Russian Chemical Reviews **73** (11) 1033 – 1039 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n11ABEH000888

Spin catalysis as a new type of catalysis in chemistry

A L Buchachenko, V L Berdinsky

Contents

I.	Spin catalysis as a new chemical phenomenon	1033
II.	Discovery of spin catalysis	1033
III.	Theory of spin catalysis	1034
IV.	Two mechanisms of spin catalysis	1036
V.	Spin catalysis by radicals and high-spin molecules	1036
VI.	Paramagnetic ions as spin catalysts	1037
VII.	Spin catalysis in reactions with activation barriers	1038
VIII.	Coherent spin catalysis	1038

Abstract. A new phenomenon, spin catalysis, *i.e.*, stimulation of chemical reactions by removing the prohibitions imposed for reasons of electron angular momentum (spin) of reactants is considered. The physical and chemical mechanisms of this phenomenon are discussed. The nature of spin catalysts, the quantitative measure of catalytic effects and the types of chemical reactions susceptible to spin catalysis are considered. The bibliography includes 37 references.

I. Spin catalysis as a new chemical phenomenon

Spin catalysis consists of stimulation of chemical reactions by changing the electron angular momenta (spins) of the reactants. This phenomenon originates from the fundamental law of spin conservation, *viz* ., only those reactions are allowed in which the total spin of the products is identical to the total spin of the reactants; all other reaction channels are strictly forbidden.

The physical sense and role of spin catalysis consist of eliminating the spin forbiddenness, changing the reactant spins and opening reaction channels closed for spin reasons. These functions are performed by a spin catalyst, *viz*., a species with its own electron spin (an atom, radical or ion). When interacting with the reaction system, the catalyst combines its own spin with those of reactants; in such a united spin system, the initially closed reaction channels are opened, *i.e*, spin-allowed.[1,2]

Like other kinds of catalysis, spin catalysis is a purely kinetic phenomenon: a catalyst modifies the reactivities of reactants thus increasing the reaction rate (often, by several orders of magnitude). Spin catalysis manifests itself at two levels: for barrierless reactions, the pre-exponential factor in the rate constant expression (the total cross-section of the reaction) increases, while for reactions with activation barriers the low-barrier channels can be opened and the activation energy can be lowered (together with the increase in the pre-exponential factor in the aforementioned equation).

Many examples of the effect of paramagnetics on the rate and direction of chemical reactions can be cited. The mechanism of these effects remained unclear and often even intriguing (*e.g*., the effect of local activation in paramagnetic polymers) for a long time.[3] It is since the discovery of the spin catalysis phenomenon in the last decade that these effects have been clearly understood.

II. Discovery of spin catalysis

The first reliable and unambiguous proof of the existence of spin catalysis[4] was obtained from studies on photolysis of optically active *d,l*-diphenylpentanone (DPP), the dissociation scheme of which was reliably established.

$$\mathrm{Ph(Me)CH\overset{\overset{\mathrm{O}}{\|}}{C}CH(Me)Ph} \overset{h\nu}{\rightleftharpoons}$$

$$\rightleftharpoons [\mathrm{Ph(Me)\dot{C}H\ \dot{C}OCH(Me)Ph}] \longrightarrow \text{products.}$$

Photodissociation of the ketone occurs in the triplet state, giving rise to a triplet radical pair of acyl and alkyl radicals, which can either recombine (following the triplet – singlet conversion) to yield the original ketone or dissociate to give free radicals which can undergo further transformation to the molecular products (predominantly through decarbonylation of the acyl radical). The inversion of the alkyl radical in the pair results in the loss of optical activity for the regenerated ketone. By separating the optical isomers into *d,l*- and *meso*-DPP and estimating their yields as a function of chemical conversion of the ketone, we can determine with a high accuracy the probability of recombination of the radical pair (P_r).

This method proposed for measuring the cage recombination[5] was used in determination of P_r for DPP decomposition in benzene at 20 °C. Under these conditions, the value of P_r turned out to be very small, *viz.,* only ~ 0.03 (3%). Hence, the spin prohibition for recombination of triplet pairs is strictly fulfilled. (For comparison, it may be mentioned that the probability of cage recombination of similar singlet pairs is 10 – 20 times greater.)

The following fact was quite unexpected: in the presence of such a strong scavenger of carbon-centred radicals as the stable iminoxyl radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl),

A L Buchachenko N N Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 117977 Moscow, Russian Federation. Fax (7-095) 938 24 84. Tel. (7-095) 939 74 90.
E-mail: spinchem@chph.ras.ru
V L Berdinsky Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-095) 576 40 09. Tel. (7-096) 522 27 74.
E-mail: bvl@icp.ac.ru

Received 2 December 2003
Uspekhi Khimii **73** (11) 1123 – 1130 (2004); translated by T Ya Safonova

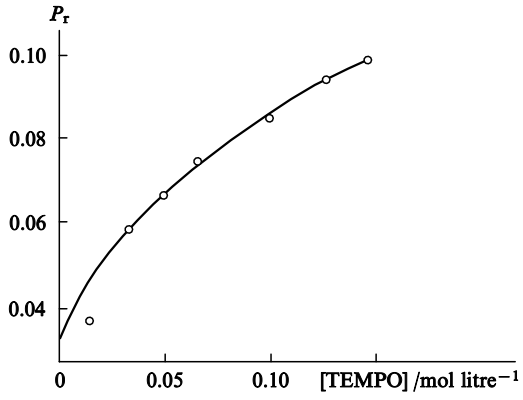
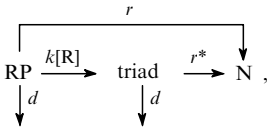


Figure 1. Probability of recombination of a triplet radical pair formed in the DPP photolysis as a function of concentration of TEMPO.[4] Points correspond to experiment, line corresponds to calculations.

the probability of recombination P_r increased with the increase in its concentration (Fig. 1).[4] This result contradicted the fact that in the presence of different strong but diamagnetic scavengers (*e.g.,* dodecanethiol) the P_r value decreased with an increase in the scavenger concentration. It is evident that the paramagnetic nitroxide catalyses the recombination of radicals; moreover, its catalytic function prevails over the traditional function of a potent radical scavenger.

