RUSSIAN
CHEMICAL
REVIEWS
Uspekhi Khimii

October 1971

U.D.C. 534.171

Chemically Induced Polarisation of Electrons and Nuclei

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The polarisation, in excess of the equilibrium value, of electrons and nuclei in the species generated in chemical reactions was observed in ESR and NMR spectra quite recently and during the last 2-3 years studies of this kind have developed vigorously. The aim of the present review is to present the principal results of studies on chemically induced polarisation of electrons and nuclei, to formulate the ideas and concepts concerning the nature of the phenomena discussed, and also to attempt an assessment of their importance and prospects.
The bibliography includes 70 references.

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I. INTRODUCTION

The ESR or NMR spectrum of a radical, ion, or molecule constitutes a kind of "portrait" of the species or fragment. The spectra contain information about the chemical structure of the species, its orientation (in a solid), the frequencies of molecular motion, and the energies of electron–electron and electron–nucleus magnetic interactions.

The usual magnetic resonance spectra do not of course provide any information about the elementary steps in the generation of the species, i.e. about the nature of the states preceding the species. The reason for this is that the magnetic resonance spectra usually recorded are the absorption spectra of the species in which the populations of the magnetic Zeeman (electronic or nuclear) levels correspond to thermal equilibrium, i.e. obey the Boltzmann distribution. However, in the steps involving the generation of the species (radicals or molecules) or in the states from which these species are produced (triplet states, radical pairs, etc.), there is a possibility of a non-equilibrium population of the Zeeman levels. Then the species generated will not give rise to the usual magnetic resonance spectra corresponding to equilibrium absorption but to spectra with an anomalously strong absorption or to emission spectra. The first case corresponds to positive polarisation of electrons or nuclei in the species in excess of the equilibrium value and the second to negative polarisation.

The observation of the effects of non-equilibrium polarisation of electrons or nuclei in ESR or NMR spectra is of course only possible immediately after the generation of the species when they "remember" the non-equilibrium polarisation induced in them during the electronic (10^{-7}–10^{-5} s) or nuclear (1–30 s) relaxation time; after this period, the species lose their polarisation in excess of the equilibrium value.

II. CHEMICALLY INDUCED NUCLEAR POLARISATION

Chemically induced nuclear polarisation (CINP)† is shown in the NMR spectra of the products of reactions occurring in the magnetic field of the NMR spectrometer. It is observed as an intense radiofrequency absorption (positive polarisation) or a radiofrequency emission (negative polarisation). The intense nuclear polarisation (exceeding by several factors of ten and sometimes hundreds the equilibrium polarisation) constitutes unambiguous evidence for the involvement in its generation of unpaired electrons and observation of the effects of nuclear polarisation constitutes a reliable criterion of the existence of radical stages in the reaction. To illustrate CINP, Fig. 1 presents the NMR spectra of the products obtained in the thermal decomposition of benzoyl and acetyl benzoyl peroxides, the spectra were recorded during the reaction.

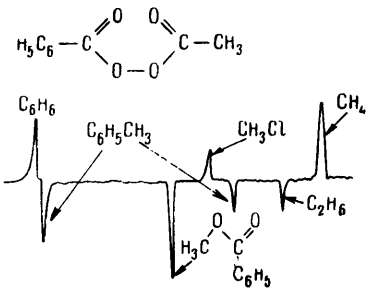
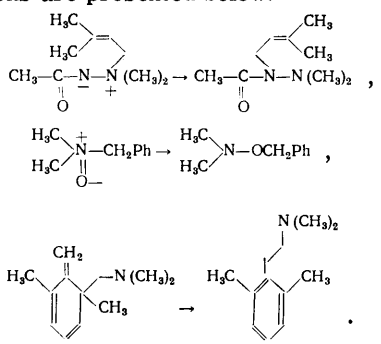


Figure 1. NMR spectrum of products with polarised nuclei in the decomposition of acetyl benzoyl peroxide at 100°C in tetrachloroethylene.

CINP was first observed by Fischer and coworkers[1] in the decomposition of benzoyl peroxide in cyclohexanone when instead of the expected benzene absorption signal an emission signal was noted.

At the present time CINP has been observed and investigated in numerous thermal decomposition reactions of peroxides and azo-compounds[1-9], thermal rearrangements of quaternary ammonium salts[10-13] and quaternary amine oxides[14], and other processes involving isomerisation with migration of molecular groups[15-17]. Examples of such reactions are presented below:



† [Usually referred to a Chemically Induced Dynamic Nuclear Polarisation in English (Ed. of Translation)].

In all these cases CINP of the migrating groups in the products was observed.

The reactions of alkyl halides with lithium alkyls have been investigated in greatest detail[18-25]. CINP has been observed in alkanes and olefins produced in the reactions and also in the molecules of alkyl halides; in the latter case CINP is shown in chemical chain reactions of the type $\dot{R} + XR \rightarrow RX + \dot{R}$. These results led to the conclusion that the reactions of alkyl halides with lithium alkyls have a radical mechanism, the first stage of which is probably a one-electron transfer.

CINP in chemical chain reactions has also been observed in the decomposition of peroxides in the presence of alkyl iodides[26], the chain processes being initiated by peroxide radicals.

Recently CINP was found in reactions of organomercury compounds, for example:

$$PhCH_2HgBr + Ph_3CBr \rightarrow PhCH_2CPh_3 + HgBr_2 ,$$

in which not only the protons of the products but also those of the initial triphenylmethyl bromide are polarised[27].

In reactions of a Grignard reagent with alkyl halides, the olefins and saturated hydrocarbons produced by the reaction of the alkyl radicals derived from the initial reaction components are polarised[28]: the observation of CINP in these reactions constitutes sufficient evidence to assume that the first stage is electron transfer from the Grignard reagent to the alkyl bromide[28].

A distinctive example of CINP in redox reactions is the emission by benzene in the reactions of phenyldiazonium salts with electron-donating reagents (alkalis, *p*-phenylenediamine, the phenoxide anion, and others)[29,30]. It is suggested that the reaction proceeds as follows:

$$PhN_2^+ \xrightarrow{D} (Ph\dot{N}_2) \rightarrow \dot{P}h + N_2 \rightarrow \text{benzene}.$$

CINP has also been observed in the products of many chemical reactions. The protons of anthraquinone were polarised in its photolysis[31]; it is postulated that CINP arises in the deactivation of the excited triplet state of the quinone to the singlet state. In the photolysis of benzophenone CINP was observed in the products of "cage" recombination[32]:

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^* + HR \rightarrow (Ph_2\dot{C}(OH)\ \dot{R}) \rightarrow Ph_2C(OH)-R .$$

In the photolysis of benzaldehyde, CINP (of the proton in the aldehyde group) was observed in addition to that of the products of the cage recombination of the above kind; it is believed that it arises as a result of chain reactions[33].

This brief description shows that the range of "reactions tested for CINP is fairly large. In most cases new, interesting, and frequently unexpected information about the reaction mechanisms, was obtained with the aid of CINP, and new concepts concerning the course of many chemical reactions have appeared and have become firmly established.

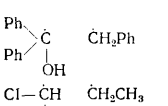
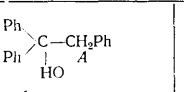
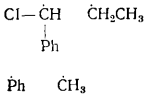
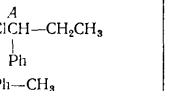
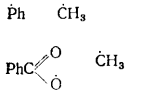
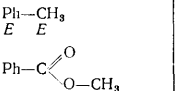
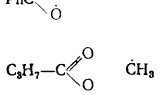
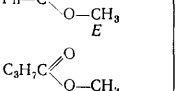
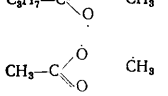
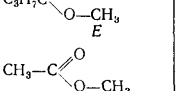
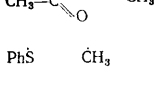
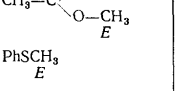
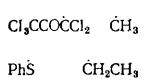
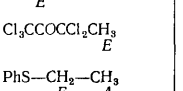
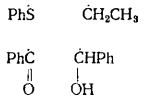
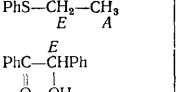
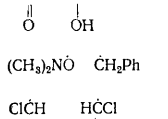
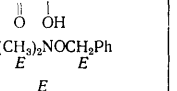
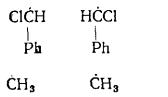
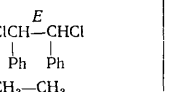
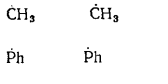
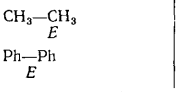
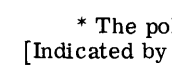
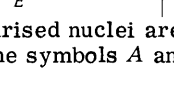
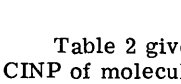
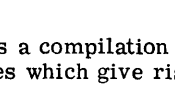
1. Characteristics of the Chemically Induced Polarisation of Hydrogen Nuclei

Reactions in which CINP has been observed are extremely varied. However, analysis of all the results obtained hitherto shows that CINP is determined mainly by the nature of the radical precursers of the product molecules and by the type of the elementary chemical

steps in which the products are formed. On this basis, a fairly simple and complete classification of nuclear polarisations is possible (Tables 1–4).

Tables 1 and 2 show the results on the CINP of the products formed in radical recombination steps. Table 1 summarises those cases where the polarisation of each group of equivalent protons is of the same sign—positive (*A*) or negative (*E*).

Table 1. CINP in recombination reactions (integral polarisation)*.

Recombining radicals	Product and sign of CINP	Reaction and conditions	References
		Photolysis of benzophenone, from triplet pair	32
		Reaction of $PhCHCl_2$ with LiC_2H_5	25
		Decomposition of peroxides	9
		Decomposition of peroxides	9
		Decomposition of peroxides	6
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Photolysis of aldehyde	33
		Meisenheimer rearrangement	14
		Reaction of $PhCHCl_2$ with LiC_2H_5	25
		Decomposition of peroxides	3,6,9
		Decomposition of peroxides	9

* The polarised nuclei are indicated in italics [Indicated by the symbols *A* and *E* (Ed. of Translation)].

Table 2 gives a compilation of the results for the CINP of molecules which give rise to NMR spectra with a multiplet structure. The spin multiplets in such molecules exhibit unusual behaviour, of a kind never observed before: the components of the multiplets in high and low fields correspond to polarisation of different signs. Thus the sign of the polarisation of any one group of equivalent nuclei depends on the spin state of another group of nuclei with which the observed group is involved in spin–spin coupling. Fig. 2 illustrates this unusual behaviour of multiplets in CINP, which has been called the multiplet effect (ME). The symbol *A/E* in Table 2 implies that the components at low field correspond to positive polarisation and those at high field to negative polarisation; the symbol *E/A* denotes the opposite situation. The multiplet effect is a property of CINP only and constitutes one of its most remarkable and distinctive features.

Table 2. CINP in recombination reactions (multiplet polarisation).

