the RP to remain in a singlet state ($\rho_{ss}{}^{S}(t)$) is determined by the equation[13]

$$\rho_{ss}^{S}(t) = 1 - 3[\Delta J/(2\Omega)]^2\sin^2(\Omega t) = 1 - 3\delta^2\sin^2(\Omega t). \qquad (8)$$

Thus, in the first case, the R^3 radical catalyzes the transition of the RP (R^1, R^2) from a triplet state to a singlet state, increasing its chemical activity, and in the second case, it plays the role of a spin inhibitor, transforming the chemically active singlet RP to the triplet unreactive RP. The key condition of spin catalysis is the nonsymmetric character of exchange interactions, *i.e.*, inequality $J_{13} \neq J_{23}$.

The next task is studying the effect of the radical-catalyst R^3 on the chemical behavior of the RP, *i.e.*, on the yield of reaction products, its rate and kinetics, and dependences of these processes on chemical and magnetic properties of radicals.

Three-spin dynamics

Let us consider the reaction of spin-dependent recombination catalyzed by the R^3 radical:

$$R^1 + R^2 \underset{k}{\overset{R^3}{\rightleftharpoons}} (R^1, R^2, R^3) \xrightarrow{w} R^1R^2 + R^3,$$

which competes with spin-independent processes of decomposition of radical triads and extracage decay of radicals. Since the rate of formation of diamagnetic molecules is proportional to the probability $\rho_{ss}(t)$, the yield ($Y(t)$) of the reaction product R^1R^2 is described by the following kinetic equation:

$$\mathrm{d}Y/\mathrm{d}t = w\rho_{ss}(t), \qquad (9)$$

where w is the rate constant of recombination (annihilation) of singlet RP, which is determined only by chemical parameters of R^1 and R^2 radicals and is a phenomenological parameter of the theory. Then

$$Y(t) = w\int \rho_{ss}(t)\mathrm{d}t + C, \qquad (10)$$

where C is the arbitrary integration constant determined by the initial condition $Y(t) = 0$. Then it is shown that $C = Y_\infty$, where Y_∞ is the yield of the product R^1R^2 at the end of the reaction.

When chemical and spin dynamics in the radical triad are taken into account, the density matrix $\rho(t)$ is the solution of the evolutionary equation

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[H, \rho] - (w/2)(P_s^{12}\rho + \rho P_s^{12}) - k\rho, \qquad (11)$$

where the last term describes the extracage decay of radicals (*i.e.*, decay of radical triads) due to spin-independent extratriad processes (k is their total rate constant), and the second term describes the geminate spin-dependent recombination of radicals R^1 and R^2. This term is presented, as a rule, as the anticommutator of the operator of the density matrix $\rho(t)$ and the operator of projecting $P_s{}^{12} = |S^{12}\rangle\langle S^{12}|$ to the singlet spin state of the RP (R^1, R^2).

Two particular kinetic scenarios of reactions in triads follow from the general equation (Eq. (11)). First of them assumes that no channels of extracage decay of radicals exist in the system, and radicals can disappear only in geminate recombination or dismutation (complete annihilation) processes. Then $k = 0$, and Eq. (11) is deduced to the expression

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[H, \rho] - (w/2)(P_s^{12}\rho + \rho P_s^{12}), \qquad (12)$$

which is applicable, in particular, for describing the spin catalysis in radical ion pairs, when dissociation of radical ions can be neglected.

On the contrary, the second scenario assumes that R^1 and R^2 radicals actively disappear in extracage reactions, and only a small portion of them recombinates. Then $w \ll k$, and Eq. (11) takes the form

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[H, \rho] - k\rho. \qquad (13)$$

It is convenient to determine solutions of Eqs. (11) and (13) in the form

$$\rho(t) = \rho'(t)\exp(-kt). \qquad (14)$$

Then for the first scenario, $\rho'(t)$ is described by Eq. (12), while Eq. (3) describes $\rho'(t)$ in the second scenario. These simplifications can be easily checked by a simple substitution of Eq. (14) into Eqs. (11) and (13). Therefore, to take into account extracage processes, it is enough to solve Eq. (3) or Eq. (12), to multiply the matrix of density $\rho'(t)$ obtained by $\exp(-kt)$, and to use this result in Eq. (10) for determining the yields of products $Y(t)$ and Y_∞.

