Russian Journal of General Chemistry, Vol. 71, No. 4, 2001, pp. 614–622. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 4, 2001, pp. 659–667.
Original Russian Text Copyright © 2001 by Skakovskii, Stankevich, Lamotkin, Tychinskaya, Rykov.

Thermolysis of Methanolic Solutions of Acetyl Propionyl Peroxide

E. D. Skakovskii, A. I. Stankevich, S. A. Lamotkin, L. Yu. Tychinskaya, and S. V. Rykov

Institute of Physical Organic Chemistry, Academy of Sciences of Belarus, Minsk, Belarus

Received June 2, 1999

Abstract—Kinetic measurements by ^{1}H NMR spectroscopy and chemically induced dynamic nuclear polarization (CIDNP) effects were used to study thermolysis of solutions of acetyl propionyl peroxide in methanol-d_4. It is found that the thermolysis may occur both by radical and by nonradical mechanisms. A scheme of the thermolysis is proposed. Parameters of the Arrhenius equation for the rate constants of the decomposition of the peroxide and the decarboxylation of acyloxyl radicals are obtained.

Thermolysis of diacyl peroxides has been considered in sufficient detail in [1–3]. The most thoroughly explored is their thermolysis in inert hydrocarbon solvents. While alcohols are available and convenient-in-operation solvents, there have only a few works [2–6] that deal with possible mechanisms of the reactions of diacyl peroxides. Thermolysis of benzoyl peroxide in ethanol, isopropanol, and *tert*-butanol [2–5], of acetyl peroxide in isopropanol, isobutanol, and *tert*-butanol [4], and of acetyl benzoyl peroxide in methanol, isopropanol, and butanol [6] have been studied.

The cited works all showed that peroxides are thermolyzed by a radical mechanism to give aldehydes and ketones. No attention in these works was paid to nonradical mechanisms. At the same time, some information [7, 8] on possible nonradical transformations of peroxides in polar solvents is available.

The aim of the present work was a detailed study of thermolysis of a diacyl peroxide in an alcohol. As the object for study we chose one of the simplest unsymmetrical diacyl peroxides, acetyl propionyl peroxide (**I**) whose thermolysis gives rise to compounds **II**–**XVIII** which can readily be identified by NMR spectroscopy.

As the solvent we took methanol-d_4, the simplest alcohol, in which, according to our expectations, a narrower range of radical reaction products would form compared with other normal alcohols, thus facilitating analysis.

Figure 1a depicts the ^{1}H NMR spectrum of compound **I**, obtained in the course of thermolysis at 353 K. The spectrum shows an ethene signal (5.57 ppm) with enhanced absorption, an emission quartet of ethyl ethanoate (CH_2 4.29 ppm), and propane multiplets with mixed type of polarization (CH_2 1.53 ppm, E + E/A; CH_3 1.10 ppm, A + E/A; here A is enhanced absorption, E is emission, E/A is

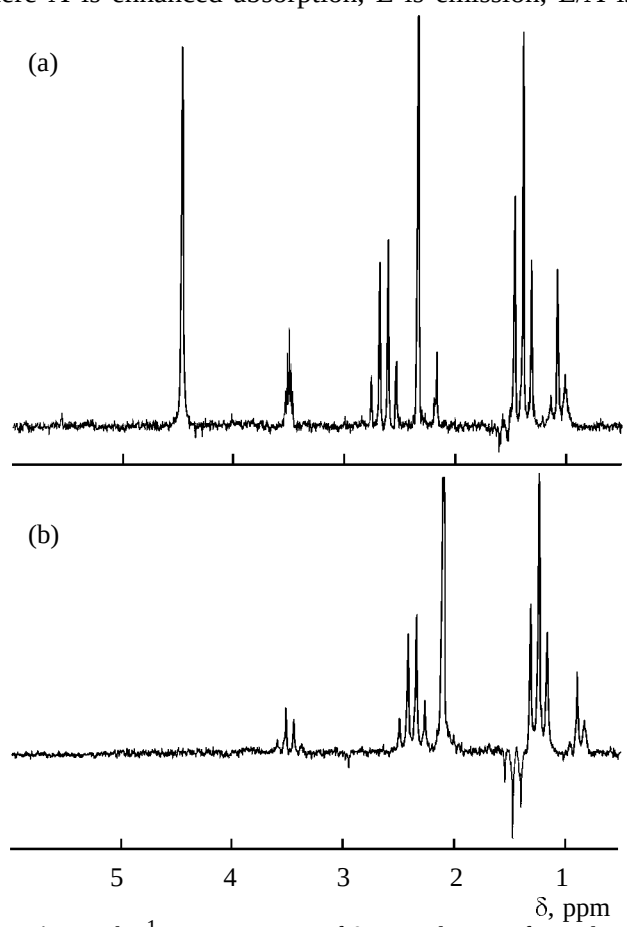


Fig. 1. The ^{1}H NMR spectra of 0.1 M solutions of acetyl propionyl peroxide in (a) methanol-d_4 and (b) carbon tetrachloride at 353 K, measured in the course of thermolysis.

1070-3632/01/7104-0614 $25.00 © 2001 MAIK "Nauka/Interperiodica"

Table 1. Yields (%) of thermolysis products of 0.1 M solutions of peroxide **I** in methanol-d_4 as a function of thermolysis time at 323 K

