

³¹P CIDNP IN THE REACTION OF ZINC DIISOPROPYLDITHIOPHOSPHATE
WITH METHYL ETHYL KETONE PEROXIDE AND CUMENE
HYDROPEROXIDE IN BENZENE

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The free-radical nature of the reactions of a series of dithiophosphate complexes of zinc with peroxides was established by ³¹P chemically induced dynamic nuclear polarization (CIDNP). The polarization coefficient, the reaction rate constant, and the nuclear relaxation rate were determined. The dependence of the polarization coefficient on the intensity of the external magnetic field was established.

It is known that the nature of the dissociation of the dithiophosphate complexes of metals determines their activity as oil additives. The majority of these reactions takes place through the free-radical state and can be studied by ³¹P CIDNP. In the present work we studied the reaction of zinc dithiophosphate with peroxide and hydroperoxide.

EXPERIMENTAL

The reaction of zinc diisopropyldithiophosphate with methyl ethyl ketone peroxide was conducted at ~20°C, and the reaction with cumene hydroperoxide was conducted at 70-80°C. The concentration of the substance was 30%, and the ratio of the reagents by weight was 1:1. The NMR investigations were conducted in a magnetic field with an intensity of 6 kOe (KGU-4 NMR instrument), 21 kOe (Bruker CXP-100), and 58 kOe (Bruker WM-250). When the reaction was conducted in the sample unit of the spectrometer, anomalous signals were observed in the NMR spectra. In the case of the peroxide an emission signal (E) was observed at δ_p 93 ppm, an anomalous absorption signal (A) was observed at δ_p 90 ppm, and a strong emission signal was observed at δ_p 81.6 ppm (Fig. 1b). In the case of the hydroperoxide, signals were observed at δ_p 93 ppm (E), δ_p 81.6 ppm (E), and δ_p 76.76 ppm (A) (Fig. 2b).

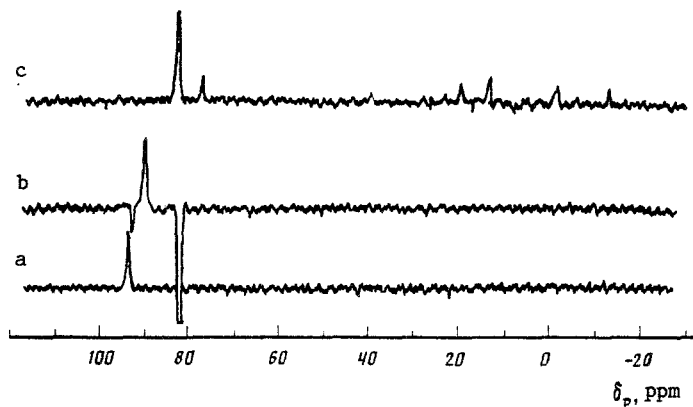


Fig. 1. ³¹P NMR spectra of the products from the reaction of zinc diisopropyldithiophosphate with methyl ethyl ketone peroxide: a) Initial; b) polarized; c) final.

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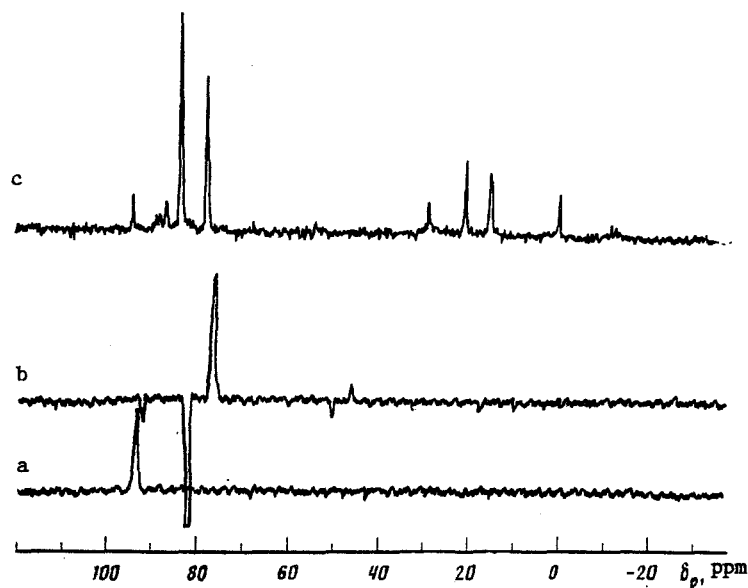
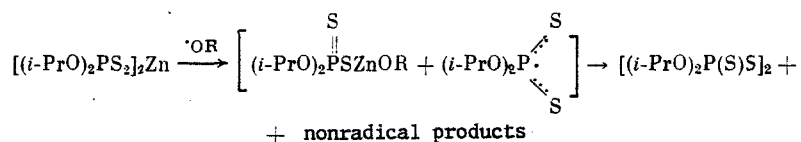


Fig. 2. ^{31}P NMR spectra of the products in the reaction of zinc diisopropyldithiophosphate with cumene hydroperoxide: a) Initial; b) polarized; c) final.

