

Electron Spin Catalysis

Anatoly L. Buchachenko* and Vitaly L. Berdinsky

Institute of Problems of Chemical Physics, Chernogolovka, Moscow Region, 142432 Russia

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Anatoly Buchachenko was born in Russia, under Archangelsk. He graduated from Gorki (Nizhny Novgorod) State University in 1958 and joined the Institute of Chemical Physics as a postdoctoral fellow. Currently he is a Professor of ICP, the Head of the Department of Chemical Kinetics at Moscow University, a full member of the Russian Academy of Sciences, and Editor-in-Chief of the *Chemical Physics Reports*. His interests include the physics of chemical reactions, spin chemistry, ESR and NMR spectroscopy, and molecular ferromagnets. He is a discoverer of the magnetic isotope effect and microwave emission of chemical reactions.

I. Introduction

Chemical reactions are known to be controlled by two fundamental parameters, energy (both free and activation energy) and angular momentum (spin) of reactants.¹ The conservation of the total angular momentum in chemical reactions is a fundamental and universal principle. It results in electron and nuclear spin selectivity of reactions: only those spin states of reactants are chemically active whose total spin is identical to that of products; chemical reaction is forbidden if transformation of reactants into products requires spin changing.² This statement is not completely adequate for the molecular systems with strong spin–orbital coupling, which induces a transfer of electron angular momentum to the orbital motion of electrons. If this coupling is strong enough it results in the electron spin changing along the reaction pathway; this phenomenon is well-known in



Vitaly Berdinsky graduated from Ural Technical University and started his career at the Institute of Chemical Physics. His current research interests concern chemical radiophysics, spin chemistry, and spin coherence in chemical reactions.

* To whom correspondence should be addressed. Phone: (095)-9397490. Fax: (095)9382484. E-mail: spinchem@chph.ras.ru.

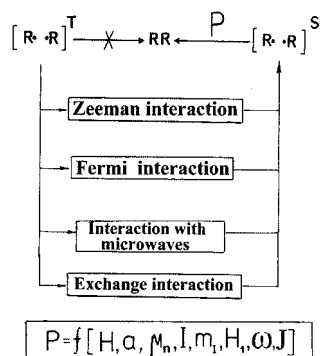


Figure 1. General scheme of spin chemistry.

spectroscopy and photochemistry as a heavy atom effect, both intra- and intermolecular.³ In the latter case the effect can be treated as a spin catalysis induced by such species as Br or I atoms;⁴ recently it was shown that even diamagnetic atoms, such as Xe, may efficiently catalyze electron spin conversion (intersystem crossing) via spin-orbital coupling.⁵⁻⁷

However, in the majority of spin-selective chemical reactions of organic molecules, the spin-orbital coupling is negligibly small and can be ignored. Nevertheless, these reactions can be also catalyzed; this *non-spin-orbital* or electron spin catalysis (for brevity we will further use the term *spin catalysis*) is the subject of the present paper.

To clearly understand principles underlying spin catalysis, it is worthy to shortly remind mechanisms of electron and nuclear spin control of the reactions. The way it functions may be illustrated by example of the triplet radical pair (R, R) prepared by photolysis, radiolysis, or encounter of freely diffusing radicals. To recombine and produce diamagnetic, zero-spin molecule RR, triplet-singlet spin conversion of the radical pair is required (Figure 1). This phase of reaction has nothing to do with chemistry: spin conversion and triplet-singlet evolution are controlled by Zeeman interaction, hyperfine (electron-nuclear or Fermi) coupling, magnetic interaction with microwaves (if they are applied to the reaction system), and exchange interaction of the partners of radical pair with a foreign, third spin carrier.

By spin changing, these interactions transform the nonreactive triplet state of the radical pair into the reactive singlet state, so that the reaction probability P is a function of parameters characterizing these interactions

$$P = f[H; a, \mu_n, m_I, H_1, \omega; J] \quad (1)$$

These parameters are listed in Table 1 in parallel

Table 1. Magnetic and Exchange Interactions Responsible for the Magnetic and Spin Effects

interaction	parameters	magnetic and spin effects
Zeeman	H , magnetic field	magnetic field effect
Fermi	a , hyperfine coupling; I , nuclear spin; m_I , nuclear spin projection μ_n , nuclear magnetic moment	magnetic isotope effect; chemically induced dynamic nuclear polarization; microwave emission (chemical maser)
interaction with microwaves	ω , frequency of microwaves; H_1 , amplitude of microwaves	chemically detected magnetic resonance; stimulated nuclear polarization; microwave-induced magnetic isotope effect
exchange	J , exchange energy	spin catalysis

with the list of magnetic and spin effects produced by magnetic and exchange interactions.

It is clear that the radical pair functions as an electron and nuclear spin-selective chemical intermediary which sorts radicals (as well as any other spin carriers) according to their nuclear spin, magnetic moment, and nuclear spin orientation and directs them into the different reaction products. The most chemically important result of the nuclear spin selection is the magnetic isotope effect, which fractionates magnetic and nonmagnetic isotopes.^{8,9}

The majority of the phenomena listed in Table 1 are induced by magnetic interactions.^{10,11} Contributing almost nothing in chemical energy, these interactions switch over the reaction between spin-allowed and spin-forbidden channels; they control chemical reactivity of spin carriers by manipulations with their spins.¹² Spin catalysis is unique; it is induced by both magnetic and nonmagnetic (exchange) interactions simultaneously. It operates in triads of spin carriers (three radicals in the simplest case); spin conversion in the pair of selected spin carriers (radical pair, for instance) is induced by pairwise exchange interaction between either of the partners of the pair and the third spin carrier; the latter acts as a spin catalyst which transforms nonreactive spin states of the pair into the reactive ones. It is purely physical catalysis which manifests itself in chemical reactions of radicals, ions, carbenes, and high-spin molecules (oxygen, in particular) and strongly affects their reaction rates and competition of reaction channels.¹³

II. Spin Catalysis in Three Spin Systems

As a model for testing three spin dynamics we consider a radical triad (R_1, R_2, R_3) in which one of the radicals, R_3 , is supposed to be a spin catalyst, two others, R_1 and R_2 , are treated as a radical pair born initially in the triplet spin state. The reaction product R_1R_2 is supposed to be generated by recombination of the pair of radicals R_i and R_j in the singlet state, so that the problem is how to find the reaction probability under action of spin catalyst R_3 .

