Photolysis of methanolic solutions of benzyl acetate

E. D. Skakovskii,[a] *S. V. Rykov,*[b]* *L. Yu. Tychinskaya,*[c] *V. L. Murashko,*[c] *M. M. Ogorodnikova,*[a]
G. S. Avrinskii,[c] *and S. A. Lamotkin*[a]

[a] *Belarus' State Technological University,*
13 ul. Sverdlova, 220603 Minsk, Belarus'.
Fax: (017 2) 261 075
[b] *A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224
[c] *Institute of Physical Organic Chemistry, Belarus' Academy of Sciences,*
13 ul. Surganova, 220072 Minsk, Belarus'.
Fax: (017 2) 394 679

Photolysis of solutions of benzyl acetate in CD_3OD has been studied. As has been established based on the effects of CIDNP and the yields of products, decomposition of the starting compound occurs from both excited singlet and triplet electronic states. The contributions of homolysis and solvolysis to the overall photochemical process have been measured, and the lifetimes of the acetoxy radicals formed have been evaluated. Toluene-d has been shown to be formed mostly by disproportionation of benzyl radicals with hydroxymethyl radicals derived from the solvent molecules.

Key words: benzyl acetate; methanol; photolysis; homolysis; solvolysis; CIDNP effects.

Esters are readily available stable compounds whose photochemical decomposition may yield the same radicals as the homolysis of peroxides, which are widely used as initiators for polymerization. However, the simplest esters absorb in the far UV region, and their photolysis is difficult. Benzyl esters do not possess this drawback and decompose rather readily through the action of light.

In a study of the photolysis of benzyl acetate (BA), it has been found[1] that BA can decompose according to both homolytic and heterolytic mechanisms. It has been shown[2] that solvolysis from the first excited state is the main reaction channel, though analogs of BA with electron-donating substituents in the ring decompose from the triplet electronic state.[3] More recently,[3,4] photochemical reactions of various benzylic compounds have been described. However, the mechanism of the photochemical reactions of BA have not been comprehensively investigated.

The purpose of the present work has been to study the mechanism of the photolysis of methanolic solutions of BA by a quantitative analysis of the effects of chemically induced dynamic nuclear polarization (CIDNP) and by studying the yields of reaction products.

Experimental

0.05 and 0.1 *M* solutions of BA in CD_3OD in sealed quartz ampules were subjected to photolysis. The ampules were sealed in such a way that the gas volume above the solution did not exceed 10 % of the internal volume of the ampule, which allowed NMR analysis of the gases formed in the reaction. The reaction was initiated by the light of a DRSh-500 mercury lamp passed through a water light filter. At certain intervals, the composition of the products was analyzed using a BS-567A NMR spectrometer.

The effects of CIDNP were studied in modified detectors of BS-487C and BS-567A spectrometers. Irradiation was carried out with the light of a DRSh-1000 mercury lamp passed through a water light filter.

The study of the effects of CIDNP, which arise predominantly from triplet precursors, was carried out using 0.1 *M* solutions of BA in CD_3OD with the addition of 0.5 *M* CD_3COCD_3 in which acetone acted as the triplet sensitizer.

The spin-lattice relaxation times were measured on the basis of the decrease in the integral intensities of the signals with polarized nuclei after the removal of the light.

The relative errors of the measurement of the yields of the reaction products and the relaxation times were about 10 %.

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Results and Discussion

Figure 1 shows the ^1H NMR spectrum of a 1 *M* solution of BA during its irradiation at 303 K. Under these experimental conditions, insignificant effects of CIDNP were observed: the protons of ethylbenzene, β-phenylethanol ($PhCH_2CD_2OD$), ethanol ($MeCD_2OD$), and some unidentified products formed in trace amounts were polarized. In addition, very weak polarization of methane (CH_4) was observed. The protons of the alcohols and methane are positively polarized, while the protons of ethylbenzene exhibit both multiplet and integral polarization: CH_2 — *A*/*E* + *A*, Me — *A*/*E* + *E* (*A* is increased absorption, *E* is emission, and *A*/*E* is multiplet polarization where the low-field lines of the multiplet reflect positive polarization, and the high-field lines reflect negative polarization of the nuclei). This character of polarization indicates that it arises in triplet radical pairs, which is in good agreement with the literature data.[4]

The intensity of the NMR signals for the groups with polarized nuclei depends substantially on the temperature of the photolysis. It is reasonable to suggest that the photochemical decomposition of BA involves its thermolysis from excited states, as in the case of diacyl peroxides.[5]

The presence of two types of polarization of the protons of ethylbenzene indicates that polarization arises in a sequence of radical pairs that can be represented by Scheme 1.

