ANALYSIS OF THE MECHANISM OF PHOTOLYSIS OF METHANOL-*d*₄ SOLUTIONS OF ACETYLPROPIONYL PEROXIDE WITH THE USE OF CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

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On the basis of the effects of chemically induced dynamic nuclear polarization of ¹H and ¹³C and the yields of reaction products, the photolysis of methanol- d_4 solutions of acetylpropionyl peroxide is investigated within the temperature interval 193–333 K. Polarization of all the protons of ethylethanoate is detected; it is shown that the latter is formed in several chemical reactions. The role of different excited states of the peroxide in the mechanism of its photolysis is discussed.

Keywords: chemically induced dynamic nuclear polarization, acetylpropionyl peroxide, photolysis.

Introduction. Diacyl peroxides provide a convenient means of carrying out a comparative analysis of photolytic and thermal modes of decomposition at relatively low temperatures. One of the simplest representatives of asymmetric diacyl peroxides is acetylpropionyl peroxide (APP). Its thermolysis and photolysis in carbon tetrachloride are studied rather thoroughly in [1, 2]. Furthermore, in [3] the parameters of the Arrhenius equation are determined for the reaction of decarboxylizing the short-lived acyloxyl radicals formed in APP decomposition. It was shown in these works that the APP decomposition is described well by the classical scheme of homolysis with the formation of acyloxyl and alkyl radicals. However, an analysis of the thermolysis of APP in methanol- d_4 [4] showed that along with the homolysis one can also observe methanolysis (the nonradical mode of decomposition), which dominates at low temperatures.

The goal of the present work is to study the photolysis of methanol- d_4 solutions of APP at different temperatures on the basis of the effects of chemically induced dynamic nuclear polarization (CIDNP).

Materials and Methods. Acetylpropionyl peroxide was prepared following the procedure described in [5]. The content of active oxygen determined by the method of iodometric titration was 99.5%. We used methanol- d_4 of grade A without preliminary purification. The degree of deuteration and the mass fraction of the basis component were 99.5%. We investigated 0.1-M and 0.5-M APP solutions. To analyze the products, the peroxide solutions were sealed in Pyrex shells with an inner diameter of 2.6 mm in such a way that the gas volume could not exceed 10% of the liquid volume. Under such conditions, all the gaseous compounds formed in APP photolysis remained almost entirely in the solution, which allowed their analysis by the NMR method. Photolysis was carried out in a quartz thermostat, filled with ethyl alcohol, at 213, 233, 253, 273, 293, and 313 K by means of the light of a DRSh-500 mercury lamp after it passed through a water light filter. At certain intervals the shells (three for each point) were withdrawn from the thermostat and placed into the ampule of an NMR spectrometer, and an NMR spectrum was recorded for each shell. The spectra were recorded

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Fig. 1. PMR spectra of 0.1-M methanol- d_4 solutions of acetylpropionyl peroxide during photolysis at 193 (a), 253 (b), and 333 K (c).

on BS-567A and AM-360 spectrometers with an operating frequency of 100 and 360 MHz, respectively. The relative error in determining the yields of the compounds, which was averaged over three measurements, was $\sim 10\%$.

The CIDNP effects were investigated in modified sensors of BS-487C and BS-567A NMR spectrometers with a controlled temperature. The light of a DRSh-1000 mercury lamp was focused on the external end of a quartz light guide, and with the aid of the latter it was guided to the side wall of the quartz Dewar of the NMR sensor [6]. Illumination was performed in broad light that passed through the water light filter. Both quartz and Pyrex NMR ampules were used.

As an internal standard we used CHD₂OD (the main admixture in CD₃OD). A signal was assigned to have a chemical shift of 3.50 ppm. In the ¹H NMR spectra the characteristic signals of APP protons (δ , ppm) were observed: 2.36 singlet [CH₃C(O)O], 2.65 quartet [CH₂], and 1.41 triplet [CH₃], while in the ¹³C NMR spectra with decoupling from protons the corresponding singlets of carbon atoms [δ , ppm] were detected: carbonyl, 171.39 [CH₂C(O)] and 161.81 [CH₃C(O)], methylene, 24.47, and methyl, 16.59 [CH₃C(O)] and 9.58 [CH₃CH₂] (the chemical shifts were determined by the multiplet CD₃OD (49.30 ppm)).