Comp. no.	Compound	Time, h					
		5	10	20	30	50	70
I	$CH_3CH_2C(O)OOC(O)CH_3$	91.4 ± 2.7	82.7 ± 1.2	69.1 ± 2.0	57.1 ± 1.9	39.4 ± 1.5	27.3 ± 2.8
II	$CH_3CH_2OC(O)CH_3$	1.1 ± 0.1	2.2 ± 0.2	3.9 ± 0.2	5.3 ± 0.3	7.2 ± 0.7	8.2 ± 0.8
III	$CH_3C(O)OD$	2.5 ± 0.2	4.9 ± 0.5	8.8 ± 0.9	12.2 ± 1.0	17.3 ± 0.9	20.7 ± 0.8
IV	C_2H_4	0.9 ± 0.1	0.9 ± 0.1	0.9 ± 0.1	0.9 ± 0.1	0.8 ± 0.1	0.7 ± 0.1
V	$CH_3CH_2C(O)OCH_3$	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
VI	C_3H_8	1.0 ± 0.1	1.9 ± 0.2	3.2 ± 0.3	4.3 ± 0.4	5.8 ± 0.5	6.7 ± 0.7
VII	CH_4	0.3 ± 0.1	1.5 ± 0.2	3.9 ± 0.4	6.5 ± 0.7	9.1 ± 0.9	10.3 ± 1.0
VIII	CH_3D	0.4 ± 0.1	1.9 ± 0.2	4.7 ± 0.5	6.5 ± 0.7	9.2 ± 0.9	11.1 ± 1.0
IX	C_2H_6	0.3 ± 0.1	1.4 ± 0.1	3.4 ± 0.3	5.1 ± 0.5	7.4 ± 0.7	8.7 ± 0.8
X	C_2H_5D	0.2 ± 0.1	0.6 ± 0.1	1.3 ± 0.1	1.8 ± 0.2	2.5 ± 0.3	3.1 ± 0.3
XI	$CH_3C(O)OCD_3$	1.5 ± 0.1	2.8 ± 0.3	4.7 ± 0.3	6.1 ± 0.6	7.6 ± 0.8	8.7 ± 0.9
XII	$CH_3CH_2C(O)OCD_3$	0.9 ± 0.1	1.8 ± 0.2	3.0 ± 0.3	3.9 ± 0.4	4.8 ± 0.5	5.2 ± 0.5
XIII	$CH_3CH_2C(O)OD$	2.2 ± 0.2	4.3 ± 0.4	7.4 ± 0.6	10.0 ± 0.8	13.3 ± 1.0	15.0 ± 1.4
XIV	CH_3CH_2OD	0.9 ± 0.1	1.9 ± 0.2	3.2 ± 0.3	4.2 ± 0.4	5.5 ± 0.4	6.2 ± 0.6
XV	CH_3OD	0.6 ± 0.1	1.2 ± 0.1	2.0 ± 0.2	2.5 ± 0.3	3.0 ± 0.3	3.1 ± 0.3
XVI	$CH_3CH(OCD_3)C(O)OD$	0.9 ± 0.1	3.4 ± 0.3	6.9 ± 0.7	9.6 ± 0.9	13.3 ± 1.3	15.4 ± 1.5
XVII	$CH_3CH_2OCD_3$	0.3 ± 0.1	0.6 ± 0.1	1.0 ± 0.1	1.3 ± 0.1	1.6 ± 0.2	1.8 ± 0.2
XVIII	C_4H_{10}	0.5 ± 0.1	1.0 ± 0.1	1.6 ± 0.2	2.2 ± 0.2	2.9 ± 0.3	3.4 ± 0.3

Table 1. (Contd.)

Comp. no.	Time, h		
	100	150	250
I	15.6 ± 1.6	6.1 ± 0.6	0.9 ± 0.1
II	8.9 ± 0.9	8.8 ± 0.9	8.2 ± 0.9
III	24.1 ± 2.5	26.8 ± 1.5	28.2 ± 2.9
IV	0.5 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
V	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.1
VI	7.5 ± 0.7	8.5 ± 0.7	9.9 ± 1.0
VII	11.1 ± 1.1	11.8 ± 1.0	12.0 ± 1.2
VIII	12.8 ± 1.3	14.3 ± 1.3	15.1 ± 1.5
IX	9.8 ± 1.0	10.0 ± 1.0	9.3 ± 1.0
X	3.5 ± 0.4	3.8 ± 0.4	3.8 ± 0.4
XI	9.7 ± 1.0	11.2 ± 1.2	14.0 ± 1.5
XII	5.3 ± 0.5	5.2 ± 0.5	5.1 ± 0.5
XIII	16.0 ± 1.5	15.7 ± 1.5	14.3 ± 1.2
XIV	6.4 ± 0.6	6.2 ± 0.7	5.7 ± 0.3
XV	3.0 ± 0.3	2.9 ± 0.3	3.0 ± 0.3
XVI	17.0 ± 1.6	17.0 ± 0.4	14.3 ± 1.4
XVII	1.9 ± 0.2	2.0 ± 0.2	2.1 ± 0.2
XVIII	3.8 ± 0.4	4.3 ± 0.4	5.0 ± 0.5

multiplet polarization, where the first letter relates to polarization of the dowlfield part of the multiplet, and the second, to the upfield part of the multiplet). Similar spectrum is observed at 343 K, but the lines of products with polarized protons are ~3 times weaker. Analysis of the CIDNP effects led us to conclude that the polarization arises in acetyloxyl–ethyl and methyl–ethyl radical pairs (RP), which is nicely consistent with our previous data for thermolysis of the same peroxide in carbon tetrachloride [9].

To gain a deeper insight into the mechanism of the thermolysis of compound **I**, we performed kinetic measurements. The resulting data are presented in Tables 1–3.

Tables 1–3, along with the concentrations of peroxide **I** at various time, show data on the accumulation of principal identified products. The main product of thermolysis of peroxide **I** in methanol-d_3 are ethanoic (**III**), propanoic (**XIII**), and 2-(methoxy-d_3)-propanoic (**XVI**) acids, ethyl ethanoate (**II**), (methyl-d_3) ethanoate (**XI**), methane (**VII**), methane-*d* (**VIII**), and ethane (**IX**). The final yields of these compounds are 10% or higher (macro products). The identified microproducts (final yield lower 10%) include (methyl-d_3) propanoate (**XII**), methanol-*d* (**XV**), ethanol-*d* (**XIV**), (methyl-d_3) ethyl ether (**XVII**),

Table 2. Yields (%) of thermolysis products of 0.1 M solutions of peroxide **I** in methanol-d_4 as a function of thermolysis time at 333 K