Kinetics of spin catalysis when $w \ll k$

The solutions of Eqs. (3) and (5) are already known for weakly recombinating radicals R^1 and R^2 (see Eqs. (7) and (8)). For initially triplet RP (R^1, R^2), substituting Eq. (7) into Eq. (14), we obtain an equation that describes the population of their singlet states:

$$\begin{aligned}\rho_{ss}^{T}(t) &= [\Delta J/(2\Omega)]^2\exp(-kt)\sin^2(\Omega t) = \\ &= \delta^2\exp(-kt)\sin^2(\Omega t).\end{aligned} \qquad (15)$$

Substituting Eq. (15) into Eq. (10), we determine the yield of the reaction product:

$$Y_\infty = [w/(2k)][\Delta J/(2\Omega)]^2/\{1+[k/(2\Omega)]^2\} = [w/(2k)][\delta^2/(1+\theta^2)], \qquad (16)$$

where $\theta = k/(2\Omega)$, and the total kinetics of accumulation of molecules R^1R^2 are described by the equation

$$Y(t) = Y_\infty\left[1-(1+\theta^2)\exp(-kt) + \theta^2\exp(-kt)\cos(2\Omega t+\varphi)/\cos\varphi\right] \qquad (17)$$

with $\varphi = \mathrm{arctg}\theta$ and $\cos\varphi = \theta/(1+\theta^2)^{1/2}$.

It is evident that the yield of the product depends on "chemical" constants w and k and on the "spin" parameters δ and θ, which characterize the ratios of ΔJ and k to the value of the doublet-doublet splitting 2Ω.

Thus, the yield of the recombination product Y_∞ increases proportionally to $(\Delta J)^2$ and $(\Delta J)^2/[k^2 + (2\Omega)^2]$ in the presence of a radical catalyst R^3. If the frequency of the doublet-doublet evolution 2Ω is very small ($2\Omega \ll k$), the yield of the product ($Y_\infty \approx w(\Delta J)^2/(2k)^3$) decreases sharply as the rate constant of the extratriad process (k) increases. In the opposite case ($k \ll 2\Omega$, but $w \ll k$), the yield of the recombination product ($Y_\infty = [w/(2k)][\Delta J/(2\Omega)]^2$) is determined by the ratio between the rate constants of cage and extracage processes (w/k), which is typical of the kinetics of parallel reactions, and by the $[\Delta J/(2\Omega)]^2$ ratio, which is the main characteristic parameter of spin catalysis. These two limits correspond to the cases when either spin conversion or molecular (diffusion) dissociation is the limiting process in the triad.

It follows from Eq. (17) that the kinetics of all reactions of spin catalysis are described by two components, one of which oscillates in time. These oscillations (quantum beats) of rates of processes and yields of products are determined by the triplet-singlet conversion of a reacting RP in a triad and are similar to quantum beats in isolated RP.[14,15] They should be most pronounced in the kinetics of intermediate objects, singlet RP (see Eq. (15)).

The normalized kinetic dependences of spin catalysis for triplet RP are presented in Figs. 2 and 3. They are obtained from Eq. (17) in which the "dimensionless" time $\tau = kt$ is used:

$$Y(\tau)/Y_\infty = 1-\exp(-\tau)\{1+\theta^2[1-\cos(\tau/\theta+\varphi)/\cos\varphi)]\} \ . \qquad (18)$$

It can be seen from Fig. 2 that for triplet RP at the initial moment ($\tau = 0$) when $\rho_{ss}{}^T(0) = 0$, the kinetic dependence $Y(\tau)$ issues out of the origin of coordinates and $dY/d\tau = 0$. This kinetic behavior is typical not only of spin catalysis, but also of all spin-dependent processes in which products of geminate recombination are formed from initially triplet RP. This resembles the kinetics of autocatalytic reactions. Despite oscillations, the curve $Y(\tau)$ monotonically increases in time (because $dY/dt = w\rho_{ss}(t) > 0$) and can change its slope only periodically.

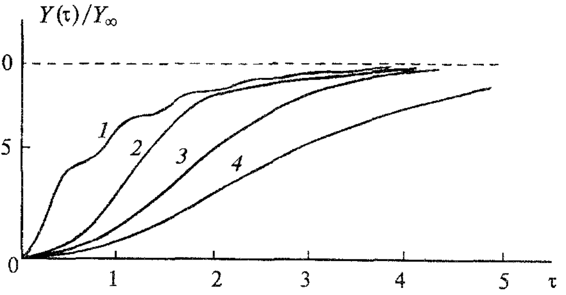

Fig. 2. Kinetics of accumulation of products of geminate recombination of triplet RP (R^1, R^2) in the presence of the spin catalyst R^3 at $w \ll k$ and $\theta = 0.1$ (*1*), 0.5 (*2*), 1.0 (*3*), and 5.0 (*4*).

