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Thermal Decomposition of Acetyl Propionyl Peroxide in Acetone-d_6

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Abstract—The kinetics of thermolysis of acetyl propinyl peroxide in acetone-d_6 in the temperature range 323–373 K was studied using NMR spectroscopy and the effect of chemically induced nuclear polarization. The peroxide decomposes in acetone at rates comparable with the rates of thermolysis in alcohols, yielding numerous products. In the examined temperature range, the solvent molecules act as efficient donors of deuterium atoms, forming acetylmethyl-d_5 radicals which recombine to a significant extent with the peroxide radicals. A scheme of the processes involved in decomposition of the peroxide was suggested. The parameters of the Arrhenius equation for the peroxide decomposition were determined.

Diacyl peroxide are widely used as initiators of polymerization and other free-radical reactions in chemical and petrochemical industries. Therefore, it seems important to analyze the products of decomposition of diacyl peroxides in cheap and available solvents commercially produced in large amounts.

One of such solvents is acetone. Data on decomposition of diacyl peroxides in acetone are scarce. Bagdasar'yan and Mulyutinskaya [1, 2] studied only the rate of thermolysis of a 0.185 solution of benzoyl peroxide at 348 K and determined the yields of benzoic acid and carbon dioxide. Leffler *et al.* studied the effect of methoxy and nitro substituents on the contributions of the radical and nonradical mechanisms in thermolysis of benzoyl peroxide [3] and determined the yield of certain products in decomposition of unstable bis(*o*-iodophenylacetyl) peroxide [4]. Dutka *et al.* [5] measured the rates of thermal decomposition of a series of diacyl peroxides and determined the contribution of the induced decomposition to the apparent constant of the process.

For aliphatic diacyl peroxides, we found only a single paper [6] in which the product yields in decomposition of acetyl peroxide in a mixture of acetone with carbon tetrachloride were reported.

Our goals were to study the effects of chemically induced nuclear polarization, perform kinetic measurements, and analyze, on the basis of the results obtained, the mechanism of thermolysis of one of the simplest unsymmetrical aliphatic diacyl peroxides, acetyl propionyl peroxide **I**, in acetone-d_6.

Figure 1 shows the ^{1}H NMR spectrum of a 0.5 M solution of **I** in the course of thermolysis. Positively polarized are the protons of ethene [δ 5.39 ppm, s (4H)], methylene protons of 2-pentanone-d_5 $CH_3CH_2 \cdot CD_2COCD_3$ [1.59 ppm, m (2H)], and methyl protons of butanone-d_5 $CH_3CD_2COCD_3$ [0.98 ppm, quintet (3H)] and propane [0.92 ppm, t (3H)]. Negatively polarized are the methylene protons of ethyl ethanoate [4.10 ppm, q (2H)] and propane [1.39 ppm, m (2H)] and methyl protons of 2-pentanone-d_5 [0.89 ppm, t (3H)] and methanes [0.19 ppm, s (CH_4); 0.17 ppm, t (CH_3D)]. Also, protons of propane and 2-pentanone-d_5 have an insignificant contribution of the multiplet
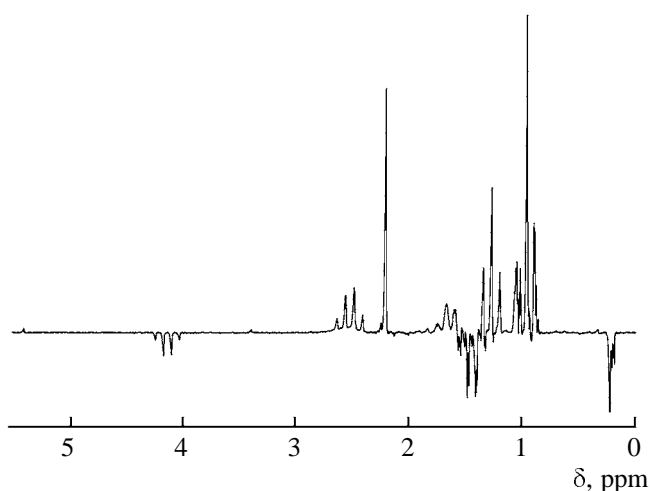
Fig. 1. ^{1}H NMR spectrum of a 0.5 M solution of peroxide **I** in acetone-d_6 at 368 K in the course of thermolysis.
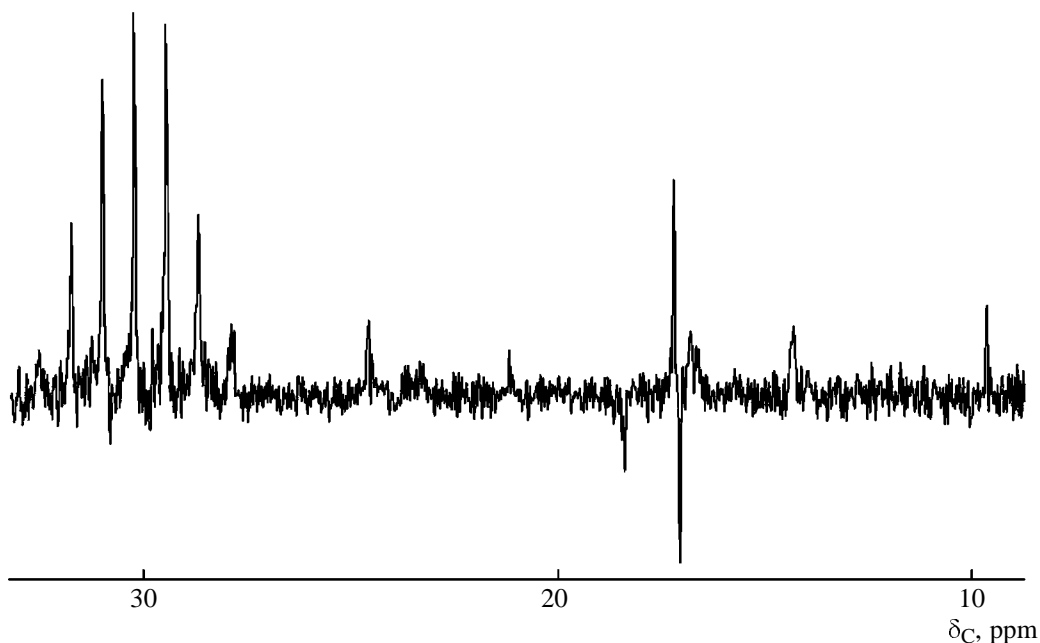
Fig. 2. ^{13}C NMR spectrum of a 0.5 M solution of peroxide **I** in acetone-d_6 at 368 K in the course of thermolysis.

