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Chemically induced dynamic nuclear polarization in reactions of trialkylaluminium and benzoyl peroxide

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Abstract

^1H and ^{13}C chemically induced dynamic nuclear polarization (CIDNP) has been detected in the interaction of Et_3Al (I) and i-Bu_3Al (II) with benzoyl peroxide (III). Polarized protons of the following products: EtOC(O)Ph (IV) (CH_2, 4.04 ppm, E; CH_3, 1.1 ppm, A), ethylene (V) (5.14 ppm, A), EtPh (VI) (CH_2, 2.37 ppm, E + EA; CH_3, 0.9 ppm, A) have been observed in proton spectra after mixing benzene solutions I and III for 20–25 sec. Polarized lines have been observed in ^{13}C NMR spectra in the main product $Et_2AlOC(O)Ph$ (VII) (CO_2, 175.39 ppm, E, C1, 145.44 ppm, E), in IV (CH_2, 62.40 ppm, A; CH_3, 15.14 ppm, E; 167.24 ppm, A; C1, 132.55 ppm, A) in V (123.70 ppm, A) and in VI (CH_2, 26.00, A).

The analysis of polarization signs shows that CIDNP occurs in the singlet radical pair (RP) of ethyl and benzoate radicals forming simultaneously with VII at the first stage of reaction. A RP recombination leads to IV, an intermediate V and benzoic acid, which then reacts with I with further to form VII and ethane. A polarized product VI has been detected with recombination of a secondary RP of ethyl and phenyl radicals, to be formed with decomposition of the benzoate radical of the first RP to CO_2 and phenyl radical. ^{13}C polarization occurs in VII with interaction of polarized benzoate radical and I.

Thus, a radical nature of the reaction has been confirmed by the CIDNP detection, and analysis of polarization signs allows us to define more exactly a reaction radical scheme proposed previously.

The reactions of benzoyl peroxide (BP) with triethylaluminium (TEA) and triisobutylaluminium (TIBA), proceeding rapidly in hydrocarbon solvents, have been studied in detail [1–3]. It was concluded [1] that the reactions are accompanied by the formation of free alkyl, but not benzoate, radicals. To explain the results obtained the authors had to resort to proposing a scheme of "latent radical" reactions assisted only by alkylaluminium radicals. The nature of the "latent radical" reaction is still ambiguous. Later EPR spectra of adducts of benzoate and alkyl radicals have been fixed with spin trapping (nitrozo-t-butane) in those reactions [4]. The formation of the above radicals has been proposed in accordance with that fact.

We have reported previously [5] that CIDNP occurred in the interactions of TEA and TIBA with BP. This paper is devoted to the study of reactions by the CIDNP method, since it permits both the identification of the intermediate radical patterns and of further transformations.

Experimental

Solvents were purified and dried in the usual way. Deuterated solvents were used without previous drying. TEA and TIBA are commercial products. TEA was used without purified purification, TIBA was distilled in vacuum.

^1H NMR spectra were recorded with a BS-467 Tesla spectrometer (60 MHz) with continuous registration and with a BS-597A Tesla Fourier spectrometer. ^{13}C NMR spectra were recorded with a "FX-90Q Jeol" spectrometer (22.5 MHz). To observe CIDNP effects on protons a suitable amount of benzoyl peroxide (0.5 M; 0.5 ml) was added to alkylaluminium solution in benzene-d_6, toluene-d_8, or dioxane-d_8 (1 M; 0.5 ml), in a spectrometer detector. CIDNP on ^{13}C NMR were registered in the same way in standard 10-mm ampoules, while the concentration and volume of TEA solutions was increased to $2M$ and 1 ml, and those of BP to $1M$ and 1 ml. Immediately after reagent mixing the recording of a spectrum was carried out within 20 sec, and a second spectrum in the next 20 sec.