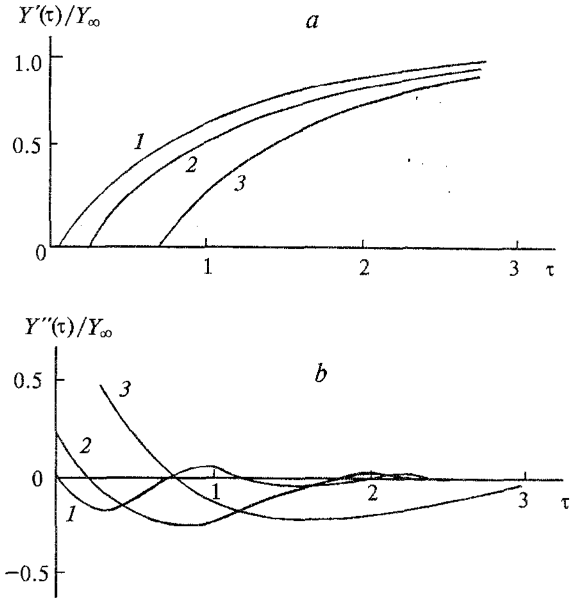

Fig. 3. Nonoscillating $Y'(\tau)$ (*a*) and oscillating $Y''(\tau)$ (*b*) components of the kinetics of accumulation of the product (R^1, R^2) of spin-catalyzed recombination of triplet RP at $w \ll k$ and $\theta = 1.0$ (*1*), 0.2 (*2*), and 0.1 (*3*).

It is seen from Fig. 3, *a* that the nonoscillating region of the kinetic curve looks like a simple exponential dependence ($1 - \exp(-kt)$) by the $\Delta\tau = \ln(1 + \theta^2) = \ln\{1 + [k/(2\Omega)]^2\}$ value shifted relative to the initial moment. At small values of $k/(2\Omega)$ ratios, this delay is equal to $[k/(2\Omega)]^2$ and always increases as the Ω frequency of the doublet-doublet evolution in radical triads decreases. This delay can be explained from the physical viewpoint by the fact that the formation of diamagnetic molecules R^1R^2 requires the time of the order of the noticeable portion of the period $T = \Omega^{-1}$ for transforming triplet RP to singlet RP. The oscillating component of the kinetics of spin catalysis is presented in Fig. 3, *b*, which distinctly shows that the initial amplitude increases as the relative oscillation frequency decreases.

The kinetics of accumulation of the recombination product (R^1R^2) of initially singlet RP in the presence of the R^3 radical can be calculated in a similar way, using Eqs. (8), (10), and (14):

$$Y^{S}(t) = Y^{S}_{\infty}\left[1 - \left(1 - \frac{\eta\theta^2}{1-\eta}\right)\exp(-kt) - \right.$$
$$\left. - \frac{\eta\theta^2}{1-\eta}\exp(-kt)\cos(2\Omega t + \varphi)/\cos\varphi\right], \qquad (19)$$

where $\eta = (3/2)[\Delta J/(2\Omega)]^2/\{1 + [k/(2\Omega)]^2\} = (3/2)\delta^2/(1 + \theta^2)$. The yield of the reaction product is equal to

$$Y^{S}_{\infty} = (w/k)\left[1 - (3/2)\delta^2/(1+\theta^2)\right] = (w/k)(1-\eta) \ . \qquad (20)$$

It follows from Eqs. (19) and (20) that in the presence of the R^3 radical the yield of the R^1R^2 product is lower by the value

$$\Delta Y^{S}_{\infty} = (3/2)(w/k)\delta^2/(1+\theta^2) = (w/k)\eta \qquad (21)$$

compared to $Y_{\infty} = w/k$ in the absence of R^3. In other words, the R^3 radical becomes an inhibitor at the starting singlet state of the RP (R^1, R^2) in the triad. Quantum beats are obvious again; however, their amplitude is $\eta/(1 - \eta)$ times lower than that for spin catalysis of triplet RP. The change in the spin multiplicity of the starting RP (singlet instead of triplet) is accompanied by inversion of the beat phase.