chemically induced nuclear polarization. In thermolysis of the 0.1 M solution, the effects of nuclear polarization are virtually the same as in thermolysis of the 0.5 M solution, except that the polarization of fully protonated methane is absent, probably because of the lower probability of hydrogen abstraction with the methyl radical.

The ^{13}C NMR spectrum of a solution of **I** in the course of thermolysis is shown in Fig. 2. Positively polarized are the carbon atoms of the methylene group in propane (δ_C 17.2 ppm) and methyl group in 2-pentanone-d_5 (δ_C 14.4 ppm). Negatively polarized are the carbon atoms of the methylene group of 2-pentanone-d_5 (δ_C 18.4 ppm) and methyl groups of propane (δ_C 17.0 ppm).

We failed to observe the polarization of the carbon atoms in ethyl ethanoate and carbon dioxide, although in the ^{13}C NMR spectrum of the final products these compounds give the strongest signals. This may be caused by low coefficients of enhancement of the chemical polarization by these nuclei.

The observed effects of chemically induced nuclear polarization suggest that the polarization of nuclei in ethene, ethyl ethanoate, and methanes arises in singlet ethyl–ethanoyloxy radical pairs (RPs). The polarization of propane is additionally manifested in ethyl–methyl radical pairs after decarboxylation of ethanoyloxy radicals. The results obtained are well consistent with our data on thermolysis of **I** in CCl$_4$ [7] and CD$_3$OD [8].

The ^{1}H NMR spectrum of propane with polarized protons coincides in shape with the spectrum of propane formed in thermolysis of peroxide **I** in CCl$_4$. Therefore, we can state that the mean constant of decarboxylation of the ethanoyloxy radical in both cases is approximately equal, ~4 × 10^9 s^{-1} [9].

The nuclear polarization in butanone-d_5 and 2-pentanone-d_5 arises in noncorrelated methyl–acetylmethyl-d_5 and ethyl–acetylmethyl-d_5 radical pairs, respectively. This fact suggests that the peroxy radicals efficiently detach a deuterium atom from the solvent molecules, and the arising acetylmethyl-d_5 radicals, though being relatively long-lived, readily recombine with the alkyl radicals.

To elucidate the mechanism of thermolysis of **I** in more detail, we performed kinetic studies.