A. Spin Wave Functions and Spin States of Triads

By ignoring for a while Zeeman and Fermi interactions (this approximation is valid for radicals with small hyperfine coupling at the nearly zero magnetic field), the spin Hamiltonian of the triad can be presented by eq 2

$$\mathbf{H} = -J_{12}(1/2 + 2\mathbf{S}_1\mathbf{S}_2) - J_{13}(1/2 + 2\mathbf{S}_1\mathbf{S}_3) - J_{23}(1/2 + 2\mathbf{S}_2\mathbf{S}_3) \quad (2)$$

It contains only exchange interactions; J_{ij} are the pairwise exchange energies for pairs R_i and R_j ($i \neq j$), \mathbf{S}_i and \mathbf{S}_j are spin operators for the unpaired electrons ($i, j = 1, 2, 3$).

Each radical as a one-half spin system may be in two spin states, so that the three-spin triad is characterized by a set of eight spin wave functions (spin states). Exchange interaction splits these eight spin states into two groups: four quartet states Q with total spin $S = 3/2$ and spin projections $S_z = \pm 3/2, \pm 1/2$ and four doublet states D and D' with total spin $S = 1/2$ and spin projections $S_z = \pm 1/2$. They are given below

$$|Q_{+3/2}\rangle = \alpha\alpha\alpha \quad (3a)$$

$$|Q_{+1/2}\rangle = 3^{-1/2}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \quad (3b)$$

$$|Q_{-1/2}\rangle = 3^{-1/2}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta) \quad (3c)$$

$$|Q_{-3/2}\rangle = \beta\beta\beta \quad (3d)$$

$$|D_{+1/2}\rangle = 6^{-1/2}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) \quad (4a)$$

$$|D_{-1/2}\rangle = 6^{-1/2}(\beta\beta\alpha + \beta\alpha\beta - 2\alpha\beta\beta) \quad (4b)$$

$$|D'_{+1/2}\rangle = 2^{-1/2}(\alpha\alpha\beta - \alpha\beta\alpha) \quad (4c)$$

$$|D'_{-1/2}\rangle = 2^{-1/2}(\beta\alpha\alpha - \beta\alpha\beta) \quad (4d)$$

The choice of these wave functions is dictated by the following requirement: they should be eigenfunctions of the total spin simultaneously;¹⁴ other details can be found in any textbook on quantum mechanics.

The energies of spin states can be derived from solution of the Schrodinger equation with spin Hamiltonian (eq 2) and spin functions (eqs 3, 4)

$$E_Q = -(J_{12} + J_{13} + J_{23}) \quad (5)$$

$$E_D = \Omega = 2^{-1/2}[(J_{12} - J_{13})^2 + (J_{12} - J_{23})^2 + (J_{13} - J_{23})^2]^{1/2} \quad (6)$$

$$E_{D'} = -\Omega = -2^{-1/2}[(J_{12} - J_{13})^2 + (J_{12} - J_{23})^2 + (J_{13} - J_{23})^2]^{1/2} \quad (7)$$

The scheme of energy levels and spin transitions in the radical triad is shown in Figure 2.

In the quartet state of the triad, neither geminate recombination $R_1 + R_2$ nor "scavenging" reactions of the partners with catalyst $R_1 + R_3$ and $R_2 + R_3$ occur; they are spin forbidden, so that these triads may disappear only by diffusional or chemical decay, and they are not subjected to spin catalysis. This is because we have agreed to ignore Zeeman and Fermi interactions for a while; later, in section III.C, we will see how to involve these quartet spin states into the spin catalysis as well.

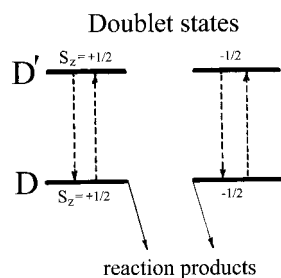


Figure 2. Doublet spin states of the radical triad. D' state corresponds to the triplet (nonreactive) state of selected radical pair (R_1, R_2); in the D state this pair is in a singlet (reactive) state. Dotted lines indicate $D'-D$ spin conversion stimulated by spin catalyst.

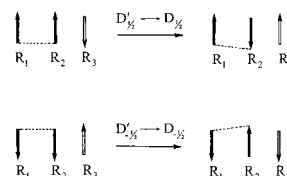


Figure 3. Visual presentation of spins in radical triad (R_1, R_2, R_3). Exchange interaction between catalyst (open arrow) and radical R_2 produces reorientation of their spins and transforms the triplet state of the pair (R_1, R_2) into the singlet state. Black arrows denote spins of the partners of radical pair (R_1, R_2).

Only doublet states D and D' are exposed to spin catalysis; the remarkable feature of this phenomenon is that neither total spin S nor its projection S_z is changed in this process.¹⁵

B. Spin Catalysis: How It Functions

By calculating eigenvalues of the total spin $S_1 + S_2$ for the pair (R_1, R_2) in the triad, it is easy to show that the two doublet states, $D_{\pm 1/2}$, correspond to the singlet state of the radical pair (R_1, R_2); the other pair of doublet states, $D'_{\pm 1/2}$, contains the radical pair (R_1, R_2) in the triplet state. It means that only $D_{\pm 1/2}$ spin states of the triad are chemically reactive; only in these triads the recombination $R_1 + R_2 \rightarrow R_1R_2$ takes place; this recombination is spin forbidden in $D'_{\pm 1/2}$ states. The key role of spin catalyst R_3 is that it transforms nonreactive $D'_{\pm 1/2}$ states of triad into the chemically reactive $D_{\pm 1/2}$ states, as shown in Figure 2.