The CIDNP effects observed are adequately described using the cooperative effect in which the nuclear polarization of the final product reflects the polarization effects that occur in all of the intermediate radical pairs.[6]

In a previous study of the thermolysis of acetyl(phenylacetyl) peroxide we also detected the formation of ethylbenzene and determined the lifetime of the acetoxy radical, which is an intermediate radical in the decomposition, using the effects of CIDNP.[7] A comparison of the ^1H NMR spectra of ethylbenzene with polarized nuclei resulting from photolysis of BA with the spectrum of a similar compound formed in the thermolysis of the peroxide studied indicates that they are similar. Therefore, on the basis of calculations[7] one may say with confidence that the lifetime of the acetoxy radicals resulting from the photolysis of BA in methanol lies in the $(1—4)\cdot10^{-10}$ s range. Notice that this is somewhat longer than the lifetimes of similar radicals that arise during the photolysis of aliphatic diacyl peroxides (10^{-11} s).[7]

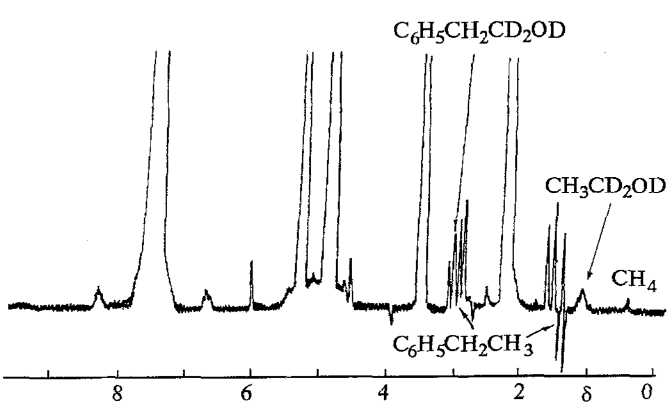
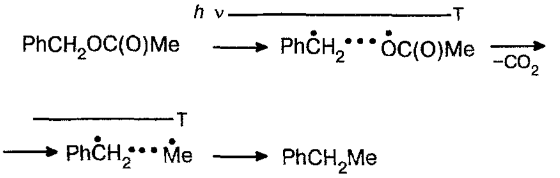


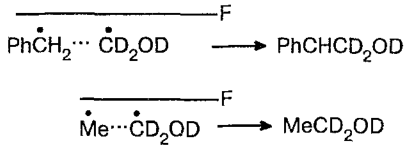
Fig. 1. The ^1H NMR spectrum of a 1 *M* solution of benzyl acetate in CD_3OD during its irradiation at 303 K (400 accumulations).

Scheme 1



The positive polarizations of β-phenylethanol and ethanol arise in the recombination of benzyl or methyl radicals with radicals of the solvent in radical pairs in which no spin correlation occurs.

To study the mechanism of photolysis in more detail, we determined the yields of the reaction products at ambient temperature as a function of the irradiation time. The results of the measurements are presented in Table 1.



From the data of Table 1 and actinometry carried out using benzophenone[8] we found that the quantum yield in the photolysis of BA varies from $6.2\cdot10^{-2}$ to $0.8\cdot10^{-2}$. By extrapolation of the quantum yields measured for the photolysis of BA to the beginning of the process, the quantum yield at the initial instant was determined to be ~0.1.

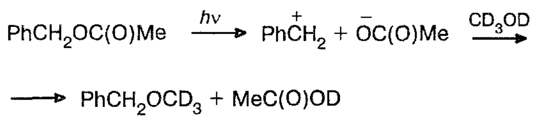
The variation of the concentration of the starting ester with time during photolysis is neither linear nor exponential. This may be due to several factors. First, the photolysis yields products that partially absorb light and decrease the rate of photolysis of the starting ester. This possibility is indicated by the fact that in the course of the photolysis the overall yield of products incorporating a benzyl fragment decreases, unlike the total yield of products with a methyl fragment. In addition, during photolysis, the walls of the quartz ampule become coated with a precipitate of insoluble products, possibly polymeric in structure. Second, the products formed may

Table 1. The yield of the products (%) of the photolysis of a 0.05 *M* solution of benzyl acetate in CD_3OD at ambient temperature depending on the time of the irradiation