The quantum yields of the APP photolysis (φ) were evaluated by the actinometry technique; for this purpose, a 0.05-M methanol solution of benzophenone was used [7].

Results and Their Discussion. The CIDNP effects on the protons of products occurring during APP photolysis at different temperatures are shown in Fig. 1. The protons of ethene CH₂ (5.57 s) and methane CH₄ (0.39 s) are polarized positively (δ , ppm); the protons of ethylethanoate CH₂ (4.29 q), CH₃C(O)O (2.20 s), methylpropanoate CH₃ (3.84 s), and methane-*d* (0.35 t) are negatively polarized; the protons of propane CH₂ (1.53 m *E/A* + *E*) and of CH₃ (1.10 m *E/A* + *A*) (here *A* is amplified absorption, *E* is emission; *E/A* is the multiplet polarization, where the first letter indicates the CIDNP type of the weak-field part of the multiplet, while the second letter pertains to the strong-field part) have a combined CIDNP (a multiplet effect with admixture of the integral one). Moreover, emission singlets are observed at 2.33 and 2.30 ppm of the unidentified compounds, which are absent in the end products of the photolysis. In our opinion, these can be the signals of the methyl protons of methyl-*d*₃-perethanoate (CH₃C(O)OOCD₃) and of hydroxymethyl-*d*₃-ethanoate



Fig. 2. PMR spectra of methanol- d_4 solutions of ethyl ethanoate during APP photolysis at 213 (a), 253 (b), 293 (c), and 333 K (d); e) the spectrum with equilibrium polarization.

 $(CH_3C(O)OCD_2OD)$. Both compounds are thermally unstable [8, 9]. Furthermore, perether must be photolyzed easily.

A change in the temperature (193–333 K) insignificantly influences the qualitative picture of the CIDNP effects. The principal differences are due to the fact that with increase in temperature there occurs an increase in the intensities of the signals of polarized nuclei due mainly to the increase in the APP decomposition rate. Ethylethanoate is characterized by a complex dependence of the amplification coefficients of CIDNP on temperature, with these coefficients being maximal at about 253 K. Moreover, on the protons of the ethyl group multiplet polarization is also observed, which is summed up with the integral one, which within the same temperature interval changes its sign from A/E at low temperatures to E/A at temperatures higher than 253 K. It should be noted that with increase in temperature, the positive CIDNP of methane is replaced by the negative CIDNP of methane-d.

Thus, the complex dependence of the amplification coefficients of CIDNP for the polarized protons of ethylethanoate and of the slightly changing amplification coefficients of CIDNP for the propane protons poorly fits into the standard picture of the cooperative effect [10] or the "memory" effect [11] for CIDNP in successive radical pairs [12].

In our opinion, the CIDNP effects observed can be explained as follows. As shown previously [2], the APP photolysis proceeds through several excited states. Here, the singlet excited state without a minimum of the potential energy, which leads to the formation of a pair of alkyl radicals, is of primary importance. The singlet excited state with a minimum of the potential energy produces a pair of acetyloxyl and ethyl and, in a smaller amount, of propionyloxyl and methyl radicals. Moreover, when methanol- d_4 is a solvent, the associates of the solvent molecules with both APP and the radicals produced are formed. The change in the chemical shifts of all the APP protons with the temperature of experiments is indicative of the presence of such associates of methanol- d_4 with APP (see Fig. 1). The formation of hydrogen bonds between the methanol- d_4 molecules and the acetyloxyl radicals prolongs the lifetime of the latter and, correspondingly, increases the yield of esters (by approximately three times higher than in carbon tetrachloride [2]). Furthermore, the interaction between the solvent and the acetyloxyl radicals is likely to cause electron density redistribution of the unpaired electron [13] in such a way that superfine interaction occurs on the acetyl group that entails polarization of the corresponding protons of ethylethanoate (2.20 ppm) and of the unidentified compounds (2.33 and 2.30 ppm).

It should be noted that in the course of irradiation we could not detect polarization of either peroxide protons or methanol- d_4 isotopomers present in the solvent. However, it is evident that the polarization of the protons of these compounds should not be a large value; it is easily masked by the proton signals of these compounds with equilibrium polarization.