Results and discussion

The integral polarization of protons of reaction products was deduced from spectra derived from the TEA and PB reactions, which took place in a benzene or toluene solution at room temperature for 40–50 sec after the reagent, were mixed in a 2/1 ratio (Fig. 1). Chemical shifts and polarization signs are listed in Table 1. The reaction hardly proceeded at all in a dioxane solution at room temperature, but at 60–70 °C it proceeded as rapidly as those in benzene and toluene, and it was followed by analogous CIDNP of protons. The ^{13}C nuclear polarization was obviously observed only in dioxane solution, owing to the insufficient solubility of PB in aromatic solvents. However, because of the CINP pictures of protons in dioxane and aromatic solvents and indications of more intense polarized lines of ^{13}C, are coincident with those observed in toluene solution, it can be concluded that the solvent type does not influence the reaction mechanism. There is an intensified absorption of ethylbenzoate carbonyl and methylene carbons and emission of diethylaluminium benzoate carbonyl carbon. Chemical shifts of ^{13}C NMR products and polarization signs are also listed in Table 1.

Proton spectra show that protons were polarized which previously belonged to ethyl groups of TEA, and in ^{13}C spectra the carbonyl atoms of carbon were more polarized. From these facts it can be concluded that the nuclear polarization first of all occurs in a radical pair (RP) of ethyl and benzoate radicals, the g-factor difference of which is not zero, and so integral effects should be observed. Polarization signs deduced on a presumption of singlet RP according to Kaptein's rule on

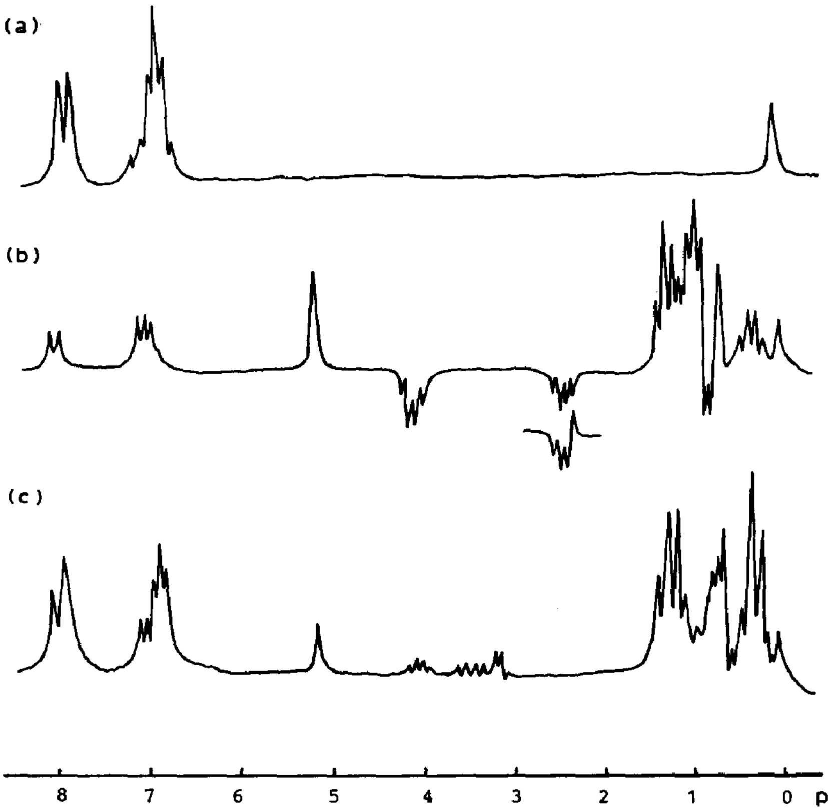
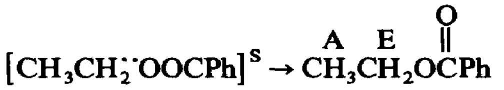


Fig. 1. ^{1}H NMR spectra obtained after mixing benzene solutions of TEA (1 *M*; 0.5 ml) and BP (0.5 *M*; 0.5 ml) at room temperature in a pulse spectrometer detector (100 MHz): (a) spectrum of BP initial solution; (b) spectrum of the reaction mixture 15 sec after mixing the reagents. Inset: a fragment in 2–3 ppm region, recorded on a spectrometer with continuous registration (60 MHz); (c) spectrum of the reaction mixture 30 min after mixing.