The dependence of the concentration of **I** on time at all the temperatures is approximately linear in the coordinates $\ln(c_0/c_t) = f(t)$, where c_0 is the initial concentration of **I** and c_t is its concentration in time t. This fact indicates that the decomposition of **I** under these conditions is an irreversible first- or second-order reaction. The rate constants (k, s^{-1}) are 4.91 × 10^{-6}, 1.90 × 10^{-5}, 5.59 × 10^{-5}, 1.76 × 10^{-4}, 5.31 × 10^{-4}, and 1.50 × 10^{-3} at 323, 333, 343, 353, 363, and 373 K, respectively. The temperature dependence of the rate constant of thermolysis of **I** is described by the Arrhenius equation:

$$k = (1.3 \pm 0.2) \times 10^{13} \exp[-(114 \pm 3)/RT].$$

Table 1. Product yields (%) in thermolysis of 0.1 M solutions of peroxide **I** in acetone-d_6 at 323 K as influenced by the thermolysis time

Comp. no.	Compound	5 h	10 h	20 h	30 h	50 h	70 h	100 h	150 h	250 h
I	$CH_3CH_2C(O)OOC(O)CH_3$	91.6	83.9	70.4	58.8	41.3	29.1	17.1	7.1	1.2
II	$CH_3CH_2OC(O)CH_3$	1.8	3.4	5.9	8.0	10.7	12.3	13.8	14.9	15.5
III	$CH_3OC(O)CH_2CH_3$	0.1	0.1	0.3	0.3	0.5	0.5	0.6	0.6	0.7
IV	$CH_3C(O)OH$	1.3	2.5	4.7	6.7	9.7	11.9	14.0	15.8	16.8
V	$CH_3CH_2C(O)OD$	0.2	0.3	0.6	0.8	1.2	1.4	1.7	1.9	2.0
VI	CH_4	0.6	1.2	2.4	3.5	5.3	6.5	7.6	8.6	9.2
VII	CH_3D	1.9	3.9	7.7	11.3	17.1	21.0	24.5	27.7	29.7
VIII	C_2H_6	0.3	0.8	1.9	2.9	4.3	5.3	6.2	6.9	7.3
IX	C_2H_5D	0.6	1.3	3.2	4.9	7.3	9.0	10.4	11.6	12.3
X	$CH_3CH_2CH_3$	0.6	1.2	2.2	3.1	4.5	5.5	6.5	7.4	7.9
XI	$CH_3CH_2CH_2CH_3$	0.1	0.2	0.3	0.4	0.6	0.8	0.9	1.1	1.1
XII	$CH_3CH_2CD_2C(O)CD_3$	1.0	2.0	3.7	5.1	7.3	8.8	10.3	11.5	12.3
XIII	$CH_3CD_2C(O)CD_3$	0.3	0.6	1.0	1.3	1.8	2.1	2.3	2.6	2.6

Table 2. Product yields (%) in thermolysis of 0.1 M solutions of peroxide **I** in acetone-d_6 at 343 K as influenced by the thermolysis time

Compound	1 h	2 h	3 h	4 h	6 h	9 h	12 h	15 h	18 h	25 h
I	81.8	66.7	54.7	44.6	29.9	16.3	8.9	4.9	2.7	0.6
II	3.7	6.5	8.6	10.4	12.6	14.5	15.5	16.0	16.2	16.4
III	0.2	0.3	0.4	0.5	0.6	0.7	0.7	0.8	0.8	0.8
IV	2.7	5.0	6.8	8.3	10.6	12.6	13.8	14.4	14.8	15.1
V	0.3	0.6	0.8	1.0	1.3	1.5	1.6	1.7	1.8	1.8
VI	1.3	2.5	3.5	4.4	5.7	6.9	7.5	7.9	8.1	8.3
VII	4.8	9.3	13.0	16.2	21.1	25.7	27.9	29.3	29.9	30.5
VIII	1.0	2.1	3.0	3.7	4.6	5.5	6.0	6.3	6.4	6.6
IX	2.0	4.3	6.1	7.6	9.4	11.2	12.2	12.9	13.1	13.5
X	1.7	3.1	4.3	5.2	6.6	7.9	8.6	8.9	9.1	9.3
XI	0.2	0.4	0.6	0.7	0.9	1.1	1.2	1.3	1.3	1.3
XII	2.9	5.4	7.3	9.0	11.4	13.6	14.8	15.4	15.8	16.1
XIII	0.6	1.1	1.4	1.7	2.1	2.4	2.6	2.7	2.7	2.8

Here the activation energy (114±3) is expressed in kJ mol^{-1}. The values obtained are somewhat lower than those characteristic of aliphatic diacyl peroxides [10]. It was shown previously [8] that a decrease in the activation energy in a polar solvent, methanol, by 5–10 kJ mol^{-1} compared to nonpolar CCl$_4$ is due to an additional nonradical pathway of the peroxide decomposition. Acetone is a polar solvent, and it was interesting to find whether nonradical reactions occur in it also.