Comp. no.	Time, h									
	5	10	15	20	25	30	40	50	60	100
I	68.4±4.0	46.8±0.3	32.0±0.2	21.7±0.2	15.0±0.5	10.2±0.2	4.8±0.2	2.2±0.2	1.1±0.1	0.5±0.1
II	3.3±0.2	5.5±0.1	7.0±0.3	8.1±0.8	8.8±0.5	9.2±0.2	9.8±0.7	10.1±0.5	10.2±0.4	10.2±0.2
III	10.5±0.9	16.7±0.5	20.7±0.1	23.3±0.6	25.1±0.7	26.2±0.5	27.4±0.6	27.8±0.5	27.7±0.9	27.5±1.0
IV	0.6±0.1	0.9±0.1	1.0±0.1	1.1±0.1	1.1±0.1	1.1±0.2	1.0±0.1	0.9±0.1	0.8±0.1	0.5±0.1
V	0.2±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.4±0.1	0.4±0.1	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1
VI	3.2±0.3	5.3±0.5	6.8±0.1	7.8±0.2	8.5±0.7	9.0±0.5	9.5±0.7	9.8±0.5	9.9±0.3	10.0±0.4
VII	4.5±0.5	7.6±0.8	9.7±0.7	11.2±0.4	12.2±1.1	12.8±1.0	13.6±1.4	14.0±1.1	14.1±1.4	14.2±0.3
VIII	6.1±0.6	10.3±0.9	13.1±0.3	15.1±0.4	16.4±1.0	17.3±1.4	18.4±1.8	18.9±1.4	19.1±0.6	19.2±0.5
IX	2.5±0.3	5.1±0.1	6.9±0.4	8.1±0.4	8.7±0.5	9.1±0.5	9.4±0.4	9.4±0.3	9.3±0.3	9.2±0.6
X	1.2±0.1	2.0±0.1	2.6±0.1	3.0±0.1	3.2±0.1	3.4±0.1	3.6±0.2	3.7±0.3	3.8±0.2	3.8±0.2
XI	3.6±0.3	5.7±0.1	7.1±0.5	8.1±0.5	8.4±0.6	8.7±0.4	9.0±0.4	9.2±0.5	9.3±0.9	9.4±0.5
XII	1.7±0.2	2.9±0.2	3.6±0.4	4.0±0.4	4.3±0.2	4.4±0.3	4.5±0.3	4.4±0.3	4.2±0.4	4.0±0.4
XIII	7.1±0.7	10.1±1.0	12.2±0.7	13.3±0.5	13.9±0.5	14.1±1.4	14.1±1.1	13.9±0.8	13.8±1.3	13.7±1.3
XIV	3.6±0.4	3.8±0.4	4.3±0.1	4.5±0.5	4.7±0.5	4.8±0.5	4.8±0.5	4.8±0.4	4.7±0.2	4.7±0.2
XV	2.1±0.2	3.2±0.1	3.7±0.1	3.9±0.2	4.0±0.3	4.0±0.3	3.9±0.2	3.7±0.3	3.6±0.2	3.3±0.1
XVI	11.2±1.4	16.0±0.9	18.2±0.2	19.2±0.9	19.4±0.6	19.4±0.7	18.8±1.2	18.4±0.6	17.6±1.8	17.0±0.6
XVII	0.6±0.1	1.0±0.1	1.3±0.1	1.4±0.2	1.5±0.2	1.6±0.2	1.6±0.2	1.6±0.2	1.5±0.2	1.3±0.1
XVIII	1.6±0.2	2.7±0.3	3.4±0.4	3.9±0.4	4.3±0.4	4.5±0.4	4.8±0.5	4.9±0.4	4.9±0.4	5.0±0.5

Table 3. Yields (%) of thermolysis products of 0.1 M solutions of peroxide **I** in methanol-d_4 as a function of thermolysis time at 343 K

Comp. no.	Time, h									
	1	2	3	4	6	9	12	15	18	25
I	78.7±1.3	62.5±2.9	49.7±0.4	39.4±0.2	24.9±0.2	12.4±0.2	6.1±0.4	3.0±0.1	1.5±0.1	0.3±0.1
II	2.2±0.2	3.8±0.3	5.1±0.6	6.1±0.4	7.6±0.4	8.8±0.9	9.5±0.5	9.8±0.9	9.9±0.4	10.1±0.9
III	5.7±0.6	10.0±1.0	13.4±0.9	16.2±0.9	20.1±2.0	23.4±1.6	25.1±2.1	25.9±1.0	26.3±0.7	26.6±1.3
IV	0.9±0.1	1.2±0.1	1.3±0.1	1.2±0.1	1.0±0.1	0.8±0.1	0.8±0.1	0.7±0.1	0.6±0.1	0.5±0.1
V	0.1±0.1	0.2±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.4±0.1	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1
VI	2.5±0.3	4.6±0.4	6.3±0.2	7.8±0.4	9.8±0.6	11.1±0.4	11.2±0.7	10.8±0.5	10.3±0.4	10.0±0.5
VII	2.3±0.3	4.7±0.5	6.7±0.3	8.2±0.4	10.0±0.3	11.4±0.4	12.0±0.5	12.1±1.0	12.2±0.4	12.3±0.7
VIII	3.3±0.3	6.5±0.7	9.2±0.2	11.2±0.8	13.9±1.4	15.9±1.0	16.7±0.4	17.0±1.1	17.0±1.5	17.1±0.6
IX	1.5±0.2	3.2±0.3	4.7±0.1	5.8±0.3	7.0±0.6	7.7±0.5	7.7±0.4	7.6±0.4	7.4±0.7	7.1±0.9
X	0.9±0.1	1.6±0.2	2.2±0.1	2.5±0.1	3.1±0.3	3.4±0.2	3.6±0.2	3.7±0.3	3.6±0.3	3.7±0.4
XI	3.1±0.3	5.2±0.5	6.8±0.7	8.0±0.8	9.7±0.9	11.0±1.0	11.7±1.2	12.1±1.2	12.3±1.0	12.5±1.0
XII	1.3±0.1	2.3±0.2	2.9±0.2	3.3±0.3	3.8±0.2	4.0±0.2	4.0±0.4	4.0±0.4	3.9±0.4	3.9±0.4
XIII	1.8±0.2	3.5±0.4	5.0±0.2	6.4±0.3	8.5±0.9	10.7±1.0	11.8±0.6	12.2±0.8	12.2±1.0	11.8±0.4
XIV	1.6±0.2	2.6±0.1	3.3±0.2	3.8±0.2	4.2±0.3	4.6±0.2	4.7±0.3	4.9±0.5	4.9±0.5	5.0±0.4
XV	1.3±0.1	2.1±0.1	2.7±0.2	3.1±0.2	3.4±0.2	3.2±0.2	2.8±0.1	2.4±0.2	2.2±0.2	2.1±0.2
XVI	4.7±0.5	8.0±0.4	10.5±0.4	12.2±0.5	14.4±0.3	15.9±1.0	16.3±0.6	16.5±0.9	16.6±0.8	16.7±0.9
XVII	0.7±0.1	1.1±0.1	1.4±0.2	1.5±0.2	1.7±0.2	1.7±0.2	1.6±0.1	1.6±0.1	1.5±0.1	1.5±0.1
XVIII	1.3±0.1	2.3±0.2	3.2±0.3	3.9±0.4	4.9±0.4	5.6±0.5	5.6±0.5	5.4±0.5	5.2±0.4	5.0±0.4

propane (**VI**), butane (**XVIII**), ethane-*d* (**X**), ethene (**IV**), and methyl propanoate (**V**).

