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Photolysis of Solutions of 3-*tert*-Butylperoxy-3-methyl-1-butyne

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Abstract—Photolysis of solutions of 3-*tert*-butyl-3-methyl-1-butyne in CD_3OD and C_6D_{12} was studied by means of ^1H NMR spectroscopy, chemical nuclear polarization of the reaction products in the range 213–333 K, and kinetic measurements. It is shown that 3-*tert*-butyl-3-methyl-1-butyne decomposes primarily from a singlet electronic state. A scheme is proposed of the most probable reactions involving the radicals formed and solvent molecules. It is found that secondary processes play an important role in the initiation of the chemical nuclear polarization and the photolysis mechanism.

Over the last years there have been extensive research into use of derivatives of acetylenic peroxides for production of peroxide-containing copolymers, grafted polymers, and surfactants, for immobilization of radical polymerization initiators on solid supports, and creation of new types of adhesives for fixing grafted copolymers on phase interfaces [1, 2].

At the same time, despite the great practical promise of acetylenic peroxides, scarce data have been available on kinetics and mechanisms of their thermolysis and photolysis [3].

The aim of the present work was to study the kinetics and mechanism of and chemical nuclear polarization effects in photolysis of 3-*tert*-butyl-3-methyl-1-butyne (**I**) in various solvents.

The ^1H NMR spectrum of a solution of peroxide **I** in methanol-d_4 at 293 K shows the following signals, δ, ppm: 1.43 s [$(CH_3)_3C$], 1.64 s $(CH_3)_2$, and 2.91 s (≡CH). As the internal reference we used a signal of CD_2HOD (3.50 ppm) which is present as admixture in methanol-d_4. In the course of irradiation, the following signals appeared, δ, ppm: 1.41 s [$CH_3)_3$; *t*-BuOH (*t*-BuOD)], 1.65 s [$(CH_3)_2$]; ethynyldimethylcarbinol (**II**)], 2.90 s (≡CH), and 2.35 s (CH_3; acetone). At deeper conversion of peroxide **I**, weak signals of methane, ethane, CH_3CD_2OD, and certain unidentified products also appeared.

Figure 1 shows the kinetic curves of consumption of compound **I** and accumulation of principal decomposition products, viz. *t*-BuOD, alcohol **II**, and acetone, in the photolysis of compound **I** in CD_3OD. The concentrations are given per 1 mol of peroxide **I**. The semilog anamorphoses of the kinetic curves of consumption of peroxide **I** in deuteromethanol are almost linear (Fig. 2), i.e. the consumption of peroxide **I** is described by a first-order equation; some deviations occur only at profound decomposition of the starting peroxide. The table lists the rate constants (k_1) of the decomposition of peroxide **I** in CD_3OD on irradiation in various conditions.

To gain insight into the mechanisms of reactions that occur in the photolysis of **I**, we studied effects of chemical nuclear polarization on protons of the reaction products. Alkyl peroxides are not suitable objects for observation of chemical nuclear polarization, since the alkoxyl radicals formed have low hyperfine coupling constants and inconsiderable electron relaxation times, which hinders appearance and retention of nonequilibrium population of Zeeman levels [4]. But here, too, chemical nuclear polarization can be induced by varying reaction conditions (initiation mode, temperature, solvent, etc.) [5].

The ^1H NMR spectra of methanol-d_4 solutions of peroxide **I**, measured in the course of the photolysis at 233 K, show, along with the peroxide and solvent signals, an emission signal of acetone protons (Fig. 3a). Raising the temperature to 273 K (Fig. 3b) increases the intensity of the acetone signal and gives rise to emission signals of ethane (1.04 ppm, s) and methane (0.38 ppm, s), as well as positively enhanced signals of ethanol methyl protons (CH_3CD_2OD) (1.35 ppm, septet). In addition, emission signals of unidentified compounds are observed: a broadened singlet at 3.66 ppm, a multiplet at 2.31 ppm, and two singlets at 1.79 and 1.72 ppm. The spectral pattern for the photolysis at 313 K (Fig. 3c) is slightly changed. Instead of the emission signal of acetone, we observe its absorption signal with equilibrium polarization, while the emission singlet of methane is replaced by