RESULTS AND DISCUSSION

The presence of the polarized signals in the NMR spectra shows that homolytic cleavage of the S—Zn—S bond occurs in addition to the heterolytic reaction of the reagents, and products involving the participation of short-lived free radicals are formed [1]. The addition of styrene does not suppress the polarization and shows unambiguously that the CIDNP is formed during the interaction of the radical pairs (RP) in the "cage" and as a result of their subsequent transformations. The general reaction scheme can be represented in the following form:



As a result of accumulation for 30 min on the Bruker CXP-100 spectrometer we obtained the spectra of the final reaction product. The main product was bis(diisopropylthiophosphoryl) disulfide at δ_p 81.6 ppm (Figs. 1c and 2c). The product with δ_p 76.76 ppm must be assigned to $(i\text{-PrO})_2\text{P(S)OR}$, where $\text{R} = \text{Me}$, Et , and $\text{Me}_2(\text{Ph})\text{CO}$. There were small amounts of the thiophosphate (according to published data, δ_p 20–28 ppm for thiophosphates [2]) and diisopropylphosphoric acid with $\delta_p - 2$ ppm. A product with δ_p 2 ppm ($J_{\text{PH}} = 550$ Hz), i.e., $(i\text{-PrO})_2\text{P(O)H}$, was isolated from the precipitate (a white colloidal mass). Intermediate products with polarized signals (E) at δ_p 52 and (A) at δ_p 44 ppm were detected in the reaction with cumene hydroperoxide.

For any reaction the kinetics of CIDNP is described in general form by the equation:

$$dM/dt = EdM_0/dt - \beta (M - M_0) \quad (1)$$

where M is the overall nuclear magnetization of a certain type of molecule, and M_0 is the equilibrium nuclear magnetization of the same molecules [3]. The first term in the equation determines the rate of creation of the nuclear magnetization (chemical pumping), and the second term determines its decomposition rate and the rate of relaxation of the nonequilibrium magnetization to its equilibrium value. The CIDNP enhancement factor E is the ratio of the nonequilibrium nuclear magnetization of the molecule at the moment of its evolution to the equilibrium magnetization:

$$E = M/M_0 \quad (2)$$

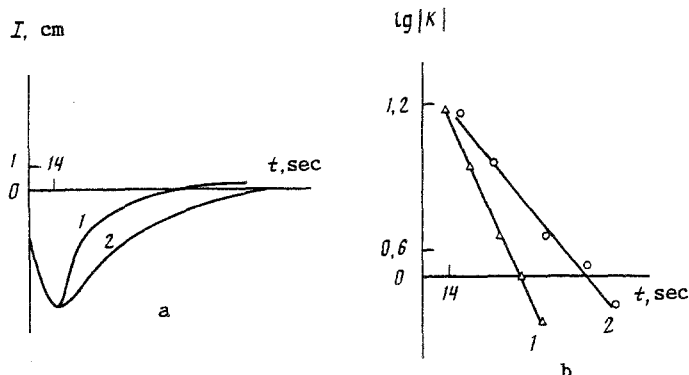


Fig. 3. Kinetics of ^{31}P CIDNP of bis(diisopropylthiophosphoryl) disulfide: a) The dependence of the NMR signal on time; b) its logarithmic form according to Eq. (4). 1) The reaction with methyl ethyl ketone peroxide; 2) with cumene hydroperoxide.

One of the constants which characterizes the kinetics of CIDNP is the β constant of the nuclear relaxation rate. Since $\beta = T_{1n}^{-1}$, by determining the recovery $T_{1n} = 8.6$ sec by the inversion method, we obtained the β value ($\beta = 11.6 \cdot 10^{-2} \text{ sec}^{-1}$).

For analysis of the experiments on the kinetics of CIDNP it is convenient to use the value of K :

$$K = (I - I_{0\infty})/I_{0\infty} = (M - M_{0\infty})/M_{0\infty} = (Ek - \beta)/(\beta - k) \cdot [\exp(-kt) - \exp(-\beta t)] - \exp(-\beta t) \quad (3)$$

Here $I_{0\infty} = \lim I_0$ when $t \rightarrow \infty$.