The content of thermolysis products is given in Tables 1–3 for 323, 343, and 373 K, respectively. Along with the consumption of **I**, we present data on accumulation of the main identified compounds. The major products of the decomposition of peroxide **I** in acetone-d_6 are methane-d **VII**, ethyl ethanoate **II**, 2-pentanone-d_5 **XII**, ethane-d **IX**, ethanoic acid **IV**, and propane **X**. For all these compounds, the final yield approaches 10% or considerably exceeds 10% (macroproducts). The major identified microproducts (final yield less than 10%) are methane **VI**, ethane **VIII**, butanone-d_5 **XIII**, propanoic acid **V**, butane **XI**, and methyl propanoate **III**. In some cases, we also identified residual ethene, but its concentration did not exceed 0.2%; therefore, it was not included in Tables 1–3. The final product yields in thermolysis of **I** at all the six examined temperatures are given in Table 4.
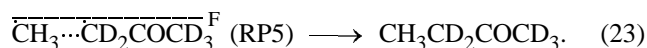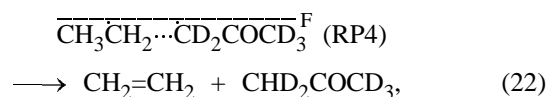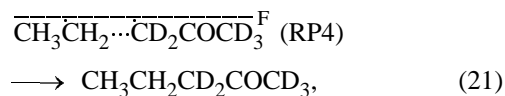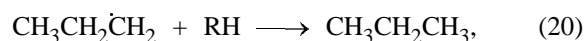
Table 3. Product yields (%) in thermolysis of 0.1 M solutions of peroxide **I** in acetone-d_6 at 373 K as influenced by the thermolysis time

Comp. no.	10 min	20 min	30 min	40 min	50 min
I	40.7	16.5	7.2	2.7	1.1
II	11.3	15.6	17.3	18.0	18.3
III	0.6	0.9	1.0	1.0	1.0
IV	7.7	10.3	11.1	11.5	11.6
V	0.9	1.3	1.4	1.5	1.5
VI	3.8	5.5	6.2	6.3	6.3
VII	19.2	27.7	31.1	31.3	31.4
VIII	2.9	4.2	4.6	4.9	4.9
IX	8.3	11.9	13.1	14.0	14.0
X	6.1	8.6	9.6	10.0	10.2
XI	0.9	1.2	1.4	1.4	1.5
XII	11.6	16.4	18.1	19.0	19.3
XIII	2.8	3.9	4.3	4.5	4.6

Table 4. Final yields of products (%) in thermolysis of 0.1 M solutions of peroxide **I** in acetone-d_6 at various temperatures

Comp. no.	323 K	333 K	343 K	353 K	363 K	373 K
II	15.7	16.1	16.5	17.2	17.8	18.5
III	0.7	0.7	0.8	0.9	0.9	1.0
IV	17.0	16.1	15.2	14.0	12.9	11.7
V	2.0	1.9	1.8	1.7	1.6	1.5
VI	9.3	8.9	8.3	8.6	7.2	6.4
VII	30.1	30.7	30.7	34.2	31.5	31.7
VIII	7.4	7.0	6.6	6.4	5.3	5.0
IX	12.4	13.2	13.6	16.5	14.7	14.2
X	8.0	8.7	9.4	9.9	10.2	10.3
XI	1.1	1.2	1.3	1.4	1.5	1.5
XII	12.4	12.5	16.2	17.2	18.1	19.5
XIII	2.6	2.7	2.8	3.1	3.6	4.7

Tables 1–4 in combination with data on the effects of chemically induced nuclear polarization suggest that the main pathways of radical generation can be described by the scheme suggested in [7, 8].