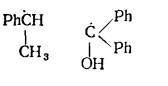
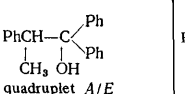
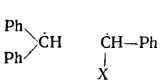
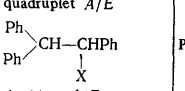
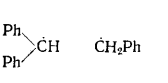
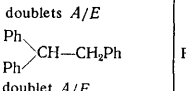
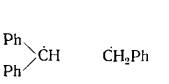
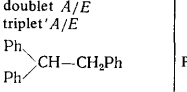
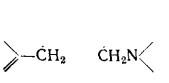
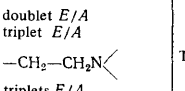
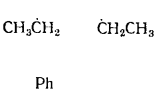
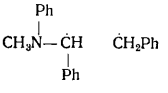
Recombining radicals	Product and sign of CINP	Reaction and conditions	References
	 quadruplet *A/E*	Photolysis of benzophenone, from triplet pair	32
	 doublets *A/E*	Photolysis of diphenyldiazomethane, from triplet pair	35
	 doublet *A/E* triplet *A/E*	Photolysis of diphenyldiazomethane, from triplet pair	35
	 doublet *E/A* triplet *E/A*	Photolysis of diphenyldiazomethane, from singlet pair	35
	 triplets *E/A*	Thermal isomerisation	15
	$CH_3CH_2CH_2CH_3$ triplet *E/A* quadruplet *E/A*	Decomposition of peroxides, reactions of LiC_2H_5 with C_2H_5I	3,21–23
	triplet *E/A* doublet *E/A*	Isomerisation	20

Table 3. CINP in scission reactions (integral polarisation).

Reaction	Product and sign of CINP	Reaction and conditions	References
$\dot{C}H_3+HR$	CH_4, *A*	Decomposition of peroxides	3,6,9
$\dot{C}H_3+ClR$	CH_3Cl, *A*	Decomposition of peroxides	3,6,9
$(CH_3)_3\dot{C}+HR$	$(CH_3)_3CH$ *E*	Decomposition of peroxides	3
$(CH_3)_3\dot{C}+ClR$	$(CH_3)_3CCl$, *E*	Decomposition of peroxides	3
$CH_3\dot{C}H_2+HR$	CH_3CH_3, *E*	Decomposition of peroxides	3
	$PhCH_2Cl$ *A*	Reaction of $PhCHCl_2$ with LiC_2H_5	25
$\dot{P}h+HR$	PhH, *E*	Decomposition of benzoyl peroxide	1,4,5
$\dot{P}h+HR$	PhH, *A*	Decomposition of acetyl benzoyl peroxide	9

As in recombination reactions, the products of abstraction reactions exhibit CINP of two types—integral and multiplet. Table 3 presents the results for the CINP in the products of the abstraction of H, Cl, etc. atoms. Here the polarisation of each group of equivalent nuclei is of one sign. It is interesting to note the behaviour of the methyl radical: it gives rise to negative polarisation in the recombination products and to positive polarisation in the products of abstraction reactions.

Thus the sign of CINP depends on the type of elementary chemical reaction from which the product is formed. Attention should also be drawn to the fact that the sign of CINP is positive for radicals with a negative hyperfine coupling constant ($\dot{C}H_3$, PhH_2) and negative for the $(CH_3)_3\dot{C}$ radical, which has a positive hyperfine coupling constant.

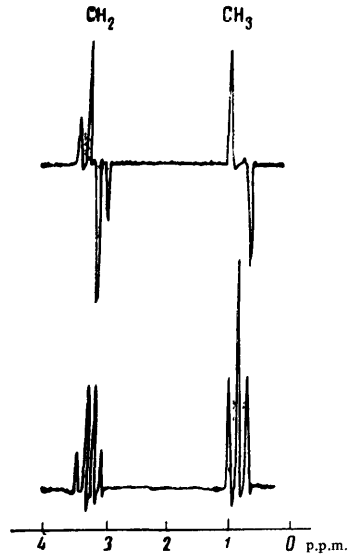


Figure 2. NMR spectrum of ethyl iodide with polarised nuclei in the reaction of ethyl lithium with alkyl iodides (the multiplet effect).

In the phenyl radical mainly the *ortho*-protons are polarised (in relation to the localised unpaired electron); the hyperfine coupling with these protons is in fact a maximum. This conclusion was based on analysis of CINP in the decomposition products of chloro-derivatives of benzoyl peroxide[8]. Trozzolo did not observe the CINP of pentadeuterobenzene in the decomposition of the fully deuterated benzoyl peroxide[8]; on this basis, it was concluded that the nucleus of the hydrogen atom transferred to the phenyl group is not polarised. The difference in the signs of the CINP of benzene in the decomposition of benzoyl and acetyl benzoyl peroxides is very remarkable (Table 3).

Table 4 summarises the results for the CINP of the products of abstraction reactions with a multiplet effect. The following relation governs the multiplet effect in abstraction reactions; a multiplet effect of type A/E is observed in the products, while in the reactants consumed (particularly in chemical relay reactions) the sign of the multiplet effect is reversed to E/A; a theoretical interpretation of these phenomena will be given below.

We may note that the sign of the multiplet effect as well as the sign of the integral polarisation depends on the type of reaction involving the formation of the product. Thus in ethyl chloride the multiplet effect has a sign corresponding to A/E, in butane to E/A, and in thiophenetole CH_3CH_2SPh (Table 1) the multiplet effect is completely absent, although the formation of all these products involves an ethyl radical.

In olefins produced by the disproportionation of radicals a multiplet effect is also observed; for example, the multiplet effect in propene is presented in Fig. 3.

Table 4. CINP in scission reactions (multiplet polarisation).

Reaction	Product and sign of CINP	Reaction and conditions	References
$CH_3\dot{C}H_2+ClR$	CH_3CH_2Cl A/E A/E	Decomposition of peroxides	3
$CH_3\dot{C}H_2+ICH_2CH_3$	CH_3-CH_2I A/E	Reaction of LiC_2H_5 with C_2H_5I	21, 22
$CH_3\dot{C}H_2+ICH_2CH_3$	CH_3-CH_2I E/A E/A	Decomposition of peroxides, chemical chain reaction	26
$(CH_3)_2\dot{C}H+ICH(CH_3)_2$	$(CH_3)_2CHI$ E/A E/A	Decomposition of peroxides, chemical chain reaction	26
$R\dot{C}H_2+ICH(CH_3)_2$	RCH_2I A/E	Decomposition of peroxides chemical chain reaction	26
$CH_3CH_2\dot{C}H_2+ClR$	$CH_3CH_2-CH_2Cl$ A/E A/E	Decomposition of peroxides	3
$CH_3CH_2\dot{C}H_2+IR$	$CH_3-CH_2-CH_2I$ A/E	Reaction of RI with LiR	20–24
$(CH_3)_2\dot{C}H+HR$	$CH_3CH_2-CH_3$ E/A E/A	Decomposition of peroxides	3
$(CH_3)_2\dot{C}H+ClR$	$(CH_3)_2$ $CHCl$ A/E A/E	Decomposition of peroxides	3
$(CH_3)_2\dot{C}H+IR$	$(CH_3)_2$ CHI E/A E/A	Reaction of RI with LiR, chemical chain reaction	22–24
$(\dot{C}H_3)_3\dot{C}+HR$	$(CH_3)_3$ CH A/E	Decomposition of peroxides, Grignard reaction	26, 28
$CH_3CH_2\dot{C}HCH_3+IR$	$CH_3CH_2\dot{C}HICH_3$ E/A	Reaction of RI with LiR, chemical chain reaction	24

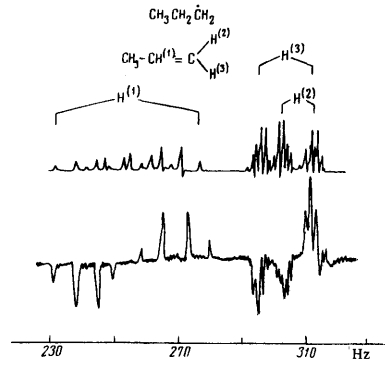


Figure 3. NMR spectrum of propene with polarised nuclei in the reaction of n-propyl iodide with butyl lithium.

The multiplet effect is of type E/A and in the spin multiplet of the proton $H^{(1)}$ only the outer doublet, corresponding to the $\alpha\alpha$ (negative polarisation of $H^{(1)}$) and $\beta\beta$ (positive polarisation of $H^{(1)}$) states of the $H^{(2)}$ and $H^{(3)}$ nuclei, is polarised. (The J_{12} and J_{13} coupling constants are positive). CINP of this type implies that the states $\beta\alpha\alpha$ and $\alpha\beta\beta$ are mainly populated in the molecules (in the series of the spin functions of $H^{(1)}$, $H^{(2)}$, and $H^{(3)}$). It is interesting that the nature of CINP in propene is independent of whether the propene is formed from the $CH_3CH_2\dot{C}H_2$

radical or from $CH_3\dot{C}HCH_3$. The nature of CINP in other olefins (butene, isobutene, etc.) is the same as in propene.

CINP has a number of surprising properties, which are not shown by the usual dynamic nuclear polarisation with radiofrequency pumping at the ESR frequency (see below). The multiplet effect and the dependence of the sign of the multiplet effect and the integral polarisation on the type of chemical reaction are two distinctive features of CINP.

2. The Magnitude of Chemically Induced Nuclear Polarisation.

A third remarkable feature of CINP is the large enhancement factor, greatly exceeding the limiting enhancement attainable in nuclear polarisation with radiofrequency pumping.

We shall now define the enhancement factor E of CINP in terms of the following equivalent relations:

$$E = \frac{M}{M_0} = \frac{I}{I_0} , \qquad (1)$$

where M is the nuclear magnetisation, I the NMR signal, and M_0 and I_0 are their equilibrium values. The value of E shows by what factor the nuclear magnetisation of the molecule exceeds the equilibrium Boltzmann magnetisation. The factor E is an important characteristic of CINP, which is necessary for the verification and experimental tests of any hypotheses and theories of CINP; its determination should be part of the study of CINP in any reaction.

It follows from the definition of E that the kinetics of CINP are associated, firstly, with the kinetics of the chemical reaction and, secondly, with the kinetics of the relaxation processes in the electronic and nuclear spin systems. The establishment of such a relation is of interest for a number of reasons: firstly, in order to be able to use CINP as a method for investigating the kinetics and mechanisms of chemical reactions; secondly, for predicting the kinetic reaction conditions necessary for the maximum development of the CINP expected in the given reactions; thirdly, for the investigation of the physical and chemical mechanisms of CINP.

In the general case the kinetics of CINP in any reaction are described by the equation[36,37]

$$\frac{dM}{dt} = E\frac{dM_0}{dt} - \beta(M - M_0) . \qquad (2)$$

Its first term determines the rate of accumulation of polarisation and is related to the kinetics of the reaction via dM_0/dt, the second term determines the rate of nuclear depolarisation, and $\beta = T_{1n}^{-1}$.

In principle, it is possible to solve Eqn. (2) for any kinetic reaction conditions. The simplest solution is obtained for first-order reactions of the type $A \xrightarrow{k} P$ (for example, decomposition, rearrangement, isomerisation, reactions etc.), when

$$\frac{dM_0}{dt} = \mu_n p_{n0} k A_0 e^{-kt} , \qquad (3)$$

where k is a first-order rate constant and μ_n the magnetic moment of the nucleus:

$$p_{n0} = th\frac{h\gamma_n H_0}{2kT} .$$

When condition (3) holds, solution (2) becomes

$$M(t) = \mu_n p_{n_0} A_0\left[\frac{Ek-\beta}{\beta-k}(e^{-kt} - e^{-\beta t}) - (1 - e^{-\beta t})\right] \qquad (4)$$

It is convenient to convert the magnetisation M into the NMR signal I [see Eqn. (1)] and into the experimentally determined effective enhancement factor K:

$$K = \frac{I(t) - I_{0\infty}}{I_{0\infty}} = \frac{Ek-\beta}{\beta-k}(e^{-kt} - e^{-\beta t}) - e^{-\beta t} \qquad (5)$$

(here $I_{0\infty}$ is the equilibrium signal at $t \to \infty$).

