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DYNAMIC POLARIZATION OF NUCLEAR SPINS DURING CHEMICAL REACTIONS

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The thermal decomposition of organic peroxides is investigated as an example of processes involving the polarization of nuclear spins in chemical reactions. The dynamic enhancement factor of nuclear polarization is taken as the basic quantitative parameter for the process. The application of the various methods proposed in this paper for obtaining and analyzing experimental data, the comparison of such data with simple model calculations, and also certain direct measurements, all lead to the conclusion that nuclear spin orientation is not conserved in chemical reactions, and that transitions involving a change of this orientation are probably the cause of the observed polarization effect.

A simple phenomenological theory of the kinetics of the nuclear magnetic moment, which takes into account the dynamic polarization of the nuclear spins during chemical reactions, is proposed and experimentally confirmed. A new experimental method, i.e., the inversion of the nuclear magnetic moment during a chemical reaction, has been developed. Simple working formulas suitable for the analysis of experimental data have been derived. The polarization of nuclear spins in the decomposition products of organic peroxides has been investigated, and the dynamic enhancement factors E for the nuclear polarization have been measured for the first time. A detailed analysis has been carried out of the predictions ensuing from the original hypothesis that the chemical polarization of nuclei occurs through the transient Overhauser effect.

The various possible consequences of the hypothesis that the nuclear spin orientation is conserved in chemical reactions are discussed, and theoretical limiting values E_i are obtained on this assumption. The dependence of these values on the reaction conditions is investigated. Comparison of the measured dynamic enhancement factors with the theoretical limiting values, the study of the dependence of these quantities on viscosity, temperature, and concentration and, finally, direct measurements of polarization in $ChCl_3$, all lead to the conclusion that the assumption that the nuclear spin orientation is conserved in chemical reactions is not valid.

THE dynamic polarization of nuclear spins during chemical reactions occurring in a magnetic field through an intermediate paramagnetic molecule (free radical) has been observed by a number of workers[1-5]. This phenomenon has been referred to as the chemically induced dynamic nuclear polarization (CIDNP) and can be classified as "chemical pumping," the idea of which was originally proposed by Basov and Oraevskiĭ[6].

Despite the large number of qualitative experiments concerned with CIDNP, there have been practically no measurements until quite recently of the main physical quantity which characterizes the phenomenon, i.e., the dynamic enhancement factor of nuclear polarization during reactions. The main aim of the present work was to carry out the necessary experiments and to compare resulting experimental data with simple theoretical models. In the first section we give a simple phenomenological theory of the kinetics of nuclear magnetic moments, which leads to a method of analysis of experimental data. In the second section we report the results of model calculations of the enhancement factor, and in the third section we give the results of our experiments and their analysis.

1. KINETICS OF THE RESULTANT NUCLEAR MAGNETIC MOMENT

CIDNP observations are usually carried out on liquids, using high-resolution NMR spectrometers (see, for example,[7]). By successively scanning the spectra, it is possible to obtain the line intensities as functions of time. This not only establishes the presence of the effect, but also allows us to identify the diamagnetic reaction product in whose molecules the polarization is conserved for time intervals of the order of the relaxation time T_{1n}.

The intensity of each line (group of lines) recorded by the spectrometer is proportional to the resultant magnetic moment M(t) of nuclei occupying certain definite positions in definite molecules. Let us consider the time dependence of the nuclear magnetic moment of diamagnetic molecules F produced from an initial material C through an intermediate stage involving radicals $\dot{R}$. This dependence is determined by the following parameters: 1) the dynamic enhancement factor E(t), 2) the concentration r(t) of radicals in the reacting mixture, 3) the probability g(t) of transition of the radicals into diamagnetic molecules, and 4) the relaxation time $T_{1n} = 1/\alpha$ of nuclei in the diamagnetic product, where α is the reaction rate. Generally speaking, these parameters will vary in the course of the reaction and are not independent. At a time t (t = 0 corresponds to the beginning of the reaction) the resultant nuclear magnetic moment produced as a result of the formation at each intermediate time t′ of molecules with anomalous polarization and the competing thermal relaxation process is given by

