Russian Chemical Reviews **64** (9) 809–816 (1995)
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UDC 541.139

The nuclear-spin selectivity of chemical reactions

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Abstract. The ability of spin-selective chemical reactions to sort nuclei in terms of two features — their spin and orientation — is discussed. The subdivision into spin (magnetic) and spin-free (nonmagnetic) nuclei constitutes the basis of the magnetic isotope effect; the subdivision of nuclei in terms of orientations and the establishment of the nuclear orientation constitute the content of a second phenomenon — chemically induced [dynamic] nuclear polarisation. The bibliography includes 50 references.

I. Introduction

Chemical reactions are selective as to the electron shells of the reacting species and this factor is the principal feature of a chemical process, namely it determines what is referred to as the reactivity. The second feature of a chemical reaction is its selectivity with respect to nuclei — with respect to their mass and angular momentum (spin). The nuclear mass selectivity of chemical reactions has long been widely known as the classical isotope effect — thermodynamic (in equilibrium processes) or kinetic (in nonequilibrium reactions). The nuclear spin selectivity is manifested by the dependence of the reaction rates on the spin, the magnetic moment, and the orientation of the nuclei of the reacting species. The selectivity of the reaction with respect to the nuclear magnetic moment has been called the magnetic (or nuclear spin) isotope effect. The selectivity with respect to nuclear orientation is the cause of the sorting of nuclei with respect to their orientations, which gives rise to magnetic nuclear polarisation in the products of chemical reactions.

Chemical reactions are selective with respect to the electron spin: they are allowed to give rise only to products the overall electron spin of which is identical with the overall spin of the reactants. Reactions are forbidden if the overall spin of the reactants does not correspond to the spin of the products. Thus, among the four spin states of a radical pair (a singlet and three triplets), only the singlet state is capable of reacting to form the standard (in the singlet spin state) molecule; the reaction involving the triplet states of the pair is forbidden. On the other hand, if the reaction product is a molecule in the triplet spin state [for example in the neutralisation of radical-ions: $M^{+\cdot} + M^{-\cdot} \Rightarrow {}^{1,3}(M^{+\cdot}M^{-\cdot}) \Rightarrow M + {}^{3}M$ with formation of the triplet molecule ^{3}M], then the singlet state of the pair $^1(M^{+\cdot}M^{-\cdot})$ is forbidden for the reaction, but the remaining three triplet states $^3(M^{+\cdot}M^{-\cdot})$ are allowed. The reaction $H + O_2 \Rightarrow HO_2$ takes place only with the doublet states of the pair $(H...O_2)$, preceding the chemical interaction. The reaction involving a quartet state of this pair (with the overall spin $S = \frac{3}{2}$) is forbidden, since the reaction product, the radical HO_2, has a spin of $\frac{1}{2}$ and is in a doublet state. The reactions in which both the reactants and the products have a zero spin (molecular and ionic reactions, electrophilic and nucleophilic substitution reactions, etc.) do not require a change of spin and are therefore allowed.

The spin-forbidden reactions are usually encountered among chemical, physical, and biochemical processes involving paramagnetic species (radicals, carbenes, triplet molecules, electrons, holes), in which the spins of the reactants can combine freely but by no means all of the possible combinations are capable of chemical reaction (for example, for a pair of spins, out of the four combinations only one can lead to the combination of the spin-carrying radicals into a diamagnetic molecule).

The spin-reactive intermediate precursors can be altered and the spin-forbidden unreactive spin states can be transformed into spin-allowed reactive states by means of three types of interactions (Fig. 1):

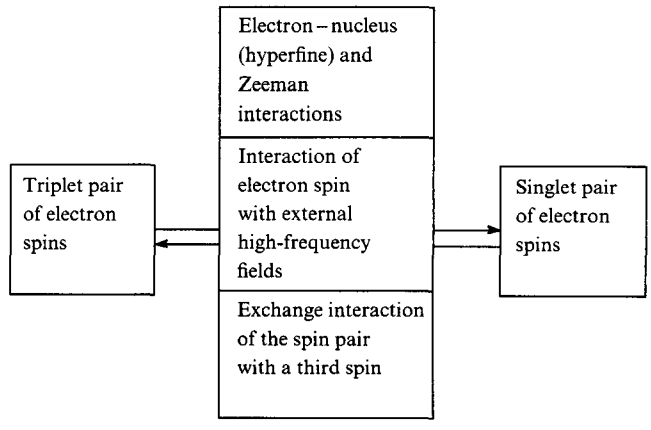


Figure 1. Schematic representation of the interactions inducing the spin conversion of spin pairs.

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Received 14 February 1995
Uspekhi Khimii **64** (9)863–871 (1995); translated by A K Grzybowski

— magnetic interactions of the electron spin with the nucleus and an external magnetic field (hyperfine and Zeeman interactions);
— interaction of the electron spin with the magnetic component of a high-frequency external field;
— exchange interaction of the electron spins with a third spin, which induces the spin triplet–singlet conversion of this pair.

They all have negligible energies, switch the reaction from spin-forbidden paths to open spin-allowed paths, and thus alter the chemical reactivity of the intermediates.

Three types of interactions, controlled by the electron spin, give rise to three generations of magnetic-spin effects. The first includes the magnetic field effect, the magnetic isotope effect, and chemically induced [dynamic] nuclear polarisation. The second generation includes the phenomenon of the chemical detection of magnetic resonance, the radio-induced magnetic isotope effect, and stimulated nuclear polarisation.

The exchange interaction of two spins with a third is not magnetic but it alters the spin of the pair. This phenomenon can be regarded as the catalytic effect of the third spin, inducing spin conversion in the first pair (spin catalysis) and it should be assigned to the third generation of spin effects.

The set of effects generated by the characteristics of the behaviour of the spins of electrons and nuclei in chemical processes is the subject of spin chemistry, to the establishment and development of which Frankevich, Sokolik, Giatsintov, Molin, Sagdeev, Salikhov, Bargon, Fisher, Ward, Kaptein, Lawler, Atkins, Turro, Closs, Step, Tarasov, Berdinskii, Anisimov, etc. have made major contributions. The principal results obtained in this field have been surveyed in a series of reviews and monographs.[1–5]

Being selective with respect to the electron spin, a chemical interaction is inevitably selective also with respect to the nuclear spin, provided that both spin subsystems — electron and nuclear — are linked by the hyperfine or Fermi interaction. The nuclear spin subsystem then acts on the electron subsystem via a hyperfine interaction (HFI), altering the electron spin and removing the spin prohibition. Since the HFI is a property of magnetic nuclei, it selects the isotopic nuclei in terms of the magnetic moment and ensures the sorting of the magnetic and nonmagnetic nuclei (the magnetic isotope effect). Furthermore, the energy of the HFI depends on the orientation of the nuclei, so that the HFI also effects the sorting of the nuclei with respect to their orientations, giving rise to nuclear polarisation in the reaction products. These two effects are the subject of the part of spin chemistry in which the nuclear spin selectivity of chemical reactions is investigated and to which this review is devoted.