The increase in P_r with an increase in the TEMPO concentration (see Fig. 1) implies that two spin-conversion channels coexist for a radical pair, namely, a direct channel induced by magnetic interactions within the pair (this provides only 3% of recombination) and a catalytic one. The contributions of these channels can be assessed quantitatively by analysing the following kinetic scheme:



which takes into account both direct recombination of the pair to yield the product N (*meso*-DPP in the case of *d,l*-DPP) and catalytic recombination. The latter involves the integration of an iminoxyl radical R into the radical pair RP with the diffusion rate constant k, which is followed by spin conversion to give N. The meanings of constants r, r^* and d in the scheme are evident.

The following expression was derived[6] for such a scheme:

$$P_r = \frac{r}{r + d + k[R]} + \frac{r^*}{r^* + d}\,\frac{k[R]}{d + k[R]}. \qquad (1)$$

The terms in this equation define the contributions to the total probability of recombination made by the two channels, namely, a direct noncatalytic channel (for $[R] = 0$) and a catalytic channel *via* spin triads. The contributions are formed independently; the former channel defines the ratio $r/d = 3.4 \times 10^{-2}$, from which it follows that $r \ll d$. A numerical analysis of the catalytic contribution carried out by a trial-and-error procedure gives a stable solution at $d = 1.8 \times 10^8$ s^{-1}, $r = 6 \times 10^6$ s^{-1} and $r^* = 3.9 \times 10^7$ s^{-1}. For these parameters, the calculated P_r values coincide with those found experimentally (see Fig. 1) for all concentrations of the radical-catalyst.

The ratio for rate constants of catalytic and direct recombination r^*/r is 6.5, *i.e.,* the recombination rate constant for a given radical pair in the radical triad (in the presence of nitroxide as the third partner) is almost an order of magnitude higher than the recombination rate constant of the original (without nitroxide) radical pair. In other words, the third radical strongly catalyses the recombination of this pair, thus accelerating its conversion.

Such a remarkable conversion of a radical scavenger into a catalyst is the result of competition between the long-range potential responsible for spin exchange (and spin conversion) and the short-range potential of chemical bond formation. This effect is illustrated in Fig. 2: at an encounter between two radicals, namely, a catalyst and a partner of the pair, the exchange interaction of their unpaired electrons and spin conversion can begin even at great distances (l_{ex}), much larger than the distance required for the formation of a chemical bond (l_{ch}); the latter is formed at the Lennard-Jones contact of of rendezvous partners. In other words, sufficient overlap of wave functions, which induces the spin exchange, occurs long before the chemical contact of partners. Such a coordinate difference between two processes, namely, the spin exchange and the chemical reaction, is explained by their different energy scales: the exchange interaction frequency sufficient for spin conversion is of the order of magnitude of $10^8 - 10^{10}$ Hz, whereas chemical interaction is significant only at an exchange potential of no less than kT, *i.e.*, several orders of magnitude larger.

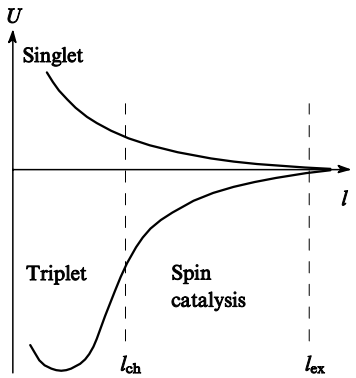


Figure 2. Potential energy (U) of triplet and singlet states of a radical pair as a function of the distance between unpaired electrons that form a chemical bond.

The relationship $l_{ex} > l_{ch}$ means that spin exchange is much more efficient than the reaction and its rate constant exceeds the cross-section of the chemical reaction. The efficiency of spin exchange (and spin catalysis) depends on details characterising the passage of the radical partners through the $l_{ex} - l_{ch}$ region (the time of their residence in this region, orientation dynamics, the extension of their orbitals and their spin delocalisation through solvent molecules).

Experiments on spin relaxation of muon-substituted radicals,[7] the transfer of spin polarisation between radicals[8–10] and other studies[11] directly confirmed the validity of the $l_{ex} > l_{ch}$ relationship. This problem is beyond the scope of this review and is not discussed below. Note that it is this relationship $l_{ex} > l_{ch}$ that is the key to the interpretation of spin catalysis as a chemical phenomenon; that is why organic paramagnetics are much more efficient spin catalysts than the chemical reactants.

III. Theory of spin catalysis

In fact, the theory of spin catalysis is a theory of spin states and spin transitions in multispin systems, namely, spin triads (where the third spin is that of the catalyst), four-spin systems (where the catalyst carries two spins, *e.g.,* an oxygen molecule or a Pr^{3+} ion), *etc.* The comprehensive theory of spin catalysis comprises two parts, namely, a static one, which studies new wave functions and spin states, and a dynamic one, which considers evolution of both the spin states and their population, and also time profiles. Both

parts are essential for the understanding of the physics of this phenomenon, purposeful selection of spin catalysts and prediction of the scope and limitations of catalysis.