$$M(t)=\mu_n p_{n0}\int\limits_0^t g(t')r(t')\,[E(t')-1]\,e^{-\alpha(t-t')}\,dt', \qquad (1)$$

where μ_n is the nuclear magnetic moment and p_{n0} is the equilibrium thermal polarization. The simplest result is obtained by assuming that both the probability of formation of the radical $\dot{R}$ from the molecule C(a) with subsequent formation of the molecule F from the radical $\dot{R}$(g) and the dynamic enhancement factor E do not change in the course of the reaction. If, moreover, $a \ll g$, then

$$M(t) = \mu_n p_{n0}\left[\frac{a}{\alpha - a} f_0 (E-1)(e^{-at} - e^{-\alpha t}) + f_0(1 - e^{-at})\right]. \quad (2)$$

This formula is very convenient for the analysis of experimental data. The quantity f_0 corresponds to the equilibrium concentration of the diamagnetic product F at the given temperature.

The following formulas are useful for calculating the dynamic enhancement factor from the observed function M(t):

$$M_{max} \approx \mu_n p_{n0} f_0 \left(\frac{a}{\alpha}\right)^{\alpha/(\alpha-a)} (E-1), \quad t_{max} \approx \frac{\ln(\alpha/a)}{\alpha - a}, \quad (3a)$$

$$t_0 \approx \frac{1}{a} \ln \frac{M_{max}}{M(\infty)} = \frac{1}{a} \ln (K-1), \quad K = \frac{M_{max} - M(\infty)}{M(\infty)}, \quad (3b)$$

$$M(\infty) = \mu_n p_{n0} f_0. \quad (3c)$$

The above expressions are valid for $|Ea| > \alpha$ and $a \ll \alpha$, i.e., for strong polarizations and relatively slow reactions. Somewhat more complicated expressions are obtained when the above assumptions are abandoned. Equation (3a) refers to the time t_{max} when M(t) passes through its extremal value M_{max}. Equation (3b) refers to the time t_0 when the deviation of the magnetic moment from the equilibrium value is equal to this value which, in turn, is given by Eq. (3c).

The reaction rate a (characteristic decomposition time 1/a) and the relaxation rate can be measured independently. It is important, however, to show that the quantities a, α, and E can, in fact, be regarded as constant during the reactions. In this connection, we propose a new experiment in which the nuclear magnetic moment M(t) under investigation is exposed to radiofrequency pulses which invert or saturate it during the reaction. Equation (2) corresponds to the following kinetic equation

$$\frac{dM}{dt} = -\alpha(M(t) - k(t)M_0),$$

$$k(t) = \left(1 + \left(\frac{a}{\alpha}E - 1\right)e^{-at}\right), \quad M_0 = f_0 \mu_n p_{n0}. \quad (4)$$

For example, after the 180° pulse Eq. (4) assumes the form

$$\left.\frac{dM}{dt}\right|_{180^\circ} = -\alpha(-M(t) - k(t)M_0),$$

i.e., the magnetic moment tends to its quasiequilibrium value $k(t)M_0$ with the relaxation rate α. This method is more convenient for strong polarizations and slow reactions, but it can also be used, for example, to determine E when M(t) does not pass through the extremum. We note that further generalization of Eq. (4) can be used to analyze measurements of the magnetic-moment kinetics of products with restricted solubility $f(\infty) \ll f_0$, for example, gases, and to determine the kinetics of two interacting magnetic moments belonging to different groups of nuclei in a given molecule (taking the Overhauser effect into account). These problems will be discussed elsewhere.