$$\text{Peroxide I} \xrightleftharpoons{k} \overline{CH_3CH_2C(O)O\cdots\dot{O}C(O)CH_3}^S \ (RP1), \ (1)$$
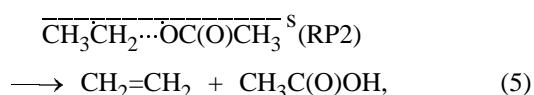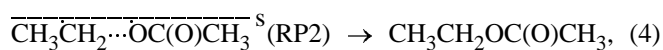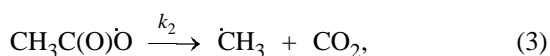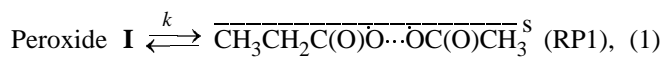
$$CH_3CH_2C(O)\dot{O} \xrightarrow{k_1} CH_3\dot{C}H_2 + CO_2, \qquad (2)$$

$$CH_3C(O)\dot{O} \xrightarrow{k_2} \dot{C}H_3 + CO_2, \qquad (3)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{O}C(O)CH_3}^S (RP2) \to CH_3CH_2OC(O)CH_3, \ (4)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{O}C(O)CH_3}^S (RP2)$$
$$\longrightarrow CH_2=CH_2 + CH_3C(O)OH, \qquad (5)$$

$$\overline{\dot{C}H_3\cdots\dot{O}C(O)CH_2CH_3}^S (RP2') \to CH_3OC(O)CH_2CH_3, \ (6)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{C}H_3}^S (RP3) \longrightarrow CH_3CH_2CH_3, \qquad (7)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{C}H_3}^S (RP3) \longrightarrow CH_2=CH_2 + CH_4, \quad (8)$$

$$CH_3CH_2C(O)\dot{O} + CD_3COCD_3$$
$$CH_3CH_2C(O)OD + \dot{C}D_2COCD_3, \qquad (9)$$

$$CH_3C(O)\dot{O} + CD_3COCD_3$$
$$CH_3C(O)OD + \dot{C}D_2COCD_3, \qquad (10)$$

$$CH_3CH_2C(O)\dot{O} + RH \longrightarrow CH_3CH_2C(O)OH + \dot{R}, \quad (11)$$

$$CH_3C(O)\dot{O} + RH \longrightarrow CH_3C(O)OH + \dot{R}, \qquad (12)$$

$$CH_3\dot{C}H_2 + CD_3COCD_3 \to CH_3CH_2D + \dot{C}D_2COCD_3, \ (13)$$

$$\dot{C}H_3 + CD_3COCD_3 \longrightarrow CH_3D + \dot{C}D_2COCD_3, \ (14)$$

$$CH_3\dot{C}H_2 + RH \longrightarrow CH_3CH_3 + \dot{R}, \qquad (15)$$

$$\dot{C}H_3 + RH \longrightarrow CH_4 + \dot{R}, \qquad (16)$$

$$CH_2=CH_2 + CH_3\dot{C}H_2 \longrightarrow CH_3CH_2CH_2\dot{C}H_2, \quad (17)$$

$$CH_3CH_2CH_2\dot{C}H_2 + RH \longrightarrow CH_3CH_2CH_2CH_3 + \dot{R}, \ (18)$$

$$CH_2=CH_2 + \dot{C}H_3 \longrightarrow CH_3CH_2\dot{C}H_2, \qquad (19)$$

$$CH_3CH_2\dot{C}H_2 + RH \longrightarrow CH_3CH_2CH_3, \qquad (20)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{C}D_2COCD_3}^F (RP4)$$
$$\longrightarrow CH_3CH_2CD_2COCD_3, \qquad (21)$$

$$\overline{CH_3\dot{C}H_2\cdots\dot{C}D_2COCD_3}^F (RP4)$$
$$\longrightarrow CH_2=CH_2 + CHD_2COCD_3, \qquad (22)$$

$$\overline{\dot{C}H_3\cdots\dot{C}D_2COCD_3}^F (RP5) \longrightarrow CH_3CD_2COCD_3. \quad (23)$$

Here the radical pairs are denoted by an overscore, and indices s and F denote their multiplicity: s, singlet and F, noncorrelated radical pairs.