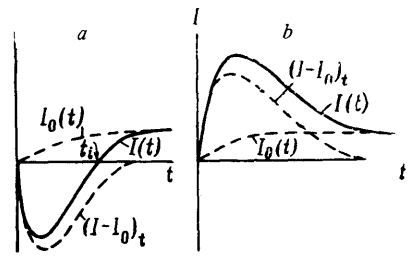


Figure 4. Theoretical CINP kinetic curves; *a*) negative CINP; *b*) positive CINP.

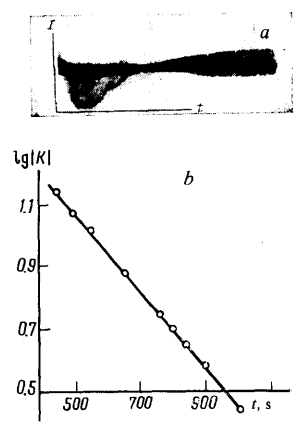


Figure 5. Kinetics of the CINP of protons in the methyl group of methyl benzoate in the decomposition of acetyl benzoyl peroxide: *a*) an experimental record obtained with a rapid scan; *b*) analysis of the kinetics in terms of Eqn. (7).

Fig. 4 presents the theoretical CINP kinetic curves and shows [as was to be expected from Eqn. (5)] that the rate of CINP passes through a maximum. The time required for the attainment of the maximum is

$$t_{max} = \frac{\ln\frac{(E-1)\beta}{Ek-\beta}}{\beta-k} . \qquad (6)$$

In the specific but very common case of fairly slow reactions ($k \ll \beta$), Eqn. (5) is

$$K = (EkT_{1n} - 1)e^{-kt} . \quad (7)$$

Fig. 5 presents an example of experimental CINP kinetics; the satisfactory agreement with the theoretical curve (Fig. 4) is evident. Fig. 5 also presents an analysis of CIPN kinetics on the basis of Eqn. (7); k and E can be immediately determined from a plot of lg $|K|$ against t.

In many cases it is convenient to saturate or invert the NMR signal during the course of the reaction by radiofrequency pulses[38]. This leads to a simplification of the initial kinetic equation (2). Thus at saturation $M - M_0 = 0$ and it is then easy to show that

$$E = \frac{(dI/dt)_{t \to t'}}{I_{\infty} k e^{-kt'}} . \quad (8)$$

Here t' is the instant of saturation (or signal inversion) and $(dI/dt)_{t \to t'}$ is the initial rate of recovery of the CINP signal after saturation (or inversion) (Fig. 6). It is significant that this method does not require a knowledge of the quantity ... [part of Russian text missing (Ed. of Translation)].

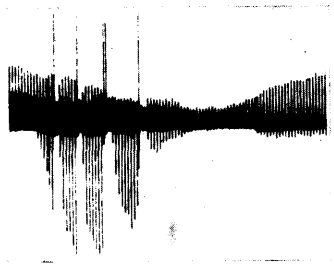
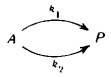


Figure 6. CINP kinetics with signal inversion by radiofrequency pulses.

In chemical kinetics situations very frequently arise where the same substance is formed by different pathways, some of which have a radical mechanism and lead to CINP, while others are non-radical and are not accompanied by CINP. Suppose, for example, that in the scheme



one of the pathways in the conversion of A into P with a constant k_1 leads to CINP, while the other pathway is non-radical.

In this case

$$K = \frac{Ek_1 + k_2 - \beta}{\beta - \Sigma k}(e^{-\Sigma kt} - e^{-\beta t}) - e^{-\beta t} , \quad (9)$$

where $\Sigma k = k_1 + k_2$. If the reaction is slow, i.e. $\Sigma k \ll \beta$, then

$$K = (Ek_1T_{1n} + k_2T_{1n} - 1)e^{-\Sigma kt} . \quad (10)$$

Using Eqns. (9) and (10) it is possible, in principle, to decide whether there really is a competition between radical and non-radical mechanisms and also to determine their kinetic parameters.

The CINP kinetics and their relation with the kinetics of chemical reactions have been considered in greatest detail by Buchachenko[39], who also examined various kinetic situations (consecutive and competing reactions, bimolecular reactions, etc.).

Eqn. (2) postulates, of course, that the product formed in the reaction, containing polarised nuclei, is not consumed in other reactions, is not precipitated, does not evaporate, etc. However, these conditions frequently break down and this must be borne in mind in the calculation of the factor E.

In particular, a method has been proposed[40] for the determination of E for a volatile product (a gas: methane, CO_2, etc.).

Finally, equations have been presented[36] for the kinetics of nuclear polarisation when, together with chemically induced polarisation, there is also radiofrequency pumping at the ESR frequency of the radicals involved in the reaction.

Table 5. Enhancement factors for CINP.

Molecule*	Type of CINP	Sign and magnitude of CINP**	References
C_6H_6	Integral	$-(80 \pm 10)$	42
CH_4	Ditto	$+10^3$	39
PhC(=O)OCH_3	»	$-(1600 \pm 100)$	42
CH_3—OC(=O)—$OCH(CH_3)_2$	»	$-(800 \pm 200)$	42
Ph, Ph, C—CH_2Ph, OH	»	$+(250 \pm 25)$	32
Ph, Ph, CH—CH_2Ph	A/E	$\pm(760 \pm 100)$ for $m_{CH_2} = \pm 1$	35
Ph, Ph, C—CH—Ph, OH, CH_3	A/E	$\pm(1300 \pm 200)$ for $m_{CH_3} = \pm 1/2$	32

* Polarised protons are designated by italic symbols.

** The enhancement factors were calculated per group of equivalent nuclei.

It is noteworthy that all the kinetic equations presented for the determination of E are independent of the mechanism of nuclear polarisation: E refers to a molecule or to a group of equivalent nuclei in the molecule. All the known values of E for CINP are listed in Table 5.

We may note that for integral polarisation the factor E in most cases greatly exceeds the maximum enhancement factors in nuclear polarisation with radiofrequency pumping (−330 for dipole relaxation and +660 for scalar relaxation[41]).

The factors E for multiplet CINP are also high. For example, for the proton in the CH group (last row of Table 5) the quadruplet lines with $m_{CH_3} = \pm\frac{1}{2}$ (inner lines) correspond to a polarisation of $\pm(1300 \pm 200)$.

The kinetic equations for CINP permit the use of such polarisation as a new kinetic method for the investigation of chemical reaction mechanisms, i.e. as a

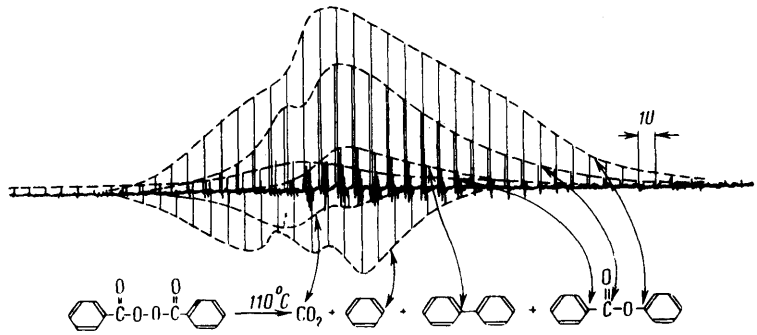


Figure 7. Kinetics of the chemically induced polarisation of ^{13}C nuclei in the decomposition of benzoyl peroxide in cyclohexanone at 110°C (proton signal saturated).

method for the determination of the rate constants and nuclear polarisation factors E. We may note that these equations are independent of the physical mechanism of CINP, since the physical information is contained in the factor E. The experimental determination of these factors and their relation with the lifetime of radicals and other experimental conditions (magnetic field strength, temperature, viscosity, the presence of radical acceptors, etc.) are important for the elucidation of the physical mechanism of CINP.

3. Chemically Induced Polarisation of ^{19}F, ^{13}C, and ^{31}P Nuclei

Tables 1–5 present the results for the chemically induced polarisation of protons. In a series of recent investigations, CINP of many-electron atoms was also observed. Fischer and coworkers [2] discovered the positive polarisation of ^{19}F in the decomposition of benzoyl peroxide in *p*-fluorobenzaldehyde and *p*-fluorostyrene. It was suggested that in the first case nuclear polarisation is induced chemically in the reaction products of aldehyde radicals of the type $-\dot{C}=O$ and in the second in the products of addition to styrene (polymerisation products). However, detailed studies on the nature of the products with CINP were not made.

Rakshys [43] observed chemically induced polarisation of ^{19}F nuclei in a fluoro-derivative of dibenzyl and in pentylbenzene (fluorine was successively substituted in the aromatic rings in the *ortho*-, *meta*-, and *para*-positions). These products were obtained by the reaction of fluorine-substituted benzyl fluoride with n-butyl-lithium. In contrast to the previous investigation, here chemically induced polarisation of ^{19}F nuclei exhibits a strong multiplet effect, which is fairly complex, so that it is difficult to interpret it unambiguously from the NMR spectra.

Chemically induced polarisation of ^{13}C nuclei forming part of the skeleton of organic molecules is of greatest interest. It was first observed [44] in the decomposition of benzoyl and acetyl benzoyl peroxides. Fig. 7 presents the kinetics of the chemically induced polarisation and the assignments of the polarised ^{13}C nuclei in the molecules. The chemically induced polarisations of ^{13}C and H nuclei are compared in Table 6. The differences in sign are discussed below.

It is remarkable that the carbonyl carbon atoms in the phenyl ester of benzoic acid and in carbon dioxide are polarised with different signs (Fig. 7) although both products are formed from the benzoyloxy-radical. Saturation of ^1H NMR (heteronuclear double resonance) does not influence the chemically induced polarisation of ^{13}C nuclei; the latter is [45] about 10^4 and, like chemically induced polarisation of protons, greatly exceeds the polarisation with radiofrequency pumping.

Table 6. Signs of the chemically induced polarisation of protons and ^{13}C nuclei.

Molecule	Group of atoms	Sign of CINP	
		protons	^{13}C
CH_4	CH_4	*A*	*E*
Ph—C(=O)—O—CH_3	CH_3	*E*	*A*
Ph—CH_3		*E*(*ortho*)	*A*(*ortho*)
	CH_3	*E*	*A*
		*E*	*E*

We may note finally that a recent communication [46] reports the observation of chemically induced polarisation of ^{13}P nuclei in various reactions involving phosphites, phosphates, and peroxides. The polarisation exhibits an extremely wide variety of signs and values but it is difficult to give a sufficiently reliable and unambiguous interpretation in these reactions owing to their complexity.

III. THEORY AND MECHANISM OF CHEMICALLY INDUCED NUCLEAR POLARISATION

The simplest mechanism of CINP depends on the Overhauser effect in free radicals during their lifetime—from the instant of generation to the instant of their conversion into diamagnetic products. This mechanism of CINP was in fact proposed in the early investigations [1,19].