2. PHENOMENOLOGICAL THEORY OF THE ENHANCEMENT OF NUCLEAR POLARIZATION

It was originally considered[1,3] that departures from equilibrium during chemical reactions are produced directly only in the system of electron spins, and that the transient Overhauser effect[8-10] in free radicals is responsible for the CIDNP phenomenon. Since it was our aim to confirm or invalidate this assumption, we introduced in the previous section the concept of the dynamic enhancement factor E which can be used for any mechanism responsible for the polarization of nuclear spins. This factor is defined by

$$p_n(\tau) = E p_{n0},$$

where p_n is the nuclear polarization and τ is the lifetime (time of recombination) of the free radical, i.e., the quantity E can equally well reflect the result of the simultaneous presence of processes occurring in the formation and recombination of the radical. Next, the main criterion for verifying the hypothesis that the transient Overhauser effect is responsible for CIDNP is the comparison of measured values of E with simple model calculations in limiting (ideal) theoretical cases, which we shall denote by E_i. For the electron polarization p_s and nuclear polarization p_n in radicals[9] we have

$$\begin{aligned} \frac{dp_n}{dt} &= -\rho(p_n - p_{n0}) - \sigma(p_s - p_{s0}), \\ \frac{dp_s}{dt} &= -\rho'(p_s - p_{s0}) - \sigma'(p_n - p_{n0}), \end{aligned} \quad (5)$$

and we have considered the solutions of these equations for a number of ideal cases (assuming that all other relaxation mechanisms apart from those due to intramolecular electron-nuclear interactions can be neglected). We have confined our attention to the case $\tau_c \ll \omega_e^{-1}, \omega_n^{-1}$, where ω_e, ω_n are, respectively, the angular frequencies of Larmor precession of the electron and nuclear spins S and I, and τ_c is the correlation time.

All the numerical results reported below refer to the case where the nuclear spin (or spins) is due to the proton:

$$S = I = {}^1/_2, \quad p_{s0}/p_{n0} \approx -660.$$

Since the paramagnetic relaxation and free-radical recombination processes are most likely to be statistically independent, the solutions of Eq. (5) should be averaged over the lifetimes of the radicals. Further simplification is achieved by abandoning this averaging but this will, of course, lead to overestimates for E_i just like all the other assumptions which we have admitted. The lifetimes of all the radicals were assumed equal, and in each case the time to reach the extremal value $p_n(t)$ for initial conditions $p_s(0) = 0$, $p_n(0) = p_{n0}$ was assumed to be the same. The time to reach the extremum and the height $p_n(\tau_i)$ of the latter are determined by the kinetic coefficients ρ, ρ', σ, σ'.[1)] Using the above assumptions for a radical containing n magnetically equivalent nuclear spins with (for purely dipole

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[1)] The results reported below were obtained on the assumption that $\rho' = n\rho$, $\sigma' = n\sigma$, $\rho = 2\sigma$. The presence of relaxation mechanisms other than the electron-nuclear mechanisms will result in an increase of ρ and ρ', i.e., in a reduction of the enhancement factor E. An example of this is the relaxation due to g-factor anisotropy of the radical, whose contribution increases with increasing magnetic field.

interaction)

$$\tau_i = \frac{1}{\rho} \ln \frac{\varkappa_\pm}{\varkappa_-}, \quad \varkappa_\pm = (n + 1 \pm \sqrt{n^2 - n + 1})\, \sigma, \tag{6}$$

we obtain

$$E_i^{\text{dip}} = \frac{p_{s0}}{p_{n0}} \frac{\varkappa_+ - \varkappa_-}{\varkappa_+ + \varkappa_-} (e^{-\varkappa_- \tau_i} - e^{-\varkappa_+ \tau_i}), \tag{7}$$

which gives $E_i \approx -125$ for $n = 1$, $E_i \approx -88$ for $n = 2$, and $E_i \approx -65$ for $n = 3$. Positive values of E_i are obtained when the scalar electron-nuclear interaction is the predominant one.