II. Sorting of isotopic nuclei

The magnetic isotope effect (MIE) was discovered by two groups of investigators in Russia in 1976,[6,7] although the possibility of its existence had been mentioned by Lawler and Evans in 1971.[8]

The sorting of the magnetic and nonmagnetic nuclei effected by the MIE is clearly illustrated by the photolysis of dibenzyl ketone, in which the molecule undergoes fragmentation in the excited triplet state into a pair of radicals — benzyl and phenylacyl. Being in the triplet state, this radical pair can recombine again, regenerating the initial molecule, or can dissociate and can generate, via the decarbonylation of the phenylacyl radical, the final photolysis products — bibenzyl and carbon monoxide. However, the recombination of the pair is possible only starting with the singlet state, which means that it must be preceded by the triplet–singlet spin conversion of the pair. The hyperfine interaction of the unpaired electron with the ^{13}C nucleus in phenylacyl accelerates the triplet–singlet conversion of the pairs with magnetic ^{13}C nuclei and stimulates their recombination, since radical pairs with nonmagnetic ^{12}C nuclei lag in their spin conversion and undergo preferential dissociation. As a result, the regenerated ketone molecules accumulate the ^{13}C nuclei, while the photolysis products — bibenzyl and CO — are depleted in this isotope. Hence, as a result of the spin selectivity and the hyperfine interaction, the radical pair sorts the nuclei in accordance with their magnetic characteristics, directing the magnetic and nonmagnetic nuclei along different reaction paths, i.e. into different chemical products.

The degree of sorting, i.e. the degree of isotope enrichment of each ketone in the ^{13}C nuclei is defined by the simple equations[9,10]

$$S = (1-F)^{\alpha}\ ; \qquad \alpha = \frac{1-\alpha_G}{\alpha_G}\ ; \qquad \alpha_G = \frac{1-P}{1-P^*}\ . \tag{1}$$

Here S is the isotope enrichment [$S = \delta/\delta_0$, where δ_0 and δ are the contents of the isotope (for example, ^{13}C) in the initial ketone and in its residue] after the attainment of the chemical conversion $1-F$ (F is the fraction of the remaining ketone), α is the coefficient of the single-stage isotope enrichment, and P^* and P are the probabilities of the recombination of the radical pairs with the ^{13}C and ^{12}C isotopes, i.e. the probabilities of the regeneration of the 'magnetic' and 'nonmagnetic' ketones respectively. Evidently, α_G is the ratio of the rates of the chemical decomposition of the nonmagnetic and magnetic ketones. Since $P^* < P$, it follows that $\alpha_G > 1$, i.e. the magnetic ketone decomposes more slowly and is retained during photolysis to a greater extent than the nonmagnetic ketone.

The ideal isotope separation takes place subject to the condition $P^* = 1$ and $P = 0$, which means that the magnetic ketone is fully regenerated, whilst the nonmagnetic ketone is fully decomposed. This regime corresponds to 'chemical isotope purification'; in this case, $\alpha_G \Rightarrow \infty$ and $\alpha = -1$. The attainment of this regime constitutes a major and intriguing problem and we shall return to its discussion below.

The photolysis of dibenzyl ketone was the first chemical process in which the MIE was observed.[6] It is a classical example of the MIE and serves as a test of the physics of this unique phenomenon.

Isotope enrichment obeys rigorously Eqn (1), while the quantity α_G depends on the properties of the medium, varying from 1.05 in hexane at 20 °C to 1.50 in glycerol and 1.37 in hexadecyltrimethylammonium chloride micelles (Fig. 2).

The studies on the MIE developed in two directions: (1) experimental search for the effects involving nuclei heavier

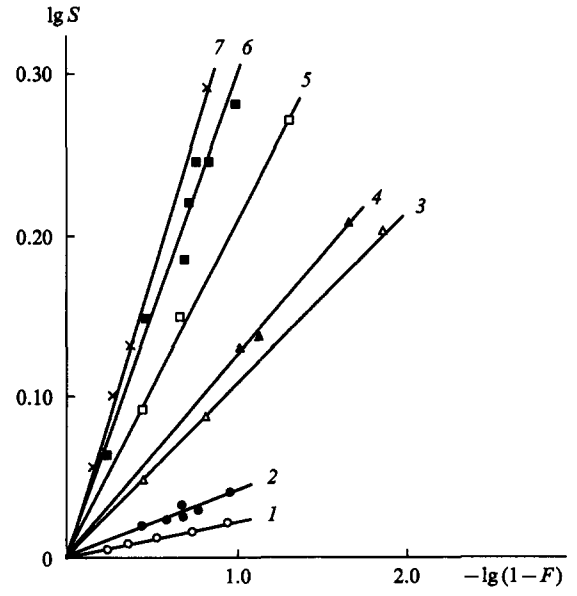


Figure 2. Isotope enrichment (S) as a function of the chemical conversion (F) in terms of the variables of Eqn (1) in the photolysis of dibenzyl ketone: (*1*) benzene; (*2*) hexane; (*3*) cyclohexanol, 20 °C; (*4*) cyclohexanol, 0 °C; (*5*) glycerol, 1700 cP; (*6*) hexadecyltrimethylammonium chloride micelles; (*7*) glycerol, 2400 cP.

than that of carbon and (2) theoretical analysis of the chemical physics of the effect in order to predict the possible ways of increasing it.

Considerable progress has been achieved in both directions: the outcome of the first will be examined briefly in this Section, while that of the second will be discussed below.