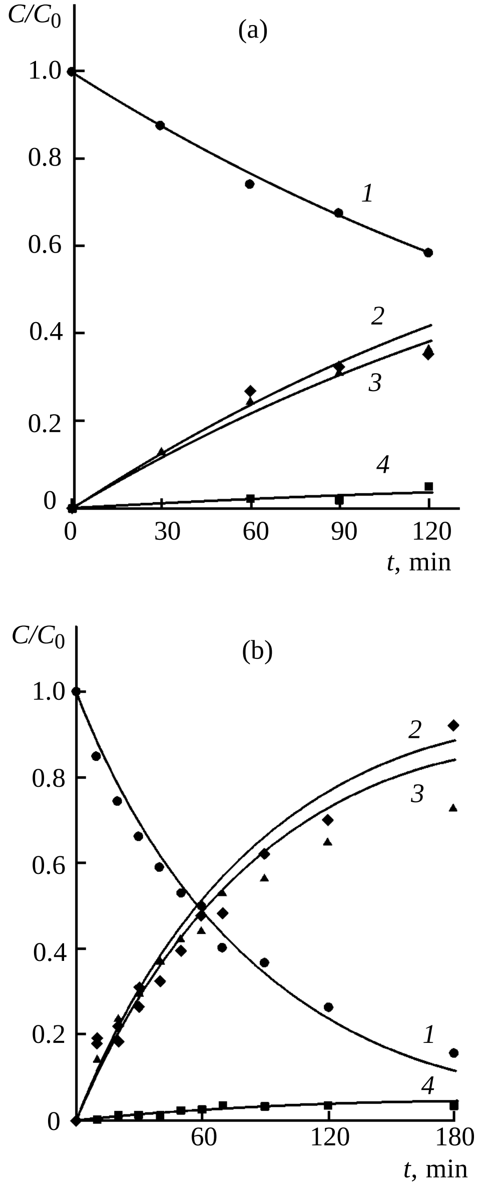

Fig. 1. Kinetic curves of (*1*) consumption of peroxide **I** and accumulation of (*2*) compound **II**, (*3*) *t*-BuOD, and (*4*) acetone on the photolysis of compound **I** in CD_3OD in (a) Pyrex and (b) quartz inserts. [**I**] 0.14 M. (Lines) Simulation and (points) experiment.

an emission triplet of its monodeuterated analog at 0.37 ppm. Moreover, all the other signals have increased intensity.

It should be noted that polarized acetone protons in the photolysis of peroxide **I** are observed immediately, not with a certain delay, as with *tert*-butyl peroxide [6]. Consequently, the polarization arises in primary processes and cannot be related to chemical nuclear polarization in radical pairs. Moreover, the extremal character of the temperature dependence of the nonequilibrium polarization of acetone and its occurrence even at a low temperature (213 K), when no other polarized protons are observed, suggests that the polarization has arisen by an optical nuclear polarization in the starting compound **I**.

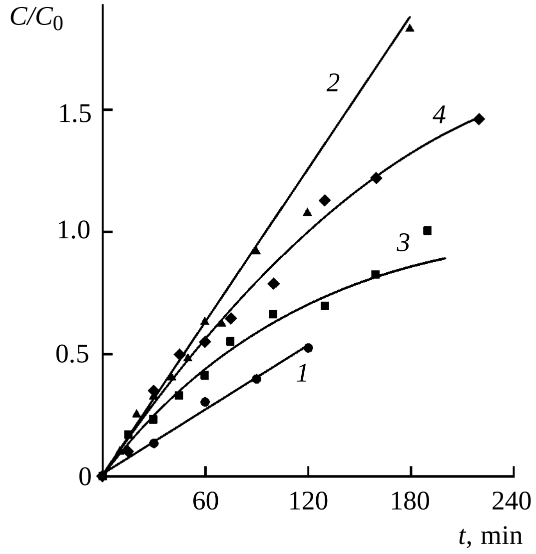

Fig. 2. Semilog anamorphoses of the kinetic curves of peroxide **I** for the photolysis in CD_3OD in (*1*) pyrex and (*2*) quartz inserts and in C_6D_{12} (quartz) at (*3*) 293 and (*4*) 333 K.