If the nuclei in the radical are not magnetically equivalent, and the electron-nuclear interaction in one of the groups is much greater than elsewhere, whereas in the diamagnetic molecule all the nuclei become equivalent, then an averaging of the polarization should occur. For example, let us consider the radical $\dot{C}_6H_5$. Here the two protons nearest to the point of localization of the unpaired electron may be polarized, and the limiting value is $E_i^{\text{dip}} \approx -88$. On the other hand, in the C_6H_6 molecule $E_i \approx -29$.

Similarly, the same hypothesis can be applied to the case where the electron-nuclear interactions with the two nuclear spins I and I′ are comparable in magnitude. Here, the electron and nuclear spin systems cannot be ascribed a common spin temperature. The cross terms between different electron-nuclear interactions in the expressions for the transition probabilities between energy levels may, in general, give rise to an appreciable difference in the relaxation rates between pairs of I levels differing by the values of I'_z. This may also lead to differences in the magnitude and even the sign of the polarization of different components of the spin multiplets in the diamagnetic molecule (this is the so-called multiplet effect[2,5]). It is clear that in this particular model the polarization of each of the multiplet components can only be smaller than the maximum possible resultant polarization.

Finally, it is important to establish, and we shall do this at the end of this section, to what extent the mechanism we are discussing did, in fact, play a part under the conditions of our experiments. Reasonable estimates of the correlation time for the inter- and intramolecular interactions in a liquid yielded a figure of 10^{-11} sec, whereas estimates of the energy of the electron-nuclear interaction (both scalar and dipole) in radicals are of the order of 10^8 Hz (in frequency units). The anisotropic part of the Zeeman interaction which also contributes significantly to the relaxation rate ρ' is of the same order. Hence, it follows that $(\rho)^{-1} \approx 10^{-6}$ sec. At the same time, the radical lifetime may be assumed to be equal to the mean time of diffusion between reacting molecules (of the order of 10^{-6} sec for concentrations of 10^{18} cm^{-3}, i.e., of the order of a few hundredths of a mole per liter). The last estimate is not very rigorous because the probability of the given reaction in each collision is unknown. Summarizing the above estimates, we are forced to the conclusion that the realization of the necessary condition $\tau\rho \approx 1$ is possible, at least in principle. Nevertheless, a large change in the relaxation time or the diffusion time may easily violate this condition. Consequently, the proposed mechanism (transient Overhauser effect) can only be realized in a relatively narrow range of experimental conditions (temperature, concentration, and viscosity).

A rigorous analysis of the above hypothesis must also take into account the following possibility. Since we are neglecting the change in the orientation of the nuclear spin in the course of the reaction, we must take into account the buildup of polarization during the subsequent reaction stages. In fact, if the reaction is of the multistage type

$$C_0 \to \dot{R}_1 \to C_1 \to \dot{R}_2 \to \ldots F,$$

the nuclear polarization at the end of the first stage will only partly approach the equilibrium state, or may even remain unaltered (if the intermediate diamagnetic state exists for a fraction of a second), and is then transferred to the newly formed radical. This is followed by the next stage, and so on. It can be shown [by solving Eq. (5) with modified initial conditions] that even in the case of two intermediate paramagnetic stages, the limiting value of the polarization that can be achieved is, for example, $E_i^{(2)} \approx -180$. If the number of such intermediate stages is allowed to increase without limit, the limiting value of the dynamic enhancement factor will tend to the value characteristic for the stationary Overhauser effect, i.e., $E_i^{(\infty)} \approx -330$.

The above hypothesis then encounters serious difficulties when it is used to explain the positive polarization which requires prolonged (of the order of 10^{-6} sec) existence of the radical pairs, or multistage transitions from one radical to another, in accordance with the scheme

$$C_0 \to \dot{R}_1 \to \dot{R}_2 \to \ldots F$$

(since, otherwise, it would be difficult to explain the time dependence of the scalar interaction).

A possible alternative is the assumption that transitions involving a change in the nuclear spin orientation which occur during the reactions (at a time of formation or recombination of the radical) contribute substantially to CIDNP. This possibility seems generally reasonable if we recall the different stability of triplet and singlet states, and the possibility of transition from the triplet to the singlet, and vice versa, during interaction between the electrons and the nuclear magnetic moment and, above all, the nonequilibrium nature of the vibrational reservoir of molecules in the transient paramagnetic state.