integral polarization signs [6], coincide with experimental ones. In fact, we have $\Delta g < 0$, $A(CH_3) > 0$, $A(CH_2) < 0$ for the ethyl radical in that RP. Then for the ethyl protons of a product of an ethylbenzoate intracell recombination we shall have:



$$[\mathrm{CH_3CH_2^{\cdot}\,{}^{\cdot}OOCPh}]^S \rightarrow \overset{A}{\mathrm{CH_3}}\overset{E}{\mathrm{CH_2}}\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Ph} \qquad (1)$$

The RP disproportion leads to the formation of polarized ethylene, the signal of which has a positive polarization, since $|A^H_{CH_3}| > |A^H_{CH_2}|$ and, therefore the positive polarization of methyl protons prevail over the negative polarization of methylene protons in an intermediate ethyl radical.

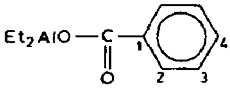
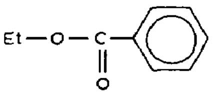
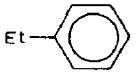
$$[\mathrm{CH_3CH_2^{\cdot}} \cdot \mathrm{OOCPh}]^S \rightarrow \overset{A}{\mathrm{CH_2}}{=}\overset{E}{\mathrm{CH_2}} + \mathrm{HOOCPh} \qquad (2)$$

Probably, a benzoic acid formed in termediately reacts rapidly with TEA according to eq. 3.

$$\mathrm{Et_3Al + PhCOOH \rightarrow C_2H_6 + Et_2AlOOCPh} \qquad (3)$$

Table 1

Chemical shifts and ^{1}H and ^{13}C nuclear polarization signs of products of the reaction of benzoyl peroxide and TEA

Substance	Group	^{1}H NMR (in benzene)		^{13}C NMR (in dioxane)	
		δ (TMS), (ppm)	CIDNP signs	δ (TMS) (ppm)	CIDNP signs
EtAl$_3$	CH$_2$	0.19q	–	0.39	–
	CH$_3$	0.99t	–	10.32	–
	CO$_2$			162.74	
	C1			134.22	
(PhCOO)$_2$	C2			130.39	
	C3			129.2	
	C4	7.77÷7.87		127.16	
	C$_6$H$_5$	6.68÷7.07			
	CH$_2$	0.32q		0.52	
	CH$_3$	1.29t		10.18	
	CO$_2$			175.39	E
	C1			145.44	E
	C2			136.69	
	C3			132.71	
	C4			130.36	
	CH$_2$	4.04q	E	62.40	A
	CH$_3$	1.1[a]	A	15.14	E
	CO$_2$			167.24	A
	C1			132.55	A
	C2			131.53	
	C3			130.09	
	C4			134.40	
CH$_2$=CH$_2$		5.14s	A	123.70	A
C$_2$H$_6$		0.69s			
C$_4$H$_{10}$	CH$_3$	0.81	E		
		0.74	E		
	CH$_2$	2.37q	E+EA	26.00	A
	CH$_3$	0.9[a]	A		

[a] A series of positive polarized signs is observed in the 0.84–1.15 ppm region. Probably, they are related to methyl protons of ethylbenzoate and ethylbenzene.

The occurrence of a positive polarized signal of the benzoic acid hydroxyl proton would be expected in the ^{1}H NMR spectrum (eq. 2) but polarization is quenched rapidly due to a short period of spin relaxation of the proton.

Ethyl radicals with positive polarized methylene and negative methyl protons diffuse to the solution at RP dissociation. A recombination of two ethyl radicals leads to polarized butane (cf. Table 1), as an intermediate decomposing to ethane and ethylene, and a proton breaking off from a molecule of the solvent leads to formation of ethane.