The time dependences of the concentration of peroxide **I** in the coordinates $\ln(c_0/c_t)$–t, where c_0 is the initial concentration of peroxide **I** and c_t is the concentration of compound **I** at time t, are close to linear for all the three temperatures. Consequently, the decomposition of compound **I** is an irreversible reaction of the first or pseudo-first order. The decomposition rate constants k are $(5.19 \pm 0.02) \times 10^{-6}$, $(2.10 \pm 0.01) \times 10^{-5}$, $(6.46 \pm 0.01) \times 10^{-5}$ s^{-1} for 323, 333, and 343 K, respectively. Using the Arrhenius equation, we obtained Eq. (1) for the apparent rate constant of peroxide **I** decomposition in methanol:

$$k = 5.0 \times 10^{13} \exp[-(116 \pm 12)/RT]. \quad (1)$$

Here the activation energy is given in kJ/mol. The resulting values for the parameters of the Arrhenius equation are in a good agreement with respective values for aliphatic diacyl peroxides [1].

Earlier we studied thermolysis of 0.5 M solutions of compound **I** in carbon tetrachloride [9]. With the rate constants obtained in that work, the Arrhenius equation can be written in form (2):

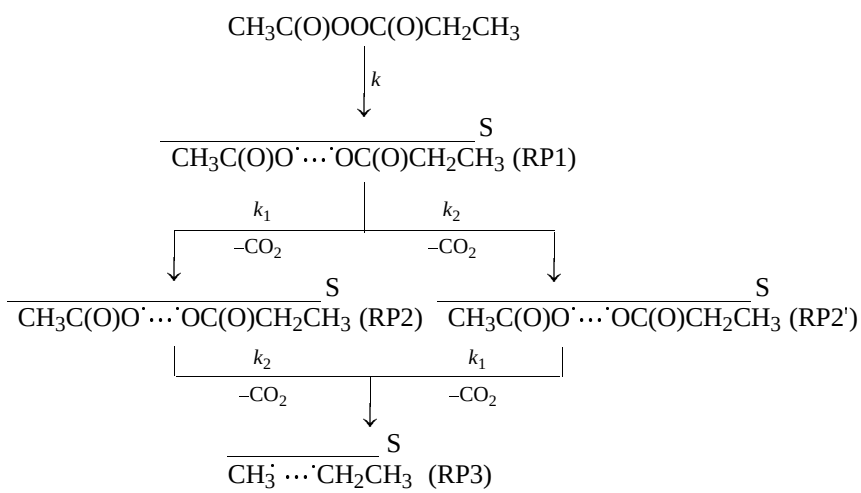
$$k = (1.4 \pm 0.4) \times 10^{14} \exp[-(123 \pm 2)/RT]. \quad (2)$$

Comparing Eqs. (1) and (2), we can state that the solvent takes an active part in thermolysis of peroxide **I** in methanol, thus accelerating the process and reducing its activation energy.

Calculations by Eq. (1) showed that compound **I** would decompose at an appreciable rate already at 275 K. The solution of peroxide **I** was kept for a year at 275 K. The resulting data are given below. Only 5 compounds could be detected: peroxide **I**, ethanoic (**III**) and propanoic (**XIII**) acids, and their methyl-d_3 esters **XI, XII**.

Comp. no.	Yield, %
I	72.4 ± 6.9
III	11.7 ± 1.3
XI	16.0 ± 1.5
XII	12.2 ± 1.3
XIII	16.8 ± 1.7

Thus, the CIDNP effects and the data in Tables 1–3 establish that peroxide **I** in methanol-d_4 is partially thermolyzed by the radical mechanism described in [1–5].



According to the above mechanism, under the action of temperature peroxide **I** decomposes to give acetoxyl and propionyloxyl radicals which form a primary geminate radical pair (RP1). The radicals in this pair can undergo various transformations: First, recombination to the starting peroxide; second, conversion to an acid, after leaving the solvent "cage" and proton or deuterium abstraction from metanol-d_4 or reaction products; and third, decarboxylation to give a secondary radical pair (RP2, RP2'). The radicals in RP2' recombine, affording methyl propanoate, and abstract hydrogen or deuterium from reaction products or methanol-d_4, yielding methane and propanoic acid after leaving the solvent "cage." The radicals in RP2, apart from recombination to ethyl ethanoate, can disproportionate, affording ethanoic acid and ethene.

Moreover, after leaving the solvent "cage" and hydrogen and deuterium abstraction they form ethanoic acid and ethane, both deuterated and not.

The CIDNP effects on ethyl ethanoate and propane protons, the appreciable yields of ethyl ethanoate and the low yields of methyl propanoate suggest that a route involving convertion of RP1 to RP2 prevails. In the scheme, the decarboxylation rate constant for propionyloxyl radicals is labeled k_1, and that for acetyloxyl radicals, k_2.

Complete decarboxylation of the acyloxyl radicals gives rise to a methyl–ethyl radical pair (RP3). The radicals in this pair recombine to give propane, disproportionate, yielding methane and ethene, and, after leaving the "cage," methane and ethane, both deuterated and not.

Earlier we proposed a procedure for estimating the decarboxylation rate constants of acyloxyl radicals [10]. According to this procedure, k_1 and k_2 are determined, based on the radical pair theory [11, 12], from a comparison of a theoretical NMR spectrum of the recombination product of RP3 with polarized nuclei with an experimental spectrum of the same product, obtained in the course of the reaction, with account for spin-lattice relaxation times. In addition, for more reliable results, theoretical and experimental yield ratios for "cage" products formed from RP2, RP2', and RP3 are compared.