Undoubtedly, quantitative measurements of the dynamic enhancement factor and its dependence on the reaction conditions, especially on the polarization of nuclei in the intermediate products, should provide an important contribution to the elucidation of the mechanism responsible for CIDNP.

3. EXPERIMENT AND DISCUSSION OF DATA

1. Experimental Conditions

We have investigated the thermal decomposition of molecules of the type $R_1\text{—CO—O—O—CO—}R_2$ (organic peroxides) in organic solvents (0.1–1N solution) in the sample-holder of the high-resolution NMR spectrometer DA-60-IL. The proton magnetic resonance frequency was 60 MHz, the volume of the specimen was about 0.4 cm^3, and the specimen temperature was maintained constant throughout the volume to within ± 2°C. The specimen reached its steady value 50—70 sec after the value was specified, or 20—30 sec after the specimen was placed in an air stream of given temperature (60—140°C). The signal was recorded by the sideband method, and the minimum time constant of the detecting device was 0.1 sec. The rate of scanning and the radio-frequency field could be varied within practically any required range, and were carefully calibrated. We have used both a frequency scan accurately linked to a pen-recorder and a periodic sawtooth field sweep. In the latter case, the reproducibility of the signal was ± 20%. The spectrometer sensitivity was sufficient to produce a signal corresponding to 10^{18} protons per cm^3 with a signal-to-noise ratio of 3 : 1.

The absence of evaporation of the reaction product under investigation from solution was checked in all the necessary and possible cases. The rate of decomposition of the original product and the relaxation rate were determined independently. Measurements of the relaxation time involving the inversion of the nuclear magnetic moment[11] and similar experiments in the course of the reaction were carried out by rapidly traversing the inverted line using a short high-power radio-frequency pulse.

2. Measurements of the Dynamic Enhancement Factor

Figures 1 and 2 show the recorded proton magnetic resonance spectra, using a frequency scan during chemical reactions. Successive recording of the spectra at given intervals of time can be used to obtain the kinetic curves for different M(t) (corresponding to different nuclei and molecules). When the aim of the experiment is to investigate the kinetics of the process, and when the line intensity is such that this can be done, a given spectral line is repeatedly recorded using a sawtooth field (Fig. 3a). The same method can be used for studies with signal inversion during reactions (Fig. 3b) and for determinations of the relaxation time (Figs. 3c and d).

The experimental data were analyzed in terms of Eq. (3) and, as already noted, some of the parameters were measured independently (especially the relaxation time).

It follows from the experiment involving the inversion of the nuclear magnetic moment in the course of the reaction, and from the analysis of the kinetic M(t) curves, that the quantities a, α, and E can, in fact, usually be regarded as constant parameters of the

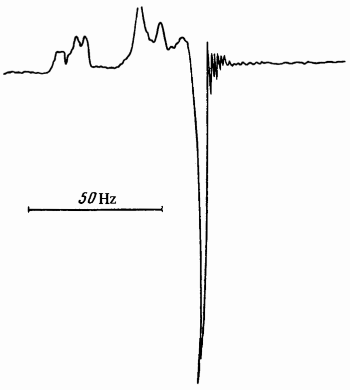

FIG. 1. High-resoltuion NMR spectra for protons in benzoyl peroxide $C_6H_5CO\text{-}OO\text{-}COC_6H_5$ decomposing at 120°C (the spectrum of the solvent $C_6H_{10}O$ is not shown). The negatively polarized single line is due to protons in C_6H_6.