For optical nuclear polarization to arise in a photochemically excited compound **I**, the latter should have a bonding triplet term. Scaiano and Wubbels [7] in their study on photochemically initiated dissociation of *tert*-butyl peroxide came to a conclusion that all lower excited singlet and triplet terms are repulsive in nature. Malkin and Shepelin [8] showed that the dissociation of the O–O bond in aromatic diacyl peroxides, induced by direct photoexcitation, occurs both from the $S_1(\pi, \sigma^*)$ state and from a triplet eximer formed by the peroxide in the $T_1(\pi, \pi^*)$ and S_0 states. Thus, unlike *tert*-butyl peroxide, peroxide **I**, due to

Rate constants for photolysis of peroxide **I** in various solvents; $[\mathbf{I}]_0$ 0.14 M

Solvent	T, K	$k_1 \times 10^{-4}$, s^{-1}	k_2/k_3	k_4/k^*
CD_3OD	293	1.90	1.15	–
CD_3OD [a]	293	0.75	2.00	–
C_6D_{12}	293	0.84	0.33	0.16
C_6D_{12}	333	1.42	0.39	0.04

[a] Irradiation in a Pyrex insert.

the presence of a triple bond, acquires a low-lying bonding triplet state.

However, like *tert*-butyl peroxide, peroxide **I** can undergo a photochemically induced homolytic O–O bond cleavage to give a singlet radical pair including *tert*-butoxyl and ethynyldimethylmethoxyl radicals. The resulting radicals abstract deuterium from methanol-d_4 to give hydroxymethyl-d_3 and, probably, methoxyl radicals [9]. This route is, however, difficult to trace by chemical nuclear polarization effects. It is known [9] that, along with deuterium cleavage, *tert*-butoxyl radical generates acetone and methyl radical.

The chemical nuclear polarization of CH_3CD_2OD, ethane, and methane can readily be explained in terms of an uncorrelated radical pair of methyl and hydroxymethyl-d_3 radicals. Ethane and methane are polarized as “outcome” products from this radical pair. Then, according to Kaptein’s rules [4] for polarization signs of protons of these products, positively polarized would be methyl protons of ethanol, and negatively, those of methane and ethane (Fig. 3).

Note that at low temperatures (273 K) methyl radical abstracts primarily hydrogen, while at higher temperatures (313 K) it can also abstract deuterium from the solvent.

Like *tert*-butoxyl, ethynyldimethylmethoxyl radical can decompose by two routes to give acetone and ethynyl radical (route *a*) or ethynyl methyl ketone and methyl radical (route *b*).

To decide between the possible decomposition routes of ethynyldimethylmethoxyl radical, we studied the chemical nuclear polarization effects on the photolysis of methanol-d_4 solutions of bis(2-methyl-3-butyn-2-yl) peroxide (**III**) at 253–333 K. In this temperature range, we observed no chemical nuclear polarization both for methane and for ethane, unlike the photolysis of compound **I** and *tert*-butyl peroxide, but observed polarization of double-bond protons.

The above findings led us to suggest that route *a* is preferred. Analysis of the final products of photolysis of peroxide **III** might clarify this problem. However, the resulting unsaturated compounds readily enter various reactions that give a great number of products and make analysis difficult.

Analysis of the variations of the concentrations of peroxide **I** and its photolysis products with time (Fig. 1) with account for the above-discussed chemical nuclear polarization effects, allow us to propose the following mechanism of the photolysis of compound **I** in deuteromethanol:

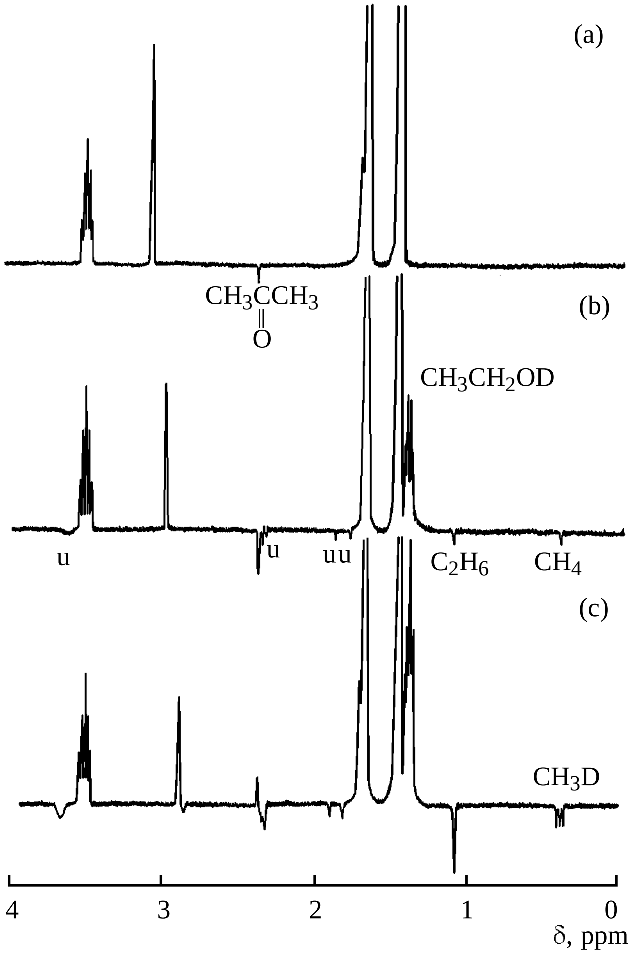

Fig. 3. ^1H NMR spectra of solutions of peroxide **I** in CD_3OD ([**I**] 0.14 M), measured in the course of photolysis at various temperatures, K: (a) 233, (b) 273, and (*c*) 313. (u) Unidentified products.

$$(CH_3)_3COOC(CH_3)_2C\equiv CH \xrightleftharpoons{h\nu} \overset{S}{\overline{(CH_3)_3CO^{\cdot}\cdot\cdot{}^{\cdot}OC(CH_3)_2C\equiv CH}}, \xrightarrow{k_1} (CH_3)_3CO^{\cdot} + {}^{\cdot}OC(CH_3)_2C\equiv CH, \quad (1)$$

$$(CH_3)_3CO^{\cdot} \xrightarrow{k_2} CH_3COCH_3 + CH_3^{\cdot}, \quad (2)$$

$$(CH_3)_3CO^{\cdot} + CD_3OD \xrightarrow{k_3} (CH_3)_3COD + {}^{\cdot}CD_2OD\ (CD_3O^{\cdot}), \quad (3)$$

$$HC\equiv CC(CH_3)_2O^{\cdot} + CD_3OD \xrightarrow{k_4} \underset{\mathbf{II}}{HC\equiv CC(CH_3)_2OD} + {}^{\cdot}CD_2OD\ (CD_3O^{\cdot}), \quad (4)$$

$$HC\equiv CC(CH_3)_2O^{\cdot} \xrightarrow{k_5} CH_3COCH_3 + {}^{\cdot}C\equiv CH, \quad (5)$$

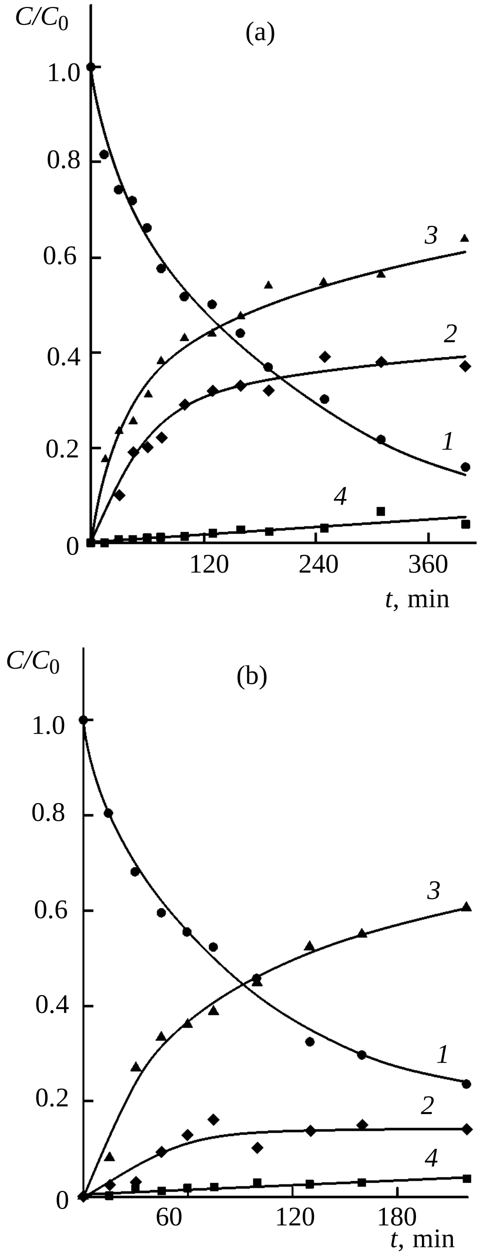

Fig. 4. Kinetic curves of (*1*) consumption of peroxide **I** and accumulation of (*2*) ethynyldimethylcarbinol, (*3*) *t*-BuOD, and (*4*) acetone on the photolysis of **I** in C_6D_{12} (quartz) at (a) 293 and (b) 313 K.