Product	*t*/min							
	30	60	90	150	210	300	480	720
$PhCH_2OC(O)Me$	69	55	45	31	21	16	5.5	1.5
$PhCH_2OD$	0.8	3.9	5.1	5.0	5.8	6.5	7.0	7.4
$PhCH_2OCD_3$	5.6	7.8	11	14	17	19	19	17
$PhCH_2CH_2Ph$	2.5	3.4	4.0	4.5	4.4	4.7	3.3	1.7
PhC_2H_5	18	21	25	27	29	27	29	25
PhMe	1.3	1.6	1.7	1.9	1.9	2.3	2.4	2.1
$PhCH_2D$	0.5	0.7	1.3	1.6	1.5	1.61	1.8	1.0
$MeC(O)OCD_3$	—	10	14	20	27	34	42	54
MeC(O)OD	8.8	6.1	7.8	10	9.8	8.8	6.7	1.7
$MeCD_2OD$	1.3	1.9	2.1	3.6	4.1	3.6	3.4	3.6
C_2H_6	0.6	1.4	1.3	1.4	1.5	1.6	1.8	2.3
CH_4	0.9	1.7	2.2	3.0	3.6	4.6	5.0	5.2
MeD	0.5	1.1	1.9	2.7	2.7	3.3	4.6	4.1
$PhCH_2CD_2OD$	1.9	2.4	3.3	4.5	4.8	5.7	6.0	3.2

lead to sensitized photolysis, which occurs at a different rate. Third, the appearance of acetic acid in the system should change the ratio between homolysis and solvolysis, which would ultimately affect the rate of the overall photolysis.

Based on the previous works and our research, the latter process can be described by the following scheme.



$$PhCH_2OC(O)Me \xrightarrow{h\nu} Ph\overset{+}{C}H_2 + \overset{-}{O}C(O)Me \xrightarrow{CD_3OD} PhCH_2OCD_3 + MeC(O)OD$$

The photolysis of solutions of BA containing dissolved oxygen and of those blown with argon showed no noticeable difference in the yields of products. Therefore, one can infer that photosolvolysis occurs from the singlet electronic state, which is in good agreement with the previous results.[2,4] However, unlike photolysis in aqueous acetonitrile, where solvolysis predominates, in the case of methanol, homolysis plays the major role at the first stages of the process. Using the data of Table 1 we calculated that the proportion of homolysis was 72 % over an irradiation period of 30 min.

It should be noted that the contribution of homolysis determined from the ratio between the yields of the reaction products slowly decreases during irradiation, and at the final stage, it is only 43 %.

By extrapolating the results obtained to the beginning of the photolysis we found that at the initial instance, the proportion of homolysis is about 85 %.

The analysis of the proportion of benzyl methyl-d_3 ether shows that initially its quantity rapidly increases, and then its yield virtually does not vary. In our opinion, this is because the ether decomposes.

To verify this assumption, we irradiated 0.05 *M* solutions of benzyl methyl ether in CD_3OD and showed that photolysis of this ether occurs somewhat more slowly and yields only methanol.

Despite the fact that acetic acid is the main product of photosolvolysis, its yield in final steps of the reaction is very low, and the yield of methyl-d_3 acetate, conversely, noticeably increases. This can be easily explained by the assumption that the acetic acid formed reacts with methanol-d_4. However, it should be noted that at the initial stage, this reaction occurs only under the action of light.

The yield of ethylbenzene varies according to a complex dependence. At the beginning, this compound intensely accumulates in the system, then the rate of its accumulation dramatically decreases, and in the final step of the photolysis, its content also decreases. This behavior can be accounted for by the fact that the proportion of the homolysis of BA decreases as the photochemical reaction proceeds, and ethylbenzene itself can undergo secondary photolysis and radical attacks. However, its high yield at the initial instant implies that, along with the photolysis of BA from the triplet electronic state, decomposition of this compound from the first excited singlet electronic state should also occur. Moreover, the decomposition from the singlet electronic state may predominate, in spite of the effects of CIDNP observed, since the amplification coefficients in singlet radical pairs are much smaller than those in triplet radical pairs.

The previous study of the photolysis of BA in acetone, where it decomposes mostly from the triplet state, showed that the yield of ethylbenzene amounts to several percent, which confirms our suggestion that in methanol, photolysis from the singlet electronic state predominates.

It is noteworthy that the yields of dibenzyl, toluenes, and β-phenylethanol exhibit extreme time dependences, unlike ethane and methanes. Therefore, the consumption of these compounds depends mostly on secondary photolysis, rather than on radical attacks.