According to the suggested scheme, under the action of temperature peroxide **I** decomposes into a primary geminal pair (RP1). The radicals of this pair can undergo various transformations: firstly, recombine to form the starting peroxide; secondly, to form one of secondary radical pairs (RP2, RP2') after de-

carboxylation of one of the radicals; and thirdly, transform into acids after escaping from the solvent cage and abstracting a hydrogen or deuterium atom from acetone-d_6 or reaction products. Radicals of the RP2 pair, along with recombination into ethyl ethanoate, can disproportionate into ethanoic acid and ethene. Also, after escaping from the solvent cage and abstracting hydrogen or deuterium atoms, they can form ethanoic acid and ethane (deuterated and nondeuterated). Radicals of the RP2' pair recombine to form methyl propanoate and also abstract hydrogen or deuterium atoms from the molecules of the reaction products or solvent to form methane and propanoic acid after escaping from the solvent cage. It was shown previously [7–9] that the rate constant of decarboxylation of the propanoyloxy radical (k_1) in CCl$_4$ and methanol is considerably higher than the rate constant of decarboxylation of the ethanoyloxy radical (k_2). The ratio of the yields of the esters in thermolysis of **I** in acetone-d_6 also indicates that in the first step the propanoyloxy radical is decarboxylated to a greater extent than the ethanoyloxy radical. After complete decarboxylation of the acyloxy radicals, the methyl–ethyl radical pair (RP3) is formed. The radicals of this pair recombine to give propane, disproportionate to give methane and ethene, and, after escaping from the cage, give methane and ethane (deuterated and nondeuterated).

Among intracage decomposition products, only ethyl ethanoate and ethanoic acid are macroproducts. The other macroproducts are primarily formed by the reactions of radicals with solvent molecules; the high concentration of the solvent results in higher yields of deuterated methane and ethane. The ethene formed inside the cage from RP2 and RP3 is permanently attacked by radicals; therefore, its concentration is low both in the course of the peroxide decomposition and after the reaction completion. Note that, in thermolysis of **I** in CD$_3$OD [8], when a part of the peroxide decomposes by the nonradical pathway, ethene is detected in appreciable amounts. Hence, the ethene concentration is an indicator of the contribution of radical processes: The larger their contribution, the lower the amount of ethene remaining in the solution. The addition of methyl and ethyl radicals to ethene in most cases yields propane and butane. Oligomerization of ethene is suggested by the decreased total yield of the products containing ethyl radical. As seen from Table 4, this quantity varies from 61 to 73% depending on the decomposition temperature, whereas the total yield of the products containing the methyl radical is approximately constant, 83–84%. An increase in the total yield of products containing ethyl radical with increasing temperature of thermolysis of **I** is well

consistent with the usually observed decrease in the molecular weight of a polymer with increasing polymerization temperature, which is due to increasing probability of chain termination. This process can be initiated by the solvent itself, i.e., by alcohols. In this case, the yield of low-molecular-weight products of addition of radicals to ethene increases (the yield of butane in methanol-d_4 is 5%, against 1.1–1.5% in acetone-d_6 [8]).

The main fraction of ethanoic acid is formed inside the cage; therefore, in Tables 1–4 its formula is given as CH$_3$COOH. On the contrary, propanoic acid is mainly formed by the reaction of the propanoyloxy radical with deuterated acetone and, to a small extent, by abstraction of the hydrogen atom from the peroxide or its decomposition products. Therefore, its formula is given as CH$_3$CH$_2$COOD. The total yield of carbonyl-containing products (esters, acids) slightly decreases with increasing temperature: from 35.4% at 323 K to 32.7% at 373 K (Table 4), which is due to an increase in the rate of decarboxylation of acyloxy radicals. Within the group of carbonyl-containing compounds, the redistribution is more significant: the yield of esters increases with temperature, whereas the yield of acids, on the contrary, decreases. Since ethanoic acid and ethyl ethanoate are formed from the same pair RP2, such variation of the acid/ester ratio suggests higher probability of recombination of radicals in this pair, compared to disproportionation. This trend is preserved in RP3: With increasing temperature, the yield of propane increases, whereas the yield of methane (disproportionation product) decreases. A decrease in the yield of ethene with increasing temperature is accompanied by an increase in the total yield of identified reaction products containing ethyl radical (the lower the yield of ethene, the lower the extent of its oligomerization).

Among all the radicals capable of abstracting a deuterium atom from the solvent, the methyl and ethyl radicals are the most reactive, as bearing larger energy compared to secondary radicals formed by abstraction of hydrogen or deuterium atoms. At the same time, the methyl radical is more active than the ethyl radical, since the excess energy is distributed among the radicals in inverse proportion with their weight. As a result, although the concentration of ethyl radicals is higher than that of methyl radicals, the yield of deuterated methane at 323 K is higher than that of ethane-d by a factor of ~2.4. As the temperature is increased to 373 K, this ratio decreases to ~2.2, with the increase in the yields of both methane-d and ethane-d.