The magnetic isotope effect in the $^{13}C/^{12}C$ diad has been known since 1976;[6,7] since then, it has been discovered in the triads $^{16}O/^{17}O/^{18}O$,[11-16] $^{28}Si/^{29}Si/^{30}Si$,[17-18] and $^{32}S/^{33}S/^{34}S$ [19] and also in the diads $^{72}Ge/^{73}Ge$ [20] and $^{238}U/^{235}U$.[21,22]

The magnetic isotope effect of ^{17}O has been discovered in the reactions involving the chain oxidation of carbochain polymers[12] and the liquid-phase oxidation of hydrocarbons[11,13] by molecular oxygen. In the first case, the oxidation reaction and the absorption of oxygen are accompanied by the enrichment of the residual oxygen in the ^{17}O and ^{18}O isotopes (Fig. 3*a*), the enrichment in the magnetic isotope ^{17}O greatly exceeding that in the nonmagnetic isotope ^{18}O, the dependence of the enrichment on the conversion obeying Eqn (1) (Fig. 3*b*). The anomalous behaviour of the magnetic isotope indicates unambiguously that the MIE is the main cause of the isotope selectivity.

The reaction involving the termination of the kinetic oxidation chains, i.e. the interaction of two peroxy radicals in accordance with the scheme

$$RO_2^{\cdot} \Longleftrightarrow (RO_2^{\cdot}\ {}^{\cdot}O_2R) \Longleftrightarrow RO_4R \Rightarrow RO_3^{\cdot} + O^{\cdot}R \Rightarrow 2\,RO^{\cdot} + O_2$$

pin-selective and hence nuclear-selective. Following their encounter, a pair of peroxy radicals either recombines to the unstable tetroxide RO_4R, which subsequently decomposes irreversibly with regeneration of molecular oxygen, or dissociates reversibly, regenerating the initial peroxy radicals. The MIE actually arises in this stage: the pairs containing the $R^{16}O^{17}O^{\cdot}$ radicals recombine faster than the radical pairs with $R^{16}O^{16}O^{\cdot}$ (or $R^{16}O^{18}O^{\cdot}$). As a result, the regenerated oxygen is enriched in the ^{17}O magnetic isotope, while the hydroperoxide $R^{16}O^{16}OH$ is depleted in this isotope. The kinetic theory of this process, developed by Buchachenko et al.,[16] defines the isotope enrichment of the molecular oxygen S as a function of its chemical conversion F in terms of the ratio of the rate constants for the quadratic kinetic chain termination. The ratio of the termination rate constants k_t was found from the $S(F)$ relation (Fig. 3*a*) in terms of the variables of Eqn (1):

$$\frac{k_t(R^{16}O^{17}O + {}^{16}O^{16}OR)}{k_t(R^{16}O^{16}O + {}^{16}O^{16}OR)} = 1.8\ ,$$

i.e. the replacement of the ^{16}O nonmagnetic nucleus by the ^{17}O magnetic nucleus ensures an increase in the rate constant for the annihilation of the peroxy radical almost by a factor of two.

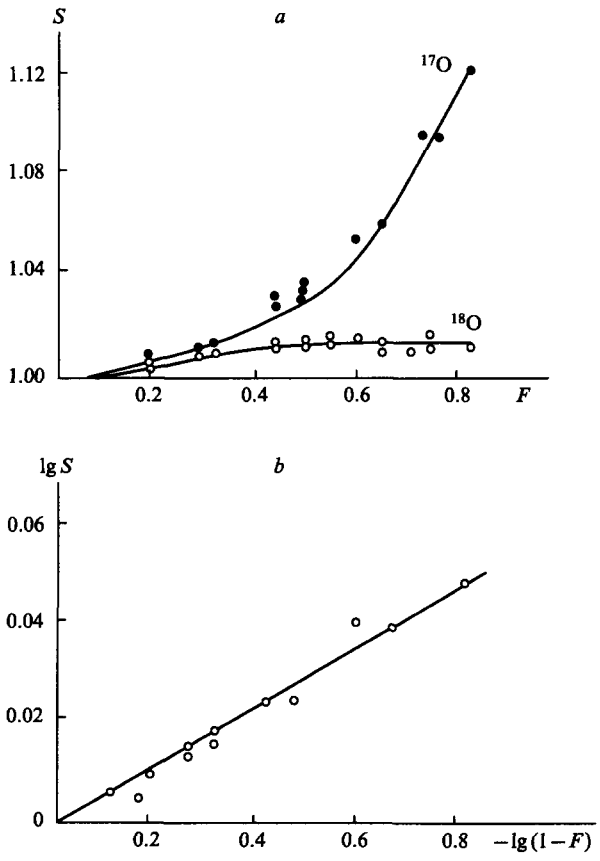


Figure 3. Dependence of the isotope enrichment on the conversion of molecular oxygen in the oxidation of polypropylene at 130 °C (*a*) and its representation in terms of the variables of Eqn 1 (*b*).

The opposite effect obtains in the liquid-phase oxidation reactions of hydrocarbons[13] — as molecular oxygen is consumed, it is depleted in the ^{17}O isotope, which means that the principal isotope-sorting process in these reactions becomes the addition of the alkyl radicals $R^{\cdot}$ to molecular oxygen. The addition of $R^{\cdot}$ to $^{17}O^{16}O$ is faster than the addition to $^{16}O^{16}O$ and the reason for this is again the acceleration of spin conversion in the pair $(R...O_2)$ as a result of the hyperfine interaction with the ^{17}O magnetic nucleus. However, the quartet–doublet conversion now takes place. The ratio of the rate constants for the $R^{\cdot} + {}^{17}O^{16}O$ and $R^{\cdot} + {}^{16}O^{16}O$ reactions is 1.011, i.e. the $^{17}O^{16}O$ molecules react faster than the $^{16}O^{16}O$ molecules to the extent of 1.1%[16] and this difference between the rates depletes the molecular oxygen in the ^{17}O isotope. The classical mass isotope effect (CIE) in the $R^{\cdot} + {}^{18}O^{16}O$ and $R^{\cdot} + {}^{16}O^{16}O$ reactions is 0.99, i.e. the first reaction is slower than the second by 1%.[16] Clearly the MIE is much greater than the CIE: it fully compensates for the CIE in the $R^{\cdot} + {}^{17}O^{16}O$ reaction and actually reverses the sign of the effect.

The difference in the behaviour of the ^{17}O isotope in two processes — the oxidation of polymers in the viscoelastic state and liquid-phase oxidation — demonstrates the leading role of molecular dynamics in the selection of the spin-selective reaction. Molecular dynamics controls the spin selectivity of the two isotope-sorting reactions (the propagation and termination of kinetic chains). The first of these predominates in solutions with a low viscosity, while the second predominates in viscous systems with greatly retarded molecular motion. The physical cause of the difference between the isotope selectivities of these two reactions is evident: rapid molecular dynamics and a short time of the diffusional 'liquid-phase' trajectories should correspond to rapid spin evolution in the $(R^{\cdot}...O_2)$ pair, while slow dynamics and a long time of the diffusional trajectories in viscous polymers should correspond to slow spin conversion in the $(RO_2^{\cdot}\ {}^{\cdot}O_2R)$ pair. The comparable times of spin conversion and diffusional motions ensure the optimum conditions for the isotope selection in two competing processes — reaction in the pair and diffusional dissociation of the pair.