In [13], we obtained k_1 and k_2 for thermolysis of 0.5 M solutions of peroxide **I** in carbon tetrachloride. Comparing the yields of "cage" products of thermolyses of compound **I** in carbon tetrachloride [13] and methanol-d_4 we noted that the ratios of the total yields of recombination products for RP2 (ethyl ethanoate and 2-chloroethyl ethanoate) and RP3 (propane and 2-chloropropane) are ~5 and ~1.3, respectively.

To find out the reasons for this difference, we measured the ^{1}H NMR spectra of 0.1 M solutions of peroxide **I** in carbon tetrachloride at 353 K (Fig 1b). Note that the ^{1}H CIDNP NMR spectra of CCl_4 solutions with various concentrations of compound **I** (0.1 and 0.5 M) are qualitatively similar to each other, except for an inconsiderable difference in the intensities of propane and chloroethane lines. As follows from a comparison of Figs. 1a and 1b, the methyl proton signals of propane are almost identical. Moreover, the yield ratios of ethyl ethanoate and methyl propanoate for thermolyses of 0.1 M solutions of compound **I** in CCl_4 and CD_3OD, are almost equal to each other (~18).

It is thus reasonable to suggest that k_1 and k_2 for the acyloxyl radicals resulting from thermolysis of peroxide **I** in carbon tetrachloride are equal to respective values for thermolysis of **I** in methanol-d_4. The same should be true of the yield ratios of "cage" products, i.e., the yield of propane from recombination of methyl and ethyl radicals should be ~3% (Tables 1–3). Consequently, ~7% of propane are formed by another reaction (see below).

Thus, by the procedure described in [10] we, taking account of the aforesaid, estimated parameters of the Arrhenius equation for decarboxylation of propionyloxyl (k_1) and acetyloxyl (k_2) radicals.

$$k_1 = 5 \times 10^{11} \exp[-(7 \pm 3)/RT], \quad (3)$$

$$k_2 = 2 \times 10^{13} \exp[-(27 \pm 6)/RT]. \quad (4)$$

Analysis of the products of the thermolysis of compound **I** (Tables 1–3) shows that the formation of some of them cannot be explained in terms of a classical scheme of radical homolysis. It is reasonable to suggest that methyl-d_3 ethanoate and methyl-d_3 propanoate are formed by methanolysis of the starting peroxide, i.e., by a nonradical reaction.

$$CH_3C(O)OOC(O)CH_2CH_3 + CD_3OD$$
$$\rightarrow CH_3C(O)OCD_3 + CH_3CH_2C(O)OOD,$$
$$\rightarrow CH_3C(O)OOD + CH_3CH_2C(O)OCD_3.$$

Therewith, methyl-d_3 ethanoate prevails at all the temperatures. At low temperatures its yield is 1.3 times higher than that of methyl-d_3 propanoate, whereas in the range 323–343 K this ratio increases to 3. These results point to a primarily nucleophilic substitution by the acetyl carbonyl.

Peroxypropanoic and peroxyethanoic acids could not be detected at any thermolysis stage, apparently because of their thermal instability. However, the possibility of formation of these products can be deduced from the fact that in the course of thermolysis of peroxide **I** in water-d_2 we found a mixture of the corresponding acids and peroxy acids, which further decomposed with acid formation.

It is known that peroxy acids can decompose by a nonradical mechanism, yielding acids and oxygen [1].

$$CH_3C(O)OOD \longrightarrow CH_3C(O)OD + 1/2O_2,$$
$$CH_3CH_2C(O)OOD \longrightarrow CH_3CH_2C(O)OD + 1/2O_2.$$

This route is prevailing both in a strongly polar liquid (D_2O) and in methanol-d_4 at low temperatures and, partially, at 323–343 K. Simultaneously, non-

radical decomposition of peroxy acids can also take place [1].

$$CH_3CH_2C(O)OOD \longrightarrow \overline{CH_3CH_2C(O)O^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP4)}$$

$$\longrightarrow \overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP5)} \longrightarrow CH_3CH_2OD,$$

$$CH_3C(O)OOD \longrightarrow \overline{CH_3C(O)O^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP6)}$$

$$\longrightarrow \overline{CH_3^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP7)} \longrightarrow CH_3OD.$$

Evidence in favor of this route is provided by the presence among final products at 323–343 K of ethanol-*d* and methanol-*d*. No CIDNP effects were observed with the alcohols, which can be explained by the low concentration of the peroxy acids and the short time of electron relaxation for hydroxyl radical [14], which, in its turn, results in a loss of spin correlation in radical pairs RP4–RP7, thus reducing the yield of the alcohols.

However, we could observe nuclear polarization in alcohols in the course of photolysis of methanolic solutions of peroxy acids and acids, which is in itself interesting in terms of magnetic and spin effect studies.

Finally, one more group of compounds exists, formed by radical reactions with thermolysis products of compound **I**. They include 2-(methoxy-d_3)-propanoic acid, methyl-d_3 ethyl ether, butanes, and most propane. The first of the listed compounds is formed by α-proton abstraction by different radicals from propanoic acid, followed by recombination of the resulting radical with methoxy-d_3 radical. The ether and alkanes are formed by addition be the ethene double bond of methoxy-d_3-ethyl and methyl radicals, respectively, followed by hydrogen abstraction.

It should be noted that methanol-d_4 gives rise primarily to methoxyl-d_3, rather than hydroxymethyl-d_3 radicals, which is consistent with data of Shannon and Harrison [15], who showed that methyl radicals more readily abstract from methanol the hydroxyl proton compared with methyl protons.

As seen from data in Tables 1–3, when the temperature is raised from 323 to 343 K, the final yields of the products do not change considerably, even though the low-temperature thermolysis is no more than methanolysis and, therefore, has a much simpler mechanism.