Let us consider in more detail how the ratio of the yields of deuterated and nondeuterated methanes and
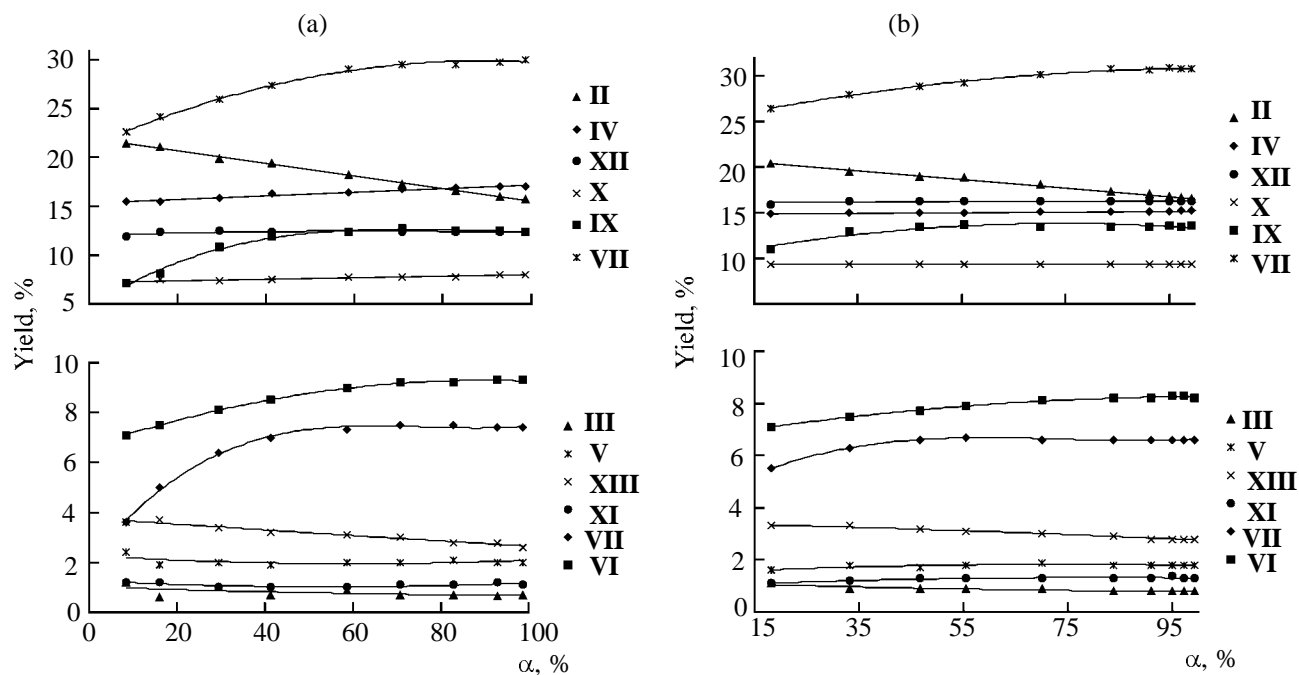
Fig. 3. Yields (recalculated on 100% thermolysis of **I**) of thermolysis products on heating a 0.1 M solution of **I** in acetone-d_6 at (a) 323 and (b) 343 K as functions of the degree α of decomposition of **I**.

ethanes varies with temperature of thermolysis of **I**. The yield of methane decreases not only because of a change in the relative rates of recombination and disproportionation of radicals in the RP3 pair, as aleady noted, but also because of a decrease in the probability of hydrogen abstraction by the methyl radical. The energy of hydrogen abstraction from the α-position of the propanoyloxy fragment is lower than that of deuterium abstraction from acetone-d_6. Therefore, despite more than fourfold higher concentration of acetone compared to the compounds containing labile hydrogen, the yield of methane is comparable with the yield of methane-d (1 : 3.2 ratio). Of course, a part of methane is formed inside the cage, and the actual ratio of CH_4 and CH_3D formed outside the cage differs from 1 : 3.2. The fraction of intracage methane is significant, as follows from indirect evidences: The yield of nondeuterated ethane formed outside the cage is comparable with the yield of nondeuterated methane. As the temperature is increased from 323 to 373 K, the $CH_4 : CH_3D$ ratio changes to 1 : 5, i.e., the selectivity of abstraction of H and D atoms by the methyl radical decreases. A similar trend is observed with the ethyl radical: The $C_2H_6 : C_2H_5D$ ratio changes from 1 : 1.7 at 323 K to 1 : 2.8 at 373 K. It is seen that the less reactive ethyl radical shows higher selectivity in hydrogen or deuteritum abstraction, especially at low temperatures.