The kinetics of accumulation of products of geminate recombination of the initially singlet RP (R^1, R^2) in the presence of the R^3 radical are described by the equation

$$Y(\tau)/Y_{\infty} = 1 - \exp(-\tau)\left\{1 - \frac{\eta\theta^2}{1-\eta}[1 + \cos(\tau/\theta + \varphi)/\cos\varphi]\right\}, \qquad (22)$$

derived from Eq. (19) with the dimensionless time ($\tau = kt$).

Kinetics of spin catalysis when $k \ll w$

The kinetics of spin catalysis under conditions when the process of geminate spin-dependent recombination of radicals in the RP (R^1, R^2) is the main ($w \gg k$) or the only ($k = 0$) process and it cannot be neglected obeys Eq. (12), which can be solved by a method analogous to the previously described method.[13] For radical triads with a starting triplet state of RP, the probability of detecting the pair in the singlet state is equal to

$$\rho^{T}_{ss}(t) = \frac{(\Delta J)^2}{(2\Omega\chi)^2 + (w\ae/2)^2}\{\exp[-w(1-\ae)t/2] \times$$
$$\times [1 - \exp(-w\ae t/2)]^2/4 + \exp(-wt/2)\sin^2(\Omega' t)\}, \qquad (23)$$

where χ is the factor of changing the frequency of quantum beats ($\Omega' = \chi\Omega$) and æ is the factor of changing rates of accumulation and recombination of singlet RP formed during spin catalysis. In fact, coefficients χ and æ describe the mutual effect of spin and chemical dynamics of radicals in processes of spin catalysis. Explicit expressions for these coefficients are the following:

$$\chi = \left\{(1/2)\left[1 - \Gamma^2 + [(1+\Gamma^2)^2 - 3\delta^2\Gamma^2]^{1/2}\right]\right\}^{1/2}, \qquad (24)$$

$$\ae = \left\{\frac{1-\Gamma^{-2}}{2} + \left[\left(\frac{1+\Gamma^{-2}}{2}\right)^2 - 3\delta^2\Gamma^{-2}\right]^{1/2}\right\}^{1/2}, \qquad (25)$$

where $\Gamma = w/(4\Omega)$.

It is evident from Eq. (23) that the population density of singlet states of RP is also described by the sum of two terms, the second of which, $\exp(-wt/2) \cdot \sin^2(\Omega' t)$, reflects decaying oscillating transitions of triplet RP to singlet RP with the Ω' frequency (quantum beats). The rate of decay of oscillations $w/2$ is determined only by recombination of RP and differs from the characteristic rates $w\ae/2$ and $w(1 - \ae)/2$, which cause the behavior of the nonoscillating component. As previously, the probability $\rho_{ss}{}^{T}(t)$ is proportional to the square of the difference in exchange energies $(\Delta J)^2$ of the interaction between the radical catalyst R^3 and partners of the RP R^1 and R^2, but, unlike Eqs. (2) and (4), not $[\Delta J/(2\Omega)]^2$ is the substantial parameter of the kinetics, but the ratio between $(\Delta J)^2$ and the combination of the doublet-doublet splitting frequency 2Ω and the recombination rate constant w.

Now the kinetics of accumulation of the recombination product R^1R^2 can be calculated using Eqs. (9) and (10). The nonoscillating component of the kinetics is described by the function

$$Y'(t) = Y_{\infty}\left\{1 - \frac{1+\ae}{2}\left[1 + \frac{(w/2)^2(1-\ae^2)}{(w\ae/2)^2 + (2\Omega\chi)^2}\right] \times \right.$$
$$\left. \times \exp[-w(1-\ae)t/2] \cdot \left[1 + \frac{1-\ae}{1+\ae}\exp(-w\ae t)\right]\right\}, \qquad (26)$$

and the oscillating component is described by the expression

$$Y''(t) = Y_{\infty}\frac{(w/2)^2(1-\ae^2)}{(w\ae/2)^2 + (2\Omega\chi)^2} \times$$
$$\times \exp(-wt/2)\cos(2\Omega' t + \varphi_0)/\cos\varphi_0, \qquad (27)$$

where $\varphi_0 = \mathrm{arctg}[w/(4\Omega')]$. Function (26) predicts the exponential accumulation of the product with the yield $Y_{\infty} = 1/3$, which means that all RP (R^1, R^2), which form triads in doublet spin states with the radical catalyst R^3 (the amount of these triads $\xi = 1/3$), are transformed to the singlet state and recombinate to form the product R^1R^2.