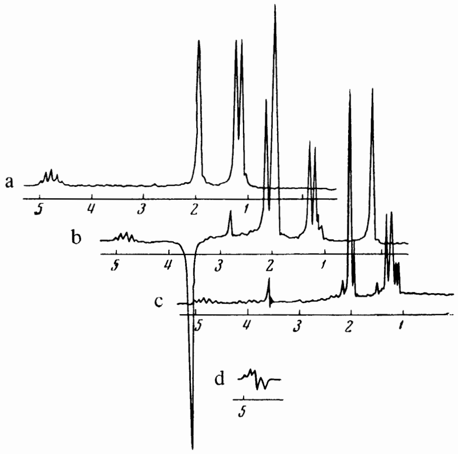

FIG. 2. High-resolution NMR spectra for protons in a solution of peracetyl isopropyl carbonate in C_2Cl_4 [the scale along the horizontal axis is in units of 10^{-6} of the field strength for the standard line of $Si(CH_3)_4$]. a – original compound; b – during reaction; c – after end of reaction; d – multiplet effect for the proton line of the CH group.

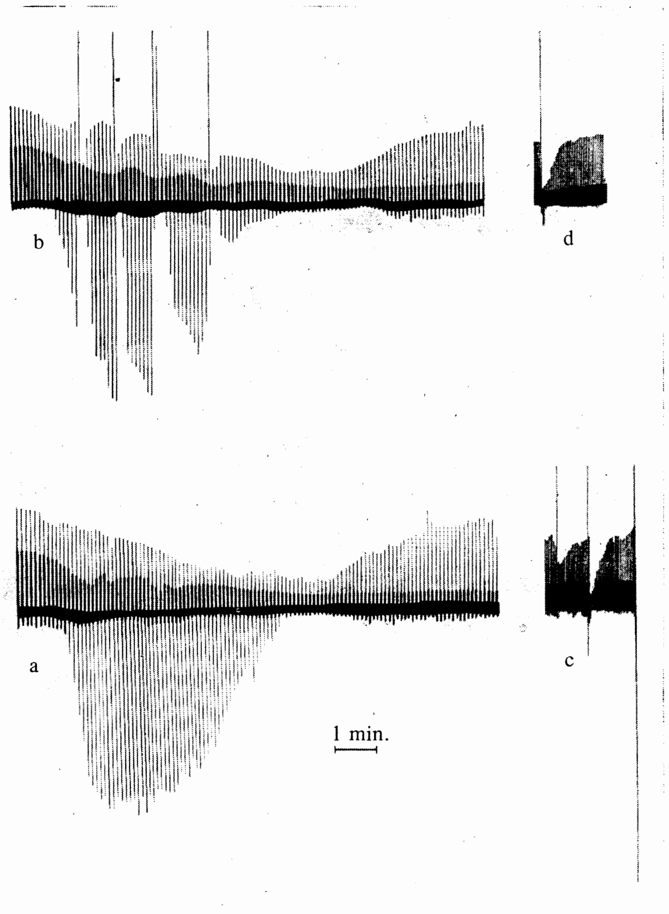

FIG. 3. Kinetics of the nuclear magnetic moment during the decomposition of benzoyl peroxide leading to the formation of benzene. a – Series of spectra obtained by repeated scan; b – ditto with inversion of the magnetic moment during the reaction; c, d – measurements of the relaxation time.

Results of experiments on the dynamic enhancement factor E for the decomposition of the peroxides $R_1-CO-O-O-CO-R_2$