Thus, for instance, the total yield of deuterated and undeuterated ethane is slightly reduced, like the total yields of alcohols and ethanoic and propanoic acids, whereas the total yield of propanoic and 2-(methoxy-d_3)propanoic acids is almost unchanged. However,

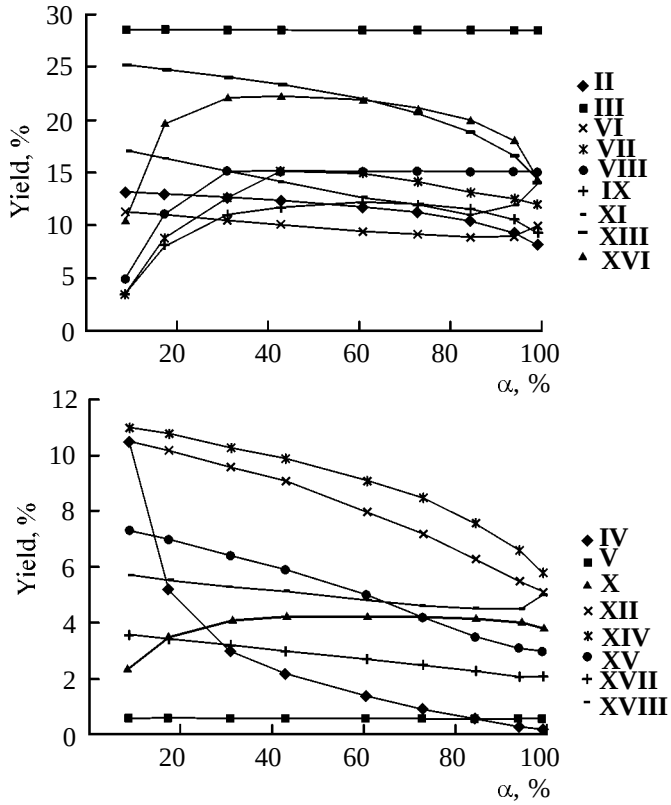


Fig. 2. Yields (reduced to 100% peroxide decomposition) of products (%) of thermolysis of a 0.1 M solution of peroxide **I** in methanol-d_4 as a function of the fraction of decomposed peroxide (α, %) at 323 K. The curve numbers are the same as the compound numbers in Tables 1–3.

the yields of thermolysis products give only a general idea of the overall process. A more interesting information on the relative contributions of the reaction routes can be gained from the ratios of the concentrations of the products to the concentration of decomposed peroxide (yield reduced to 100% peroxide decomposition) for all the time points.

Figures 2 and 3 depict the plots of the reduced yields of thermolysis products as a function of the fraction of decomposed peroxide (α) at 323 and 343 K. For clarity sake, the yields of macro and micro-products are given in different scales.

The first observation is that the yield of ethene (**IX**) decreases with increasing α. This fact provides evidence for our assumption that part of propane and, probably, all butane are formed by addition of methyl and ethyl radicals to ethene. The resulting propyl and butyl radicals are not very active and abstract hydrogen rather than deuterium. The main source of hydrogen are, in our opinion, the least strongly bound α-

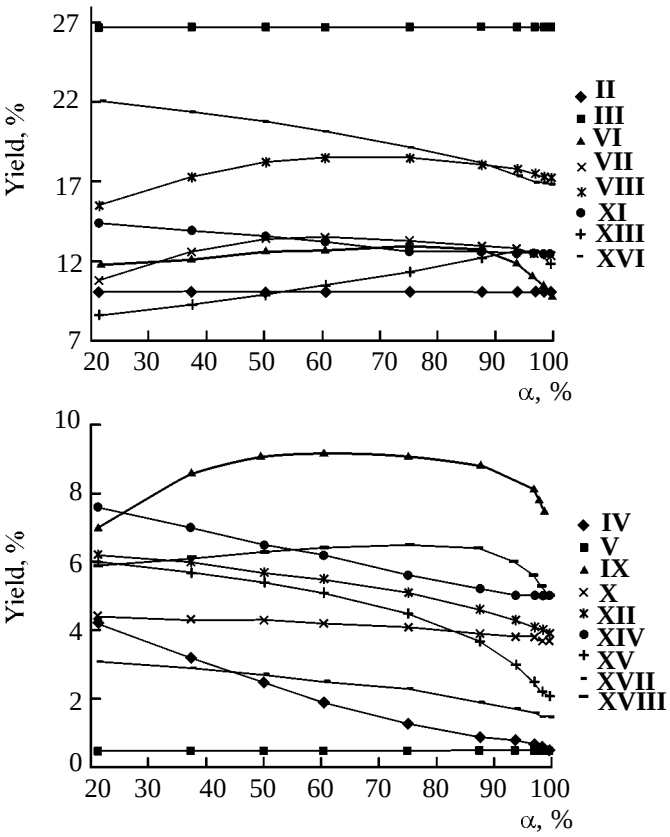


Fig. 3. Yields (reduced to 100% peroxide decomposition) of products (%) of thermolysis of a 0.1 M solution of peroxide **I** in methanol-d_4 as a function of the fraction of decomposed peroxide (α, %) at 343 K. The curve numbers are the same as the compound numbers in Tables 1–3.

CH_2 protons of propanoic acid (much this acid is formed by thermolysis). The more reactive ethyl and, especially, methyl radicals are less selective and can abstract deuterium from methanol-d_4 to form ethane-*d* and methane-*d*.

We determined the yield ratios for protonation and monodeuteration of these radicals. The ratio $[CH_4]/[CH_3D]$ varies from 0.86 ± 0.06 to 0.72 ± 0.01, and the ratio $[C_2H_6]/[C_2H_5D]$, from 2.68 ± 0.14 to 2.13 ± 0.08, as the temperature is raised from 323 to 343 K. Thus, the fraction of deuterated products increases with temperature, implying that the activation energy of duterium abstraction from the solvent is higher than that of hydrogen abstraction from various compounds. Therewith, the yield ratio is independent of the depth of thermolysis and, consequently, of the concentration of the starting peroxide.

Unlike the above case, the relative total yield of methyl-deuterated esters decreases with inreasing depth of thermolysis, implying increasing contribution of the nonradical mechanism of thermolysis with increasing peroxide concentration.

The aforesaid also applies to alcohols, since their yield depends on the contribution of nonradical decomposition. The latter processes prevail at low temperatures, which corresponds to their lower activation energies compared with radical processes.