There is one more group of compounds whose

formation necessarily involves solvent molecules. We identified only two compounds of this group: 2-pentanone-d_5 and butanone-d_5, both formed in appreciable yields. These ketones are formed by recombination of ethyl and methyl radicals with acetyl-methyl-d_5 radical. 2-Pentanone-d_5 can be additionally formed by the reaction of the $CD_3C(O)\dot{C}D_2$ radical with ethene, followed by hydrogen abstraction. The yields of the ketones increase with temperature.

We considered above the influence of various factors on the product ratio after complete decomposition of the peroxide. Additional information on the reaction pattern can be derived from variation of the concentrations of the products (yields recalculated on 100% decomposition of **I**) and unchanged **I** with time. The yields of the thermolysis products based on the decomposed peroxide **I** at 323 and 343 K are plotted in Fig. 3. For clearness, the yields of the macro- and microproducts are given on different scales.

It is seen that the yields of the majority of products are quasi-constant at different degrees α of decomposition of **I**. However, the yield of ethyl ethanoate decreases with an increase in α, and the yields of methanes and ethanes increase. We believe that such a change in the yields of these compounds in the course of thermolysis is due to the contribution of induced decomposition of **I** at concentrations close to the initial concentrations. An additional cause of the increase

in the yield of the alkanes may be an increase in their solubility as the gas pressure in the ampule grows; this trend is the most pronounced in the initial period of thermolysis.

It should be noted in conclusion that we detected neither alcohols no ethers; this fact indicates that the methyl and ethyl radicals do not add to the solvent molecules to a noticeable extent.

Thus, peroxide **I** decomposes in acetone at rates comparable with the rates of thermolysis in alcohols, yielding a large set of products. In the examined temperature range, the solvent molecules act as efficient donors of D atoms, transforming into acetylmethyl-d_5 radicals which recombine to a significant extent with the radicals generated from the peroxide.

EXPERIMENTAL

Peroxide **I** was prepared as described in [11]. The content of available oxygen, determined by potentiometric titration, was 99.5%.

We studied 0.1 and 0.5 M solutions of **I** in acetone-d_6 (weight fraction of the main substance 99.5%, degree of deuteration 99%). The qualitative and quantitative compositions of the products were determined from the ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra were measured on BS-567A and AM-360 spectrometers operating at 100 and 360 MHz, respectively. The ^{13}C NMR spectra were taken on BS-567A and BS-587A spectrometers operating at 25 and 20 MHz, respectively. To study the effects of chemically induced nuclear polarization in the ^{1}H and ^{13}C NMR spectra, 0.5 M solutions of **I** in sealed ampules were placed in the BS-567A NMR probe preheated to 360 K, and after a 120-s period the accumulation was started. The number of accumulated scans sufficient to obtain an acceptable spectrum was several tens for ^{1}H and 1000 for ^{13}C.

To analyze the reaction products, solutions of **I** were sealed in glass inserts with inner diameters of 2.6 mm for ^{1}H NMR and 6.0 mm for ^{13}C NMR, so that the gas volume did not exceed 10% of the liquid volume. Under such conditions, all the gaseous compounds formed by thermolysis of the peroxide virtually fully remained in the solution, which allowed their quantitative analysis. The thermolysis was performed in an oil thermostat at 323, 333, 343, 353, 363, and 373 K. At definite intervals, the inserts (three for each temperature point) were removed from the thermostat

and placed in an NMR ampule with the outer diameter of 5 (for recording the ^{1}H NMR spectra) and 10 mm (for recording the ^{13}C NMR spectra). With each insert, the NMR spectrum was recorded in the quantitative mode. The relative error in the yield of the products averaged over three measurements was ~8%.

As internal reference in the ^{1}H NMR spectra we used CHD_2COCD_3 (isotope impurity in CD_3COCD_3), δ 2.05 ppm, quintet, and in the ^{13}C NMR spectra, the solvent signal: $δ_C$ 30.2 ppm (CD_3). In the ^{1}H NMR spectra, we observed the characteristic proton signals of peroxide **I** (δ, ppm): 2.17 s [3H, $CH_3C(O)O$], 2.47 q (2H, CH_2), 1.22 t (3H, CH_3), and in the proton-decoupled ^{13}C NMR spectra, the singlets ($δ_C$, ppm) at 170.5 [C(O)O], 167.0 [C(O)O], 24.1 (CH_2), 16.7 [CH_3C(O)O], and 9.6 (CH_3).

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