This spin catalytic process is visualized in Figure 3. Suppose, in the triad (R_1, R_2, R_3), the exchange interaction between one of the partners (R_2 , for instance) of the radical pair and catalyst R_3 is switched on; it results in exchange of spin orientations of R_2 and R_3 (we will see later how it occurs), so that the nonreactive $D'_{+1/2}$ state is converted into the reactive $D_{+1/2}$ state (Figure 3a). Similarly, spin catalyst R_3 mixes $D'_{-1/2}$ and $D_{-1/2}$ states (Figure 3b) and populates the singlet state of the radical pair (R_1, R_2). Neither total spin S nor its projection S_z are changed in this spin catalytic transformation of the triad; however, a selected pair of radicals (R_1, R_2) undergoes triplet-singlet conversion and acquires chemical reactivity. Spin oscillation of the selected radical pair is accompanied by in-phase periodical reorientation of the catalyst spin.

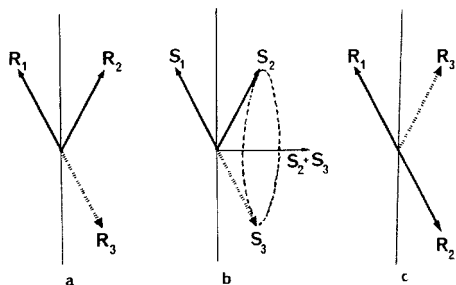


Figure 4. Vector model of spin transformation in triad (R_1, R_2, R_3). Dotted arrow indicates spin of the catalyst (see text).

Now we address the question how catalytic spin reorientation in the triad happens. Figure 4 visualizes this phase of spin catalysis by vector model. Suppose we have a triad (R_1, R_2, R_3) in the $D_{1/2}$ state (Figure 4a) with the pair of radicals (R_1, R_2) in the triplet state (both spins S_1 and S_2 are oriented up, spin S_3 of spin catalyst R_3 is directed down). Assume now that the exchange interaction J_{23} between R_2 and R_3 is switched on; it induces precession of spins S_2 and S_3 around the vector of total spin $S_2 + S_3$ (Figure 4b). After the time interval τ , such as $J_{23}\tau = \pi$, the permutation of spins occurs (Figure 4c) in such a way that the triad is now in the $D_{1/2}$ spin state with the pair of reactive radicals R_1 and R_2 fixed in the singlet state. The change of spin in the pair (R_1, R_2) is compensated by the spin change of catalyst; ultimately, both total spin S and its projection S_z are conserved, but the chemical reactivity of the triad is dramatically changed.

C. Two Mechanisms of Spin Catalysis

Spin catalysis described above is exclusively driven by nonmagnetic, exchange interaction. This conclusion remains valid even if we take into account Zeeman interaction and hyperfine coupling, i.e., instead of spin Hamiltonian (eq 2) we will use extended spin Hamiltonian of the triad

$$\mathbf{H} = \sum_{i=1-3} g_i \beta H + \sum_{i=1,2} a_i m_i - \sum_{i \neq j} J_{ij} S_i S_j \quad (8)$$

where g_i , a_i , and m_i are g -factors, hyperfine coupling constants, and nuclear spin projections and J_{ij} are pairwise exchange potentials between i and j partners.

The inclusion of Zeeman and Fermi interactions only slightly modifies energy levels of all eight spin states, both quartets and doublets; much more important is that these interactions induce additional channels $Q_{\pm 1/2} - D_{\pm 1/2}$ and $Q_{\pm 3/2} - D_{\pm 1/2}$ of spin conversion which are forbidden in the absence of Zeeman and Fermi interactions (these transitions are similar to those between T_0 and S states in an isolated radical pair). Moreover, in low magnetic field the other channels, $Q_{\pm 3/2} - D_{\pm 1/2}$ and $Q_{\pm 3/2} - D_{\pm 1/2}$, operate (they are analogous to $T_+ - S$ transitions in isolated radical pair). Thus, in contrast to spin triads with spinless nuclei, in triads with magnetic nuclei hyperfine coupling induces quartet-doublet transitions and provides additional pumping of both reactive D and nonreactive D' states of the triad. Stimu-

lating $D'-D$ transitions, spin catalysis ultimately enhances the yield of reaction products.

This mechanism of spin evolution in triads with magnetic nuclei is not too important for spin catalysis itself because in any case the spin catalyst mixes only D' and D states and has nothing to do with $Q-D'$ and $Q-D$ transitions. However, spin catalysis in spin triads with magnetic nuclei may enhance nuclear spin selectivity and isotope fractionation in chemical reactions.¹⁶

Another mechanism of spin catalysis proceeds from the contribution of dipolar electron-electron interaction into the spin evolution of the triad. Contrary to exchange interaction, which induces only $D'-D$ transitions, the dipolar interaction, being a magnetic one, does not influence $D'-D$ transitions but stimulates direct $Q-D$ transitions. Such a magnetic relaxation of R_1 and R_2 under the influence of R_3 populates chemically reactive D states, accelerates spin conversion of the triad, and increases the yield of reaction products.

Physical mechanisms of spin catalysis can be summarized as follows. Exchange (nonmagnetic) interaction accelerates transitions between doublet spin states and transforms nonreactive D' states into the reactive D states; total spin is conserved in this process. Dipolar (magnetic) interaction involves into the spin evolution spin-forbidden quartet states and produces $Q-D$ mixing, opening an additional reaction channel; total spin is not conserved in this case.