The high-temperature oxidation of polyaromatic[15] polymers (polypyromellitimide, polyphenylquinoxaline) by molecular oxygen is accompanied by the enrichment of the latter in the ^{18}O isotope and its depletion in the ^{17}O isotope. The kinetics of the oxidation (the absence of autocatalysis and of the inhibiting effect of antioxidants) and the composition of the oxidation products (mainly quinones) indicate a nonchain oxidation mechanism, in which the spin-selective stage is the interaction of molecular oxygen with low-lying excited and thermally accessible triplet states of the polyaromatic fragments of the macromolecules. The product of this reaction is an *endo*-peroxide. Among the nine spin states of the pair of two triplets (oxygen plus the triplet fragment of the macromolecule), only one (singlet) state gives rise to the *endo*-peroxide. The hyperfine interaction in the oxygen with ^{17}O partly removes the spin prohibition and opens an additional reaction path involving other spin states. As a result,

the ^{17}O isotope-containing oxygen reacts faster and its transfer to the products depletes the molecular oxygen in the ^{17}O isotope. The enrichment of the oxygen in the ^{18}O isotope in this reaction takes place due to the CIE.

A magnetic isotope effect of ^{17}O with the opposite sign has been observed by Turro and Chow[14] in the reverse reaction involving the decomposition of *endo*-peroxides. There is no doubt that the decomposition takes place via the singlet state of the biradical $Ar^{\bullet}-OO^{\bullet}$, where Ar is the aryl component of the *endo*-peroxide. The biradical may decompose, generating singlet oxygen, or may be transformed into a triplet state, generating triplet molecular oxygen on decomposition. Clearly in the biradicals with ^{17}O the latter process should predominate and singlet oxygen should therefore be depleted in the ^{17}O isotope, while triplet oxygen should in fact be enriched in this isotope. These predictions have been fully confirmed by experiment.[14]

The discovery of the MIE of ^{29}Si arose from the synthesis of the silicon-containing ketone $PhCH_2COSiMe_2Ph$, which is similar to dibenzyl ketone structurally and to its photolysis in micelles.[18] It was shown with the aid of chemically induced [dynamic] nuclear polarisation that both direct and triplet-sensitised photolysis occur, as in the photolysis of dibenzylketone via radical pairs.

$$PhCH_2\overset{O}{\overset{\|}{C}}SiMe_2Ph \Longleftrightarrow (PhCH_2^{\bullet}\ \ {}^{\bullet}\overset{O}{\overset{\|}{C}}SiMe_2Ph) \Longrightarrow \text{products}$$

The direct photolysis begins with the excited singlet state, which generates the singlet radical pair (RP). On the other hand, the sensitised photolysis proceeds via the triplet RP.[23] The variation of the silicon isotope composition of the ketone as a function of the chemical conversion of the latter is illustrated in Fig. 4.

The first important result which follows from Fig. 4 is that the enrichment of the ketone in the ^{29}Si magnetic isotope greatly exceeds its enrichment in the ^{30}Si nonmagnetic isotope. Clearly the HFI involving the ^{29}Si nucleus in the triplet RP accelerates its triplet – singlet spin conversion and stimulates the recombination of the pairs with ^{29}Si, whereas the triplet – singlet conversion of the pairs with ^{28}Si lags behind and these pairs dissociate and are converted into other products, the excess ^{28}Si nuclei being removed in these products.

The second striking result which follows from Fig. 4 is that the direct photolysis leads to the depletion of the initial ketone in the ^{29}Si isotope, i.e. the inversion of the spin multiplicity of the RP in the direct and sensitised photolysis is accompanied by the inversion of the sign of the MIE: the enrichment of the ketone in the ^{29}Si isotope in the sensitised photolysis (starting with the triplet) is replaced by depletion in the direct photolysis (starting with the singlet). The cause of the inversion is evident: the initial singlet pairs with ^{29}Si are transformed faster into the triplet pairs and subsequently dissociate, carrying away ^{29}Si and other products and depleting the regenerated ketone in this isotope. We may note that the enrichment of the ketone in the ^{30}Si nonmagnetic isotope is due to the CIE and is therefore insensitive to the spin multiplicity of the RP and to the direction of spin conversion — from the triplet to the singlet or back again.

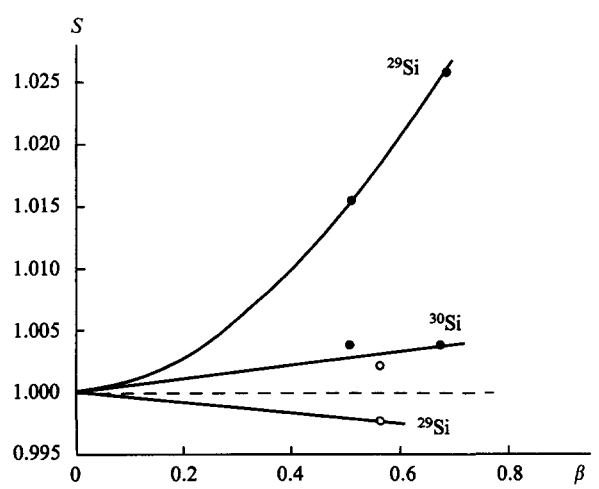


Figure 4. Enrichment in the ^{29}Si and ^{30}Si istopes as a function of the chemical conversion β in the direct (open circles) and sensitised (filled circles) photolysis of silyl ketone.

The ^{33}S magnetic isotope effect was first observed in 1990[19] in the direct micellar photolysis of a sulfur-containing ketone, which was shown with the aid of chemically induced [dynamic] nuclear polarisation to proceed via triplet RP in accordance with the scheme

$$PhC\overset{O}{\overset{\|}{C}}H_2SO_2Ph \rightleftharpoons (PhC\overset{O}{\overset{\|}{C}}H_2^{\bullet}\ \ {}^{\bullet}SO_2Ph) \Longrightarrow \text{products.}$$

The pairs with the ^{33}S magnetic isotope recombine faster and return this isotope to the regenerated ketone molecules, the enrichment of which in ^{33}S increases with increase in the chemical conversion of the ketone (Fig. 5). The marked predominance of the ^{33}S isotope enrichment over the enrichment in the ^{34}S nonmagnetic isotope demonstrates unambiguously the predominance of the MIE over the CIE.