"Weak" spin catalysis

In real systems, spin catalysis is often realized in radical triads in which distances between radicals R^1 and R^2 in RP are considerably shorter than distances between them and the radical catalyst R^3. Since the exchange interaction $J(r)$ is short-range, the following relationships are valid for these triads:

$$J_{13}, J_{23} << J_{12} , \tag{28}$$

$$\delta = \Delta J/(2\Omega) << 1 . \tag{29}$$

Then

$$\ae = 1 - \gamma \tag{30}$$

and

$$\chi = 1 - \gamma\Gamma^2/8 , \tag{31}$$

where

$$\gamma = 3\delta^2/(1+\Gamma^2) = 3\Delta J^2/[(2\Omega)^2 + (w/2)^2] << 1 . \tag{32}$$

This is a case of "weak" spin catalysis in which the dynamics of population of singlet RP is described by an equation similar to Eq. (23):

$$\rho^T_{ss}(t) = (\gamma/6)\Big\{\exp(-w\gamma t/2)\cdot\{1 - \exp[-w(1-\gamma)t/2]\}^2 + \\ + 4\exp(-wt/2)\sin^2(\Omega' t)\Big\} . \tag{33}$$

The equation for the kinetics of accumulation of R^1R^2 is obtained by substituting Eq. (33) into Eq. (10). The nonoscillating kinetic component obeys the equation

$$Y'(t) = Y_\infty\left\{1 - \left(1 + 2\gamma\frac{\Gamma^2}{\chi^2+\Gamma^2}\right)\exp(-w\gamma t/2) \times \right. \\ \left. \times\ [1\ + (\gamma/2)\exp(-wt)]\right\} \approx Y_\infty[1 - \exp(-w\gamma t/2)] \tag{34}$$

and can be characterized by a new effective rate constant $w\gamma/2$, which is $\gamma/2$ times lower than the recombination rate of analogous singlet isolated RP. Therefore, $k \ll w\gamma/2$ is a more rigorous condition of applicability of the "weak" spin catalysis theory. At $t \to \infty$ the yield of the product approaches to the asymptotic limit: $Y_\infty = 1/3$.

The oscillating part of the kinetic curve, which describes quantum beats, has the form

$$Y''(t) = Y_\infty\left(2\gamma\frac{\Gamma^2}{\chi^2+\Gamma^2}\right)\exp(-wt/2) \times \\ \times \cos(2\Omega' t + \psi_0)/\cos\psi_0, \tag{35}$$

where $\psi_0 = \mathrm{arctg}(\Gamma/\chi)$ and can be noticeable in the transition process only at its initial regions, when $t \ll (w\gamma/2)^{-1}$. At $t \geq w^{-1}$ the singlet-triplet evolution of RP has the nonoscillating character.

Exact kinetics

According to Eq. (14), when the dynamics of population density of singlet states of RP at $k = 0$ is known, it can also be determined for such pairs in a more complicated case, when extracage spin-independent reactions cannot be neglected, *i.e.*, when $k \neq 0$. Then

$$\rho^T_{ss}(t) = (1/8)\frac{\Delta J^2}{(w\ae/2)^2 + (2\Omega\chi)^2}\exp[-(k + w/2)t] \times \\ \times [\mathrm{ch}(-w\ae t/2) - \cos(2\Omega\chi t)]. \tag{36}$$

As in all previous cases, the kinetics of accumulation and consumption of singlet RP are described by the sum of two functions, oscillating and nonoscillating. It follows from Eq. (36) that spin-independent extracage radical reactions do not change the frequency of S—T-conversion of RP.