Product No.	Product	213 K						253 K					313 K		
		t, min													
		10	20	40	60	90	120	10	20	40	60	90	10	20	40
1	CH ₃ CH ₂ C(O)OOC(O)CH ₃	96.5	92.6	86.8	80.8	72.0	64.5	94.9	90.6	82.2	76.3	69.0	90.9	84.3	73.3
2	CH ₂ CH ₂	0.3	0.5	0.9	1.4	2.1	2.8	0.4	0.7	1.1	1.3	1.6	0.6	0.6	0.7
3	CH ₃ CH ₂ OC(O)CH ₃	0.3	0.5	1.1	1.6	2.5	3.3	0.4	0.8	1.4	2.0	2.6	0.6	1.2	1.9
4	CH ₃ CH ₂ C(O)OCH ₃	_	_	0.1	0.2	0.3	0.4	_	0.1	0.2	0.3	0.4	-	0.1	0.2
5	CH ₃ CH ₂ C(O)OD	_	_	_	_	_	_	-	-	-	-	-	-	-	0.3
6	CH ₃ C(O)OCD ₃	_	_	_	_	_	0.6	_	-	-	0.2	0.3	-	-	-
7	CH ₃ C(O)OD	0.3	0.6	1.3	2.0	2.9	3.9	0.5	0.9	1.8	2.7	4.1	1.1	2.2	4.4
8	CH ₃ CH ₂ CH ₃	1.9	4.1	7.2	10.6	15.4	19.5	2.8	5.2	9.6	12.9	16.5	5.0	7.9	11.9
9	CH ₃ CH ₃	0.3	0.5	0.9	1.4	2.1	2.7	0.3	0.6	1.3	1.7	2.1	0.6	1.2	1.8
10	CH ₃ CH ₂ CH ₂ CH ₃	0.2	0.3	0.6	0.9	1.4	1.8	0.3	0.6	1.0	1.3	1.6	0.5	0.9	1.5
11	CH4	0.2	0.4	0.6	1.0	1.4	1.9	0.4	0.7	1.2	1.5	1.8	1.3	2.3	3.5
12	CH ₃ CH ₂ OD	-	_	_	_	_	_	-	-	-	-	1.6	0.6	1.1	2.3
13	CH ₃ D	-	-	—	—	—	—	-	-	-	-	-	0.8	1.4	2.1
14	CH ₃ CH(OCD ₃)C(O)OD	_	_	_	_	_	_	-	-	-	-	-	0.8	2.0	6.0

TABLE 1. Yields (%) of the Decomposition Products of 0.1-M CD₃OD Solutions of Acetylpropionyl Peroxide at 213, 253, and 313 K as a Function of Photolysis Time (t)

We detected a decrease in the intensities of the signals of CHD_2OD in the solvent at temperatures higher than 253 K upon irradiation of the APP solutions, but the effect observed is mainly due to the fact that starting from this temperature the formed radicals effectively separate hydrogen atoms from the solvent rather than from the reaction products, thus decreasing the amount of this compound.

We believe that there are two more possibilities for the occurrence of polarization of methyl protons in the acyl part of esters and perether. First, in [14, 15] it is noted that acyloxyl radicals can be of σ - and π -type, with the π -type radicals, according to calculations, having smaller energy [14]. In that work, the hydrogen and carbon constants of superfine interaction were also calculated for different configurations of formyloxyl and benzoyloxyl radicals of σ - and π -type. The calculations showed that for σ -radicals distinct far-field constants of superfine interaction appear. It is reasonable to presume that the same is typical of the acetyloxyl radicals. Since the radicals formed in photolysis can possess an excess energy, we can expect that in our experiments a great number of σ -acetyloxyl radicals appear, thus leading to nuclear polarization of the methyl groups of the compounds indicated.

The second possibility lies in the fact that, along with CIDNP, in the present situation the optical polarization that occurs with allowance for the triplet APP terms is also possible. This is evidenced by the results of [16], where it is shown that in the case of direct photoexcitation of aromatic diacyl peroxides the O–O-bond dissociates from both the state $S_1(\pi, \sigma^*)$ and the triplet eximer formed by peroxide in the $T_1(\pi, \pi^*)$ state, with the molecule being in the S_0 state.