	1	2	3	4	5	6	7
R_1	C_6H_5	C_6H_5	C_6H_5	C_6H_5	C_6H_5	CH_3	CH_3
R_2	C_6H_5	C_6H_5	CH_3	CH_3	CH_3	$OCH(CH_3)_2$	$OCH(CH_3)_2$
N, mole/l	0.8 N	0.8 N	0.8 N	0.8 N	0.3 N	0.6 N	0.6 N
T, °C	120	120	120	120	140	90	90
Solvent	cyclohexanon	cyclohexanon	C_2Cl_4	C_2Cl_4	silicone oil	CCl_4	CCl_4
Reaction product	C_6H_6*	C_6H_6*	C_6H_6*	CH_3*$OCOC_6H_5$	CH_3* $OCOC_6H_5$	CH_3 *$OCOCH-(CH_3)_2$	CH* Cl_3
Relaxation Time T_{1n}, sec	16 ± 3	25 ± 10	30 ± 5	35 ± 5	15 ± 5 ****	15 ± 8	55 ± 10
Characteristic decomposition time							
$1/a$, sec	250 ± 50	270 ± 70	100 ± 20	120 ± 30	1100 ± 200	900 ± 300	900 ± 300
K	-3.2 ± 0.2	-3.2 ± 0.2	$+5.0 \pm 0.5$	-40 ± 1	-3.0 ± 0.2	-30	-6 ± 1
E**	-50 ± 15	-40 ± 20 ***	$+15 \pm 5$	-120 ± 30	-180 ± 90	-1800 ± 900	-90 ± 40

*Anomalously polarized protons.

**E calculated from Eq. (3).

***Value of T_{1n} obtained from experiments on magnetic moment inversion.

****T_{1n} estimated from Eq. (3).

process, and that Eq. (2) gives a satisfactory representation of the equation of motion of the resultant nuclear magnetic moment during the reaction.

As a rule, the absolute magnitudes of the negative enhancement factor E substantially exceed the limiting theoretical values expected when the Overhauser effect is predominant. In some cases, the values of E were found to exceed in absolute magnitude the limiting theoretical value for the stationary Overhauser effect, although the experimental errors were considerable (see the table, col. 6).[2] Positive enhancement factors are, as a rule, smaller in their numerical value than negative factors, and the observed qualitative regularities in the behavior of a particular polarization sign cannot as yet be regarded as firmly established. The only conclusion that can be drawn is that neither the type of the radicals participating in the formation of the molecule nor the expected type of reaction leading to its formation will by itself determine even the sign of the polarization. It would appear that the sign is also affected by the conditions under which the radical is formed (for example, the molecule C_6H_6 is formed from the peroxide with $R_1 = CH_3$, $R_2 = C_6H_5$ with positive polarization, whereas it is formed with negative polarization from the peroxide with $R_1 = R_2 = C_6H_5$).

The most important and the most characteristic experimental results are summarized in the table. Some of them were discussed above and the remainder will be considered below.

3. Direct Experimental Verification of the Hypothetical Buildup of Polarization in Intermediate Products and the Conservation of Nuclear Spin During Reactions

The brief review of experimental data given above indicates that the above hypothesis on the role of the transient Overhauser effect in CIDNP is clearly inadequate. It is desirable to carry out a more direct experimental verification of this hypothesis. After a search for a system on which this experiment could be performed, we finally selected solutions of peroxides in carbon tetrachloride. When the peroxides decompose in these solutions the side product is chloroform, $CHCl_3$, whose protons are negatively polarized (see the table).

Virtually the only way in which chloroform can be formed would seem to be the two-stage reaction

$$\dot{R} + CCl_4 = RCl + \dot{C}Cl_3, \quad HX + \dot{C}Cl^3 = CHCl_3 + \dot{X}.$$

Thus, first, the Overhauser effect cannot determine the polarization of the protons in chloroform because the radicals do not contain these protons. Second, if we consider that when the chloroform is formed, i.e., during the transfer of hydrogen atoms from the hydrogen-containing molecules CCl_3, the proton spin orientation is unaltered and the polarization of the chloroform protons when they are formed should be equal to the mean proton polarization in all the molecules of the specimen.[3] A very convincing fact that refutes this assump-

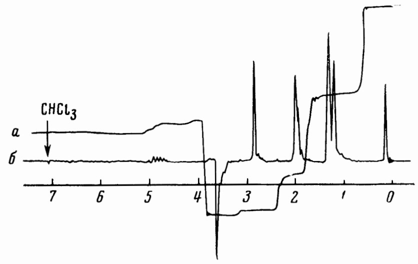

FIG. 4. Experiment on the sign of the mean proton polarization under the conditions of formation of negatively polarized $CHCl_3$. Figure shows the spectrum (a) and the integral curve (b). The scale along the horizontal axis is in units of 10^{-6} of the field strength for the standard line of $Si(CH_3)_4$.