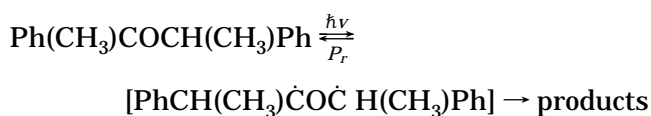
There is a very clear criterion to discriminate these two mechanisms: exchange-induced spin catalysis should depend on the spin of catalysts, dipolar-induced spin catalysis is expected to be a function of the magnetic moment of catalyst. The relative contribution of these mechanisms into the total spin catalytic effect is determined by relaxation time T_1 of spin catalyst and by molecular motions in triad which modulate both exchange and dipolar interactions. Some examples will be given later.

III. Spin Catalysis by Radicals

Many spin carriers can serve as the spin catalysts; they can be added into the reactor as a component of the reagent mixture (stable radicals, paramagnetic ions, oxygen molecules) or can be formed as unstable reaction intermediates (active radicals, carbenes, excited triplet molecules, etc.). Some of them are chemically reactive and function simultaneously as the spin catalysts and reactants, the others (paramagnetic ions, in particular) serve only as the spin catalysts.

A. Radicals as the Spin Catalysts

The first direct experimental demonstration of spin catalysis¹⁷ has been obtained in the photolysis of optically active D,L-diphenylpentanone (DPP) which follows the scheme



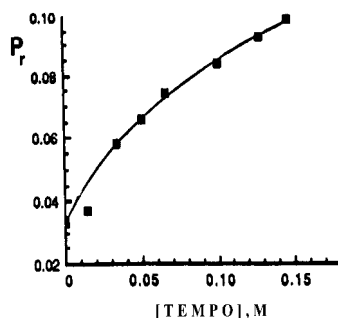


Figure 5. Recombination probability of the triplet radical pair generated by photolysis of DPP in benzene as a function of the concentration of TEMPO, tetramethylpiperidyl-1-oxyl, radical. (Reprinted with permission from ref 17. Copyright 1994 American Chemical Society.)

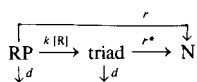
The Norrish α -cleavage of DPP occurs in the triplet state of the molecule and generates a triplet radical pair, which can recombine (after triplet–singlet spin conversion) regenerating the starting molecule or dissociate resulting in free radicals and their products. Geminate recombination of the pair is accompanied by the loss of optical activity of regenerated ketone; it is a result of inversion or rotation of alkyl radical in the pair. By measuring diastereomeric purity of DPP (by separation of both diastereoisomers, *D,L*-DPP and *meso*-DPP) as a function of chemical conversion, the recombination probabilities P_r of the radical pair in benzene at 20 °C were determined.

The real surprise was that in the presence of stable nitroxide radical TEMPO, which is known to be a powerful scavenger of carbon-centered radicals, the recombination probability P_r was shown to increase as the concentration of TEMPO increases (Figure 5).

These results contrast with the observation that the addition of *diamagnetic* scavenger, such as dodecanethiol, decreases P_r ; they unambiguously demonstrate that *paramagnetic scavenger catalyzes radical recombination*. What is even more impressive is that the catalytic effect strongly dominates over the traditional function of nitroxide to be a radical scavenger.

The increase of P_r by nitroxides shown in Figure 5 implies that there are two coexisting pathways of the radical pair spin transformation: a direct pathway, induced by intrapair magnetic interactions, and a catalytic pathway, stimulated by nitroxide radicals. Their contributions to the total recombination probability P_r can be estimated by considering the kinetic scheme shown in Scheme 1.

Scheme 1



It takes into account the direct recombination of the radical pair RP into the product N (*meso*-DPP in the case of *D,L*-DPP) and catalytic recombination, which includes the entering of the nitroxide radical R into the RP with diffusional rate constant k and the following transformation of radical triad into the product N. The scheme provides also for the diffu-

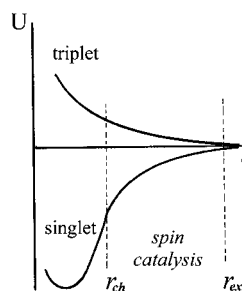


Figure 6. Potential energy profiles $U(r)$ of triplet and singlet states for the chemical bond formation process; spin catalysis operates in the range between r_{ex} and r_{ch} , the distances of exchange and “chemical” interactions.

sional separation of both the radical pair and triad with rate constant d .

By fitting of the experimental data (Figure 5) to the kinetic equation for the P_r , derived from the kinetic scheme, the ratio of the rate constants of catalytic and direct recombination r^*/r was found to be 6.3. It demonstrates that the rate constant of recombination in the radical triad is almost an order of magnitude higher than that in the radical pair. Therefore, nitroxide radical catalyzes spin conversion of the triplet radical pair and stimulates its recombination.

The amazing transformation of the powerful radical scavenger into the radical catalyst is a result of competition between the long-range exchange potential, responsible for the spin exchange, and the short-range potential, resulting chemical bond formation.

Figure 6 visualizes this statement; at the encounter of two radicals the exchange interaction and spin exchange start to operate at the long distance of approach r_{ex} , much longer than the distance of bond formation r_{ch} ; the latter is assumed to occur at the Lennard–Jones contact distance between the encountering partners. In other words, the sufficient overlap of the wave functions, which induces spin exchange, happens far before the two partners have reached the Lennard–Jones contact distance required for the bond formation. The difference between r_{ex} and r_{ch} results in that the cross-section (or the rate constant) if spin exchange exceeds that for the bond formation; the efficiency of the spin exchange (and spin catalysis) depends on the details of passage of the region $r_{ex} - r_{ch}$ by radical partners (residence time, orientational mobility, etc.).