1. Three-spin system

The three-spin system is a theoretical model of a radical triad (R^1,R^2,R^3), in which one of radicals (let it be R^3) is a spin catalyst, while the others, *i.e.*, R^1 and R^2, are the components of the reacting system, *e.g.*, a radical pair (note that these two spins can also pertain to any chemical bond which reacts in the presence of a spin catalyst, *e.g.*, to the π-bond of an alkene in its *cis–trans*-isomerisation or a carbene). Let the reacting spin pair (R^1 and R^2) be in the triplet state; the reaction product R^1R^2 is formed by recombination of the (R^1,R^2) pair in the singlet state. Hence, we have to find the probability of formation of R^1R^2 under the action of the spin of the third radical R^3. (Note that the problem is merely inversed if the original reacting spin pair is in the singlet state.)

If we neglect the Zeeman and hyperfine electron–nuclear interactions, the spin Hamiltonian of the triad can be presented as follows:[12]

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

This expression contains only exchange energies J_{ij} for pairs R^i and R^j ($i \neq j$; $i, j = 1, 2\ 3$); S_i and S_j are spin operators of spins i and j. Each spin in a triad has two spin states, so that the total number of states in the triad is eight (2^3). The exchange interaction (the spin-dependent part of the Coulomb interaction) splits these states into two groups: four quartet states Q with the total spin $S = 3/2$ and spin projections $S_z = \pm 3/2, \pm 1/2$ and four doublet states D and D' with the total spin of each state $S = 1/2$ and projections $S_z = \pm 1/2$. The spin functions of all four states are as follows:

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

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

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

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

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

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

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

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

These functions are eigenfunctions of energy and total spin; the energies of spin states are derived from the Schrödinger steady-state equation with the spin-Hamiltonian (2) and functions (3), (4)

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

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

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

Figure 3 illustrates the energy levels and spin transitions in a radical triad. In the quartet states, both the $R^1 + R^2$ recombination and scavenging reactions $R^1 + R^3$, $R^2 + R^3$ are spin-forbidden; these 'quartet' triads can only decompose due to diffusion or disappear due to some ' foreign' chemical reactions.

Of four doublet states in a triad, namely, $D_{\pm 1/2}$ and $D'_{\pm 1/2}$, only two ($D_{\pm 1/2}$) correspond to the singlet state of the reaction pair (R^1,R^2), *i.e.*, the $R^1 + R^2$ recombination occurs only in this state; the $D'_{\pm 1/2}$ state corresponds to the triplet state of the (R^1 , R^2) pair, for which recombination is forbidden. This is the point where spin catalysis is 'switched on', as a result of which the triads pass from non-reactive states D' to chemically active states D. This process is illustrated in Fig. 4. Let the exchange interaction be switched in the (R^1,R^2 ,R^3) triad between one of reacting pair partners, *e.g.*, R^2, and the spin catalyst R^3 . Then, the non-reactive state $D'_{+1/2}$ (corresponding to the triplet state of the reacting pair) is converted into a chemically active state $D_{+1/2}$ in which the (R^1,R^2) pair is a

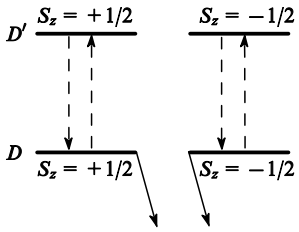


Figure 3. A scheme illustrating the doublet spin states of a radical triad. State D' corresponds to the triplet (chemically inert) state of the radical pair chosen (R^1 ,R^2); state D corresponds to the singlet (chemically active) state of the pair. Dashed lines indicate spin-catalytic $D' - D$ transitions.

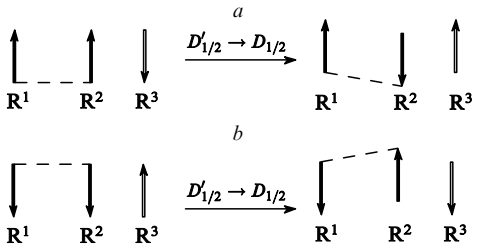


Figure 4. A scheme illustrating $D' - D$ transitions.
Triplet states of the radical pair (R^1,R^2) are transformed into the singlet state upon the interaction with a spin catalyst R^3; (*a*, *b*) are explained in the text.

singlet and hence can undergo recombination (see Fig. 4 *a*). This occurs due to the combining of S_2 and S_3 spins and their exchange (the mechanism of this process is shown below).

A spin catalyst converts $D'_{-1/2}$ into $D_{-1/2}$ by the same mechanism (see Fig. 4 *b*) and populates the chemically active singlet state of the (R^1,R^2) pair. Note that in these spin-catalytic processes neither the total spin S, nor its projection S_z, change. It is only the spin exchange within the triad that occurs in such a way that the chosen pair (R^1 ,R^2) undergoes a triplet–singlet conversion and becomes chemically active.

The spin exchange mechanism between a spin catalyst and an (R^1,R^2) pair partners can be clearly demonstrated in terms of the vector model. Let there be a triad in the $D'_{+1/2}$ state (Fig. 5 *a*), in which the chosen pair (R^1, R^2) is in a non-reactive triplet state (both its spins are oriented upwards, while the catalyst spin is directed downwards). Now, let the exchange interaction J_{23} between the radicals R^2 and R^3 be switched (say, as a result of their approach to one another within the triad). This interaction induces the precession of spins S_2 and S_3 around the total spin vector $S_2 + S_3$ (Fig. 5 *b*). In time τ such that $J_{23\tau} = \pi$, reorientation of S_2 and S_3 spins occurs (Fig. 5 *c*). Now, the triad is in the $D_{+1/2}$ state, *i.e.,* the (R^1 , R^2) pair becomes a singlet and is ready to react: its spins S_1 and S_2 are oppositely oriented, while the catalyst

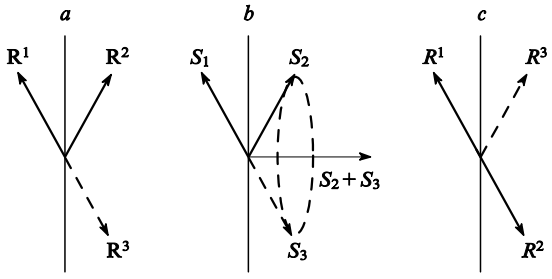


Figure 5. A vector model of spin conversion for a radical pair (R^1,R^2) from triplet to singlet state, induced by a spin catalyst R^3; (*a*, *b*) are explained in the text.

spin is oriented upwards. Moreover, both the triad total spin and spin projections are retained, whereas the chemical activity of the reacting system chosen changes dramatically.