Equation (36) can be presented in the form, which is more convenient for analyzing:

$$\rho^T_{ss}(t) = (1/8)\frac{\delta^2}{(\ae\Gamma)^2 + \chi^2}\Big\{\exp\{-[k + w(1-\ae)/2]t\} \times \\ \times [1 - \exp(-w\ae t/2)]/2 + 2\exp[-(k + w/2)t]\sin^2(\Omega\chi t)\Big\} , \tag{37}$$

whence it follows that extracage processes accelerate the disappearance of singlet RP. Using Eq. (37), the following expression for the complete kinetics of accumulation of recombination products $Y(t)$ and the yield of products of the catalyzed reaction Y_∞ can be obtained:

$$Y_\infty = \frac{2w(k + w/2)\Delta J^2}{4k(k+w)\left[(k + w/2)^2 + 4\Omega^2\right] + 3w^2\Delta J^2} . \tag{38}$$

At $k = 0$, the yield of products ($Y_\infty = 1/3$) completely corresponds to the previously obtained results. An increase in distances in the radical triad, *i.e.*, a decrease in ΔJ, decreases the yield of recombination products proportionally to ΔJ^2. The same effect is caused by an increase in the rate of extratriad and extracage processes: at high k the yield $Y_\infty \sim k^{-3}$, and when $w \ll k$ the limiting value of Y_∞ coincides with the results of calculations according to Eq. (16).

The exact kinetics of accumulation of products of spin-catalyzed geminate recombination are described by a rather awkward expression, which can be simplified by introducing the following subsidiary values:

$$\varepsilon = (w\ae/2)/(k + w/2) , \tag{39}$$

$$\nu = 2\Omega\chi/(k + w/2) . \tag{40}$$

The nonoscillating component of the kinetics has the form

$$Y'(t) = Y_\infty\left\{1 - \frac{1+\varepsilon}{2}\left(1 + \frac{1-\varepsilon^2}{\nu^2+\varepsilon^2}\right)\exp\{-[k + w(1-\ae)/2]t\} \times \right. \\ \left. \times\left[1 + \frac{1-\varepsilon}{1+\varepsilon}\exp(-w\ae t)\right]\right\} , \tag{41}$$

and the oscillating component is described by the equation

$$Y''(t) = Y_\infty \frac{1-\varepsilon^2}{\nu^2+\varepsilon^2} \exp[-(k+w/2)t] \times$$
$$\times \cos(2\Omega\chi + \psi)/\cos\psi, \qquad (42)$$

where

$$\cos\psi = (1+\nu^2)^{-1/2} \qquad (43)$$

and ψ = arctg ν. For the yield of products we have

$$Y_\infty = \frac{w\Delta J^2}{2(k+w/2)^3(1-\varepsilon^2)(1+\nu^2)}. \qquad (44)$$

***

Exchange interactions between the R^3 radical and the R^1 and R^2 radicals in the triad (R^1, R^2, R^3) induce spin-triplet conversion in the isolated RP (R^1, R^2) and change the yield of products of geminate recombination or dismutation of these radicals. Thus, the R^3 radical (or a paramagnetic ion) is the spin catalyst of geminate reactions of the initially triplet RP (R^1, R^2). On the contrary, for the initially singlet RP (R^1, R^2), the R^3 radical serves as a spin inhibitor of their recombination.

Spin catalysis is possible only for RP (R^1, R^2) that form with R^3 a radical triad with a total electron spin $S = 1/2$. For radical triads in the quartet state ($S = 3/2$), neither spin catalysis nor pair recombinations are possible, and radicals from such triads can disappear only due to extracage and extratriad processes.

Singlet-triplet conversion of RP (R^1, R^2) occurs due to doublet-doublet evolution of radical triads (R^1, R^2, R^3); both processes occur synchronously, their rates are proportional to $\sin^2(\Omega' t)$, and Ω' is determined by the value of doublet-doublet splitting in the radical triad and the rate constant w of geminate spin-dependent radical recombination. The key condition of spin conversion of correlated RP (R^1, R^2) and spin catalysis is the inequality $J_{13} \neq J_{23}$, *i.e.*, spin catalysis occurs only for nonsymmetric exchange of partners of the RP (R^1, R^2) with the radical catalyst R^3.

The spin-catalytic yield of products of geminate recombination of radicals R^1 and R^2 is proportional to ΔJ^2 and the recombination rate constant w and is inversely proportional to k^3, and the kinetics of spin catalysis is the sum of nonoscillating and oscillating terms, which describe quantum beats in spin catalysis.

Spin is the most important property of electrons, nuclei, collective excitations in condensed media, and other elementary particles, and spin-dependent reactions and processes are observed not only in chemical systems, but they also occur in plasma, molecular crystals, and organic and inorganic semiconductors, and are studied in high energy physics. Therefore, it is evident that spin catalysis will be found in chemical and physical processes in which spin selectivity plays a substantial role.

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