Chemically induced dynamic nuclear polarization and reaction of Et_3Al with CCl_4 catalyzed by $Ni(acac)_2$

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The influence of $Ni(acac)_2$ added in catalytic amounts on the chemically induced dynamic nuclear polarization (CIDNP) effects, the mechanism of interaction, and the products of reaction between Et_3Al and CCl_4 were studied. The radical intermediates were identified and the routes for their transformations were proposed. The thermal reaction of Et_3Al with CCl_4 occurs by a radical mechanism. However, in the presence of $Ni(acac)_2$, the reaction proceeds mainly *via* a nonradical route and gives large amounts of ethylene and ethane.

Key words: organoaluminum compounds, carbon tetrachloride, free radicals, radical mechanism, chemically induced dynamic nuclear polarization, homogeneous catalysis by transition metal complexes.

Previously,[1] in a chemically induced dynamic nuclear polarization (CIDNP) study of the reaction of trialkylaluminum with CCl_4, a scheme has been proposed, according to which this reaction occurs mostly by a free radical mechanism. Subsequently it was found that the rate of this reaction and the CINDP effects depend appreciably on the presence of catalyic amounts of transition metal complexes.[2]

In this work, we outline the results of a study of the reaction of triethylaluminum (TEA) with CCl_4 in the presence of catalytic amounts of $Ni(acac)_2$.

Results and Discussion

It is known that mixing of concentrated solutions of TEA and CCl_4 results in an explosion.[3] When TEA is diluted by a hydrocarbon solvent to a concentration of 1 mol L^{-1}, the reaction rate decreases and becomes too low for CIDNP effects to be observed reliably. On heating, the reaction accelerates and signal polarization is permanently recorded.[1] Sharp acceleration of the reaction can be attained by adding catalytic amounts of $Ni(acac)_2$ to a solution of TEA in cyclohexane. In addition, in this case, the reaction yields much more gaseous products than that conducted without additives. For example, the addition of 0.3 mol. % $Ni(acac)_2$ with respect to TEA results in the formation of 0.77 moles of a gas consisting of ethane (61%) and ethylene (39%). When the reaction mixture is hydrolyzed, 1.4 moles of a gas consisting of ethane (98%) and ethylene (1.7%) is evolved per 1 mole of TEA. The amount of the gas increases with an increase in the content of $Ni(acac)_2$.

The ^1H NMR spectrum of the reaction mixture, recorded after the reaction, demonstrated the presence of Et_2AlCl (δ 1.07 (t); 0.2 (q)), EtCl (δ 3.4 (q)), and ethylene (δ 5.3 (s)). After hydrolysis of the reaction mixture, ethyl chloride, unreacted CCl_4, hexachloroethane, tetrachloroethylene, and dichloromethane were identified by GLC and GC/MS analyses. The mixture also contained traces of 1,1,1-trichloropropane, 1,1-dichloropropane, and unidentified chlorinated hydrocarbons.

The acceleration of the reaction in the presence of $Ni(acac)_2$ is accompanied by a sharp increase in the polarization effects and by inversion of the CINDP signs with respect to those observed in the thermal reaction (Fig. 1, Table 1). For comparison, Fig. 2 also contains the polarization ^1H NMR spectrum recorded during the reaction, which was carried out without a catalyst. The opposite signs are not the only difference between these two variants. Whereas in the thermal reaction, the protons in ethylene, chloroform, and 1,1,1-trichloropropane are strongly polarized, in the presence of the catalyst, polarization is observed for chloroform and 1,1,1-trichloropropane and is not observed for ethylene. During the thermal reaction, polarization of all signals disappears almost simultaneously over a period of 1 min. In the catalytic reaction, polarization of protons in 1,1,1-trichloropropane is observed for 1.5—2 min, while the chloroform proton remains polarized for an unusu-