2. Four-spin system

The spin dynamics in a four-spin triad (R^1,R^2,K) formed by a radical pair (R^1,R^2) and a third two-spin partner K, which may represent a biradical, a triplet molecule (*e.g*, O_2), a triplet carbene or a metal ion, resembles in principle the spin dynamics in the three-spin system.

Spin states of a four-spin system (the total number of states $2^4 = 16$) differ in energy, in total spin S and its projection S_z to the z axis and can be divided into three groups, *viz.,* five quintet states with the total momentum $S = 2$, nine states with the total momentum $S = 1$ (triplet states) and two four-spin singlet states ($S = 0$). Being induced by exchange interactions, the spin-catalytic triplet – singlet conversion of the (R^1,R^2) radical pair is only possible for the group of triplet states. The conservation laws for the total spin of the triad and the total spin of the catalyst prohibit the triplet – singlet conversion of the radical pair for triads in quintet and singlet states. The general theory of spin catalysis in the four-spin system was discussed in Ref. 13.

IV. Two mechanisms of spin catalysis

Two mechanisms were proposed for spin catalysis: the first was discussed in detail in the previous section and is realised due to the exchange (nonmagnetic) interaction of electron spins; the second mechanism is purely magnetic and realised due to interaction of spins as the magnetic dipoles.

When discussing the exchange mechanism in the previous section, we ignored the Zeeman and hyperfine interactions by assuming the absence of the magnetic field and magnetic nuclei in reactants. Including the Zeeman and hyperfine interactions does not affect the exchange mechanism. In this case, the energy levels of all eight states are modified only to a small extent, and additional channels of quartet – doublet spin conversion appear. Transitions $Q - D$ and $Q - D'$ forbidden in the absence of hyperfine coupling become partly allowed (like triplet – singlet transitions in isolated radical pairs). They create additional channels for populating the D and D' states of Q quartets. Populating these states increases the efficiency of spin catalysis; moreover, additional nuclear spin selectivity of spin-catalytic reactions and isotope fractionation are observed as side effects.[14] Spin transitions induced by hyperfine coupling can be reliably calculated in terms of spin chemistry (although it should be mentioned that these transitions are not directly related to spin catalysis).

Another mechanism of spin catalysis is purely magnetic and induced by the dipole – dipole interaction of electron spins. In contrast to the exchange mechanism, which stimulates only transitions between D and D' states, the dipole mechanism induces all transitions including $Q - D$ and $Q - D'$; moreover, the total spin and its projections are also changed (recall that both spin and its projections are retained for the case of exchange mechanism).

There is a clear criterion which allows distinguishing these two mechanisms: the exchange-induced spin catalysis is determined by the angular momentum (spin) of the catalyst, whereas the dipole-induced spin catalysis is unambiguously defined by the catalyst magnetic moment. The relative contributions of these mechanisms depend on the time of magnetic relaxation of the catalyst (T_1) and molecular dynamics, which modulates both spin and dipole interactions. Analysing the experimental results, we can see that the exchange mechanism contribution to spin catalysis prevails; the dipole effect is insignificant and operates only in exceptional cases.

V. Spin catalysis by radicals and high-spin molecules

The first clear example that opened up the spin catalysis as a new phenomenon in chemistry was discussed above (see Section III). Later, the spin-catalytic effect of the iminoxyl radical TEMPO in the recombination of a pair of isopropyl and acylisopropyl radicals was studied for photolysis of diisopropyl ketone by the method of chemically induced dynamic nuclear polarisation (CIDNP).[15]

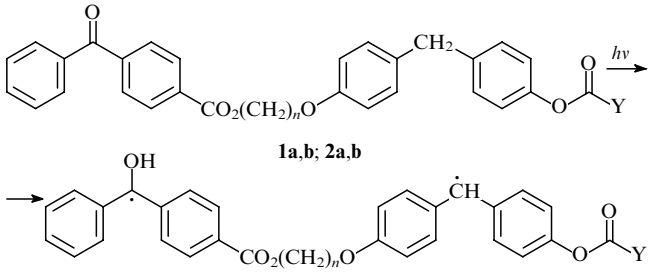
Spin catalysis is also performed by biradicals. Interaction of alkyl radicals R with nitroxide biradicals B proceeds in two steps

$$B + R \xrightarrow{2k_B} M,$$

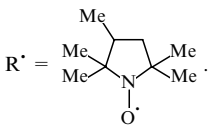
$$M + R \xrightarrow{k_M} MR.$$

The addition of R to any terminus of the biradical transforms it to a monoradical M, which in turn adds to another alkyl radical; the rate constants for these two reactions (k_B and k_M) should be strictly equal, because the radical fragments in the biradicals studied are absolutely identical. However, it turned out that the ratios k_B/k_M reliably measured for different biradicals and various radicals R always exceed unity [16] being equal to 1.1 – 1.5, *i.e*., the addition of the first radical occurs 1.1 – 1.5 times faster as compared with the second radical. It is evident that one of the radical fragments operates as the reactant, while the other operates as the spin catalyst accelerating the reaction of the former fragment. It is also clear that the catalysis proceeds for coiled conformations of flexible-chain biradicals — it is here that chains and nitroxide fragments are closer to one another and can form a spin triad with the reacting radical R. According to rough estimates, the fraction of coiled conformations is $\sim 10\%$; bearing in mind such a population of spin triads, we can assess the ratio of rate constants for catalytic and noncatalytic reactions, *viz*., $r^*/r \approx 2 - 5$ (this agrees with much more precise results shown in Section II).