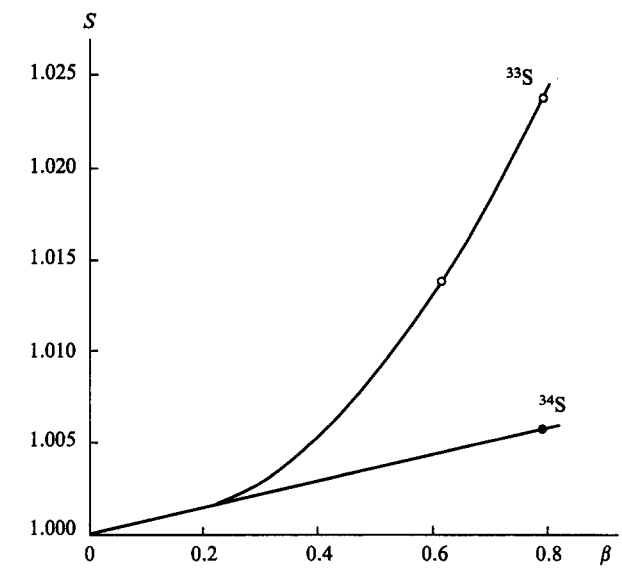


Figure 5. Enrichment in the ^{33}S and ^{34}S isotopes as a function of the chemical conversion in the photolysis of a sulfur-containing ketone.

The ^{73}Ge magnetic isotope effect was discovered quite recently[20] in the photolysis of methyltriphenylgermane in micelles; the initial compound was enriched in the ^{73}Ge magnetic isotope relative to the nonmagnetic ^{72}Ge. The enrichment in ^{73}Ge depends greatly on the magnetic field, whereas the content of the ^{72}Ge isotope does not change, demonstrating the 'classical' origin of the effect involving ^{72}Ge.

The mechanism of the decomposition reaction suggests that the selection of the magnetic and nonmagnetic germanium nuclei takes place in accordance with the same principle as the sorting of the ^{13}C nuclei in the decomposition of dibenzyl ketone.

$$Ph_3GeMe \Longleftrightarrow (Ph_2MeGe^{\bullet}\ Ph^{\bullet})^{T} \Rightarrow \text{products}$$

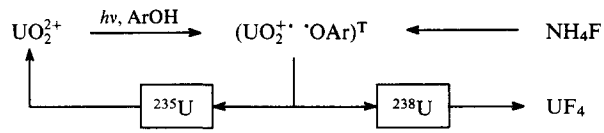
The hyperfine interaction involving the ^{73}Ge nucleus in the radical $Ph_2MeGe^{\bullet}$ is unknown, but one can make the reliable assumption that its magnitude is hardly likely to differ greatly

from that known for the $Ph_3Ge^{\cdot}$ and $Me_3Ge^{\cdot}$ radicals.[24,25] As a result of the HFI, the ^{73}Ge-containing radical pairs rapidly evolve to singlet species and recombine, returning the ^{73}Ge magnetic nuclei to the regenerated methyltriphenylgermane molecule.

Finally, the MIE involving uranium nuclei has been observed independently by two groups of investigators.[21,22] The search for the MIE of uranium nuclei required the solution of three problems: (1) the search for reactions of uranium compounds which could generate paramagnetic intermediates — spin carriers (radicals or radical-ions); (2) the search for spin-selective stages in the reactions of these intermediates; (3) the study of the proportions of the isotopes in the products. The solution of the last of the three problems is the most problematical, because there is no guarantee that the outer unpaired electron in the uranium-containing paramagnetic intermediate is capable of 'breaking through' the thick electron shell consisting of more than 90 electrons and reaching the nucleus in order to give rise to the appreciable HFI necessary to ensure the nuclear spin selectivity.

Among the various reactions of uranium-containing compounds, the photoreduction of uranyl salts was chosen for the search for the MIE. The first stage of this reaction is the reduction of the uranyl ion UO_2^{2+} to the paramagnetic uranoyl ion UO_2^{+}. In three series of elegant experiments {the observation of chemically induced [dynamic] nuclear polarisation in the reactions of the uranyl ion,[26] the observation of the magnetic field effect in a uranyl-photosensitised polymerisation reaction,[27] and the detection of electronic polarisation transferred from the excited UO_2^{2+} ion to the nitroxyl radical[28]}, it was shown unambiguously that the uranyl ion UO_2^{2+} reacts in the excited triplet state, generating the uranoyl ion UO_2^{+}, which subsequently participates in spin-selective reactions, which sort the isotopic nuclei (the magnetic ^{235}U nuclei and the nonmagnetic ^{238}U nuclei).[29]

The most convincing results were obtained in the photolysis of uranyl perchlorate in an aqueous micellar solution of sodium dodecyl sulfate in the presence of NH_4F and 2,6-diphenyl-4-stearoylphenol.[30] The reaction mechanism and the paths followed in the migration of the isotopic nuclei are illustrated below.



The photolysis of uranyl generates a triplet RP made up of the uranoyl ion UO_2^{+} and the phenoxyl radical. The reaction pairs with ^{235}U magnetic nuclei undergo rapid triplet–singlet conversion and disproportionate with regeneration of the initial uranyl enriched in ^{235}U. The 'nonmagnetic' pairs with ^{238}U are converted into tetravalent uranium products (of the type of the insoluble UF_4). The initial uranyl is enriched on photolysis in the light but magnetic ^{235}U isotope, while the product of the photolysis of UF_4 is enriched in the heavy nonmagnetic ^{238}U isotope. This result conflicts with the predictions based on the CIE (it was found that the UO_2^{2+} ions with the heavy isotope are more reactive than those with the light isotope) and indicates unambiguously a contribution by the MIE, which exceeds the CIE in magnitude, compensating for the latter and actually leading to a change in sign. Later the ^{235}U MIE was confirmed in the photolysis of uranyl succinate containing 30% of ^{235}U. On 85%–90% conversion in methanol, the content of ^{235}U in the initial uranyl succinate increases by 6% relative to the initial value.[31]

Fig. 6 summarises the values of α_G for all the MIE discovered hitherto. It provides a clear idea about the quantitative scales of the MIE and the CIE.