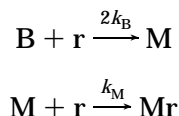
A series of excellent papers recently appeared in favor of this concept. By using the beautiful muon spin relaxation technique, Roduner et al.¹⁸ studied gas-phase spin exchange and reaction kinetics of the muon-substituted ethyl radical $\mu\text{CH}_2\text{CH}_2$ with oxygen. They found that the rate constant of collisions between $\mu\text{CH}_2\text{CH}_2$ and O_2 , measured by muon spin relaxation, is larger by 30–50% than that accurately estimated from the Lennard–Jones collision limit. It is a direct and reliable proof of the relation $r_{ex} > r_{ch}$.

Lawler et al. quantitatively showed by studying liquid-phase reactions of small radicals that the spin exchange occurs faster than the recombination of radicals and that the effective radius of spin exchange, r_{ex} , is several times larger than the reaction radius, r_{ch} .¹⁹ Turro et al. in a series of brilliant papers

on electron spin polarization transfer, studied by time-resolved ESR, came to the conclusion that the rate of spin exchange (and polarization transfer between polarized radical and nitroxide radical) is faster than that of radical recombination.^{20–22} The domination of spin catalytic effect over the spin scavenging is a direct outcome of the long-range character of exchange interaction between the radical partners.

B. Biradicals and Triradicals

The interaction of alkyl radicals with nitroxide biradicals occurs as a two-step reaction

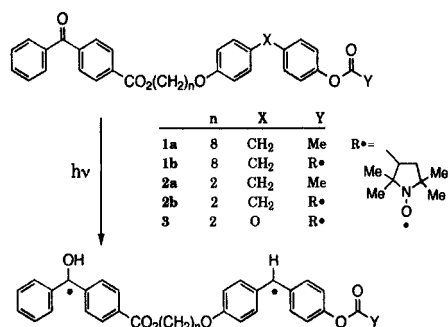


The addition of alkyl radical r to either of the biradical termini transforms biradical B into the monoradical M , which yields further the reaction product by scavenging of the second alkyl radical. By taking into account spin statistical factors, it was rigorously shown that the ratio of the rate constants k_B/k_M should be equal to unity. However, experimentally measured ratios k_B/k_M for different biradicals and alkyl radicals were shown to be in the range 1.1–1.5, i.e., chemical reactivity of nitroxide with respect to alkyl radical depends on the presence of the third spin.²³ For this reason, the first recombination of biradical is faster by 10–50% than the second recombination.

Spin catalytic effect operates only in spin triads in which all partners are coupled by exchange interaction. However, in the biradicals under study, the extended molecular conformations with far distant termini dominate, so that only a small part of biradicals are in coiled conformations, able to generate triads with alkyl radicals. By taking into account the relative populations of extended and coiled conformations and keeping in mind that only the latter exhibit a spin catalytic effect, one can estimate the ratio of the rate constants of catalytic and direct recombinations $r^*/r \approx 10$, which is in agreement with that found for the radical pair generated by photolysis of DPP (see section IV.A).

A beautiful example of spin catalysis by radicals was demonstrated by Hayashi et al.²⁴ By photolysis of ketones (see Chart 1), the chain-linked biradicals

Chart 1



were generated via an intramolecular hydrogen abstraction reaction if $Y = \text{CH}_3$; for the ketones with paramagnetic substituent Y (nitroxide fragment), this reaction generates chain-linked triradicals. As the intramolecular reaction produces a pair of radicals in the triplet state, biradicals 1a and 2a are also in the triplet state, so that in triradicals 1b and 2b only Q and D' states are populated (see section III.A). The decay of triradicals 1b and 2b is expected to be much faster than that of biradicals 1a and 2a since the nitroxide fragment, as a spin catalyst, stimulates $D-D$ transitions in the triad and accelerates intramolecular recombination (cyclization). This prediction is confirmed experimentally: by monitoring of the decay time profiles it was established that the decay rate constants of 1b and 2b are an order of magnitude larger than those of 1a and 2a.

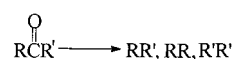
Moreover, the magnetic field dependence of the decay rates of 1b was shown to be similar to that of 1a; this result unambiguously demonstrates that the spin catalytic effect in triradicals is caused mainly by exchange interaction, whereas magnetic interaction between the nitroxide spin and the pair of reactive radicals is not significant. Experimentally observed magnetic field dependence of the time profiles both in biradicals and triradicals should be attributed to the intramolecular magnetic interactions, Zeeman and Fermi, in the pair of chemically active radicals.

Similar arguments may be applied to describe dynamic behavior and magnetic field effects in ion-radical biradicals and triradicals; they were generated by laser-induced electron transfer from triplet 10-methylphenothiazine to electron acceptor linked with diamagnetic or paramagnetic (nitroxide fragments) substituents.²⁵ In the latter case, triradicals are formed in spin states Q and D' . The yield of free ions from triradicals was shown to be lower than that from biradicals; this result is an indication that the nitroxide catalyzes spin conversion $D-D$ in the ion-radical pair and allows back transfer of an electron, partly preventing escape of free ions.

IV. Paramagnetic Ions as the Spin Catalysts

The influence of the paramagnetic metal ions on the chemical reactions has been the subject of many papers; these ions were shown to have an effect on the magnetic field dependence of the reaction rates, on the yield of reaction products, on the lifetime of biradicals, on the decay of radical pairs, etc.^{26,27} As pointed out by Turro,²⁸ no quantitative interpretation of these observations was given. At best, paramagnetic ions were qualitatively treated as the spin relaxators; their effects were not perfectly deliberated.