The same result was obtained by Hayashi *et al*.;[17] with the only difference that all three triad partners were chemically bound within a single molecular system. In the photolysis of ketones, biradicals in the triplet state were generated by an intramolecular reaction of hydrogen abstraction (if Y = Me); for ketones where Y was a paramagnetic substituent (nitroxide fragment), this reaction generated triradicals.



Compound	*n*	Y
1a	8	Me
1b	8	R˙
2a	2	Me
2b	2	R˙



By studying the dynamics of intramolecular cyclisation of bi- and triradicals, it was discovered [17] that cyclisation rate constants in a triradical exceed similar constants for biradicals by an order of magnitude, although both cyclisation reactions are absolutely chemically identical. This is an example of spin catalysis where the third spin (on the nitroxyide fragment) induces the spin conversion of the triplet radical pair involved in cyclisation.

Similar examples of catalysis were observed for electron transfer reactions;[18] triplet radical pairs were found to be generated during photolysis. Their disproportionation (the reverse electron transfer) was dramatically accelerated in the presence of a spin label, *viz.*, a nitroxide fragment chemically attached to the radical-ion pair. In this case (as in the previous one), nitroxide was not involved in the reaction at all and served only as the spin catalyst inducing the triplet–singlet conversion of the reacting radical ion pair.

The function of the spin catalyst can be performed not only by bi- and polyradicals, but also by different high-spin molecules, *e.g.*, O_2. Thus catalytic effects of iminoxyl radicals and oxygen were observed in the reactions of 7-silanorbornadiene and dimethylsilane (carbene).[19—21]

VI. Paramagnetic ions as spin catalysts

Like iminoxyl radicals, paramagnetic ions can also catalyse barrierless reactions of radical recombination. An analysis of the spin-catalytic functions of ions was performed on the example of recombination of a triplet radical pair built of two benzyl radicals one of which is *para*-substituted in the phenyl ring; non-symmetrical dibenzyl represented the recombination product.[22] Figure 6 shows the dependence of its yield (the cage effect or recombination probability) on the lanthanide ion concentration in the micellar solution. This dependence is the same as for radicals (see Fig. 1); moreover, the spin-catalytic effect of ions is adequately described by Eqn (1). Figure 7 shows the rate constant ratio of catalytic and noncatalytic recombination r^*/r as a function of spin S_i; a clear correlation between the spin catalyst efficiency and its electron spin can be traced, which unambiguously suggests that the catalysis is governed by the exchange interaction between the radical pair and a paramagnetic ion. No correlation with the magnetic moments of ions was revealed, which additionally confirms the dominating role of the exchange mechanism in the catalysis.[23]

Figure 7 also shows the rate constant for cyclisation of a triplet biradical obtained by photodissociation of 2,10-diphenylcyclododecanone[24] as a function of the catalyst (lanthanide ion)

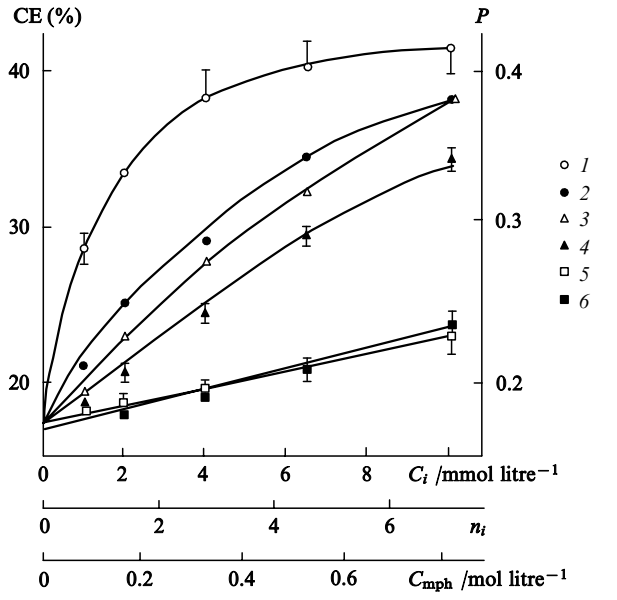


Figure 6. Dependences of the cage effect (CE) and the probability of recombination P for a triplet pair of benzyl radicals in micelles on the concentration of lanthanide ions. C_i is the concentration of ions in the micellar solution, C_{mph} is their concentration in the micellar phase; n_i is the average number of ions in each micelle; (*1*) $GdCl_2$, (*2*) $SmCl_3$, (*3*) $NdCl_3$, (*4*) $EuCl_3$, (*5*) $LaCl_3$, (*6*) $LuCl_3$.

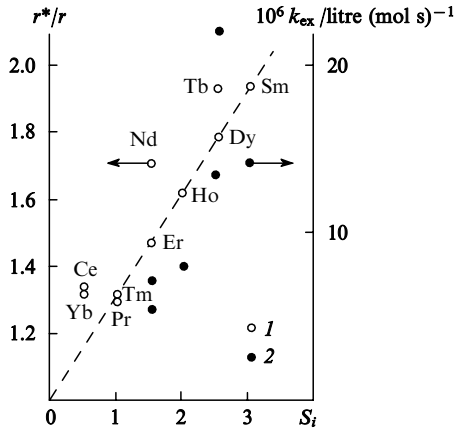


Figure 7. Dependences of (*1*) the rate constant ratio of catalytic and noncatalytic recombination of a radical pair ($PrCH_2$ CH_2Ph) and (*2*) the rate constant of catalytic recombination of the biradical on the catalyst electron spin (S_i).

spin. This dependence is also linear, which confirms the dominating contribution of the exchange mechanism of spin catalysis.