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[2] The large error is due to the slowness of the reaction and the low yield of the product, i.e., insufficient signal-to-noise ratio and low reproducibility of the results.

[3] We have carried out an experiment under conditions for which the probability of removal of hydrogen atoms from all the molecules was practically equal (removal from the CH_3 groups).

tion is that the integrated electron spectrum of the reacting mixture (see Fig. 4) gives a positive mean polarization for the entire specimen, whereas the polarization of the chloroform protons is negative. Finally, an additional experiment involving the depolarization of the strongest lines by rf radiation (resonance saturation) shows that this does not affect the polarization of chloroform. Thus, the polarization of the intermediate products not only does not determine the polarization of the protons in $CHCl_3$ but does not even contribute appreciably to it. Direct experiment confirms that the dynamic polarization of the proton spins during the formation of $CHCl_3$ is associated with the formation of the diamagnetic molecule.4)

4. Effect of Temperature, Concentration, and Viscosity

We have investigated the polarization of protons in the decomposition products of peroxides with $R_1 = CH_3$, $R_2 = C_6H_5$ in broad ranges of viscosity and concentration. This reaction and a number of other reactions were investigated in solutions containing different chemically active impurities. The observed regularities can be summarized as follows. The reaction conditions have a much stronger effect on the relative and absolute yields of the various products and the rates at which they are formed than on the magnitude of the dynamic enhancement factor (this was confirmed in special cases by chemical analysis). Reduction of temperature was found, as a rule, to lead to an increase in the enhancement factor, although the observed effect was reduced by the reduced relaxation time and increased reaction time [cf. Eq. (3)]. Experiment has shown that the quantity $|E|$ for protons in the OCH_3 group in very viscous silicone oil (viscosity $\eta \approx 45$ cp) is not smaller than for the usual organic solvents (which have $\eta \approx 0.3$ cp at the same temperature).

It is still difficult to determine any definite regularities in some of the observed changes of the multiplet effect. In this part of our work we restricted our attention largely to the polarization of single lines. The final data appear to be sufficient to enable us to reject the original hypothesis that the nuclear spin orientation is conserved in chemical reactions.5)

5. Feasibility of a Maser Based on Negatively Polarized Nuclear Spins

The following expression (which can readily be obtained from the usual expression given in[14]) determines the conditions necessary for self-excitation

$$|np_{n0}(K-1)\mu_n| > 2/\gamma T_2 Q\zeta V, \qquad (8)$$

where Q is the effective Q-factor of the radio-frequency circuit, T_2 is the transverse relaxation time of the nuclei, γ is their gyromagnetic ratio, V is the volume of the coil, ζ is the duty coefficient, n is the number of nuclei in the specimen, and K is the enhancement factor for the resultant nuclear magnetic moment. If the reaction is carried out in a continuous flow system we can ensure that $K \approx E$ but even then generation is difficult to achieve. For example, the above condition is satisfied for $Q \geq 100$, $n \gtrsim 10^{22}$, $K \gtrsim 100$ in a magnetic field of the order of 10^4 Oe and at temperatures of the order of 400°K. By increasing the magnetic field, by selecting a reaction with a higher yield and by using lower temperatures, the system may become technologically possible.

We are greatly indebted to G. S. Bylina, V. A. Dodonov, and their coworkers for supplying us with the organic peroxide specimens, to the staff of the Institute of Chemical Physics and the Institute of Organic Chemistry, Academy of Sciences of the USSR, who helped us in this research, and to I. V. Aleksandrov and G. M. Zhidomirov for advice and discussions.

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4)The detailed mechanism responsible for negative CIDNP in $CHCl_3$ is at present being investigated by I. V. Aleksandrov and G. M. Zhidomirov.

5)It is clear that this also applies to the interpretation of the results reported in [12,13].

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