The most clear and easily interpretable results were presented by Turro et al.²⁶ They studied photolysis of p -methyl-substituted dibenzyl ketone in sodium dodecyl sulfate micelles



where $R = \text{PhCH}_2$ and $R' = p\text{-CH}_3\text{PhCH}_2$. The yield

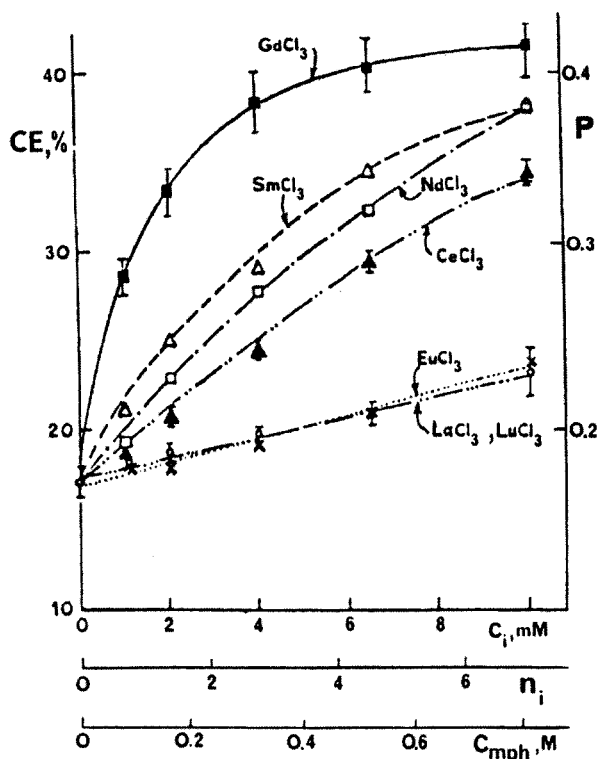


Figure 7. Cage effect, CE, and recombination probability, P , of the triplet pair of benzyl radicals in micelles as a function of concentration of lanthanide ions; C_i is the ion concentration in micellar solution, C_{mph} is that in micellar phase, and n_i is an average number of ions in each micelle. (Reprinted with permission from ref 29. Copyright 1998 Publisher.)

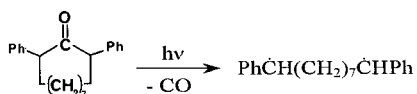
of the cage product RR' , certified as a cage effect, was shown to increase as the concentration of lanthanide ions increases (Figure 7).

The cage effect refers to the recombination in the secondary radical pair (R, R') originating from the primary pair of alkyl and acyl radicals by decarbonylation of the latter.

The recombination probability as a function of the lanthanide ion concentration (Figure 7) is similar to that shown in Figure 5 for the spin catalysis by nitroxide radicals; in principle, the kinetic Scheme 1 is also suitable to describe the effect of the lanthanide ions. The ratios r^*/r of the rate constants of catalytic and direct, noncatalytic recombination are shown in Figure 8 as a function of the spin S_i of the catalyst, lanthanide ion.²⁹

Turro et al. measured the lifetimes of triplet biradicals²⁸ generated by photolysis of 2,10-diphenylcyclododecanone in methanol, see Chart 2.

Chart 2



The biradical lifetime was shown to decrease by addition of lanthanide ions. Bimolecular rate constants for the La^{3+} -induced biradical decay range from 0 to $2 \times 10^8 M^{-1} s^{-1}$; they are also plotted in Figure 8 as a function of the lanthanide spin.

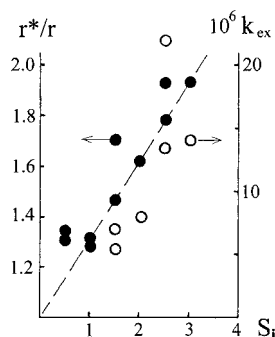


Figure 8. Ratio r^*/r of catalytic and noncatalytic recombination of radical pair ($Ph\dot{C}H_2\dot{C}H_2Ph$) (\bullet) and the rate constant k_{ex} of catalytic recombination of biradical (\circ) as a function of electron spin S_i of catalysts.

Table 2. Efficiency of the Spin Catalysis as a Ratio r^*/r of the Rate Constants of Catalytic and Noncatalytic Radical Recombination

spin catalyst	r^*/r	spin catalyst	r^*/r
Pr^{3+}	1.28	Tb^{3+}	1.93
Tm^{3+}	1.31	Gd^{2+}	4.4
Yb^{3+}	1.31	Co^{2+}	4.4
Ce^{3+}	1.34	Cu^{2+}	4.4
Er^{3+}	1.47	Fe^{2+}	5.3
Ho^{3+}	1.62	Mn^{2+}	5.7
Nd^{3+}	1.71	Ni^{2+}	5.7
Dy^{3+}	1.78	Cr^{3+}	6.2
Sm^{3+}	1.93	nitroxide	6.3

The figure demonstrates the correlation between the efficiency of lanthanide ion as the spin catalyst and its electron spin in recombination of radical pairs and biradicals. This correlation clearly and unambiguously argues in favor of the exchange interaction as the main driving force of spin catalysis. No correlation between the catalytic effect and magnetic moment of catalysts was found; it provides additional support in favor of the first, nonmagnetic mechanism of spin catalysis (see section III.C).

Turro et al. reported the influence of the lanthanide ions on the photoinduced emulsion polymerization of styrene.³⁰ Besides the lanthanide ions, Hayashi et al. also studied transition-metal ions as the spin catalysts in the photolysis of naphthoquinone in micelles.³¹ They monitored the decay of transient optical absorption due to naphthoquinone radical and naphthoquinone anion-radical by time-resolved laser technique; time-resolved ESR has been also used to monitor transient dynamic spin polarization generated in radical pairs of naphthoquinone and alkyl radicals. Transition-metal ions appear to be effective as the spin catalysts at the level of Gd^{3+} , the best catalyst among the lanthanide ions.