The same type of polarization on protons, occurring in a singlet RP of ethyl and benzoate radicals, was observed in thermal decomposition of propionyl peroxide [7]. Similarly [7], in our experiments on a spectrometer with continuous registration with quartet of ethylbenzene methylene protons, we found three components to be polarized negatively, and the fourth one at positive high field. The quartet is related to ethylbenzene methylene protons. The analogous polarization of the above quartet, observed previously in decomposition of propionyl benzene peroxide, was explained by the authors [8] as a process of decarboxylation of the benzoate radical with formation of a secondary RP of ethyl and phenyl radicals with preservation of the singlet state, in which protons of ethyl radical acquire a multiplet polarization with EA phase due to $g = 0$. An overlapping of two types of polarization, E + EA, accounts for the observed effect.

$$[CH_3CH_2^{\cdot} \cdot OOCPh]^S \xrightarrow{-CO_2} [\overset{A}{CH_3}\overset{E}{CH_2^{\cdot}}{}^{\cdot}Ph]^S \rightarrow \overset{E+EA}{CH_2CH_2Ph} \qquad (4)$$

It is interesting to note, that in our experiments a similar polarization [9] is not observed on the impulse spectrometer values there is a previous saturated pulse, without this only a quartet emission is recorded. The ethylbenzene formation has not been detected previously [1] in studies of this reaction. In our experiments a quartet at 2.37 ppm is observed only in the course of polarization. This fact is consistent with very small yield of the product. The yield of another product, ethylbenzoate, is also small in accordance with ^1H NMR spectra (~ 5%). The difference from previous results [1] is probably explained by higher concentration of initial reagents in our experiments.

To observe the further behaviour of benzoate radicals we have registered CIDNP spectra on ^{13}C. The data obtained either confirmed the above described results or supplemented them. Thus, the polarization signs of carbon in ethylbenzoate correspond completely to intracell recombination of initial RP, since for the ^{13}C atoms $A^C_{CH_3} < 0$, $A^C_{CH_2} > 0$, $A^C_{CO_2} < 0$, and $A^C_{Cl} < 0$ (cf. Table 1) [6]; the polarization signs in ethylene and ethylbenzoate also correspond to the scheme proposed. The major observation is the very emission at 175.4 ppm. This signal remains rather intensive in product spectra after the reaction, so it probably corresponds to carboxylic hydrocarbon of the main reaction product, diethylaluminium benzoate. The negative polarization of that carbon indicates, that the product was formed in the interaction of initial TEA with the polarized benzoate radical to leave the primary RP (eq. 5). Such a substitution of alkyl groups of organometallic compound series Al, B, Zn, Cd, etc. by $RO^{\cdot}$ radicals has been detected previously [10].

$$\overset{E}{PhCO\dot{O}} + Et_3Al \rightarrow \overset{E}{PhCOOAlEt_2} + Et^{\cdot} \qquad (5)$$

Another way by which $PhCOOAlEt_2$ is formed via benzoic acid, mentioned above (eq. 2 and 3), should lead to the counter positive polarization of carbonyl carbon. However, taking into account the fact that the ethylene yield is rather small (> 6% [1]), it was concluded to be unlikely. Thus, the strong emission of carbonyl carbon occurring for the first main route is of greater significance than the positive polarization.

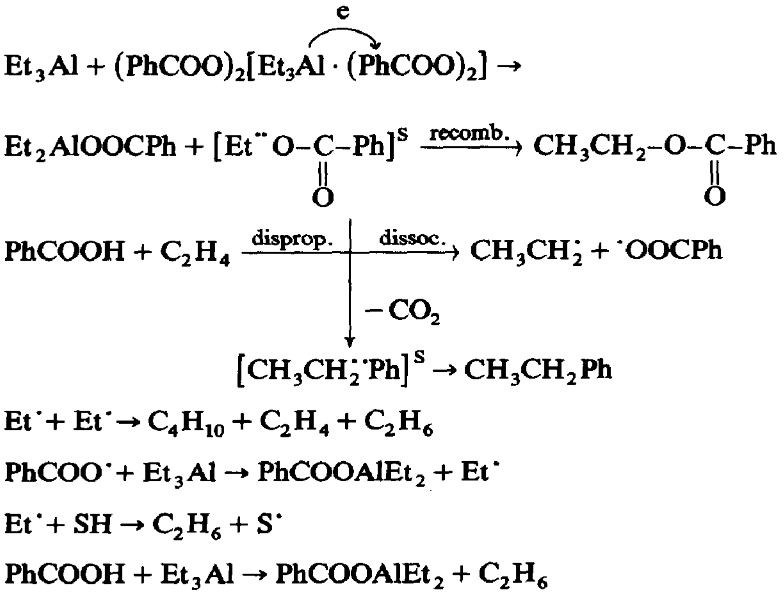
Since in ref. 1 the experiments were carried out in the presence of styrol we were interested in the excess effect of styrol on CIDNP. The presence of 5-fold styrol in relation to TEA is the reason for the lack of change in the CIDNP picture. Thus, in ^1H NMR spectra in benzene and dioxane solutions the negative polarized butane lines disappear on the addition of styrol, and in their place a series of novel