To study the decomposition of BA from the triplet electronic state, we considered the effects of CIDNP that accompany the photolysis of methanolic solutions in the presence of acetone. Figure 2 presents the ^1H NMR spectrum of this solution recorded during its irradiation at 303 K. Unlike the previous case, we observe intense CIDNP effects for a number of products. In fact, the aromatic protons of ethylbenzene, the methylene protons of β-phenylethanol ($PhCH_2CD_2OD$), the methyl protons of toluene ($PhCH_2D$) and ethanol ($MeCD_2OD$), and the protons of methane (CH_4) are positively polarized, ethane is negatively polarized, and the protons of ethylbenzene (CH_2 — $A/E + A$, CH_3 — $A/E + E$) and methane (MeD — $A/E + A$) exhibit mixed polarization.

It should be noted that the spectra are qualitatively similar, but there are also some distinctions. First, the

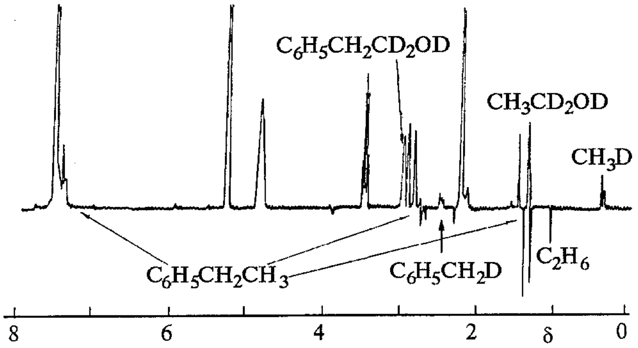


Fig. 2. The ^1H NMR spectrum of a 0.1 *M* solution of benzyl acetate in CD_3OD with 0.5 *M* CD_3COCD_3 during its irradiation at 303 K.

greater contribution of the integral polarization to the total polarization of ethylbenzene indicates that sensitized photolysis yields "colder" acetoxy radicals. Second, the emission of ethane cannot be explained only by the participation of BA radical pairs. In our opinion, it is reasonable that polarization of ethane be regarded as a "memory" effect in the methyl-hydroxymethyl noncorrelated radical pair.

$$\overline{\dot{M}e\cdots\dot{C}D_2OD}^{\,F} \longrightarrow \text{Yield}$$

$$\dot{M}e + \dot{M}e \longrightarrow MeMe$$

Third, the positive polarization of the methyl protons in toluene ($PhCH_2D$) indicates that polarization results from disproportionation, rather than from a "memory" effect of the primary radical pair, in the case when toluene is formed by the abstraction of a deuterium atom by a benzyl radical.

$$\overline{Ph\dot{C}H_2\cdots\dot{C}D_2OD}^{\,F} \longrightarrow PhCH_2D + CD_2O$$

We can evaluate the contributions of various reactions to the formation of toluene-d. For this purpose, it is necessary to use the ratio between the integral intensities of the lines that correspond to polarized nuclei and to the nuclei existing in the heat equilibrium between β-phenylethanol and toluene. Taking into account relaxation times, this ratio for the lines of the products during irradiation was 6.5, and the ratio for the products under steady-state conditions was 3.3. Assuming that the coefficients of amplification of CIDNP for the protons of toluene resulting from disproportionation and for toluene formed by the abstraction of deuterium from the solvent are similar, and taking into account the fact that the intensities of the lines for nuclei with nonequilibrium polarization are subtracted and those for nuclei with equilibrium polarization are added, we found that 80 % of the toluene molecules result from disproportionation of benzyl radicals with hydroxymethyl radicals.

The presence of multiplet polarization, *A*/*E*, at the protons of methane (MeD) indicates that polarization can also occur through disproportionation. However, in this case, the quantitative estimates are even more tentative.

Thus, the study of the photolysis of methanolic solutions of benzyl acetate showed that it decomposes from both the singlet and the triplet electronic states, and the decomposition from the singlet state predominates. At the initial stages, homolysis to give the acetoxybenzyl radical pair is the main process. The lifetime of the resulting acetoxy radicals exceeds the lifetimes of the same radicals that arise in the photolysis of diacyl peroxides. The molecules and radicals of the solvent are significant for both solvolysis and homolysis.

At the relatively high density of the luminous flux used in the experiments ($I \sim 10^{17}$ quant s^{-1}) the possibility of double quantum processes appears. However, no obvious dependence of the yields of the photolysis products on the intensity of the light was observed. We believe that double quantum processes are possible (especially in photolysis *via* the triplet state), but in the case under consideration, their contribution is small.

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