An interesting feature of the polarization of ethylethanoate protons is the extreme dependence of the change in the intensities of the multiplet lines on the photolysis temperature (Fig. 2). We think that this type of behavior of the polarization of protons can be attributed to the fact that ethylethanoate is formed not only in geminal recombination of ethyl and acetyloxyl radicals but also in recombination of the same radicals formed from different APP molecules. The increase in the APP homolysis rate observed with increase in temperature entails an increase in the intensities of the signals of the polarized protons. However, starting from 253 K the decarboxylizing of acetyloxyl radicals makes a substantial contribution that results in the decrease of the ethylethanoate yield (Table 1) and in an increase in the share of uncorrelated radical pairs that decrease the total amplification coefficients of CIDNP. The latter phonomenon leads to one more interesting consequence. Since in our system the solvent molecules efficiently associate with the APP molecules and, moreover,



Fig. 3. The ¹³C NMR spectra of methanol- d_4 solutions of acetylpropionyl peroxide containing 1 M ¹³CH₃OH: a) during photolysis at 313 K; b) 20 min after photolysis.

the share of the alkyl radical pairs formed from different peroxide terms is high, the proton polarization of ethylethanoate bears evidence of the multiplet polarization initiated from the methyl–ethyl radical pairs. Note that at low temperatures they preserve spin correlation, but starting from 253 K the contribution of the radical pairs that lost this correlation prevails.

The question concerning the contribution of the optical nuclear polarization to the total nuclear polarization could have been closed after investigations of the polarization of carbon atoms. However, we failed to observe noticeable polarization of the carbon atoms of reaction products in photolysis of the 0.5-M APP solutions in a regime of accumulation with decoupling from protons. On the one hand, this can be related with the limited sensitivity of the BS-567 A spectrometer, but, on the other hand, it correlates well with the fact that in the ¹H spectra the multiplet CIDNP prevails on the products' nuclei, while the integral CIDNP is not substantial.

To evaluate the role of a solvent in photochemical reactions, we investigated the nuclear polarization effects of carbon in photolysis of 0.5-M APP solutions containing 1-M methanol enriched with a ¹³C isotope by 85% at 313 K (see Fig. 3a). Positive polarization of methylene carbon atoms of the ethyl (58.63 ppm) and propyl (65.02 ppm) alcohol is observed. This type of polarization indicates that it occurred in uncorrelated radical pairs

$$\overline{CH_3}^{\bullet} \dots {}^{\bullet 13} CH_2 OH \stackrel{F}{\to} CH_3^{13} CH_2 OH ,$$

$$\overline{CH_3 CH_2}^{\bullet} \dots {}^{\bullet 13} CH_2 OH \stackrel{F}{\to} CH_3 CH_2^{13} CH_2 OH$$

and that along with separation of the hydrogen (deuterium) atom from the hydroxyl group that prevails in the APP thermolysis in methanol [4], there occurs its separation from the methyl group of the solvent.

In an effort to analyze in detail the mechanism of chemical reactions, we studied the kinetics of the APP photolysis at the indicated temperatures and evaluated the quantum yields of its decomposition extrapo-



Fig. 4. Recalculated yields of the products of APP photolysis based on the share of decomposed peroxide (Nos. of the curves correspond to the numbering of the products in Table 1).

lated to the initial period of decomposition. Under our experimental conditions, they were as follows: $\varphi_{213} = 0.32$, $\varphi_{233} = 0.38$, $\varphi_{253} = 0.46$, $\varphi_{273} = 0.55$, $\varphi_{293} = 0.68$, and $\varphi_{313} = 0.83$. The measurement results revealed that with increase in the temperature the quantum yield changes nonlinearly, and its value is slightly higher as compared to the APP photolysis in CCl₄ ($\varphi_{293} = 0.40$) [2].

Table 1 presents data on the amount of APP and of the products of its photolysis at different temperatures depending on the photolysis time. The yields of the products are given for a degree of peroxide decomposition of \sim 30%, since in more profound photolysis the secondary processes that are typical mostly of elevated temperatures become pronounced. The yields of the photolysis products at 233, 273, and 293 K have intermediate values between those for the corresponding neighboring pairs of temperatures and are not cited in the present work. It is seen from Table 1 that at none of the temperature values can the APP photolysis be described by a constant of zero order, which is consistent with the conclusion made in [2] about the peroxide photolysis from several terms.