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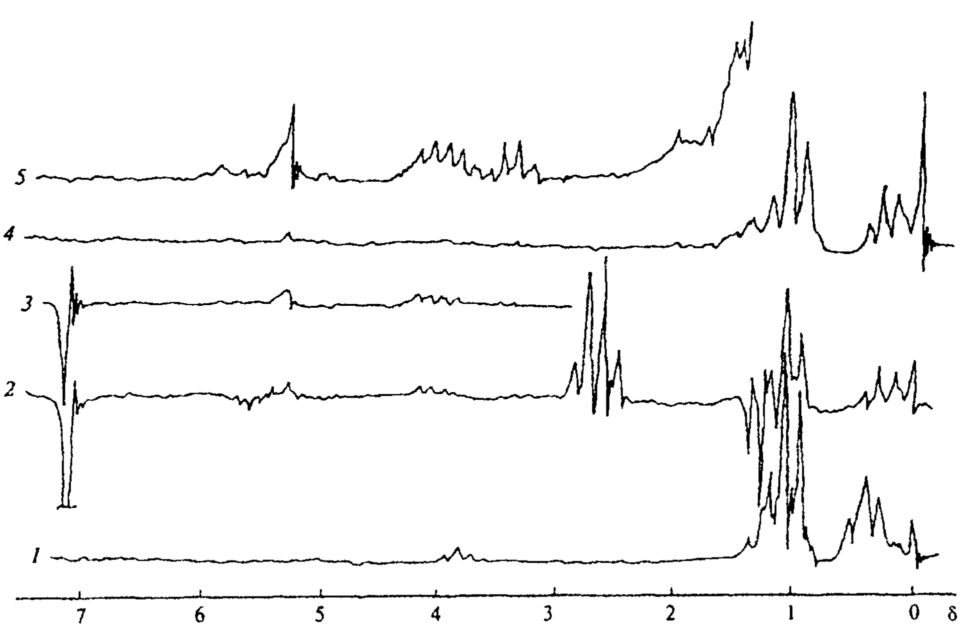


Fig. 1. ^1H NMR spectra (60 MHz, CW) recorded during the reaction of TEA with CCl_4 in deuteriocyclohexane in the presence of $Ni(acac)_2$ at room temperature: initial Et_3Al with $Ni(acac)_2$ (*1*), after 5 (*2*) and 20 (*3*) s after the addition of CCl_4, and reaction products (*4*, *5*).

ally long period of up to 5 min; moreover, the signal for chloroform is manifested only as gradually vanishing emission, while a normal absorption signal is not observed at all. In addition, in the case of the catalytic reaction, the spectrum exhibits a weakly polarized triplet for 1,1-dichloropropane, which is missing in the thermal variant.

In both cases, only integral polarization is observed; thus, polarization arises in radical pairs (RP) with nonequivalent *g*-factors.[4] As has been noted previously,[1] during the thermal reaction, the starting TEA and CCl_4 in a hydrocarbon solvent are converted *via* a single-electron transfer into a radical-ion pair $[Et_3Al]^{\cdot +}[CCl_4]^{\cdot -}$, which is then transformed into Et_2AlCl and a singlet radical pair (RP), $[^{\cdot}Et^{\cdot}CCl_3]^S$. Since $g(Et) < g(CCl_3)$, intergral polarization does appear in this RP. Subsequently the polarization is transferred to the products of transformations of the radicals and can be observed experimentally (see Table 1). An inversion of polarization signs, similar to that discovered

Table 1. Signs of proton polarization in the products of thermal reaction of Et_3Al with CCl_4 in C_6D_{12} and those for the reaction in the presence of $Ni(acac)_2$

Product	Group	δ	CIDNP signs	
			Thermal reaction	Reaction with $Ni(acac)_2$
Ethylene	CH_2	5.28	A	None
$CHCl_3$	CH	7.2	A	E
$CH_3CH_2CCl_3$	CH_3	1.25	A	E
	CH_2	2.7	E	A
CH_3CH_2Cl	CH_3	1.43	None	None
	CH_2	3.45	None	None
$CH_3CH_2CHCl_2$	CH	5.6	—	E
	CH_2	2.1	—	A
	CH_3	1.3	—	E