$$\overline{\mathrm{CH}_3^{\bullet}\cdots{}^{\bullet}\mathrm{CD_2OD}}^{\,F} \longrightarrow \mathrm{CH_3CD_2OD},$$

$$\overline{\mathrm{CH}_3^{\bullet}\cdots{}^{\bullet}\mathrm{CH_3}}^{\,F} \longrightarrow \mathrm{CH_3CH_3},$$

$$\mathrm{CH}_3^{\bullet} + \mathrm{CD_3OD} \longrightarrow \mathrm{CH_3D} + {}^{\bullet}\mathrm{CD_2OD}\ (\mathrm{CD_3O}^{\bullet}),$$

$$\mathrm{CH}_3^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{CH_4} + \mathrm{R}^{\bullet},$$

$$\mathrm{CD_3O}^{\bullet} + \mathrm{RH} \longrightarrow \mathrm{CD_3OH} + \mathrm{R}^{\bullet},$$

RH = compound **I**, *t*-BuOD, compound **II**, acetone, etc.

It should be noted that for the photolysis of compound **I** in CD_3OD, the relation $[\mathbf{I}]_0 - [\mathbf{I}] \rightleftarrows [\mathbf{II}]$ is valid (Fig. 1). Apparently, in the experimental conditions, $k_4[CD_3OD] >> k_5$, and reaction (5) can be neglected in calculations.

The ratios of the rate constants of the decomposition of *tert*-butoxyl radical (k_2) and abstraction by this radical of D from CD_3OD (k_3), calculated as k_2/k_3 = [acetone][CD_3OD]/[t-BuOD], are listed in the table.

In solving the direct kinetic task, k_2 was let be equal to the rate constant of $(CH_3)_3CO^{\bullet}$ elimination in CCl_4 (1.2×10^2 s^{-1} at 293 K) [9], and $k_3 \rightleftarrows k_4$. The kinetic curves of consumption of compound **I** and accumulation of principal products of the photolysis in CD_3OD, obtained by computer simulation with experimental and published [9] rate constants, fairly fit experimental data (Fig. 1).

The decomposition of the starting peroxide and the accumulation of products in the photolysis of **I** in C_6D_{12} have more complicated, temperature dependent patterns (Fig. 4.)

Analysis of the ln$[\mathbf{I}]_0/[\mathbf{I}]$–time dependence for the photolysis of compound **I** in C_6D_{12} (Fig. 2) shows that with increasing time of irradiation the reaction slows down, which is apparently associated with changed conditions of absorption of the UV light with the system. The decomposition of compound **I** in C_6D_{12} is a first-order reaction only at initial stages, when the conversion of compound **I** is no higher than 40–50%. The rate constants for the decomposition of peroxide **I** in C_6D_{12} are listed in the table. When the temperature is increased from 293 to 333 K, the decomposition rate constant increases by a factor of 1.7. Concurrent themolysis of peroxide **I** in these conditions is unlikely, since it is known [1, 9] that dialkyl peroxides begin to decompose at appreciable rates at temperatures higher than 373 K. Probably, the above acceleration of the reaction is explained by the fact that photoexcitation of compound **I** at 333 K occurs from a higher vibrational level of the S_0 state, thus resulting in absorption of a stronger longer wavelength irradiation. On the other hand, not excluded is also acceleration of induced decomposition of the peroxide under the action of radicals resulting from photolysis.

The ^1H NMR spectra of a cyclohexane solution of compound **I** shows the following signals, δ, ppm: 1.24 s [$(CH_3)_3C$], 1.45 s $(CH_3)_2$, and 2.11 s (≡CH). The internal reference was $C_6D_{11}H$ (δ 1.40 ppm) which was present as an admixture in C_6D_{12}. In the course of irradiation of the solution, the following signals appear, δ, ppm: 1.22 s [$(CH_3)_3$; *t*-BuOD], 1.46 s [$(CH_3)_2$; compound **II**], 2.16 s (≡VH), and 2.01 s (CH_3; acetone). No polarization of protons of these compounds was observed. However, in the range of signals characteristic of double-bond protons (5–6 ppm), absorption and lines of reaction products appear which are not observed in the stedy state. The intensity of these signals is slightly higher at 333 K. Thus, the photolysis of peroxide **I** in cyclohexane-d_{12} gives rise to a weak chemical polarization of protons of products with double bonds.