The results of the present study allow the mechanism of thermolysis of peroxide **I** in methanol-d_4 to be described by reactions (5)–(37):

$$\text{Peroxide } \mathbf{I} \longrightarrow \overline{CH_3CH_2C(O)O^{\cdot}\cdots{}^{\cdot}OC(O)CH_3}^{S}\ (RP1), \quad (5)$$

$$CH_3CH_2C(O)O^{\cdot} \longrightarrow CH_3CH_2^{\cdot} + CO_2, \quad (6)$$

$$CH_3C(O)O^{\cdot} \longrightarrow CH_3^{\cdot} + CO_2, \quad (7)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}OC(O)CH_3}^{S}\ (RP2) \longrightarrow CH_3CH_2OC(O)CH_3, \quad (8)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}OC(O)CH_3}^{S}\ (RP2) \longrightarrow CH_2{=}CH_2 + CH_3C(O)OH, \quad (9)$$

$$\overline{CH_3^{\cdot}\cdots{}^{\cdot}OC(O)CH_2CH_3}^{S}\ (RP2') \rightarrow CH_3OC(O)CH_2CH_3, \quad (10)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}CH_3}^{S}\ (RP3) \longrightarrow CH_3CH_2CH_3, \quad (11)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}CH_3}^{S}\ (RP3) \longrightarrow CH_2{=}CH_2 + CH_4, \quad (12)$$

$$CH_3CH_2C(O)O^{\cdot} + CD_3OD \longrightarrow CH_3CH_2C(O)OD + CD_3O^{\cdot}, \quad (13)$$

$$CH_3C(O)O^{\cdot} + CD_3OD \longrightarrow CH_3C(O)OD + {}^{\cdot}CD_3O, \quad (14)$$

$$CH_3CH_2C(O)O^{\cdot} + RH \longrightarrow CH_3CH_2C(O)OH + {}^{\cdot}R, \quad (15)$$

$$CH_3C(O)O^{\cdot} + RH \longrightarrow CH_3C(O)OH + {}^{\cdot}R, \quad (16)$$

$$CH_3CH_2^{\cdot} + CD_3OD \longrightarrow CH_3CH_2D + CD_3O^{\cdot}, \quad (17)$$

$$CH_3^{\cdot} + CD_3OD \longrightarrow CD_3O^{\cdot} + CH_3D, \quad (18)$$

$$CH_3CH_2^{\cdot} + RH \longrightarrow CH_3CH_3 + {}^{\cdot}R, \quad (19)$$

$$CH_3^{\cdot} + RH \longrightarrow CH_4 + {}^{\cdot}R, \quad (20)$$

$$CH_2{=}CH_2 + CH_3CH_2^{\cdot} \longrightarrow CH_3CH_2CH_2CH_2^{\cdot}, \quad (21)$$

$$CH_3CH_2CH_2CH_2^{\cdot} + RH \longrightarrow CH_3CH_2CH_2CH_3 + {}^{\cdot}R, \quad (22)$$

$$CH_2{=}CH_2 + CH_3^{\cdot} \longrightarrow CH_3CH_2CH_2^{\cdot}, \quad (23)$$

$$CH_3CH_2CH_2^{\cdot} + RH \longrightarrow CH_3CH_2CH_3 + {}^{\cdot}R, \quad (24)$$

$$CH_2{=}CH_2 + CD_3O^{\cdot} \longrightarrow CD_3OCH_2CH_2^{\cdot}, \quad (25)$$

$$CD_3OCH_2CH_2^{\cdot} + RH \longrightarrow CD_3OCH_2CH_3 + {}^{\cdot}R, \quad (26)$$

$$\text{Peroxide } \mathbf{I} + CD_3OD \longrightarrow CH_3CH_2C(O)OOD + CH_3C(O)OCD_3, \quad (27)$$

$$\text{Peroxide } \mathbf{I} + CD_3OD \longrightarrow CH_3C(O)OOD + CH_3CH_2C(O)OCD_3, \quad (28)$$

$$CH_3CH_2C(O)OOD \longrightarrow CH_3CH_2C(O)OD + 1/2O_2, \quad (29)$$

$$CH_3C(O)OOD \longrightarrow CH_3C(O)OD + 1/2O_2, \quad (30)$$

$$CH_3CH_2C(O)OOD \rightarrow \overline{CH_3CH_2C(O)O^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP4)}, \quad (31)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP5)} \longrightarrow CH_3CH_2OD, \quad (32)$$

$$\overline{CH_3CH_2^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP5)} \longrightarrow CH_2{=}CH_2 + HOD, \quad (33)$$

$$CH_3C(O)OOD \longrightarrow \overline{CH_3C(O)O^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP6)}, \quad (34)$$

$$\overline{CH_3^{\cdot}\cdots{}^{\cdot}OD}^{S,F} \text{ (RP7)} \longrightarrow CH_3OD, \quad (35)$$

$$CH_3CH_2C(O)OD + {}^{\cdot}R \longrightarrow CH_3^{\cdot}CHC(O)OD + RH, \quad (36)$$

$$\overline{CH_3^{\cdot}CHC(O)OD\cdots{}^{\cdot}OCD_3}^{F} \text{ (RP8)} \longrightarrow CH_3CH(OCD_3)C(O)OD. \quad (37)$$

The apparent rate constant of the decomposition can be represented by Eq. (38):

$$k = k_{rad} + k_{nonrad}[CD_3OD]. \quad (38)$$

Here k_{rad} and k_{nonrad} are the rate constants of radical and nonradical peroxide decomposition.

As follows from the thermolysis scheme, the nonradical route is described by the second-order equations (27) and (28); therewith, k_{nonrad} is given by Eq. (39):

$$k_{nonrad} = W/[I][CD_3OD]. \quad (39)$$

Here W is the sum of the accumulation rates of methyl-deuterated esters (Tables 1–3), measured at the onset of decomposition of compound **I**.

The resulting k_{nonrad} ($mol^{-1}\ s^{-1}$) values were $(6.65 \pm 0.09) \times 10^{-8}$, $(1.59 \pm 0.07) \times 10^{-7}$, $(6.05 \pm 0.08) \times 10^{-7}$ for 323, 333, and 343 K, respectively.

Using Eq. (38), the corresponding k_{rad} (s^{-1}) were calculated: $(3.73 \pm 0.09) \times 10^{-6}$, $(1.75 \pm 0.07) \times 10^{-5}$, and $(5.13 \pm 0.08) \times 10^{-5}$.

By the Arrhenius equation we estimated the apparent rate constants of thermolysis of 0.1 M solutions of peroxide **I** in methanol-d_4.

$$k_{nonrad} = 1 \times 10^9 \exp[-(102 \pm 15)/RT], \quad (40)$$

$$k_{rad} = 3 \times 10^{14} \exp[-(120 \pm 16)/RT]. \quad (41)$$

Thus, the activation energy of the radical decomposition, as we expected, is higher than that of the nonradical decomposition and almost equals the activation energy of thermolysis of peroxide **I** in carbon tetrachloride.