Table 2

Chemical shifts and proton polarization signs in products of the TIBA and BP reaction in benzene-d_6

Substance	Group	δ (TMS) (ppm)	CIDNP signs
$[(CH_3)_2CHCH_2]_3Al$	CH_2	0.28d	
	CH_3	1.0d	
	CH	1.92m	
$[(CH_3)_2CHCH_2]_2AlOOCPh$	CH_2	0.51d	
	CH_3	1.2d	
	CH	2.17m	
$(CH_3)_2C{=}CH_2$	CH_2	1.71 septet	E
	CH_3	1.63t	E
$(CH_3)_2CHCH_3$	CH_3	0.9d	
$(CH_3)_2CHCH_2OOCPh$	CH_2	4.08d	E
$(CH_3)_2CHCH_2Ph$	CH_2	2.37d	E

polarized signals occurs corresponding probably to the products of interaction of styrol and radicals derived from RP. Thus, it can be concluded that styrol intercepts rather effectively polarized ethyl radicals, which have diffused from RP into a solution. This prevents the formation of polarized butane which might occur following diffusion, collision and recombination of polarized ethyl radicals. This conclusion conforms with the data relating to butane yields. Previous workers [1] have detected that butane yield decreases from 6.3% to 1.6% in relation to TEA on addition of styrol in the course of the reaction, and most of the butane originates from hydrolysis of the reaction mixture after reaction. This fact may be explained by the nonradical nature of butane. For instance, there is a possibility that ethylene formed in the course of the reaction is introduced into an Al–C bond of TEA with the formation of diethylbutylaluminium [11], further hydrolysis of which leads to the formation of butane.



$$Et_3Al + (PhCOO)_2[Et_3Al\overset{e}{\cdot}(PhCOO)_2] \rightarrow$$

$$Et_2AlOOCPh + [Et^{\bullet\bullet}\,O{-}\underset{\overset{\|}{O}}{C}{-}Ph]^S \xrightarrow{\text{recomb.}} CH_3CH_2{-}O{-}\underset{\overset{\|}{O}}{C}{-}Ph$$

$$PhCOOH + C_2H_4 \xleftarrow{\text{disprop.}}\;\xrightarrow{\text{dissoc.}} CH_3CH_2^{\bullet} + {}^{\bullet}OOCPh$$

$$\downarrow -CO_2$$

$$[CH_3CH_2^{\bullet}\,{}^{\bullet}Ph]^S \rightarrow CH_3CH_2Ph$$

$$Et^{\bullet} + Et^{\bullet} \rightarrow C_4H_{10} + C_2H_4 + C_2H_6$$

$$PhCOO^{\bullet} + Et_3Al \rightarrow PhCOOAlEt_2 + Et^{\bullet}$$

$$Et^{\bullet} + SH \rightarrow C_2H_6 + S^{\bullet}$$

$$PhCOOH + Et_3Al \rightarrow PhCOOAlEt_2 + C_2H_6$$

Scheme 1

In CIDNP ^{13}C NMR spectra made in the presence of styrol attention should be given to the decrease in intensity of the negative polarized signal of carbonyl carbon $Et_2AlOOCPh$. This fact confirms the truth of the reaction proposed (eq. 5), as styrol in this case intercepts a part of polarized benzoate radicals.

Similarly, TIBA reacts with BP. Data of ^1H NMR spectra and polarization signs of protons in products are listed in Table 2. Regarding that reaction, it should be noted that integral polarization occurs in singlet RP of isobutyl and benzoate radicals. Taking into account this moment, everything described above for TEA is also true for TIBA.

Summarizing the data obtained, a new set of pathways for radicals in the TEA and PB reaction can be proposed (see Scheme 1), namely the formation of a 1/1 complex and, probably, single-electron transfer leading to formation of a radical in the first stage.

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