In addition to lanthanide ions, transition metal ions were also studied as spin catalysts of recombination of triplet pairs formed upon photolysis of naphthoquinones;[25] these ions proved to be potent catalysts, *viz.*, at the same level with Gd^{3+}, the best catalyst among lanthanides.

Table 1 shows the data on the efficiency of spin catalysts studied, which is represented as the ratio of rate constants for catalytic and noncatalytic recombination of radicals.

Table 1. Efficiency of spin catalysts.

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

Diamagnetic ions (Sc^{3+}, La^{3+}, Zn^{2+}) or ions with zero angular momenta (Eu^{3+}) exhibit no catalytic effects. Lanthanide ions with unpaired electrons located in deep 4f electron shells and hence strongly shielded by upper electron layers are catalysts of low efficiency; the strongest catalyst is Gd^{3+} ($r^*/r = 4.4$). Note, by the way, that the latter ion drops out of the dependence shown in Fig. 7, its efficiency being higher than that predicted by the exchange mechanism. Probably, this is precisely that extraordinary case where the dipole-magnetic mechanism of spin catalysis operates together with the exchange mechanism.

Ions of transition metals with unpaired electrons in less shielded 3d electron shells display a catalytic activity substantially higher than that of lanthanide ions. Their activity increases systematically in the series from Co^{2+} to Cr^{3+} and approaches the highest value corresponding to the iminoxyl radical with an unpaired electron in the outer shell.

The quantitative hierarchy of spin catalysts with respect to their spin-catalytic activity agrees with a theory that predicts that the rate of spin conversion in a triad should be proportional to the exchange interaction energy of the catalyst with any partner of the

radical pair. Hence, it unambiguously follows that spin carriers with 'outer' unpaired electrons (radicals, oxygen) are much more potent spin catalysts than those spin carriers whose unpaired electrons are 'hidden' within the electron shell. However, being potent catalysts, the former function also as reactants (radical scavengers), whereas the latter are weak catalysts and as a rule chemically inactive, which is their practical advantage. In essence, the strategy of spin catalysis is to find a compromise between these two functions of spin catalysts, *viz*., to serve as a catalyst or a chemical reactant. This is not difficult to achieve by selecting suitable radicals or ions and varying their concentrations. Note that neither ionic radii nor the magnetic moments of ions are related to the catalytic activity. The absence of these dependences indicates that the exchange mechanism is the main driving force of spin catalysis.

VII. Spin catalysis in reactions with activation barriers

To this end, we analysed the spin catalysis in barrierless and low-barrier reactions such as recombination of radicals and disproportionation of radical ions. In reaction with activation barriers, spin catalysts not only increases the total reaction cross-section but also opens new earlier forbidden reaction channels.

A vivid example illustrating this idea is the spin catalysis of *cis*–*trans*-isomerisation of alkene derivatives. Rotation of one part of the molecule with respect to another by the angle π around the double bond occurs through a singlet channel but requires surmounting a high energy barrier ($\sim 50-60$ kcal mol^{-1}). The top of this barrier corresponds to the rotation angle $\pi/2$ where the parts of a molecule undergoing isomerisation are orthogonal to one another. However, there is another reaction trajectory along the reaction coordinate (the rotation angle φ) on the potential-energy surface of the triplet state of the molecule. At angles $\varphi = 0$, π, this surface lies well above the ground state energy; however, at $\varphi = \pi/2$ it has minima and lies well below the top of the singlet channel barrier. The overlap of singlet and triplet channels occurs at angles $\varphi \approx 40-50^\circ$ and $130-140^\circ$.

Kinetics of liquid-phase *cis*–*trans*-isomerisation of dimethyl maleate to dimethyl fumarate was studied.[26] Direct isomerisation proceeds slowly with a rate constant

$$k_d = 10^5 \exp\left(-\frac{27\,000}{RT}\right).$$

In the presence of stable iminoxyl radicals, isomerisation sharply accelerates, which is accompanied by neither their scavenging nor the formation of side products; moreover, the isomerisation rate is proportional to the concentration of iminoxyl radicals. For the unit concentration of iminoxyl (1 mol litre^{-1}), the rate constant of catalytic isomerisation is as follows:

$$k_c = 10^{12} \exp\left(-\frac{27\,000}{RT}\right).$$

A comparison of k_d and k_s constants provides grounds for the unambiguous explanation of these results. First, the identity of activation energies and their low values indicate that both the catalytic and noncatalytic reactions cross the coordinate $\varphi = \pi/2$ through the triplet channel; the spin-allowed singlet channel is too high to be surmounted for energy reasons.

Second, the small pre-exponential factor in the rate constant expression of the noncatalytic reaction suggests that the triplet channel of direct reaction is spin-forbidden. This prohibition is removed only partly due to the spin–orbit coupling along the reaction coordinate. Then, the spin changeover with the transition from the singlet channel to the triplet one at angles $\varphi\,40-50^\circ$ and $130-140^\circ$ is compensated for by the changes in the orbital angular momentum. However, in molecules containing carbon atoms, the spin–orbit coupling is very weak; hence, the triplet channel remains virtually closed.