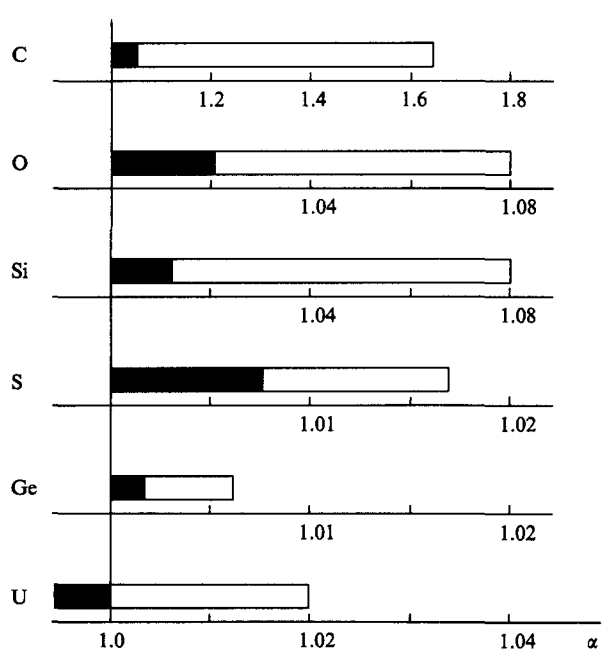


Figure 6. The single-stage isotope enrichment coefficients α_G. The open rectangles indicate the region of α_G for the MIE in the $^{13}C/^{12}C$, $^{17}O/^{16}O$, $^{29}Si/^{28}Si$, $^{33}S/^{32}S$, $^{73}Ge/^{72}Ge$, and $^{235}U/^{238}U$ isotope pairs. The filled rectangles characterise the CIE for the $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{30}Si/^{28}Si$, $^{34}S/^{32}S$, $^{73}Ge/^{72}Ge$, and $^{235}U/^{238}U$ isotope pairs.

III. Properties of the magnetic isotope effect

Table 1 summarises the characteristic properties and features of the MIE and compares them with those of the CIE. The first fundamental feature of the MIE, which is also its essential feature, is its nuclear spin dependence (in contrast to the nuclear mass dependence of the CIE).

The effectiveness of the nuclear spin selection is controlled by the HFI energy: the higher the HFI energy, the stronger the effect of the nuclear spin system on the electron system with removal of spin prohibition and differentiation of the rates of the triplet–singlet conversions of the 'magnetic' and 'nonmagnetic' radical pairs. The dependence on the HFI energy constitutes the second feature of the MIE, which, in contrast to the CIE, can lead to measurable isotopic enrichments of the atoms at a considerable distance from the reaction centres. The reason for this is that the distribution of the spin density among the chemical bonds in the radicals is not attenuated regularly and may give rise to intense HFI involving remote atoms. At any rate, this attenuation is much gentler than the transfer of perturbations of the molecular vibrations induced by isotope substitution (this is why the CIE is localised at the reaction centre).

The third feature of the MIE is its high sensitivity to molecular dynamics and all the factors influencing the latter: viscosity, temperature, restriction of the reaction in closed volumes — microreactors of the type of micelles or zeolite cavities. The spin conversion develops in a dynamic system — a radical pair, where the partner radicals move apart as a result of diffusion, some of them return and are involved in repeated encounters, move apart again, etc. During the diffusional migrations, spin conversion, induced by the hyperfine and Zeeman interactions, takes place. For the occurrence of nuclear selection, it is important that the diffusional migration times of the partner radicals should be comparable with the spin conversion times of the pair.

The high sensitivity of the isotope enrichment to the molecular-dynamic properties of the medium is demonstrated by Fig. 2. The isotope enrichment coefficient [α_G in Eqns (1)] depends greatly on the visocity: in viscous solutions (cyclohexanol, glycerol), α_G is much greater than in solutions with a low

Table 1. Comparison of the features of the MIE and the CIE.

Feature	MIE	CIE
Selectivity parameter	Nuclear spin and magnetic moment	Nuclear mass
Hyperfine interaction	Strong dependence	No dependence
Magnetic field	Strong dependence	No dependence
Molecular dynamics	Strong dependence	No influence
Chemical dynamics and lifetime of radicals	Dependence	No dependence
Effect of temperature	Strong	Weak
Spin multiplicity	Strong dependence of magnitude and sign	No dependence

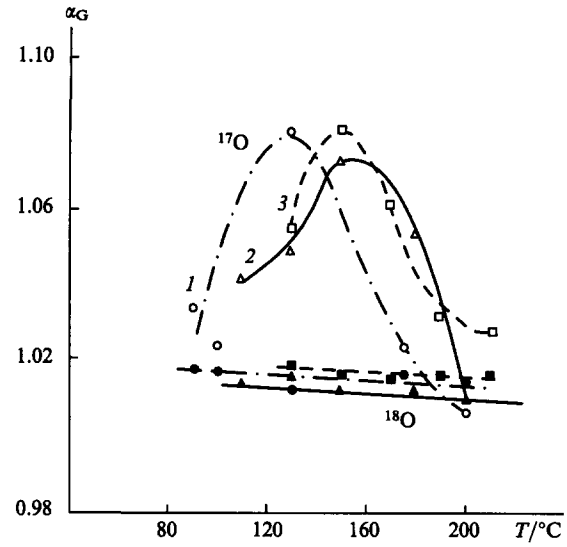


Figure 7. Temperature dependence of the single-stage isotope enrichment coefficient α_G in the oxidation of polyethylene (curve *1*), polypropylene (curve *2*), and poly-4-methylpentene (curve *3*). The open circles, squares, and triangles correspond to ^{17}O, whilst the filled symbols correspond to ^{18}O.

viscosity (benzene, hexane). Thus, for the photolysis of dibenzyl ketone, α_G is 1.054 in hexane[6] and 1.039 in benzene,[32] whereas in vitreous cyclohexanol $\alpha_G = 1.113$[33] and in glycerol (with a viscosity of 2400 cP) $\alpha_G = 1.50$.[34] Turro was the first to show that α_G attains large values when the reaction is carried out in closed microreactors (micelles and the cavities in zeolites or porous glasses). Thus $\alpha_G = 1.37$ in hexadecyltetramethylammonium chloride micelles[35] and $\alpha_G = 1.39$ in the corresponding bromide micelles.[36] The physical causes of such high isotopic selectivity of the reactions in closed microreactors are discussed below.