The main products of photolysis at 213 K are ethene, ethylethanoate, ethanic acid, propane, ethane, and methane. For all these substances the final yield reaches or substantially exceeds 10% (macroproducts). The group of identified macroproducts (the final yield is less than 10%) includes methylpropanoate, methyl- d_3 -ethanoate, and butane. An increase in temperature leads to the appearance of ethanol-d (253 K), methane-d (273 K), and 2-methoxy- d_3 -propanic acid (293 K). Thus, unlike the APP thermolysis in methanol- d_4 [4], its photolysis proceeds virtually only homolytically (at least at low temperatures). We cannot indicate unambiguously the mechanism by which the products of heterolysis at temperatures exceeding 253 K appear. In all probability, their formation is related with dark processes.

Additional information can be obtained from consideration of the relationship between the concentrations of the compounds formed and the residual peroxide concentration (the yield (Y, %)) of the products calculated per 100% APP decomposition) for all the time points.

Figure 4 presents the changes in the yields calculated as a function of the share of the decomposed peroxide (α) at 213 K. It is seen that the values of Y for ethene, ethylethanoate, ethane, methane, propane, and butane increase slightly, while in the case of ethanic acid Y at first increases and then decreases.

The slight increase in Y for ethene is observed only at low temperatures. The increase in the photolysis temperature leads to the decrease in Y in the course of the reaction, which is typical of APP thermolysis. This behavior of Y for ethene points to its participation in the telomerization reactions with positive activation energy, which is quite consistent with the data of [17].

Since, during photolysis, the Y of methane increases insignificantly at 213 K and the Y of the ethanic acid even decreases, and with allowance for the fact that the separation of hydrogen from isotopomers of the solvent is manifested at a temperature higher than 253 K, it is reasonable to assume that at a low temperature

methane and ethanic acid are the main products formed in disproportionation reactions of geminal radical pairs. Consequently, the high yield of ethylethanoate (approximately twice as large as that in APP photolysis in CCl_4) can be attributable to the fact that it is formed (with the exception of the recombination reactions) according to the following scheme:

$$APP + hv \rightarrow \overline{CH_3CH_2}^{\bullet} \dots {}^{\bullet}CH_3 \xrightarrow{S} \rightarrow CH_4 + CH_2 = CH_2,$$

$$APP + hv \rightarrow \overline{CH_3C(O)O^{\bullet}} \dots {}^{\bullet}CH_2CH_3 \xrightarrow{S} \rightarrow CH_3C(O)OH + CH_2 = CH_2,$$

$$CH_3C(O)O^{\bullet} + CH_2 = CH_2 \rightarrow CH_3C(O)OCH_2CH_2^{\bullet},$$
(1)

$$CH_{3}C(O)OCH_{2}CH_{2}^{\bullet} + RH \rightarrow CH_{3}C(O)OCH_{2}CH_{3} + R^{\bullet}, \qquad (2)$$

$$\overline{\text{CH}_{3}\text{C}(\text{O})\text{OCH}_{2}\text{CH}_{2}^{\bullet}\dots^{\bullet}\text{CH}_{2}\text{CH}_{3}}^{\text{S},\text{F}} \rightarrow \text{CH}_{3}\text{C}(\text{O})\text{OCH}_{2}\text{CH}_{3} + \text{CH}_{2} = \text{CH}_{2}.$$
(3)

Note that, as in the case of the thermolysis of APP in methanol- d_4 [4], a noticeable amount of propane can be formed upon adding methyl radical to ethene with subsequent separation of the hydrogen atom from different compounds by the formed radical or upon disproportionation of the propyl and ethyl radicals.

According to the scheme presented, if reactions (1) and (2) proceed efficiently, then in ethylethanoate produced by reaction (2) the multiplet CIDNP, which was initiated in the singlet radical pair of methyl and ethyl radicals, should be manifested following the "memory" effect. Moreover, the practically multiplet CIDNP should proceed also in the radical pairs of reaction (3). Its sign will depend on whether the initial spin correlation will be retained in the newly formed radical pairs or not.

Thus, the high concentration of the alkyl radicals produced in photolysis of APP from an antibonding term leads to manifestation of combined CIDNP on the protons of ethylethanoate.

It should be noted that at low temperatures of photolysis the alkyl radicals with an excess energy upon APP decomposition from the antibonding term lose it quickly and cannot separate the deuterium atom from the solvent. We have detected this possibility for the methyl radical at temperatures higher than 273 K, while for the ethyl radical it was not detected within the temperature interval studied.

Thus, the investigations performed have shown that in addition to the classical mechanism of photolysis typical of diacyl peroxides [17], the photolysis of APP in methanol- d_4 possesses a number of special features that allowed us to study its elementary stages in more detail.

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