The kinetic curve of CIDNP for sufficiently long times falls exponentially (Fig. 3a). When $\beta \gg k$, Eq. (3) for $t \gg T_{1n}$ can be written in the following form:

$$K = (EkT_{1n} - 1) \exp(-kt) \quad (4)$$

The logarithmic form of the curve for Eq. (4) is shown in Fig. 3b, from which it is easy to determine the rate constant $k = 2.7 \cdot 10^{-2} \text{ sec}^{-1}$. From Eq. (3) it is possible to determine the kinetic parameters of the reaction. Polarization passes through a maximum, the time for which is given by

$$t_{\max} = 1/\beta - k \ln(E - 1)/\beta(Ek - \beta) \quad (5)$$

where E is determined from the kinetics and is equal to -16.6 with a magnetic field strength of 21 kOe . Substituting the values of β and k in Eq. (5), we obtain $t_{\max} = 14.45 \text{ sec}$, and this satisfies the data on the reaction kinetics. From Eq. (5) it is easy to write the condition for which it is possible in general to observe the kinetics of CIDNP with a maximum (the condition of the existence of a maximum):

$$|Ek - \beta| \neq 0 \quad (6)$$

In order to check the reliability of the obtained values of k and E it is possible to use the point where the signal passes through zero. At this point t_i with emission $I = 0$ and $K = -1$, from which

$$t_i = 1/k \ln(|E|kT_{1n} + 1) \quad (7)$$

Substituting the values in Eq. (7), we obtain $t_i = 86.9 \text{ sec}$, which gives good agreement with experiment.

The value of E determined experimentally from the kinetics is calculated on the molecule or on some nuclear-spin transition between the ab and $a'b'$ states. The averaged difference in the nonequilibrium populations is therefore contained in Eq. (8):

$$E = P_{ab} - P_{a'b'}/P_{ab}^0 - P_{a'b'}^0 \quad (8)$$

TABLE 1. Dependence of the Polarization Coefficient of the Disulfide on the Intensity of the External Magnetic Field*

Reagents	Magnetic field intensity, kOe		
	6	21	58
Methyl ethyl ketone peroxide	-29,2 (-29,4)	-16,6 (-16,67)	-5,6 (-8,2)
Cumene hydroperoxide	-28,3 (-29,4)	-16,4 (-16,7)	-4,3 (-8,2)

*The theoretically calculated values of the polarization coefficient are given in parentheses.

The relation between E and the populations of the nuclear-spin states is:

$$E_{\text{rec}}^S = -(1-\alpha)/\alpha (P_{ab} - P_{a'b'})/(P_{ab}^0 - P_{a'b'}^0) \quad (9)$$

where α is the probability of recombination in the pair and varies in the range of 0.5-0.99.

Strong hyperfine coupling for the phosphorus-containing radical pairs leads to the need to take account of the second-order corrections of perturbation theory [4]. The spin Hamiltonian $|H|$ has the following values:

$$\begin{aligned} |H|_{\alpha_e\alpha_n} &= (a/4 + \Delta g\beta H/2); & |H|_{\beta_e\alpha_n} &= (a/4 + \Delta g\beta H/2 + a^2/4g\beta H) \\ |H|_{\alpha_e\beta_n} &= (a/4 - \Delta g\beta H/2 - a^2/4g\beta H); & |H|_{\beta_e\beta_n} &= (a/4 - \Delta g\beta H/2) \end{aligned} \quad (10)$$

The rate of the $S \rightleftharpoons T_0$ evolution therefore depends on the nuclear spin not only on account of the $a/4$ term but also on account of the quadratic term $a^2/4g\beta H$.

In the molecule formed from the singlet pair as a result of secondary recombination, the difference in the populations is equal to:

$$P_{ab}^S - P_{a'b'}^S = -(1-\alpha)\alpha\pi^{1/2}m(|H_{ab}|^{1/2} - |H_{a'b'}|^{1/2}) \quad (11)$$

Equation (11) holds when $\tau \gg H_{ab}^{-1}, H_{a'b'}^{-1}$, where τ is the lifetime of the radical. Solving Eq. (11) with Eq. (10) and substituting the values $a^P = 25$ Oe, $g = 2.0203$, $m = 4.35 \cdot 10^{-6}$ sec^{1/2}, and $\beta = 9.27 \cdot 10^{-24}$ A·m² (the Bohr magneton), and $\alpha = 0.99$ in Eq. (11) and taking account of Eq. (8), we obtain E for various external magnetic field intensities. The theoretically calculated values give good agreement with experiment (Table 1).

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