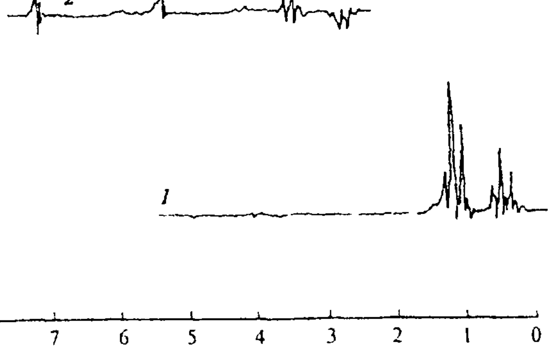
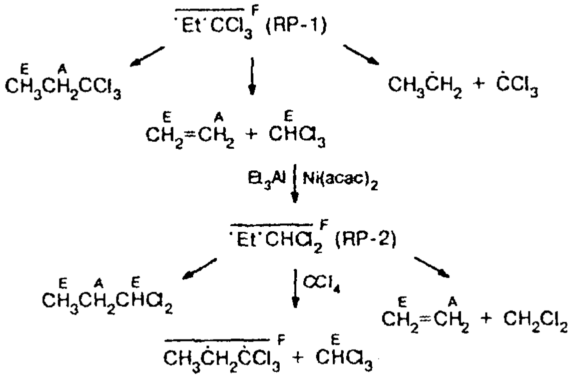


Fig. 2. ^1H NMR spectra (60 MHz, CW) recorded during the thermal reaction of TEA in C_6D_{12} at 70 °C: initial TEA (*1*), during the reaction (*2*), and reaction products (*3*, *4*).

in this study, had been observed previously in the same reaction carried out without a catalyst and in dioxane instead of a hydrocarbon solvent. In conformity with the CIDNP theory, this situation is possible in the case where nuclear polarization is induced in a noncorrelated diffusion RP, whose unpaired electrons occur in the triplet state. The absence of a geminate singlet RP in dioxane can be explained by the fact that dioxane tends to form fairly strong complexes with R_3Al. The incorporation of the dioxane molecule in the first coordination sphere of the organoaluminum compound might prevent the formation of singlet RP at the instant of origination of the radicals. The radicals meet somewhat later, but at that time, their spins have become non-correlated. Presumably, a similar situation is realized in the presence of nickel ions. The assumption of the formation of a diffusion RP is confirmed by the fact that addition of styrene completely suppresses nuclear polarization in the case of the catalytic reaction. Indeed, styrene acts as an efficient radical trap; it binds the radicals that have emerged from the "cage" and thus prevents formation of the diffusion RP.

The generation of nuclear polarization in the reaction products can be rationalized in terms of the following sequence of transformations of a diffusion pair formed by ethyl and trichloromethyl radicals (RP-1) (Scheme 1).

Scheme 1



Recombination of the RP-1 yields 1,1,1-trichloropropane; the signs of proton polarization for this product coincide with those predicted by the Captain rule for the integral polarization.[4] Disproportionation of the RP-1 gives ethylene and chloroform with the negatively charged proton. Ethylene is not polarized in the experiments, probably due to the fact that the α- and β-protons of the ethyl radical, which are characterized by opposite polarization signs, become equivalent in ethylene and their effects partly cancel each other. The excessive emission of the methyl β-protons is masked by signals from ethylene molecules, formed *via* a nonradical pathway. Chloroform was not found among the reaction products. Presumably, it reacts again with TEA. It was shown in a special experiment that chloroform enters into a catalytic reaction with TEA; this is accompanied by intense emission from protons of the starting chloroform. This can be explained by assuming that a dichloromethyl radical, incorporated in the diffusion radical pair RP-2, abstracts a chlorine atom from the initial chloroform molecule and is thus converted into a polarized chloroform molecule, *i.e.*, they undergo exchange (the asterisk marks polarized protons).

$$[\cdot Et\cdot CH^{*}Cl_2]^F + CHCl_3 \longrightarrow [\cdot Et\cdot CHCl_2]^F + CH^{*}Cl_3$$

It can be assumed that similar exchange also occurs in the case of CCl_4, as shown in Scheme 1. This yields again the RP-1 and a polarized chloroform molecule. Recombination of the RP-2 affords polarized 1,1-dichloropropane. The weak emission of the triplet signal from the proton in position 1 of this compound can be observed in the spectrum. Disproportionation of the RP-2, apparently, does not occur, because polarized dichloromethane does not manifest itself in the spectra.