The magnetic isotope effect depends greatly on the lifetime of the radicals, because the joint molecular and spin dynamics of the pair are limited by its chemical lifetime. For the nuclear spin selection to be successful, it is necessary that the spin conversion time and the lifetime of the pair are comparable. This property of the MIE, namely the dependence on the chemical dynamics of the pair, constitutes its fourth fundamental feature.

Thus the generation of the molecule from the RP is the result of the combined efforts and interactions due to three types of dynamics — spin, molecular, and chemical. Their joint effect prepares the pair for an important event — recombination: the spin dynamics ensures the required (singlet) spin state of the pair, the molecular dynamics guarantees contact between the recombining partners by this instant, and the chemical dynamics ensures the survival of the pair. For this reason, the isotope separation based on the MIE depends on the parameters which influence the molecular and chemical dynamics — temperature[37] and viscosity,[38] the presence of radical acceptors, the wavelength of the photolysis,[39] the size of the micelles,[40] etc.

As an illustration, Fig. 7 shows the enrichment of molecular oxygen in the ^{17}O and ^{18}O isotope as a function of temperature[12] in the chain oxidation of polymers. The enrichment in ^{18}O decreases only slightly with increase in temperature, in conformity with the predictions based on the CIE. However, the MIE-induced enrichment in ^{17}O depends greatly on temperature, passing through a maximum at T_{max}, which reflects the condition for the most effective isotope selection: the time between repeated diffusional encounters of radicals is comparable to the spin conversion time for the pair. On either side of the maximum, the characteristic times of these two dynamic processes (molecular and spin) are not comparable and the MIE decreases sharply. At high temperatures $T > T_{max}$, the lifetime of the RP diminishes sharply (rapid diffusion) and there is insufficient time for the pair to effect spin conversion and isotope sorting. On the other hand, for $T < T_{max}$ the diffusional lifetime of the RP is too long and during it the spin correlation is lost for all the pairs — both 'magnetic' and 'nonmagnetic'. In both extreme cases, the isotope sorting in the pairs is ineffective.

The sign of the CIE is unambiguously dictated by the ratio of the isotope masses; however, the sign of the MIE is determined by the spin multiplicity of the radical pairs (or other electron spin carriers). Strictly speaking, it depends on the direction of the spin conversion — from the triplet to the singlet or conversely. This is an obvious property: in the initial triplet state, the 'magnetic' pairs evolve more rapidly to the singlet state and the recombination product is enriched in the magnetic isotope; in the initial singlet state, the 'magnetic' pairs pass through the triplet state for the same reason and dissociate, depleting the recombination product in the magnetic isotope. An example of the inversion of the sign is provided by the MIE based on the ^{29}Si nuclei (see above). Another example of the inversion of the sign of the MIE is the triplet-sensitised photolysis[7] and thermolysis of benzoyl peroxide.[38] The photochemical reaction involves triplet RP and triplet–singlet conversion, whereas the thermal reaction begins with singlet pairs and involves singlet–triplet spin conversion. These two chemically identical reactions lead to different isotope redistributions: in the first case, the cage product (phenyl benzoate) is enriched in the ^{13}C isotope, while in the second case the excess ^{13}C is found in the reaction product outside the cage — in benzene.[38] Such dependence of the sign of the MIE on the direction of the spin evolution is a reliable test for the identification of the spin multiplicities of the reactants.

Finally, there is yet another important property of the MIE: as a rule, the effect arises in chemical steps which do not limit the overall rate of the process (for example, the formation of chemical bonds on recombination), whereas the CIE occurs in energy consuming chemical decomposition or substitution reactions.

IV. Problems and prospects of the isotopic-spin selectivity

The magnitude of the classical isotope effect is determined by the ratio of the isotope masses, which greatly limits the nuclear mass selectivity of the reactions (provided that tunnelling is excluded). It was shown above that the nuclear spin selectivity is as a rule

much more pronounced, so that the isotope enrichment induced by the MIE can exceed the value expected from the CIE by 1–2 orders of magnitude.

The limiting nuclear spin selectivity and ideal isotope separation are attained for $P = 0$ and $P^* = 1$ [see Eqn (1)]. These are very severe conditions, which fully prohibit the recombination of nonmagnetic RP and at the same time require the complete recombination of pairs with magnetic nuclei. Whether or not these contradictory conditions can be satisfied is a problem which we shall now discuss.

The first step on the way towards a high spin selectivity involves directing the reaction along the path with participation of paramagnetic intermediates (spin carriers), i.e. the adjustment of the chemistry to promote the spin-selective reactions. Naturally, this is not always possible and is not always necessary. For example, it is pointless to seek the nuclear spin selectivity in hydrolytic or nucleophilic substitution reactions. When the reaction proceeds via two parallel competing paths, one of which is radical and spin-selective whilst the other is nonradical, the single-stage isotope enrichment coefficient assumes the following form:

$$\alpha_G = \frac{1 - P\theta}{1 - P^*\theta}, \qquad (2)$$

where θ is the partial contribution of the radical path. For $\theta = 1$, the coefficient α_G is a maximum and Eqn (2) then reduces to Eqn (1). However, if θ diminishes, then α_G also falls and for $\theta = 0$ (the radical path vanishes) there is no nuclear spin selectivity ($\alpha_G = 1$). Eqn (2) may be used also to determine the contribution by the nonradical path. Thus, in the sensitised photolysis of a silicon-containing ketone in micelles, it was found that the radical path (via triplet RP) coexists with the decomposition reaction via a siloxycarbene, which is inserted in the O–H bond of the water molecule; this path amounts to approximately 2/3 of the overall reaction flux and is not spin-selective, which greatly reduces the ^{29}Si MIE.[18]

The second important condition is high reversibility of the spin-selective reaction, which guarantees the possibility that each molecule can undergo repeated reactions of this kind (e.g. dissociation–recombination–regeneration cycles). Each of these repeating cycles is isotope-selective, so that the overall isotope selection is multiplied repeatedly in the multicascade process.