We shall now examine the Overhauser effect in qualitative terms. Consider the simplest electronic-nuclear system consisting of one electron and one proton: its Zeeman levels are shown schematically in Fig. 8. If there is magnetic coupling between the unpaired electrons and the proton (isotropic or dipolar) in such a system, then in principle there exist four types of relaxation processes between the Zeeman electronic and nuclear levels: (1) purely electronic transitions when the magnetic quantum number of the electron M changes but the nuclear spin quantum number m does not; these are $\Delta M = \pm 1$ and $\Delta m = 0$ vertical transitions corresponding to ESR; (2) purely nuclear transitions--$\Delta M = 0$ and $\Delta m = \pm 1$ horizontal transitions (NMR transitions); (3) $\Delta M = \Delta m = \pm 1$ flip-flop transitions; (4) $\Delta M = -\Delta m = \pm 1$ flip-flop transitions. In the last two transitions there is simultaneous flipping of the spins of the electron and of the nucleus in the same or in the opposite directions; there is at the same time a change in the population of the Zeeman levels of the electronic and nuclear spin systems[47].

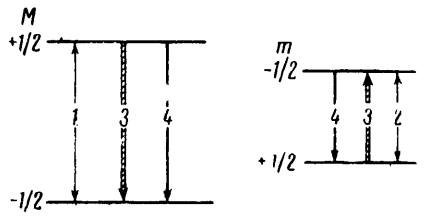


Figure 8. A schematic representation of the Zeeman levels and transitions in an electron–nucleus system with a spin of 1/2.

Usually in the observation of nuclear polarisation two frequencies are used: one for the saturation of the vertical transitions (ESR) and for the equalisation of the populations of the electron levels and the other for the detection of changes in the populations of the nuclear Zeeman levels (NMR). After the removal of the saturating field at the ESR frequency, the electronic Zeeman system tends to return to equilibrium, corresponding to the Boltzmann distribution of electron spins among the Zeeman levels. Then processes (1) are accompanied by transitions (4), in which there is an increase in the population of the lowest nuclear level (positive polarisation), and transitions (3), which increase the population of the highest nuclear level and can actually lead to inversion of the populations (negative polarisation). Positive polarisation predominates when the main contributions to relaxation come from isotropic hyperfine coupling and negative polarisation predominates when dipolar coupling is dominant. Negative polarisation is usually employed in radiofrequency masers[47].

In principle, nuclear polarisation may be induced by a chemical reaction and not radiofrequency pumping of the electronic levels. If the chemical reaction involves the formation of radicals, it may happen that the electronic Zeeman levels will have equal populations or, in the general case, non-equilibrium populations. Next a Boltzmann distribution of the populations of the electronic levels is established in the radical with an electronic relaxation time T_{1e} and a new population of nuclear levels (polarisation of nuclei) arises owing to transitions (3) and (4). If the radical is further converted into a molecule (by a chemical reaction) nuclear polarisation appears in the product molecule and is detected in it. It is then necessary that the lifetime of the radical τ_R should be longer than or comparable to T_{1e}, i.e. that there is sufficient time for the occurrence of the relaxation processes (3) and (4). However, τ_R must not be too long so that the nuclear polarisation can be transferred to the molecule before disappearing in the radical with a nuclear relaxation time $T_{1n}^{(R)}$. Thus $T_1 \ll \tau_R < T_{1n}^{(R)}$, or

$10^{-7}-10^{-6}$ s $< \tau_R < 10^{-4}-10^{-5}$ s.

Within the framework of the above mechanism, chemically induced polarisation differs from the usual polarisation only by the method of pumping to electronic Zeeman levels. If this mechanism of CINP is valid, there should be three main consequences.

1) The sign of the nuclear polarisation of the radical and hence the sign of the CINP of the product molecules into which it is converted is predictable on the basis of its chemical structure. Thus the radical $\dot{C}H_3$ should have negative polarisation, while in the $CH_3\dot{C}H_2$ radical one may expect positive polarisation of the protons in CH_3 and negative polarisation of the protons in CH_2, etc.

2) The products derived from the radicals should exhibit the polarisation established in the radicals and its sign should be determined solely by the nature of the radical and should be independent of its origin, of its further reactions, and of the nature of the product formed.

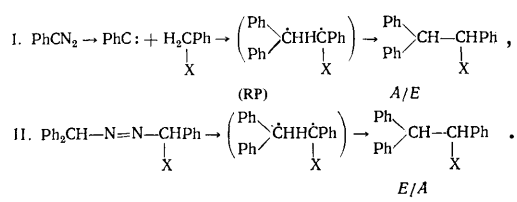
3) The magnitude of CINP should not exceed –330 for dipolar electronic-nuclear relaxation in the radical and +660 for scalar relaxation.

The three main characteristics of CINP formulated in the preceding section quite unambiguously contradict these conclusions. This implies that the mechanism of CINP based on the simple Overhauser effect cannot account for its characteristics and the relations which it exhibits. One must assume that elementary chemical steps involved in the generation and destruction of radicals are responsible for CINP and therefore the mechanism of such polarisation should be sought in the chemical steps.

1. Theory and Mechanisms of Chemically Induced Nuclear Polarisation Involving $S-T_0$ Transitions.

The concepts concerning the mechanisms of CINP arose from simple and elegant experiments by Closs and coworkers[48,49], in which the same products were obtained in different ways and CINP was observed in them. An example of the preparation of the same product in different ways is presented below. Pathway I consists of the decomposition (photochemical or thermal) of diphenyldiazomethane; this yields diphenylcarbene, which has a triplet ground state. One may assume that, regardless of the state in which the carbene is generated, during its lifetime it passes to the ground state and reacts in the triplet state, abstracting a hydrogen atom from a neighbouring molecule in the solution. This results in the formation of a radical pair (RP) in the triplet state, which can subsequently give rise to either recombination products (for this, a preliminary triplet–singlet transition in

the radical pair is necessary) or the radical pair can dissociate into individual radicals, which are released into the bulk phase:



Pathway II consists of the dissociation of the azo-compound accompanied by the liberation of a nitrogen molecule and the formation of the same radical pair as in the first case but only in the singlet state. Recombination of radicals with the radical pair yields the same product as in the first case.

Thus in the first case the precursor of the final reaction product is the radical pair in the triplet state and in the second case the radical pair in the singlet state. Different types of CINP in the final product correspond to the different spin multiplicities of the precursor: in the first case the multiplet effect in the CH−CH group corresponds to A/E and in the second to E/A.

Hence one can immediately conclude that a possible mechanism of CINP is a selection of nuclear-spin states in the radical pairs (precursors of the products) as a result of singlet−triplet transitions.

We shall now consider briefly the simplest theories of CINP based on $S-T$ transitions[48-52] in radical pairs. Suppose that we have the radical pair

$$(H\dot{R}_1\dot{R}_2)\begin{cases}\nearrow HR_1{-}R_2 & \text{(recombination)}\\ \searrow H\dot{R}_1+\dot{R}_2 & \text{(radical pair dissociation),}\end{cases}$$

which can either recombine or dissociate: suppose further that the radical pairs liberated participate in substitution reactions (for example, they abstract atoms from solvent molecules, becoming thereby converted into stable products).

We shall now calculate the probabilities of the transfer to the recombination products of an $H\dot{R}_1$ proton with a spin α_n and β_n. We shall consider the singlet state of the pair with the wave function $S = 1/\sqrt{2}(\alpha\beta - \beta\alpha)$ and the triplet state $T_0 = 1/\sqrt{2}(\alpha\beta + \beta\alpha)$ (other triplet states, T_{+1} and T_{-1}, will be disregarded at present, since they are separated from the S and T_0 levels by the energy of the electronic Zeeman interaction).

The complete wave functions of the pair consist of the combination of the states S and T_0:

$$\begin{aligned}\psi^+(t) &= [c_S^+(t)\,S + c_{T_0}^+(t)\,T_0]\,\alpha_n\,,\\ \psi^-(t) &= [c_S^-(t)\,S + c_{T_0}^-(t)\,T_0]\,\beta_n\,;\end{aligned} \qquad (11)$$

$c_S^{\pm}(t)$ and $c_{T_0}^{\pm}(t)$ determine the proportions of the states and the superscripts + and − refer to states with nuclear spins α_n and β_n respectively.

Suppose that the pair is initially in a triplet state, i.e. $|c_S^{\pm}(0)|^2 = 0$ and $|c_{T_0}^{\pm}(0)|^2 = 1$. The problem is to find the evolution of the triplet wave function in the system to the singlet wave function under the influence of the perturbing Hamiltonian:

$$\mathcal{H} = \beta H_0(g_1S_1 + g_2S_2) - JS_1S_2 + aIS_1\,. \qquad (12)$$

Here the first term describes the energy of the Zeeman interaction (g_1 and g_2 are the g-factors of the radicals in the pair), the second term is the exchange energy operator, and the third term describes the hyperfine interaction.

The exchange interaction in the pair alters as a result of fluctuations in the geometry of and the distances in the pair under the influence of thermal motion in the liquid; the mixing of the S and T_0 states takes place as a result of the difference between the Zeeman energy $(g_1 - g_2)\,\beta H_0$ and the hyperfine coupling energy.

The result of operation using the Hamiltonian (12) may be obtained by solving the Schrödinger equation for the coefficients $c_S^{\pm}(t)$ and $c_{T_0}^{\pm}(t)$. Then

$$\begin{aligned}c_S^{\pm}(t) &= -i\frac{{}^1/_2\beta H_0\Delta g \pm {}^1/_4 a}{D^{\pm}}\sin D^{\pm}t\,,\\ c_{T_0}^{\pm}(t) &= \cos D^{\pm}t - \frac{iJ}{D^{\pm}}\sin D^{\pm}t\,,\end{aligned} \qquad (13)$$

where $D^{\pm} = [(\frac{1}{2}\beta H_0\Delta g \pm \frac{1}{4}a)^2 + J^2]^{1/2}$.

The probability of the formation of the recombination product from the triplet pair at time τ is equal to the proportion of the S state $|c_S^{\pm}(\tau)|^2$ at this instant:

$$|c_S^{\pm}(t)|^2 = \frac{{}^1/_2\Delta g\beta H_0 \pm {}^1/_4 a}{(D^{\pm})^2}\sin^2 D^{\pm}\tau\,. \qquad (14)$$

By averaging over the lifetime of the radical pair, we finally obtain the rates of population of the nuclear-spin states in the recombination product:

$$w^{\pm} = k_0\frac{2\,(1/2\,\Delta g\beta H_0 \pm 1/4\,a)^2\tau^2}{1 + 4\,(D^{\pm})^2\tau^2}\,, \qquad (15)$$

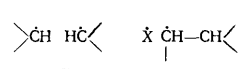
where k_0 is the overall rate of formation of the radical pair and τ is its lifetime.

It follows from Eqn. (15) that the rates of formation of molecules with hydrogen spins α_n and β_n are proportional to $(\Delta g\beta H_0 + \frac{1}{2}a)^2$ and $(\Delta g\beta H_0 - \frac{1}{2}a)^2$ respectively. Clearly the probabilities of observing the α or β spins of the proton in the molecule formed on recombination of the radical pair are different and depend on the magnitude and sign of $\Delta g = g_1 - g_2$ and the hyperfine coupling constants. Thus, when $\Delta g < 0$ and $a < 0$, we have $w^+ > w^-$, i.e. positive polarisation obtains in the recombination product from the triplet pair, while the radicals liberated from the radical pair and converted into other products in the bulk phase are negatively polarised.