Table 2 integrates a collection of spin catalysts according to their efficiency.

Diamagnetic ions (Sc^{3+} , La^{3+} , Zn^{2+}) or ions with zero angular momentum (Eu^{3+}) exhibit no catalytic effect. Lanthanide ions having deep lying and strongly screened unpaired 4f electrons are catalysts of low efficiency; the largest catalytic effect was observed for Gd^{3+} (r^*/r is 4.4, Table 2). Transition-metal ions with unpaired electrons in the less screened 3d layer display catalytic activity which is much higher than

that of the majority of lanthanide ions. It increases in the sequence from Co^{2+} to Cr^{3+} , approaching the highest activity of nitroxide radical with the outer unpaired electron.

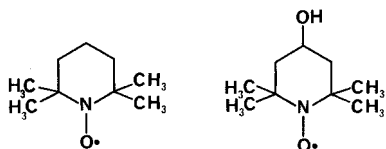
The quantitative hierarchy of spin carriers with respect to their spin catalytic efficiency is in excellent agreement with theory, which predicts that the rate of spin conversion in the radical pair has to be proportional to the exchange energy between the spin catalyst and either of the radical pair partners.¹⁶ This statement undoubtedly implies that the spin carriers with outer unpaired electrons are much more powerful as spin catalysts than those with inner unpaired electrons. However, although the former spin carriers are effective spin catalysts, they are usually also chemically reactive radical scavengers, whereas the latter carriers being rather low efficiency spin catalysts are usually chemically inert. The strategy of spin catalysis is indeed a compromise between these two functions of spin carrier, to be simultaneously spin catalyst and spin scavenger.

At last, it is worthy of mentioning that neither ion radii nor ion magnetic moments relate to the spin catalytic efficiency of paramagnetic ions; this is another piece of strong evidence in favor of exchange interaction as a dominating driving force of spin catalysis.

V. Cis–Trans Isomerization

Cis–trans isomerization of ethylene derivatives is known to be catalyzed by paramagnetic molecules (oxygen, NO, atomic bromine and iodine, etc). McConnell postulated that catalysis occurs in the complex of reactant with paramagnetic catalyst.^{32,33} The direct kinetic and structural evidences in favor of McConnell's idea was presented in catalysis of cis–trans isomerization of dimethylmaleate by stable nitroxide radicals I and II, see Chart 3.

Chart 3



The reaction was shown to be strongly accelerated by these radicals.³⁴ Neither decay of nitroxides nor formation of any byproducts was observed, so this is the case of true paramagnetic catalysis. The reaction rate is a linear function of the catalyst concentration; the rate constants k_d and k_c of direct and catalytic isomerization are expressed by equations

$$k_d = 10^5 \exp(-27\,000/RT), \text{ s}^{-1}$$

$$k_c = 10^{12} \exp(-27\,000/RT), \text{ s}^{-1}$$

The activation energy of the catalytic reaction was shown to coincide with that of direct isomerization; however, the frequency factor of the former appears to be 7 orders of magnitudes larger than that of the

latter. Both these arguments are in favor of “nonenergetic” catalysis, which was kinetically proved to occur in the 1:1 paramagnetic complex of reactant with catalyst.

The existence of these weakly bound complexes was unambiguously demonstrated by studies of paramagnetic shifts and broadening of the NMR lines of dimethylmaleate induced by its complexation with nitroxide radicals.³⁵ By studying the concentration dependence of the paramagnetic shifts for both olefinic and methyl protons of dimethylmaleate, the transfer of spin density of unpaired electron from nitroxide radical to ligand molecule, dimethylmaleate, was detected; it results in hyperfine coupling constants -0.08G and -0.06G for olefinic and methyl protons, respectively. It corresponds to approximately 3×10^{-3} of π -electron spin density transferred to ligand.^{36,37}

Cis–trans isomerization is known to predominantly occur along the adiabatic pathway which requires singlet–triplet transition in the twisted conformation of the molecule (nonadiabatic pathway along the singlet potential energy surface is assumed to take too high an activation energy and its contribution is considered to be negligible). In the direct isomerization reaction the singlet–triplet conversion along the adiabatic pathway is induced by spin–orbital coupling, which is rather weak in carbon molecules and inefficient; this is the reason of the low frequency factor in the rate constant of direct reaction.

Spin catalysis is supposed to manifest itself in a twisted conformation of the molecule. A pair of π -electrons of the double bond and the third, unpaired electron of the spin catalyst in the complex are united in the spin triad, in which singlet–triplet conversion in the twisted double bond takes place. Now the adiabatic pathway becomes spin allowed; it strongly increases the probability of the adiabatic reaction and agrees well with the experimentally observed increasing of the frequency factor by 7 order of magnitudes.

One should keep in mind that on the adiabatic reaction pathway from cis to trans, the system overcomes two spin transitions: singlet–triplet in the entrance channel and triplet–singlet in the exit reaction channel. One can suppose that the spin catalyst accelerates both transitions since the residence time of the paramagnetic three-spin complex in the twisted conformation is comparable with or shorter than the lifetime of the complex, so that the internal rotation around the $\text{C}=\text{C}$ bond occurs almost inertially, in one direction. However, even if it is not the case and both channels, entrance and exit, are reversible and equilibrated in the transition state (which is not necessary to exactly coincide with the twisted conformation), the result of the spin catalysis would be, in principle, the same.

VI. Dynamics of Spin Catalytic Processes

In principle, one can imagine two limiting chemically important spin catalytic situations, static and dynamic.