A high reversibility of the reaction can be induced in two ways—by spatial and by physical 'enforcement'. The former implies that the reaction is carried out in closed microreactors (micelles, the cavities in zeolites and porous glasses, microcavities in stressed polymers, etc.), in which the reflecting walls limit diffusion and give rise to the 'capture' of the radical pairs. The theory of microreactors from the standpoint of nuclear spin selectivity has now been fairly thoroughly developed.[33,41]

The physical 'enforcement' is less trivial and merits special consideration. The magnetic isotope effect is a result of the spin conversion induced by the electron-nucleus HFI, so that the greater the extent of the HFI, i.e. the stronger the linkage between the electron and nuclear spin subsystems, the greater the isotope selection. However, the HFI is by no means the only physical interaction giving rise to the triplet–singlet (or any other, for example, quartet–doublet) spin conversion. The spin-rotation, spin-orbit, dipolar, and exchange interactions all induce electron relaxation and hence spin conversion. This additional relaxation path competes with the HFI path and is traditionally regarded as the harmful spin leakage path, because it does not involve the nuclear spin system and thus does not give rise to the MIE. In such cases, the reaction remains selective with respect to the electron spin but loses its selectivity with respect to nuclear spin.

However, even if the contribution of the HFI to the spin conversion is low but the electron relaxation is rapid and stimulates effectively the spin conversion and recombination of the triplet pairs (i.e. forces the radical pairs to recombine), ultimately the isotopic selectivity increases. This paradoxical result has a simple explanation: not only the isotope selection in each reaction step but also the number of such steps undergone by each molecule is important. Here the multicascade nature of the spin-selective process is again manifested.

Thirdly, in order to ensure an appreciable MIE, it is necessary to modify the reaction mechanism in such a way that the spin-selective processes begin with the triplet state of the RP. This is one of the reasons why the triplet-sensitised photolysis is preferable for the observation of the MIE and isotope selection.

The fourth factor controlled by the MIE is the extent of the HFI in radicals participating in spin-selective processes: the greater the extent of the HFI, the greater the difference between the probabilities P and P^*, and the greater the value of α_G. However, the quantities P and P^* themselves are determined by the interaction of three dynamic processes—spin, molecular, and chemical, so that the synchronisation of these dynamic processes in time is an important factor which influences the difference $P^* - P$ (this has already been discussed in the section concerning the properties of the MIE).

Finally, the MIE and isotopic selectivity may be strengthened by the selective microwave pumping of the RP having magnetic nuclei. By acting on the electron spin, the magnetic component of the resonance hyperfine frequency field accelerates the spin conversion and stimulates the selective regeneration of molecules with magnetic nuclei without affecting the RP with nonmagnetic nuclei. This remarkable effect has been called the radio-induced MIE;[42,47] it belongs to the second generation of magnetic effects, namely those which are due to the action of microwave magnetic fields on chemically reacting spin systems.[5] The first generation of magnetic effects are induced by static magnetic fields—external or internal (of the type of HFI). The magnetic field effect, the MIE, and chemically induced [dynamic] nuclear polarisation are effects of this kind.

As an example of the radio-induced MIE, one may quote the enrichment of dibenzyl ketone in the ^{13}C isotope during its photolysis in micelles as a function of the chemical conversion plotted in terms of the variables of Eqn (1). The slope of this plot, which determines the single-stage enrichment coefficient α_G, increases with microwave pumping.[43]

The prospects for the radio-induced MIE are still more promising when one employs a combination of two types of microwave pumping: the low amplitude pumping of the 'magnetic' RP, which stimulates their recombination and the high-amplitude pumping of the 'nonmagnetic' RP, which slows down or altogether suppresses the spin conversion of these pairs, preventing their recombination (the spin locking effect).[44] Under these conditions, the isotope selection is most effective.

Thus there are diverse and almost limitless possibilities for regulating the nuclear spin selectivity of chemical reactions. There is a problem in the choice of the reactions and the methods and conditions for carrying them out; in other words, the problem of controlling the chemistry and physics of the reactions which are a part of spin chemistry—the science of the behaviour of the angular momenta of electrons and nuclei in chemical reactions.

V. Sorting of nuclei in accordance with spin orientations

Thus, by virtue of the MIE, the reaction sorts the magnetic and nonmagnetic nuclei. The next level in nuclear spin selectivity involves the sorting of magnetic nuclei in accordance with their orientations. The hyperfine interaction, which makes it possible to separate nuclei in terms of their magnetic properties, depends on the orientation of the nucleus and in the simplest case is defined as am, where a is the HFI constant proper and m is the projection of the nuclear spin specifiying the orientation of the nucleus. Clearly, the HFI-induced rate of spin conversion depends on m, so that both the conversion and the competition

between the reactions in the RP depend on the orientation of the nuclei. As a result, the reaction directs nuclei oriented in different ways into different products. Thus molecules with oriented (polarised) nuclei are generated. However, the reaction is capable not only of sorting the nuclei in accordance with orientations but also of orienting them. This occurs in very weak magnetic fields, where the external magnetic field $H \ll a$ and is still incapable of rupturing the electron–nucleus linkage. The spin conversion in the electron system is then accompanied by conversion of the nuclear spin. In other words, the change in the electron spin is compensated by the change in the orientation of the nuclear spin (because the overall angular momentum of the electron–nucleus system is conserved).

The phenomena involving the sorting of nuclei and their orientation in chemical reactions are combined under the term chemically induced [dynamic] nuclear polarisation (CIDNP).[1,45,46] The orientation of the nuclei is equivalent to the nonequilibrium (excess) population of the nuclear Zeeman levels in the molecules of the chemical reaction products and is therefore detected by nuclear magnetic resonance methods and is manifested in the NMR spectra as an anomalous absorption or emission (depending on which Zeeman levels are overpopulated and which orientations of the nuclei predominate in the molecules).

Chemically induced [dynamic] nuclear polarisation was discovered independently by two groups of workers (Bargon and Fisher[47] and Ward and Lawler[48]); Sagdeev, Molin, Kaptein, Osterhoff, Closs, Roth, Lippmaa, etc. have made major contributions to the CIDNP. Stimulated CIDNP was a remarkable discovery (Sagdeev, Grishin, Molin, etc.). The idea underlying it was formulated by Sagdeev et al.[49] Stimulated CIDNP is generated by the selective microwave pumping of assemblies of radical pairs with a selected orientation of the nuclei, which leads to the spin conversion of such assemblies and forces them to react. As a result, nuclei with the specified orientation are forcibly directed into the molecules of products and are detected in the latter by NMR methods.

Chemically induced [dynamic] nuclear polarisation is widely used in its diverse variants (in the stationary and time-resolved variants, in the static and flow variants, etc.) in chemistry and biochemistry as a method for the identification of reaction mechanisms, for the detection of radicals and radical stages, and as a method for the study of chemical kinetics and chemical physics (see, for example, Refs 1, 5, and 50).

This review was written with financial support from the Russian Fundamental Research Fund (grant No. 93-03-05227).

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