If the initial pairs are in the singlet state, then $w^- > w^+$ since pairs with an α spin are more rapidly converted into the triplet state and then dissociate. In this case the recombination products are depleted in α spins and an excess of β spins remains, i.e. the polarisation is negative; positive polarisation now appears in the reaction products of the free radicals.

Thus for specified values and signs of a and Δg, the sign of CINP depends on the spin multiplicity of the radicals in the pair and hence on the spin multiplicity of the reacting species—the precursors of the radical pair.

Similarly it is possible to obtain expressions for the multiplet chemically induced nuclear polarisation by considering a radical pair of the type



The rates of population of different nuclear-spin states or the rates of $S-T_0$ transitions are proportional to

the squares of matrix elements of the type $\langle S|\mathcal{H}|T_0\rangle$ calculated with the Hamiltonians

$$\mathcal{H}_{\mathrm{I}} = \beta H_0 (g_1 S_1 + g_2 S_2) - J S_1 S_2 + a_1 S_1 I_1 + a_2 S_2 I_2 , \quad (16)$$

$$\mathcal{H}_{\mathrm{II}} = \beta H_0 (g_1 S_1 + g_2 S_2) - J S_1 S_2 + (a_1 I_1 + a_2 I_2) S_2 , \quad (17)$$

for pairs of types I and II respectively.

Table 7. Relative rates of $S-T_0$ transitions.

Nuclear-spin states	Pair (I)	Pair (II)
$\alpha_n\alpha_n$	$(\Delta g\beta H_0/2+a_1/4+a_2/4)^2$	$(\Delta g\beta H_0/2+a_1/4-a_2/4)^2$
$\alpha_n\beta_n$	$(\Delta g\beta H_0/2+a_1/4-a_2/4)^2$	$(\Delta g\beta H_0/2+a_1/4+a_2/4)^2$
$\beta_n\alpha_n$	$(\Delta g\beta H_0/2-a_1/4+a_2/4)^2$	$(\Delta g\beta H_0/2-a_1/4-a_2/4)^2$
$\beta_n\beta_n$	$(\Delta g\beta H_0/2-a_1/4-a_2/4)^2$	$(\Delta g\beta H_0/2-a_1/4+a_2/4)^2$

Table 7 lists the relative rates of population of various states of a system of two nuclei (protons) in the recombination product.

For example, when $a_1 < 0$ and $a_2 < 0$ and the initial type I radical pair is in the triplet state, the populations of the nuclear-spin states $\alpha_n\alpha_n$ and $\beta_n\beta_n$ in the recombination product $\rangle$CH−CH$\langle$ increase and the $\alpha_n\beta_n$ and $\beta_n\alpha_n$ states become depleted. This leads to the appearance of chemically induced nuclear polarisation with an A/E multiplet effect (the populations and polarisations are illustrated schematically in Fig. 9). A multiplet effect of this type was in fact observed by Closs[48] in the decomposition of diphenyldiazomethane. Clearly the sign of the multiplet effect in the reaction products of the radicals liberated from the radical pair is opposite to that of the multiplet effect in the recombination products, since the nuclear states $\alpha_n\beta_n$ and $\beta_n\alpha_n$ in the liberated radicals become enriched.

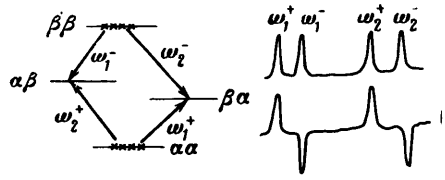


Figure 9. Schematic representation of multiplet CINP in the $\rangle$CH−CH$\langle$ molecular fragment from a triplet radical pair.

Within the framework of the theory of chemically induced nuclear polarisation involving $S-T_0$ transitions in radical pairs, it is possible to predict the signs of the integral CINP and of the multiplet effect as a function of the signs of Δg and a; these results are summarised in Tables 8 and 9.

It is now possible to make a number of generalisations concerning CINP.

1. The integral polarisation and the multiplet effect in the products of the recombination of the radicals in pairs and of the reactions of free individual radicals should have opposite signs.

Table 8. Integral CINP in recombination products.

Multiplicity of radical pair	$\Delta g<0,\ a<0$ $\Delta g>0,\ a>0$	$\Delta g<0,\ a>0$ $\Delta g>0,\ a<0$
Singlet	*E*	*A*
Triplet	*A*	*E*

A—positive polarisation (absorption).
E—negative polarisation (emission).

2. If $\Delta g = 0$ in the pair, only multiplet CINP should be observed, its value being proportional to a^2; if $\Delta g \neq 0$, integral CINP proportional to $\Delta g\beta H_0 a$ should be observed. Frequently both types of CINP may be observed.
3. The signs of the integral CINP and of the multiplet effect depend on those of Δg and a (as shown in Tables 8 and 9) and also on the type of radical pairs [(I) or (II)] and their spin multiplicity.

Table 9. Multiplet CINP in recombination products.

Multiplicity of radical pair	Pair (I)		Pair (II)	
	$a_1<0,\ a_2<0$	$a_1<0,\ a_2>0$	$a_1<0,\ a_2<0$	$a_1<0,\ a_2>0$
Singlet	*E*/*A*	*A*/*E*	*A*/*E*	*E*/*A*
Triplet	*A*/*E*	*E*/*A*	*E*/*A*	*A*/*E*

Extensive experimental data have now been obtained in various laboratories, which makes it possible to verify the consequences and characteristics of CINP formulated above. It was found that in the vast majority of cases the experimental data are consistent with these consequences, i.e. at least in the region of high fields (of the order of several thousand gauss) the mechanism based on $S-T_0$ transitions in radical pairs generates CINP fairly effectively and gives a correct qualitative description of its characteristics.

2. Analysis of the Mechanisms of Chemical Reactions from the Standpoint of Chemically Induced Nuclear Polarisation

We shall now consider the significance of CINP for chemistry and chemical physics.

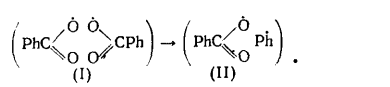
1. In the first place the very fact of the observation of CINP indicates the presence of radical stages in the reaction, i.e. the involvement in the reaction of intermediate paramagnetic species—ions or radicals. In this sense detection of CINP has become a new and powerful method for the investigation of the mechanisms of chemical reactions.

2. The appearance in chemical reactions of CINP with the properties described above implies that the reactions involve the formation of radical pairs. It is also possible to determine whether the g-factors of the radicals differ, whether there is hyperfine coupling, and the type of the radicals in the pair [(I) or (II)]. Moreover, at the present time CINP is used with increasing frequency as a quantitative method for the determination of the g-factors of the radicals in the pair (or their differences) and also the values and signs of the hyperfine coupling constants.
3. When the values of a and Δg for the radicals in the pair are known, it is possible to determine from the signs of the integral CINP and of the multiplet effect the spin multiplicity of the radical pairs (precursors of the products) and hence the spin multiplicity of the reacting species generating the radical pairs. Analysis of CINP shows that thermal and photochemical decomposition reactions of peroxides and azo-compounds take place in the singlet state and that the primary radical pairs are in this state. Singlet pairs are also formed in thermal rearrangement and isomerism reactions, in the Wurtz and Grignard reactions, and others. Photochemical decomposition of peroxides sensitised by ketones and also thermal decomposition of diazo-compounds take place with formation of primary triplet pairs. The multiplicity of the reacting species is an extremely important characteristic of the reaction mechanism and this information is carried by CINP.

Above (see p. 808) it was shown how Closs and coworkers obtained the same products from singlet and triplet radical pairs. The third method consisted in an independent generation of the same radicals as separate species, new radical pairs with so called non-correlated spins being subsequently generated in the encounters between these radicals in solution. Since the S and T_0 states are being produced statistically in the same way, one may assume that CINP should not be observed in the products from such secondary radicals of pairs (the CINP in the singlet and triplet pairs should mutually cancel out). However, experiments showed that the recombination products from secondary pairs exhibit the CINP characteristic of triplet pairs[52]. This implies that the lifetime of the triplet pairs is longer than that of the singlet pairs and consequently the steady-state concentration of the triplet pairs in solution is higher than that of the singlet pairs. This is an important and non-trivial result for the dynamics of chemical reactions.
5. It follows from the previous two conclusions that the products obtained from primary radical pairs and those generated from secondary radical pairs, i.e. from pairs of freely colliding radicals, may be resolved. This permits a deeper and more detailed understanding of the chemistry of the processes, i.e. the mechanisms of the chemical reactions.

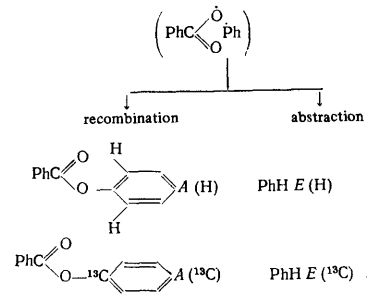
We shall now consider the mechanisms of a number of reactions from the standpoint of CINP.

The decomposition of benzoyl peroxide takes place with formation of a radical pair:



(I) (II)

The radical pair (I) can be either converted into (II) or can recombine with formation of the initial molecule. Such recombination is well known from experiments involving the transfer of an ^{18}O tracer from the carbonyl to the ester group[53]. However, neither H nor ^{13}C nuclei show CINP, since $\Delta g = 0$ in pair (I). In pair (II) $\Delta g \neq 0$ and CINP should obtain in its reaction products:



In the phenyl radical $a_{^{13}C} > 0$, $a_{H(ortho)} > 0$, and $g_{PhCOO} > g_{Ph}$ and consequently the signs of the chemically induced polarisation of the H and ^{13}C nuclei in the recombination products correspond to recombination in a singlet pair (Table 8). In benzene formed from the liberated radicals the CINP is of the opposite sign, as predicted by the theory.

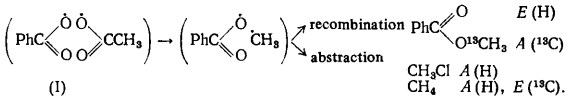
There is reason to believe that $a_{^{13}C} < 0$ ($\rho^{\pi}_{^{13}C} < 0$, as in the allyl fragment) in the $Ph^{13}C(=O)O\cdot$ radical, so that the ^{13}C nucleus in the product of the recombination of this radical with the phenyl radical in pair (II) should exhibit positive chemically induced polarisation if pair (II) is in the singlet state. This prediction is found to be valid (Fig. 7). Moreover, in the radicals $Ph^{13}C(=O)O\cdot$ liberated from the pair ^{13}C should be negatively polarised and, in the decarboxylation of these radicals, the CO_2 molecules should be negatively polarised; this prediction is also fulfilled (Fig. 7).

Thus the signs of the chemically induced polarisation of the H and ^{13}C nuclei in the principal thermal decomposition products of benzoyl peroxide show that the decomposition takes place in the singlet state. The same signs are observed in direct photolysis and photochemical decomposition sensitised by aromatic hydrocarbons, which implies that the decomposition in this case proceeds via excited singlet states. In the photochemical decomposition sensitised by ketones having the energy of the lowest triplet level (>56 kcal mole^{-1}), the signs of CINP in the decomposition products are reversed (for instance benzene protons are positively polarised and the *ortho*-protons of the phenoxy-ring in phenyl benzoate are negatively polarised). This implies that the decomposition of the peroxide in the presence of ketones proceeds via the triplet state[54,55].