In the catalytic reaction, a spin catalyst removes the spin-prohibition and opens the triplet channel of isomerisation; the latter becomes allowed so that for the unit concentration of the catalyst the pre-exponential factor in the expression for the catalytic reaction rate constant increases by seven orders of magnitude as compared with the similar factor for the non-catalytic reaction. The three-spin system susceptible to spin catalysis is formed by the catalyst spin and two electron spins of the double bond, which are weakly coupled in the coiled conformation and resemble the spin of a radical pair. The exchange interaction of the catalyst with this spin pair affords their triplet–singlet conversion by switching the reaction from the high-energy singlet channel to the low-energy triplet one.

Evidence for the spin catalyst interaction with the double bond by the exchange mechanism was obtained by analysing the paramagnetic shifts and paramagnetic broadening of NMR lines for dimethyl maleate in the presence of iminoxyl radicals.[27] It was reliably established that dimethyl maleate forms weakly bound complexes with nitroxide (the binding energy of $1-2$ kcal mol^{-1}), in which the spin density is transferred from the radical to the ligand (dimethyl maleate).[28,29] It is in this complex that the three-spin system is formed and the spin-catalytic event occurs.

Numerous examples of catalysing the *cis*–*trans*-isomerisation of alkenes by atoms and paramagnetic molecules (Br, I, NO, O_2, *etc*.) are known. McConnel referred to this phenomenon as 'paramagnetic catalysis',[30,31] although its physical sense had not yet been fully understood. Particularly, for Br and I atoms it had been assumed that the catalysis is realised due to spin–orbit coupling in their complexes with alkenes. The internal spin–orbit coupling in these atoms is substantial, whereas the intermolecular interaction should be weak and incapable of sustaining the efficient spin conversion of the alkene double bond, which always seemed puzzling. Now, however, it is clear that paramagnetic catalysis is, in fact, purely by spin catalysis in which the electron spin plays the key role.

Spin catalysis as a phenomenon may prove to be much more common than it seems at present. Charge separation and water oxidation during photolysis, C–H bond activation in CH_4 by metal complexes, ethylene activation by atoms and clusters, dissociative adsorption on metals, the performance of peroxidases, catalases and other metal enzymes — in many complex reactions involving spin carriers the role of spin catalysis in selecting the reaction pathways can turn out to be significant. This cannot be claimed for all cases, but the possibility of this should never be ignored.[6,32–36]

VIII. Coherent spin catalysis

The triad spin state D' corresponds to the non-reactive triplet state of a radical pair chosen (see Section III). The probability of spin conversion of D' to D in which this pair is in the chemically active singlet state is determined by the solution of a nonstationary Schrödinger equation. This solution is as follows:

$$\rho_{ss}(t) = \left(\frac{\Delta J}{\omega}\right)^2 \sin^2\left(\frac{\omega t}{2}\right). \tag{8}$$

Here, $c_{ss}(t)$ is the probability that the pair is in the singlet state, ΔJ is the difference in exchange energies of the spin catalyst and each partner of the radical pair

$$\Delta J = |J_{13} - J_{23}|; \tag{9}$$

ω is energy splitting of the doublet states D' and D, which is determined by equations (6) and (7)

$$\omega = 2[(J_{12}-J_{13})^2 + (J_{12}-J_{23})^2 + (J_{13}-J_{23})^2]^{1/2}. \tag{10}$$

It follows from equation (8) that both conjugated processes, *viz*., the doublet–doublet evolution of the triad and the triplet–

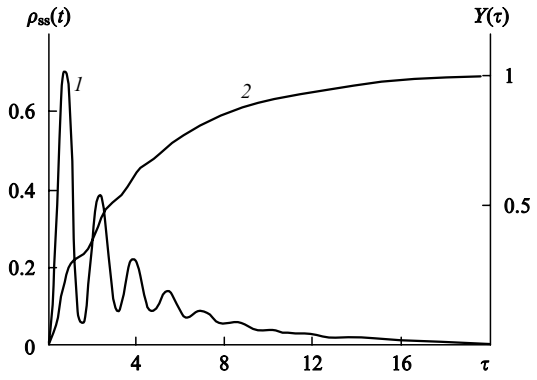


Figure 8. (*1*) Oscillating probability $\rho_{ss}(t)$ of the occurrence of (R^1,R^2) pair in the singlet state during its interaction with a spin catalyst R^3 and (*2*) the kinetics of accumulation of the recombination product.[37]

singlet conversion in the chosen pair of this triad, oscillate in time with a period $\mathbf{t} = \omega^{-1}$ (Fig. 8). In this case, both the total spin and its projection are retained.

The yield of reaction products (*e.g.*, as a result of recombination in ensembles of selected pairs) also oscillates in time with a frequency ω (Fig. 8). These oscillations (or quantum beats) can be observed in static triads with fixed distances between the partners, if the ensemble of these triads has been formed instantaneously and coherently, *i.e.*, in a fixed spin state and with the same phase. In such ensembles (or coherent wave packets), one can realise and observe the coherent spin catalysis with oscillating generation of the reaction product.[37]

A photosynthesis centre, *i.e.*, a molecular arrangement in which all the partners of a spin triad are rigidly organised, can serve as an example of a static triad. The photoinduced charge separation gives rise to a radical-ion pair, in which spin evolution is defined by the exchange interaction with Fe^{3+} ions as spin catalysts.

In non-rigid triads, the molecular motion induces random and incident changes in the distances between partners and modulates the exchange interaction, thus varying the frequencies of quantum beats. Ultimately, this motion modulates the phases and rates of spin evolution, upsetting coherency and suppressing quantum beats. The coherent spin catalysis has not yet been observed experimentally; however, it would be worthwhile to pursue its research in order to understand the structure and dynamics of spin triads.