A. Static Model and Quantum Beats

A static model of spin catalysis implies that the spacial positions of partners in the spin triad are fixed; the pairwise exchange potentials are time independent. As an example of such a static model of spin catalysis, one can consider a photosynthetic reaction center, a molecular device in which all participants are rigidly organized. Photoinduced charge separation generates an ion–radical donor–acceptor pair: triplet–singlet spin evolution in the pair is influenced by exchange interaction with paramagnetic Fe^{3+} ion as the spin catalyst.

If the starting spin state of the pair is triplet (it corresponds to D state of the triad), then the probability to find this pair in the singlet state (it corresponds to D state of the triad) is¹⁶

$$\rho_S(t) = (\Delta J/2\Omega)\sin^2 \Omega t \quad (9)$$

where Ω is defined by eq 6 and ΔJ is the difference of exchange energies between spin catalyst and each of the partners of the radical pair, $\Delta J = |J_{13} - J_{23}|$. Both conjugated processes, triplet–singlet conversion of the pair and doublet–doublet evolution of the triad, oscillate in time with a period $\tau = (2\Omega)^{-1}$ and keep unchanged the total spin S and spin projection S_z . Neither spin conversion of the triad nor spin evolution of the pair are conceivable if $J_{13} = J_{23}$; it implies that there is no driving force of spin catalysis, this is the case when the spin triad is locked. Besides for ΔJ there are no other limits on the distance and geometry requirements for the spin catalysis in triads.

The yield of reaction product generated, for instance, by recombination of the radical pair in triad oscillates with frequency 2Ω . These oscillations (or quantum beats) can be observed in static triads, prepared instantaneously and coherently, i.e., in the certain spin state.³⁸ It can be performed by laser photolysis of ketone spin labeled by nitroxide $\dot{\text{R}}$



or by reactions mentioned in section IV.B.

It is evident that in nonrigid triads molecular motions randomly vary distances between partners and modulate J_{ij} , changing 2Ω , the frequency of quantum beats. Ultimately, they randomly modulate the rate and phase of spin evolution and kill quantum beats and spin coherency.

To detect quantum beats in triads, one needs to generate triads in media with restricted molecular mobility (viscous solutions, glasses, crystals, etc); then the characteristic time τ of the motions in triads would be much less than the time of spin evolution, i.e., $\tau \ll \Omega^{-1}$. Although the quantum beats in triads were not yet experimentally observed, their search has a sense to gain information on the structure and dynamics of spin triads.

B. Dynamic Model

In solutions molecular diffusion randomly varies distances between the partners so that the dynamics

of triad is a combined result of spin, molecular, and chemical dynamics. It is almost an unsolvable problem; however, it can be simplified by taking into account the short-range character of exchange potential J_{ij} . Then the rate constant k of spin conversion in the selected pair can be presented as a product of two values

$$k = k_{\text{enc}} p_{\text{ex}} \quad (10)$$

where k_{enc} is the rate constant of the encounters of spin catalyst with either of the partners of the pair and p_{ex} is the probability of spin changing in the encounter pair. The rate constant k_{enc} can be found, for instance, from the Smoluchowsky equations; the parameter p_{ex} depends on the residence time of spin catalyst in the encounter pair and on the paramagnetic relaxation time of catalyst. Different dynamic situations and the corresponding expressions for the parameter p_{ex} are considered by Molin et al.³⁹ Equation 10 is adequate to describe the kinetics of liquid-phase spin-catalyzed reactions as well as paramagnetic quenching of the electronically excited molecules and positronium atom.

VII. Conclusion

Spin catalysis was proved to operate in radical recombination (termination reaction in chain processes), biradical decay, cis–trans isomerization of molecules, low-temperature recombination of spin-aligned hydrogen atoms (in this case it prevents their Bose condensation),¹³ spin conversion of positronium atom, primary light-harvesting reactions in photosynthetic centers, paramagnetic quenching of excited molecules, etc.

Possibly the extent of the phenomenon may be larger than one can imagine at the level of our current knowledge. Any process of generation of radical or ion–radical pair by catalytic decomposition or by electron transfer may be accompanied by spin catalysis, so that metal ions or metal complexes being chemical catalysts may function as the spin catalysts. It is valid also for the biocatalytic, enzyme processes; at least among those reviewed by Grissom,⁴⁰ which are magnetic field sensitive, there are some examples in which spin catalysis may operate.

As mentioned in the Introduction, the concept of spin catalysis is frequently used in extended treatment when chemical reactivity induced by spin–orbital coupling is also considered as a spin catalytic effect. Indeed, in many reactions, such as oxygenation and carbonylation of hemoglobin, metalloenzyme reactions, methane monooxygenation, charge separation and water oxidation by photosystem II, the C–H bond activation of methane by transition-metal complexes, ethylene activation by Pd and Pt atoms, hydrogen activation by Pt clusters, etc., both effects, electron spin catalysis and spin–orbital coupling, coexist, so that the routes and the rates of chemical reactions are the combined result of these two effects.^{41–45}

As a driving force of spin conversion in triads the exchange interaction competes with magnetic interactions (Zeeman and Fermi) in the pairs of spin

carriers. This competition results in the two effects. (i) Spin catalysts (such as paramagnetic ions) destroy or suppress magnetic effects (magnetic field effect, chemically induced or stimulated nuclear polarization, electron spin polarization, etc). As a rule, in spin-catalyzed reactions magnetic effects are very small; moreover, the higher efficiency of spin catalyst correlates with lower magnetic effects.⁴⁶ (ii) Spin catalysis may depend on the magnetic field. For instance, at low magnetic field the rate of spin evolution may be fast and controlled by strong Fermi interaction; however, in high fields it can be suppressed and retarded; then exchange interaction and spin catalysis become dominating. Both these effects are additional arguments in favor of exchange interaction as a paramount factor of electron spin catalysis.

VIII. Acknowledgments

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