We may note that, according to theory, chemically induced polarisation of the nuclei in the adjacent carbon atoms of the two benzene rings of biphenyl should have the same sign as in benzene if both these products are obtained from phenyl radicals liberated from the primary singlet pair (II). In fact the sign of the chemically induced polarisation of the ^{13}C nucleus in biphenyl is opposite to that of the ^{13}C nucleus in benzene. This implies that benzene is mainly obtained directly from the radicals liberated from the pairs, whereas biphenyl is obtained from radicals which had sufficient time after

liberation from the primary pair to be involved in collisions with other radicals of the type $PhC(=O)O\cdot$. In such secondary pairs with non-correlated electron spins CINP of the same sign as in triplet pairs is generated. Thus the "short-lived" phenyl radicals are converted into benzene and the "long-lived" radicals participate in secondary collisions and yield biphenyl with chemically induced polarisation of ^{13}C nuclei of the opposite sign.

Acetyl benzoyl peroxide is decomposed by the same mechanism:



(I)

Evidently the signs of CINP in the CH_3 group of the recombination products correspond to their formation from a singlet pair (see Table 8; $\Delta g < 0$, $a_H < 0$, and $a_{^{13}C} > 0$).

CINP in the reaction products of radicals liberated from pair II has the opposite sign (in agreement with theory). It is interesting that, as for biphenyl, the ethane formed in the decomposition of benzoyl peroxide is negatively polarised (in contrast to methane). This implies that methane (and CH_3Cl) are formed from the "short-lived" methyl radicals, whereas ethane is formed mainly from the "long-lived" radicals involved in secondary (triplet) collisions in which they acquire negative polarisation.

We shall now consider the mechanism of the reactions of secondary radicals generated in the decomposition of benzoyl peroxide in the presence of various additives. Fischer and coworkers investigated CINP in the decomposition of benzoyl peroxide in the presence of a mixture of molecules of different types (RX and R'X'); the free radicals $\dot{R}$ and $\dot{R}'$ appeared in the system independently under these conditions [56]. The signs of CINP in the asymmetric recombination products R–R' corresponded to the case where the same products were produced from triplet pairs. This implies that the recombination of independently generated radicals takes place in the pairs with non-correlated spins (in agreement with the results of Closs and coworkers [52]; (see p. 808 above).

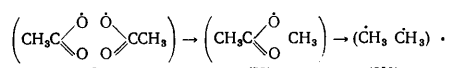
The signs of CINP in the reaction products of radicals liberated from asymmetric pairs (i.e. in R'R', RR, R'X, and RX') are opposite to those of CINP in the asymmetric recombination products (as would be expected from the theory of CINP with $S-T_0$ transitions).

Rykov et al. [34] investigated the decomposition of benzoyl peroxide in the presence of methyl iodide. Here $\dot{C}H_3$ radicals were generated independently and it might have been expected that in the CH_3 group of methyl benzoate and in methane the signs of CINP should correspond to *A* and *E* respectively (as in the products formed from pairs with non-correlated spins). In fact it was found that the signs of CINP in these products correspond to *E* and *A*, i.e. as in the products from singlet pairs. In order to account for this effect, one may assume that the radicals $PhC(=O)O\cdot$ (or $\dot{P}h$) react with CH_3I in the primary pair (I) or (II); this involves the immediate formation of the singlet secondary pair ($PhC(=O)O\cdot\ \dot{C}H_3$) resembling pair (II) in the decomposition of acetyl benzoyl peroxide.

CINP of the CH_3 protons in methyl benzoate and in methane arises in this secondary pair. CINP in ethane and in the CH_3 group of toluene is negative, which is consistent with the formation of these products from the "long-lived" CH_3 radicals, i.e. from pairs with non-correlated spins.

The hypothesis that the primary pair is immediately converted into a secondary pair is equivalent to the hypothesis of a comparatively high reactivity of radicals in the primary pairs. Subsequently we shall consider other examples consistent with this hypothesis.

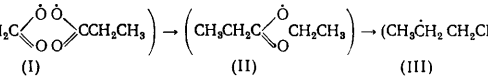
The decomposition of acetyl peroxide takes place with successive formation of pairs:



(I) (II) (III)

In the OCH_3 group of methyl acetate and in CH_4 (or CH_3Cl) the signs of CINP correspond to *E* and *A* respectively; this implies that these products are formed mainly from the singlet pairs (II). However, in the products of the recombination of CH_3 with solvent radicals ($PhSCH_3$ in thiophenol and $CH_3-CCl_2COCCl_3$ in hexachloroacetone), the signs of CINP of the CH_3 groups should be positive, since these products should be formed from pairs with non-correlated spins (random collisions). In fact the signs of CINP of these products are negative (as in singlet pairs). Thus here too one must assume that the radicals in the primary pairs exhibit an enhanced reactivity and therefore the primary pairs are rapidly converted into secondary singlet pairs of the type ($\dot{C}H_3\ \dot{S}Ph$) or ($\dot{C}H_3\ \dot{C}Cl_2COCCl_3$). CINP of ethane is negative. Its origin can be explained if it is assumed that the ethane is formed from the pair (III) and the polarisation in the latter persists from the preceding pair. Possibly this is also the explanation of the CINP of biphenyl formed from benzoyl peroxide.

The decomposition of propionyl peroxide is interesting:



(I) (II) (III)

The decomposition proceeds via singlet pairs, because in butane the sign of the multiplet effect corresponds to *E/A* and in CH_3CH_2Cl [the reaction products of the $CH_3\dot{C}H_2$ radical liberated from the pair (II) or (III)] the multiplet effect has the opposite sign (corresponding to *A/E*). In the photochemical decomposition of this peroxide sensitised by ketones the signs of the CINP of these products are reversed [54], which implies that the decomposition proceeds via an excited triplet state.

$PhS-CH_2CH_3$ with CINP of the CH_2 (*E*) and CH_3 (*A*) groups is formed in the decomposition of propionyl peroxide. The signs of CINP correspond to the formation of this product from the singlet pair ($\Delta g < 0$, $a_{CH_2} < 0$, $a_{CH_3} > 0$) and not from pairs with non-correlated spins as would have been expected. Thus here too one must assume that the primary singlet pairs are rapidly converted into secondary pairs, i.e. the reactivity of the radicals in the primary pairs is enhanced, so that their reactions in the pair successfully compete with the liberation of the radicals from the pair by diffusion.

We shall now consider CINP in chemical chain reactions. The iodide $CH_3(CH_2)_9CH_2I$ with an *A/E* multiplet effect is formed in the decomposition of undecyl peroxide $[CH_3(CH_2)_9CH_2COO]_2$ in the presence of ethyl iodide [26]. This corresponds to the liberation into the bulk phase of the radical $CH_3(CH_2)_9\dot{C}H_2$ from the primary singlet pair.

At the same time $CH_3\dot{C}H_2$ is generated and is in turn transformed by a chemical chain reaction into ethyl iodide with an E/A multiplet effect. This sign of the multiplet effect arises in radicals liberated from pairs with non-correlated spins. Thus ethyl radicals produced in the decomposition of the peroxide undergo random collisions and form pairs with non-correlated spins. On liberation from such pairs, they acquire multiplet E/A CINP and, on being converted into ethyl iodide, transfer this polarisation to the molecule of the latter.

This mechanism accounts for the previously mentioned (p. 804) characteristics of CINP in chain reactions: the signs of the multiplet effect in the products formed and in the reactants consumed (iodides) are opposed. The explanation is that the products are generated from singlet pairs and CINP in the reactants arises in radical pairs with non-correlated spins.

The CINP of the iodides formed and consumed in Wurtz reactions can be explained in the same way. Thus, in the reaction of CH_3CH_2Li with $(CH_3)_2CHI$, ethyl iodide has a multiplet effect with the sign corresponding to A/E and isopropyl iodide has the sign corresponding to E/A. Other examples are presented in Table 4.

It is interesting that in the reaction of ethyl-lithium with ethyl iodide both radicals are identical and the opposite signs of the multiplet effects in the ethyl iodide molecules consumed and formed should cancel out. In fact a multiplet effect with the sign corresponding to A/E is observed, which implies that the CINP of ethyl iodide formed from the primary singlet pair predominates.

Analysis of the CINP of the products of the Wurtz reaction, thermal isomerisation, and rearrangements shows that the products are formed mainly from primary pairs on disproportionation or recombination and their CINP is generated in the primary pairs. The results for CINP show that, as in the thermal decomposition of peroxides, the primary pairs in the Wurtz and thermal isomerisation reactions are in the singlet state.

3. Mechanisms of the Chemically Induced Nuclear Polarisation Involving $S-T_{-1}$ Transitions.

The behaviour of the singlet and triplet levels in molecules dissociating into radicals (or conversely in a pair of recombining radicals) is shown in Fig. 10. The above mechanism of CINP in radical pairs involving $S-T_0$ transitions postulates that the distances R between the radicals in the radical pair are fairly large, i.e. one considers radical pairs beyond the point of intersection of the S and T_{-1} levels when the S and T_0 levels converge closely and the T_{-1} levels are separated by the Zeeman interaction energy. In $S-T_0$ transitions the nuclear spins are not inverted and there is only a selection, i.e. sorting of the radicals with respect to nuclear spins, some of which, with a specific orientation of the nuclei, pass to the recombination products, while others, with the opposite orientation of the nuclei, are liberated into the bulk phase and are converted into other molecules. $S-T_0$ transitions are induced by changes in the exchange energy J in fluctuations of the distances in the radical pairs and are due to the secular component of the hyperfine coupling. Thus in $S-T_0$ transitions the elementary chemical step itself does not give rise to polarisation. However, CINP can be generated also by another mechanism, namely one involving $S-T_{-1}$ transitions which are due to the non-secular component of the hyperfine coupling, $\mathcal{H}_{\text{non-sec}} = \frac{1}{2}a\,(I_+S_- + I_-S_+)$, and which are accompanied by a reorientation of the nuclear spins in the recombination or dissociation step.

The $S-T_{-1}$ transition should be particularly effective at the quasi-intersection point of these levels (Fig. 10). The point is at $R \simeq 3-4$ Å‡.

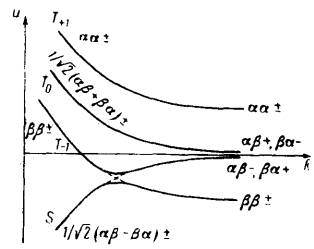


Figure 10. Behaviour of energy levels in the radical pair.

Fig. 10 shows on the left the states of molecules or radical pairs and on the right the states formed non-adiabatically (i.e. when the point of intersection is rapidly traversed). If the motion along the levels takes place slowly and adiabatically, then, for example in dissociation in the singlet state, the matrix elements $\langle\alpha\beta^-|\mathcal{H}_{\text{non-sec}}|\beta\beta^+\rangle$ are not zero and consequently triplet pairs will be enriched in the $\beta\beta^+$ states and singlet pairs will be depleted in the $\alpha\beta^-$ states. This implies that in the products of the recombination of singlet pairs there will be an excess of nuclear spins with negative polarisation and in the radicals liberated from triplet pairs there will be positive polarisation. Clearly in this case the reaction plays an active role in the generation of CINP, since the nuclei are reoriented in the elementary chemical recombination steps itself.