Our study showed that thermolysis of peroxide **I** in methanol-d_4 is an intricate process involving both radical and nonradical reactions, whose contribution depends on the temperature and the concentration of the peroxide.

EXPERIMENTAL

The ^1H NMR spectra were obtained on BS-567A and AM-360 spectrometers at operating frequencies of 100 and 360 MHz, respectively.

Acetyl propionyl peroxide (**I**) was prepared by the procedure in [16]. The active oxygen content, as determined by iodometric titration, was 99.5%. Methanol-d_4 of brand A was used as received. The deuteration degree and the weight fraction of the main substance were 99.5%. 0.1 M solutions of compound **I** were used. For analysis of the reaction products, the peroxide solutions were sealed in glass inserts (2.6 mm i.d.) so that the volume of the gas phase was 10% the volume of the liquid. Under such conditions all gaseous products almost completely remained in the solution and thus could be analyzed. Thermolysis was performed in an oil thermostat at 323, 333, and 343 K. In addition, decomposition of the peroxide solutions at a refrigerator temperature (~275 K) was followed over the course of a year. Periodically, the inserts (by 3 for each measument) were taken off from the thermostat, placed in an NMR tube, and ^1H NMR spectra were measured in the quantitative mode.

To determine the yields of thermolysis products, the ^1H NMR spectra of the initial solutions were first measured and integral intensity ratios of signals of compound **I**, reduced per one proton, to residual proton (OH, CHD_2) signals of methanol-d_4 were determined (correction factors). Further for each time point the integral intensitities of signals of products, reduced per one proton, were related to the integral intensities of residual proton signals of the solvent, and, with account for the correction factors, the yields of the corresponding products were estimated. For control, the yields of compounds formed from different fragments of peroxide **I** [$CH_3C(O)O^{\cdot}$, $CH_3CH_2C(O)O^{\cdot}$] were summarized with the amount of peroxide **I**. This sum was always only slightly less than 100%, thus attesting the analytical procedure.

Unfortunately, the above procedure was unsuitable for analysis of carbon dioxide. However, since the knowledge of its total content carried, by our opinion,

no important mechanistic information, we made no additional efforts to determine the yield of this gaseous product.

The relative error in the yields, averaged over 3 measurements, was ~10%.

Further insight into the thermolysis mechanism was obtained by ^{1}H CIDNP NMR studies on a BS-567A spectrometer using as the internal reference CHD_2OD which is present as the main admixture in CD_3OD, δ 3.50 ppm. The ^{1}H NMR spectra showed characteristic signals of peroxide **I**, δ, ppm: 2.36 s [$CH_3C(O)O$], 2.65 q (CH_2), 1.41 t (CH_3). The spin-lattice relaxation times for the propane line were measured using 180°–τ–90° pulse sequences. The relaxation times differed only slightly.

REFERENCES

1. Antonovskii, V.L., *Organicheskie perekisnye initsiatory* (Organic Peroxide Initiators), Moscow: Khimiya, 1972, pp. 266–340.
2. Rakhimov, A.I., *Khimiya i tekhnologiya organicheskikh perekisnykh soedinenii* (Chemistry and Engineering of Organic Peroxide Compounds), Moscow: Khimiya, 1979, pp. 72–96.
3. Ol'dekop, Yu.A. and Maier, N.A., *Sb. Nauchn. Rabot Akad. Nauk BSSR, Inst. Fiz. Org. Khim.*, 1961, no. 9, pp. 138–218.
4. Walling, Ch., *Free Radicals in Solution*, New York: Wiley, 1957. Translated under the title *Svobodnye radikaly v rastvore*, Moscow: Inostrannaya Literatura, 1960, pp. 374–404.
5. Bagdasaryan, Kh.S., *Teoriya radikal'noi polimerizatsii* (Theory of Radical Polymerization), Moscow: Mir, 1966, pp. 41–50.
6. Razuvaev, T.A. and Latyaeva, Z.N., *Zh. Obshch. Khim.*, 1956, vol. 26, no. 7, pp. 1986–1991.
7. Dutka, V.S., Pankevich, R.V., and Koval'skii, Ya.P., Abstracts of Papers, *Vsesoyuznoe Soveshchanie "Kinetika radikal'nykh reaktsii v zhidkoi faze"* (All-Union Conf. "Kinetics of Liquid-Phase Radical Reactions"), Gorki, 1987, p. 108.
8. Dutka, V.S., Pankevich, R.V., and Soltys, M.N., Abstracts of Papers, *IX Vsesoyuznaya konferentsiya po khimii organicheskikh i elementoorganicheskikh peroksidov* (All-Union Conf. on Chemistry of Organic and Organoelement Peroxides), Gorki, 1990, p. 133.
9. Skakovskii, E.D., Stankevich, A.I., Lamotkin, S.A., Tychinskaya, L.Yu., and Rykov, S.V., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 6, pp. 881–887.
10. Turetskaya, E.A., Skakovskii, E.D., Rykov, S.V., Glazkov, Yu.V., and Ol'dekop, Yu.A., *Dokl. Akad. Nauk BSSR*, 1980, vol. 24, no. 1, pp. 57–59.
11. Kaptein, R., *J. Am. Chem. Soc.*, 1972, vol. 94, no. 18, pp. 6262–6269.
12. Hollander, J.A. Den, *Chem. Phys.*, 1975, vol. 10, no. 1, pp. 167–184.
13. Skakovskii, E.D., Lamotkin, S.A., and Tychinskaya, L.Yu., *Zh. Prikl. Spektrosk.*, 1997, vol. 64, no. 3, pp. 306–311.
14. Gragerov, I.P., Kiprianova, L.A., and Levit, A.F., *Khimicheskaya polyarizatsiya yader v issledovanii mekhanizma reaktsii organicheskikh soedinenii* (Chemical Nuclear Polarization in Investigation of Mechanisms of Organic Reactions, Kiev: Naukova Dumka, 1985.
15. Shannon, T.W. and Harrison, A.G., *Can. J. Chem.*, 1963, vol. 41, no. 10, pp. 2455–2461.
16. El'nitskii, A.P., Ol'dekop, Yu.A., Bezborodov, V.S., Stankevich, A.I., Glazkov, Yu.V., and Skakovskii, E.D., *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, 1976, no. 2, pp. 58–61.