* * *

Spin catalysis is the universal phenomenon typical of multispin molecular systems. This is observed in chemical reactions (both barrierless and with activation barriers), biological systems (primary light-accumulating reactions in photosynthesis centres, redox enzymes), in physical phenomena (the recombination of spin-oriented hydrogen atoms, which prevents their Bose-condensation, the spin conversion of positronium, the paramagnetic quenching of excited molecules). Scientists are often even unaware of its existence, although its abundance is much wider than seems at present. Any process of generation of radical or radical-ion pairs during catalytic or thermal decomposition or electron transfer can be accompanied by spin catalysis, so that such chemical catalysts as metal ions or metal complexes (especially, bi- and polynuclear) can also operate as spin catalysts. Such a coexistence of spin and chemical catalysis is also true for biocatalytic processes. Spin catalysis can also occur in heterogeneous processes such as hydrogenation, isomerisation, oxidation on zeolites, metals, oxides, *etc*.

The review was written with a financial support of the Russian Foundation of Basic Research (Project No. 02-03-32753), Program 'Integration', Federal Program 'Leading Scientific Schools of Russia' (Project NSh-1221.2003.03) and programs of the Division of Chemistry and Materials Science and the Presidium of the Russian Academy of Sciences.

References

1. A L Buchachenko, V L Berdinsky *Chem. Rev.* **102** 603 (2002)
2. A L Buchachenko *Pure Appl. Chem.* **72** 2243 (2000)
3. A A Berlin, S I Bass *Izv. Akad. Nauk SSSR, Ser. Khim.* 1492 (1962) [a]
4. E N Step, A L Buchachenko, N J Turro *J. Am. Chem. Soc.* **116** 5462 (1994)
5. V F Tarasov, N D Ghatlia, A L Buchachenko, N J Turro *J. Am. Chem. Soc.* **116** 228 (1994)
6. A L Buchachenko, V L Berdinsky *J. Phys. Chem.* **100** 18292 (1996)
7. H Dilger, M Schwager, P Tregenna-Piggott, E Roduner, I Reid, D Arseneau, J Pan, M Senba, M Shelley, D Flemming *J. Phys. Chem.* **100** 6561 (1996)
8. N J Turro, I V Khudyakov, D W Dwyer *J. Phys. Chem.* **97** 10530 (1993)
9. N J Turro, I V Khudyakov *Res. Chem. Intermed.* **25** 505 (1999)
10. N J Turro, I V Khudyakov *J. Phys. Chem.* **99** 7654 (1995)
11. D M Bartels, A D Trifunac, R G Lawler *Chem. Phys. Lett.* **152** 109 (1988)
12. A L Buchachenko, V L Berdinsky *Chem. Phys. Lett.* **242** 43 (1995)
13. V L Berdinsky, A L Buchachenko *Kinet. Katal.* **37** 659 (1996) [b]
14. A L Buchachenko, V L Berdinsky *Chem. Phys. Lett.* **298** 279 (1998)
15. I M Magin, V S Shevel'kov, A A Obynochny, A I Kruppa, T V Leshina *Chem. Phys. Lett.* **357** 351 (2002)
16. A L Buchachenko, L V Ruban, E N Step, N J Turro *Chem. Phys. Lett.* **233** 315 (1995)
17. Y Mori, Y Sakaguchi, H Hayashi *Chem. Phys. Lett.* **301** 365 (1999)
18. Y Mori, Y Sakaguchi, H Hayashi *J. Phys. Chem. A* **104** 4896 (2000)
19. M Taraban, O Volkova, A Kruppa, V Plusnin, V Grivin, Yu Ivanov, T Leshina, M Egorov, O Nefedov *J. Organomet. Chem.* **566** 73 (1998)
20. M Taraban, A Kruppa, O Volkova, I Ovcharenko, R Musin, T Leshina, E Korolenko, K Kitahara *J. Phys. Chem. A* **104** 1811 (2000)
21. O Volkova, M Taraban, V Plusnin, T Leshina, M Egorov, O Nefedov *J. Phys. Chem. A* **107** 4001 (2003)
22. N J Turro, X Lei, I K Gould, M B Zimmt *Chem. Phys. Lett.* **120** 397 (1985)
23. V L Berdinskii, A L Buchachenko N J Turro *Kinet. Katal.* **39** 325 (1998) [b]
24. J Wang, K Welsh, K Waterman, P Fehler, C Doubleday, N J Turro *J. Phys. Chem.* **92** 3730 (1988)
25. Y Sakaguchi, H Hayashi *Chem. Phys. Lett.* **106** 420 (1984)
26. A L Buchachenko, L V Ruban, E G Rozantsev *Kinet. Katal.* **9** 915 (1968) [b]
27. N A Sysoeva, A V Karmilov, A L Buchachenko *Chem. Phys.* **7** 123 (1975)
28. N A Sysoeva, A V Karmilov, A L Buchachenko *Chem. Phys.* **15** 313 (1976)
29. N A Sysoeva, A V Karmilov, A L Buchachenko *Chem. Phys.* **15** 321 (1976)
30. H McConnell *J. Chem. Phys.* **20** 1043 (1952)
31. H McConnell *J. Chem. Phys.* **23** 2440 (1955)
32. B Minaev, H Agren *Coll. Czech. Chem. Commun.* **60** 339 (1995)
33. H Agren, O Vahtras, B Minaev *Adv. Quantum Chem.* **27** 71 (1999)
34. H Agren, B Minaev *Int. J. Quantum Chem.* **72** 581 (1999)
35. B Minaev, H Agren *J. Mol. Catal. A: Chem.* **149** 179 (1999)
36. P E M Siegbahn *J. Am. Chem. Soc.* **118** 1487 (1996)
37. A L Buchachenko, V L Berdinsky *Izv. Akad. Nauk, Ser. Khim.* 1646 (1995) [a]

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*