According to this mechanism, the sign of CINP should be independent of the signs of a and Δg (in contrast to the mechanism involving $S-T_0$ transitions). These features make it possible to distinguish these two mechanisms. Analysis of the experimental data shows that in high fields the mechanism with $S-T_0$ transitions mainly operates. This means that the dissociation and recombination processes take place non-adiabatically, i.e. the point of intersection of the levels is traversed rapidly and apparently only once. This conclusion is important for the understanding of the physical mechanisms of chemical processes.

Evidently in weak fields (of the order of tens or hundreds of gauss when the Zeeman interaction is comparable to the hyperfine interaction) the point of intersection of the levels is displaced to the region where $R \simeq 6-8$ Å; clearly in this region the contributions of $S-T_{-1}$ transitions to the generation of CINP will increase appreciably owing to the repeated traversing of the point of intersection in the fluctuations of the geometry of the radical pair. In general, in weak fields all $S-T$ transitions will contribute to CINP.

‡ This quantity may be estimated from the approximate relation $J \simeq J_0 e^{-\alpha R}$, where J_0 is the exchange integral corresponding to the bond energy, J is of the order of magnitude of the energy of the Zeeman interaction, and $\alpha \simeq 1$ Å^{-1}.

This is also indicated by the behaviour of the sign of CINP as a function of field strength. Thus, it has been shown[9,57] that in the decomposition of benzoyl peroxide benzene protons are positively polarised in weak fields. This polarisation increases with field strength to a maximum at 20 G and then falls, reaching zero at about 100 G. When $H_0 > 100$ G, CINP becomes negative. A change in the sign of CINP as a function of the field has also been observed in many other investigations. In all these cases the reaction was performed in weak fields (outside the magnetic field of the NMR spectrometer) and the specimen was then rapidly transferred to the NMR transducer of the spectrometer and CINP generated in weak fields was detected in high fields. In one study[5] the reaction (decomposition of benzoyl peroxide) was carried out and CINP was detected in fields of 30–47 G. The observed CINP was negative, but this result does not contradict other data[8,57], since in NMR detection in weak fields the overall NMR signal of all kinds of protons is observed and one cannot rule out the possibility that the main contribution to the NMR signal comes from the negative CINP of products other than benzene.

The next step in the theory of CINP will probably consist in a correct allowance for all the transitions in radical pairs and the calculation of their probabilities. In chemical kinetics, the solution of this problem will yield information about the states and interactions in radical pairs, about the dynamics of the motion of radicals in the pair, and about the probability of the recombination or collision of the radicals.

4. Chemically Induced Nuclear Polarisation in Atom Transfer Steps

The CINP of products of substitution reactions (or atom transfer reactions) has the same properties as in recombination (Tables 3 and 4). The mechanisms of CINP were examined in the preceding Sections. They are based on the hypothesis of $S-T$ transitions in the radical pairs, the dissociation of which gives rise to free radicals with polarised nuclei. These mechanisms have received reliable experimental confirmation.

However, the problem of whether CINP can be generated in elementary atom transfer steps and whether there are mechanisms capable of generating CINP in such steps is significant. The idea that CINP can arise in atom transfer steps was put forward by Rykov et al.[34] It arose from the following experimental finding: in the decomposition of peroxides in carbon tetrachloride, chloroform with negative CINP is detected. It was postulated that this polarisation arises in the steps involving the abstraction of hydrogen atoms by $\dot{C}Cl_3$ radicals from solvent molecules. However, this evidence is not unambiguous; CINP could arise in chloroform owing to the disproportionation of radicals in radical pairs by the mechanism discussed above (p. 809).

We have seen that in recombination reactions selection with respect to states takes place in triplet–singlet transitions. By analogy with recombination, the involvement of excited states in atom transfer steps can also be postulated. Such an analogy was drawn by Gerhart and Osterman[58].

The transition state in the transfer reaction $\dot{R} + XR' \rightarrow RX + \dot{R}'$ is regarded formally as a set of three radicals ($\dot{R}X\dot{R}'$) in the doublet state. As in the recombination reactions, the mixing of multiplet states owing to hyperfine coupling is considered and by analogy only the secular component of the isotropic hyperfine coupling is taken into account as a perturbation and the non-secular component and dipole–dipole interactions of the radical spins are neglected. The starting point in this treatment is the concept of a symmetrical wave function (s) of the transition state. Next follows the hypothesis that the decomposition of the state (activated complex) into the final products is facilitated by the mixing of the symmetrical (s) and antisymmetric (a) states owing to isotropic hyperfine coupling. Such mixing leads to the preferential population of levels with a minimum overall projection of nuclear spins (as in the recombination steps in the singlet state).

The introduction of antisymmetric spin states is equivalent to allowance for the excited states of the activated complex (by analogy with $S-I$ transitions in radical pairs in recombination). This hypothesis has evident consequences for CINP.

1. In the product RX of the reaction $R + XR' \rightarrow RX + \dot{R}'$ the states with the minimum overall projection of nuclear spins will be more populated and therefore in R'X these states will be depleted. This implies that the signs of the multiplet effect will be opposed and will correspond to A/E in RX and to E/A in R'X. This behaviour does indeed obtain (see Table 4 and the relevant comments).
2. The sign of the multiplet effect can also change when the direction of the reaction alters, i.e. the reaction $R + XR' \rightarrow \dot{R}X + R'$ is transformed into $\dot{R}' + XR \rightarrow R'X + \dot{R}$. This corollary has not been tested directly.
3. If R' = R, the multiplet CINP should be zero. This corollary hardly ever holds.
4. The enhancement factor E should depend on the nuclear spin in the multiplet because the probabilities of the transitions between the symmetrical and antisymmetrical states in the activated complex depend on the hyperfine interaction energy.

Despite the apparent confirmation of the idea of transitions between symmetrical (s) and antisymmetric (a) states there are two arguments which give rise to serious doubts about the validity of this mechanism.

Firstly, $s-a$ transitions are considered only in the step involving the decomposition of the activated complex. However, reverse transitions of the same type should occur in the formation of the activated complex, which should apparently lead to the cancellation of CINP in the atom transfer step.

Secondly, the magnitude of CINP should depend on the difference Δ between the energies of the s and a states and should be defined by the approximate relation $E \simeq a/\Delta$. Since $a \simeq 10^8-10^9$ s^{-1} and $E \simeq 10^3$, it follows that $\Delta \simeq 10^{11}-10^{12}$ s^{-1}. Thus, to be effective, the mechanism of CINP invoking excited states of the activated complex must involve the mutual approach of the ground and excited levels to within an energy of the order of a vibrational quantum. It is unlikely that such a situation can be realised; the real energy is of the order of one electron-volt.

Thus CINP in atom transfer steps can hardly be explained by invoking excited states of the activated complex. The problem of the intrinsic mechanisms of CINP in steps involving the transfer of atoms from the molecule to the radical remains open.

IV. CHEMICALLY INDUCED ELECTRONIC POLARISATION

Chemically induced electronic polarisation (CIEP) is revealed in the ESR spectra of atoms and radicals.

As in CINP, the polarisation of electrons is of two types - multiplet and integral. CIEP was observed for the first time by Fessenden and Schuler[59] in the ESR spectrum of hydrogen atoms in the radiolysis of liquid hydrocarbons: the low field component of the doublet corresponded to emission and the high field component corresponded to strong absorption. The hyperfine coupling constant for the hydrogen atom is positive and therefore the above spectrum implies that the hydrogen atoms are generated predominantly in the $\alpha\alpha_n$ and $\beta\beta_n$ spin states (the first symbol denotes the spin function of the electron and the second of the proton; the α-electron is oriented along the field and occupies the upper Zeeman level, because $\gamma_e < 0$). The $\alpha\alpha_n$ states give rise to an emission spectrum and the $\beta\beta_n$ states to an absorption spectrum (multiplet effect of type E/A). An analogous spectrum with multiplet polarisation was obtained for deuterium atoms[59].

Initially this effect was not understood; an attempt was made to attribute it to the technical conditions in the observation of ESR (modulation amplitude and phase, level of microwave power, etc.). However, five years after the publication of the paper of Fessenden and Schuler[59] a similar multiplet effect was observed by Smaller et al.[60] in the ESR spectra of radicals in the pulse radiolysis of liquid hydrocarbons. Thus all the low field components of the ESR spectrum of cyclopentyl radicals with $m_\alpha = \pm\frac{1}{2}$ and $m_\beta > 0$ corresponded to emission and all the high field components with $m_\alpha = \pm\frac{1}{2}$ and $m_\beta < 0$ corresponded to absorption (m_α and m_β are the quantum numbers of the projections of the nuclear spins of the α- and β-hydrogen atoms in the radical). Since the hyperfine coupling constant for β-protons is positive, such a spectrum corresponds to exactly to the same population of the electronic-nuclear spin levels as in hydrogen and deuterium atoms: the electron with an α-spin "escapes" to nuclei with α-spins and the electron with a β-spin "escapes" to nuclei with β-spins. One may postulate that, for a negative hyperfine coupling constant, the $\alpha\beta_n$ and $\beta\alpha_n$ states will be populated preferentially.

It was also shown[60] that the multiplet ESR spectrum is converted into the usual spectrum over a period of several microseconds. The kinetics of the variation of the emission signal from one of the hyperfine components are presented in Fig. 11. As in CINP (p. 805) a polarisation maximum is observed; the electronic relaxation times may be determined from the rate of depolarisation: they vary in the range 6–60 μs and depend on m_β, i.e. on the hyperfine interaction energy.

The problem of the mechanism of the multiplet polarisation of electrons will now be considered. If radicals are formed in the dissociation of molecules, all the processes occurring under these conditions can be treated as in recombination, i.e. the concept of $S-T$ transitions in dissociating radical pairs may be invoked (by analogy with the previous treatment of CINP in terms of recombining pairs). Then $S-T_0$ transitions will lead to multiplet CIEP, while $S-T_{\pm 1}$ transitions can give rise to appreciable integral CIEP; in this case there is clearly a complete analogy with the mechanisms of CINP in recombination products.

The difference consists in the model adopted to describe the motion along the dissociation reaction coordinate. We shall consider as an example a study by Fischer[61], in which it was postulated that motion along the reaction coordinate is so slow that the S and T_0 states vary adiabatically. The spin-Hamiltonian for a pair of radicals is of the usual type:

$$\mathcal{H} = g\beta H_0(S' + S) - {}^1/_2 J(1 + 4\,SS') + h\Sigma a I_z S_z + h\Sigma a' I'_z S'_z .$$

Within the framework of the approximation employed, the problem reduces to the solution of a quadratic equation and for adiabatic conditions we obtain

$$\psi^+ = \frac{1}{\sqrt{2}}(AS + BT_0); \qquad (18)$$

$$\psi^- = \frac{1}{\sqrt{2}}(AT_0 - BS); \qquad (19)$$

$$A = \left(1 + \frac{1}{\sqrt{1+x^2}}\right)^{1/2}; \; B = \frac{x}{|x|}\left(1 - \frac{1}{\sqrt{1+x^2}}\right)^{1/2};$$

$$S = \frac{1}{\sqrt{2}}(|\alpha\beta m_I m_{I'}\rangle - |\beta\alpha m_I m_{I'}\rangle); \qquad T_0 = \frac{1}{\sqrt{2}}(|\alpha\beta m_I m_{I'}\rangle + |\beta\alpha m_I m_{I'}\rangle);$$

$$x = \frac{\Sigma a m_I - \Sigma a' m_{I'}}{2|J|}; \; J = J_0 e^{-t/\tau} .$$

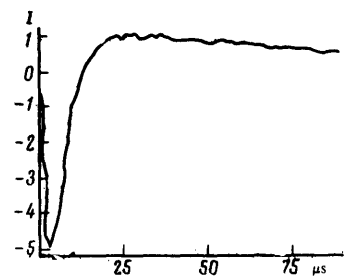


Figure 11. Kinetics of the variation of the amplitude of the component with $m_\beta = +1$ and $m_\alpha = -1/2$ in the ESR spectrum of cyclopentyl radicals.