The yield of alcohol **II** in deuterocyclohexane is higher than in deuteromethanol, especially at 333 K (Fig. 4b). This is apparently explained by a much increased contribution of polymerization in the mechanism of the decomposition of compound **I**, as evidenced by the observation in the ^{1}H NMR spectrum of deuterocyclohexane solutions of peroxide **I** of signals of unidentified reaction products, probably, of those with double bonds.

It the photolysis of compound **I** in C_6D_{12}, the fraction of ethynyldimethylsilyl radicals invoved in deuterium abstraction from the solvent, leading to alcohol **II** formation, decreases from 0.7 from 0.2 as the temperature is raised from 293 to 333 K. The ratio of the rate constant of deuterium abtraction from C_6D_{12} (k_4) to the overall rate constant (k^*) of the conversion of ethynyldimethylmethoxyl radical by reaction (5) and oligomerization reactions, calculated as $k_4/k^* = [\mathbf{II}]/([\mathbf{I}]_0 - [\mathbf{I}] - [\mathbf{II}])[C_6D_{12}]$, much decreases as the photolysis temperature increases (see table). The ratio k_2/k_3 (see table) was estimated in the assumption that, like with CD_3OD, the contribution of reaction (5) in the mechanism of the decomposition of compound **I** is insignificant.

In simulating the decomposition of compound **I** in C_6D_{12}, the k_2 values, like with deuteromethanol, was set equal the rate constant of $(CH_3)_3CO^{\cdot}$ elimination (solvent CCl_4) (1.2–10^2 and 2.3–10^3 s^{-1} at 293 and 333 K, respectively) [9], and $k_3 \rightleftarrows k_4$. The resulting kinetic curves of consumption of peroxide **I** and accumulation of principal products of the photolysis in C_6D_{12} fairly fit experimental results at low degress of decomposition of the starting peroxide.

Thus, our study showed that compound **I** decomposes primarily from a singlet electronic state. The chemical nuclear polarization effects and the photolysis mechanism are much contributed by secondary processes associated with photolysis products and solvent.

EXPERIMENTAL

3-(*tert*-Butylperoxy)-3-methyl-1-butyne (**I**) and bis-(2-methyl-3-butyn-2-yl) peroxide (**III**) were synthesized by the procedures described in [10, 11]. The purity of the peroxides was no less than 99%.

The photolytic and chemical nuclear polarization studies were performed in two solvents, cyclohexane-d_{12} and methanol-d_4, since they both are transparent in the near UV light but give radicals with different physicochemical characteristics, cyclohexyl and hydroxymethyl and methoxyl, respectively.

The kinetics of photolysis of compound **I** were studied in methanol-d_4 at 293 K and in cyclohexane-d_{12} at 293 and 333 K. The concentration of peroxide **I** was 0.14 M. The solutions were irradiated in quartz and Pyrex inserts 3 mm in internal diameter and 60 mm in length, sealed in such a way that the gas-to-liquid volume ratio was no more than 1 : 9. Under these conditions all gaseous photolysis products almost completely remained in the solution and thus could be analyzed, both qualitatively and quantitatively. Irradiation was performed with an RSh-500 mercury lamp with a heat filter.

The ^{1}H NMR spectra of initial solutions and photolyzates were recorded on a Tesla VS-567A spectrometer at 100 MHz.

The yields were determined at a relative error of about 10%.

The chemical nuclear polarization effects were performed in a modified temperature-controlled NMR probe. The light of the DRSh-1000 mercury lamp was focused on an outer end of a quartz light guide and thus passed to a wall of a rotating quartz ampule [12]. Methanol-d_4 solutions of compounds **I** and **III** were illuminated at temperatures from 213 to 313 K and from 213 to 333 K, respectively, while cyclohexane-d_{12} solutions, at 293 and 333 K.

Kinetic schemes of photolysis of compounds **I** in various solvents were simulated using the KINETICS (Version 2) program designed for solving the direct kinetic task by the Gear method [13].

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