Hexachloroethane, discovered among the reaction products, arises most likely upon recombination of two trichloromethyl radicals. Tetrachloroethylene might result from recombination of two dichlorocarbene species, which have been assumed[5] to be intermediates in a study of the reaction of trialkylalanes with CCl_4.

An important point is that the ^1H NMR spectra recorded for the reaction mixture after the reaction virtually do not contain any longer the signals polarized during the reaction. Only ethylene and ethyl chloride, which are not polarized, can be reliably detected. This is consistent with the above results of the analysis of the products, which indicate that only traces of 1,1,1-trichloropropane and 1,1-dichloropropane are formed.

Thus, it can be concluded that $Ni(acac)_2$ catalyzes mostly the nonradical route of the reaction between CCl_4 and Et_3Al. The radical route is also accelerated, but it is apparently a side process; however, it is the latter route that is responsible for the CIDNP effects.[6]

Experimental

A 1—2 *M* solution of a commercial sample of TEA (92.8%) in cyclohexane or hexane was used. CCl_4 was dried over $CaCl_2$ and distilled. ^1H NMR and CIDNP spectra were recorded in cyclohexane-d_{12} with 0.1% impurities and a degree of deuteration of 99.5%.

1,1,1-Trichloropropane, ethyl chloride, 1,1-dichloropropane, and Et_2AlCl were identified by comparing their spectra with those of authentic samples.

To record CIDNP, the reaction was carried out directly in the probe of an NMR spectrometer at room temperature. Carbon tetrachloride was injected under argon with a syringe into a 5-mm tube in the transducer and containing a solution of TEA and a known amount of $Ni(acac)_2$. ^1H NMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz, CW).

The gases evolved during the reaction were analyzed on an Agat gas chromatograph (*n*-hexadecane, 25% on C-22 zeolite, 40—60 mesh, 6.8 m × 4 mm column, room temperature, TC detector, hydrogen as the carrier gas). *n*-Butane was used as the reference compound.

The liquid reaction mixture was analyzed without separation by the GC/MS method on a FINNIGAN-4021 instrument. A 50-m long capillary column and SE-30 stationary phase were used under conditions of linear temperature programming (6 deg $\min^{-1}$) in the range from 50 to 250 °C. Compounds in the mixture were identified using the database contained in the instrument computer.

To analyze the products, the reaction was carried out under argon in a three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser. A 2 *M* solution of TEA (5.1 mL, 10.2 mmol) in hexane was added into a flask containing $Ni(acac)_2$ (15.9 mg, 0.5 mol. % in relation to TEA). The flask was connected to a gas meter. At 0 °C, a 1 : 5 solution of CCl_4 in hexane (2.8 mL) was slowly added dropwise over a period of 30 min, in order to avoid overheating, to the dark solution formed in the flask, and then the remaining CCl_4 (0.58 mL) was added (total 10.8 mmol). During the reaction, 210 mL (s.t.p.) of a gas evolved; this makes 0.9 moles per mole of TEA. The gas consisted of ethane (62%) and ethylene (38%). Hydrolysis was started with cooling, continued at room temperature, and brought to completion by adding 10% HCl. During the hydrolysis, 400 mL of a gas (1.8 moles per mole of TEA) comprising 97.4% ethane and 2.6% ethylene was collected. The organic layer, separated from the aqueous phase using a separating funnel, was dried with $MgSO_4$ and subjected to GC/MS analysis.

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