Next it is postulated that at a certain instant $t = \tau'$ there is an instantaneous breakdown of the radical pair, which leads either to decomposition into free radicals, or to recombination, or transfer reactions. Since these processes are assumed to be fast (in the sense that they do not involve a change in the population of the magnetic states), the resulting populations are calculated by a simple projection of Eqns. (18) and (19) on to the relevant states of free radicals or molecules. Thus we have the following relative populations of the states of radicals in the decomposition of a singlet molecule:

$$a_{\alpha\alpha m_I m_{I'}} = 0; \quad a_{\alpha\beta m_I m_{I'}} = {}^1/_4(A + B)^2; \quad a_{\beta\alpha m_I m_{I'}} = {}^1/_4(A - B)^2;$$

$$a_{\beta\beta m_I m_{I'}} = 0; \; J = J_0 e^{-\tau'/\tau} .$$

These populations explain qualitatively the multiplet polarisation of electrons. The value of Fischer's work consists in the fact that he clearly formulated the principal reason for the change in the populations of the magnetic states in the dissociation step. This consists in the fact that the conditions which obtain for motion along the dissociation reaction coordinate are adiabatic.

However, an important comment must be made concerning the calculation itself. The point is that the redistribution of populations takes place mainly in the region where $J \simeq a$, i.e. when the traversal is never adiabatic. On the other hand, the applicability of

adiabatic conditions, discussed by Fischer refers to the region where $J \gg a$, which should not apparently make a significant contribution to chemically induced polarisation of nuclei and electrons.

A somewhat different dissociation model was considered by Kaptein and Oosterhoff[62]. Suppose that a molecule HX dissociates via the mechanism

$$H{-}X \rightarrow (\dot{H}\ \dot{X}) \rightarrow \dot{H} + \dot{X}$$

and one has to calculate the probability of the population of the levels of the hydrogen atom formed. The Hamiltonian for the pair is of the form

$$\mathcal{H} = \omega_e (S_1^z + S_2^z) - JS_1S_2 + a(S_1^z + S_2^z) I^z .$$

Here the non-secular terms are neglected and only the $T_0 - S$ transitions are considered (as for CINP, p. 809). It is postulated that in the dissociation J falls sharply to a value of the order of a, the pair remains in the singlet state, and subsequently dissociates with formation of an H atom in one of the states. (We may note that these are in fact the same approximations as those employed by Voss to account for the multiplet CINP in recombination products). Suppose that the nuclear spin is α_n; then the state of the radical pair is described by the wave function

$$\varphi^+(t) = [c_S(t)\, S + c_{T_0}(t)\, T_0]\, \alpha_n .$$

On substituting this function into the time dependent Schrödinger equation, we obtain a set of equations for the coefficients $c_S(t)$ and $c_{T_0}(t)$:

$$i\dot{c}_S = Jc_S + Ac_{T_0} ,$$
$$i\dot{c}_{T_0} = Ac_S - Jc_{T_0} ,$$

where $A = \frac{1}{4}a$. After finding the coefficients for the boundary conditions $c_S(0) = 1$ and $c_{T_0}(0) = 0$, we have

$$\varphi^+(t) = [\cos \omega t S - i\omega^{-1} \sin \omega t (JS + AT_0)]\, \alpha_n ,$$

and for the wave function with a nuclear spin β we have

$$\varphi^-(t) = [\cos \omega t S - i\omega^{-1} \sin \omega t (JS - AT_0)]\, \beta_n ,$$

where $\omega = (A^2 + J^2)^{1/2}$. Now the (oscillating) spin density at the H atom may be calculated:

$$\rho^{\pm} = 2 \langle \varphi^{\pm}(t) | S_1^z \delta(r_1) | + S_2^z \delta(r_2) | \varphi^{\pm}(t) \rangle = \pm 2AJ\omega^{-2} \sin^2 \omega t .$$

This equation shows that the electron with a nuclear spin α has a higher density at the a nucleus.

If the spin density is now averaged over the lifetime of the pair $(\dot{H}\ \dot{X})$, we obtain the selectivity parameter

$$\delta^{\pm} = \frac{1}{\tau} \int_0^{\infty} \rho^{\pm}(t) e^{-t/\tau} dt = \pm \frac{4AJ\tau^2}{1 + 4\omega^2\tau^2} .$$

The rates of population of the levels in the H atom are

$$\alpha\alpha_n\ {}^1/_4 k(1 + \delta^+), \qquad \beta\alpha_n\ {}^1/_4 k(1 - \delta^+),$$
$$\alpha\beta_n\ {}^1/_4 k(1 + \delta^-), \qquad \beta\beta_n\ {}^1/_4 k(1 - \delta^-),$$

where k is the rate constant for the formation of the pairs. Evidently the $\alpha\alpha_n$ and $\beta\beta_n$ states are populated preferentially; this leads to a multiplet effect in the ESR spectrum of the hydrogen atom and the multiplet polarisation is proportional to δ and depends on J, a, and τ in the radical pair. Evidently the sign of ME in the ESR spectrum depends on the state in which the atom or radical is formed—the singlet or triplet state (as in CINP).

The multiplet polarisation of electrons has been observed in radicals formed not only in dissociation steps but also in transfer steps. Fischer and coworkers[63] investigated the electron spin resonance of the radicals $\dot{C}H_2CH_2COOH$ and $CH_3\dot{C}HCOOH$ from propionic acid by a flow method in the $Ti^{3+} - H_2O_2$ redox system. As in the work of Smaller et al.[60], the hyperfine coupling components with $m_\alpha = \pm 3/2$ gave rise to emission; other lines with $m_\beta > 0$ were found to have a lower amplitude, since here absorption was partly compensated by emission.

We must now note the following important factor. Since the probabilities of the population of various electronic-nuclear levels of the radical in a chemical reaction are different, one can consider the variation of the rate constant for the chemical reaction with nuclear spin, i.e. with the hyperfine coupling energy in the radicals formed (and possibly also destroyed). Thus the multiplet effects in the chemically induced polarisation of nuclei and electrons can be explained even when the difference between the rate constants amounts to only a few per cent. However, usually the rate constants measured in chemical kinetics are overall quantities averaged over the nuclear-spin states and there is no point in considering their variation with the spin. In other words, the integral rate constants k (see above). are independent of the spin, while the quasidifferential constants $k(1 \pm \delta)$ do depend on the nuclear spin. At present the only method for the measurement of the differential (with respect to the nuclear spin) reaction cross-sections is based on chemically induced polarisation. It would be interesting to attempt to find this type of relation between reaction cross-section and the spin in experiments with magnetically oriented molecular beams (provided that this is possible in principle).

The ESR spectra do not reveal solely multiplet CIEP. Recently reports have appeared[64,65] of the preparation of radicals with a completely inverted population of the Zeeman electronic levels; their ESR spectrum exhibited total emission over a period of several microseconds after preparation and was then converted into the normal ESR absorption spectrum. The radicals were obtained by pulse or continuous illumination of benzophenone, benzaldehyde, 2- and 4-chlorobenzaldehydes, acetophenone, dibenzyl, and anthraquinone by light from a nitrogen gas laser (λ = 3371 Å) or from a mercury lamp.

The causes of the total emission are so far obscure. One can only put forward certain hypotheses. On irradiation, excited triplet states are formed, which on reaction with the solvent form triplet radical pairs. If one of the radicals relaxes rapidly, then, owing to the non-secular component of the exchange interaction $JS_{\pm 1}S_{\mp 2}$, there may be an inversion of population in the second radical (as in the Overhauser effect). It is also possible that some of the triplet excited states (for example T_0 and T_1) are rapidly deactivated; the remaining T_{+1} states react with formation of a T_{+1} pair, which dissociates into radicals with electron spins α. Such selective deactivation of triplets in a magnetic field was observed in a solid on the basis of ESR and phosphorescence spectra[66], but it is not clear whether such a mechanism can operate in a liquid. A mechanism involving $S - T_{-1}$ transitions should also be effective (as in CINP, p. 813).

Finally, we may note that cosmic radiofrequency emission by hydroxyl radicals is also associated with the inverted population of their magnetic-rotational states[67]. This emission comes from regions of ionised gas near young and newly formed stars; such a region with a high concentration of hydroxyl radicals with an inverted population operates as a gigantic cosmic oscillator or

possibly as an amplifier—a celestial maser. Little is known about the mechanisms of inverted population; optical pumping has been mainly considered, but this hypothesis involves many difficulties and therefore one cannot rule out the possibility of chemical pumping[67-70].

V. THE IMPORTANCE AND PROSPECTS OF CHEMICALLY INDUCED NUCLEAR POLARISATION

In order to understand how chemically induced polarisation of electrons and nuclei takes place, it is first necessary to discover how the elementary chemical step occurs, what is its physical mechanism, and what is its physical model. It is already quite clear that many details of elementary chemical reactions may be understood with the aid of chemically induced polarisation of electrons and nuclei. This is in fact why chemically induced polarisation constitutes at present a "hot spot" at the junction of a number of disciplines: theory of the elementary step, magnetic relaxation, radiofrequency spectroscopy, chemical kinetics, and others; this has given rise to much interest in the phenomena of chemically induced polarisation.

Many fundamental problems in the theory of chemically induced polarisation are still obscure. However, what has already been achieved has proved very fruitful. The dual role of elementary chemical reactions is clear in principle: the passive role, consisting in the selection of radicals and molecules with respect to electronic-nuclear and nuclear spin states, and the active role, leading to the induction of polarisation in the elementary steps themselves. Such separation has already significantly aided the solution of the problem. Clearly CINP and CIEP contain information about electron–electron and electron–nucleus interactions in the activated reaction complex, about the time variation of these interactions, about the behaviour of the energy levels in the activated complex, etc. There is no doubt that the development of the theory of chemically induced polarisation will be closely related to the development of the theory of the elementary step.

The role of CINP as a new and powerful research method for the kinetics and mechanisms of chemical reactions must be emphasised; the sensitivity of CINP as a method for the identification of radical stages is higher by several powers of 10 than the sensitivity of the ESR method.

It is significant that CINP is shown not only in the reaction products of alkyl and phenyl radicals, where there is a powerful electron–nucleus magnetic interaction, but also in the reaction products of oxy-radicals where such interaction is weak[6]. This greatly extends the scope of the CINP method. A large-scale application of the CINP method in the study of various chemical reactions is at present of great interest both for the reactions and the method itself. The phenomena of chemically induced polarisation are also of some interest for physicists, since they give rise to new methods for the polarisation of nuclei and electrons.

The fundamental tasks in the field of chemically induced polarisation are, firstly, further development of the qualitative and quantitative theories of the phenomena associated with the theory of the elementary chemical steps and, secondly, a large-scale application of the chemically induced polarisation methods in a wide variety of chemical and biological processes.

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