Brief Communications

CIDNP study of the Ni(acac)$_2$-catalyzed reaction of triethylaluminum with chloroform

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CIDNP effects were found in the Ni(acac)$_2$-catalyzed reaction of Et_3Al with $CHCl_3$. The effects appear in the products of transformation of the diffusion radical pair of the ethyl and dichloromethyl radicals. The radical route is a side process in this reaction, and the main products, Et_2AlCl, ethane, and ethylene, are formed by a nonradical route. A general mechanism of the reactions of Et_3Al with $CHCl_3$ and CCl_4 including radical and ion-coordination processes was suggested.

Key words: organoaluminum compounds, polyhalomethanes, free radicals, catalysis by transition metal compounds, chemically induced dynamic nuclear polarization.

The influence of a catalytic amount of Ni(acac)$_2$ on the effects of chemically induced dynamic nuclear polarization (CIDNP) in the reaction of Et_3Al with CCl_4 has been considered in a recent report,[1] and Et_2AlCl, ethylene, and ethane were shown to be the main products of this reaction. The reaction products are formed *via* the heterolytic route, and CIDNP is due to a side radical process.

In this work, we analyzed the CIDNP effects in the reaction of Et_3Al with $CHCl_3$ and suggested a general mechanism of the process.

Results and Discussion

It was found in preliminary experiments that $CHCl_3$ does not react with Et_3Al dissolved in hexane in the absence of the catalyst. When Ni(acac)$_2$ is introduced into the reaction mixture, a vigorous exothermic reaction occurs to form Et_2AlCl, ethane, and ethylene.

For example, when a twofold excess of chloroform (20 mmol) was added to a 1 *M* solution of Et_3Al (10 mmol) in hexane in the presence of Ni(acac)$_2$ (1 mol.% relative to Et_3Al), 0.44 mole of a gas consisting of ethylene (27%) and ethane (73%) was evolved per mole of Et_3Al. The amount of the evolved gas increases as the catalyst concentration increases.

When the reaction was carried out in a 5-mm NMR tube directly in the detector of a spectrometer, the ^1H NMR spectra recorded during the reaction exhibited the effects of integral CIDNP (Fig. 1, *a*). The signs of proton polarization in the reaction products are presented in Table 1. The polarized products have apparently a radical origin. Their signals were reliably found in the spectra only when they existed in polarized form,

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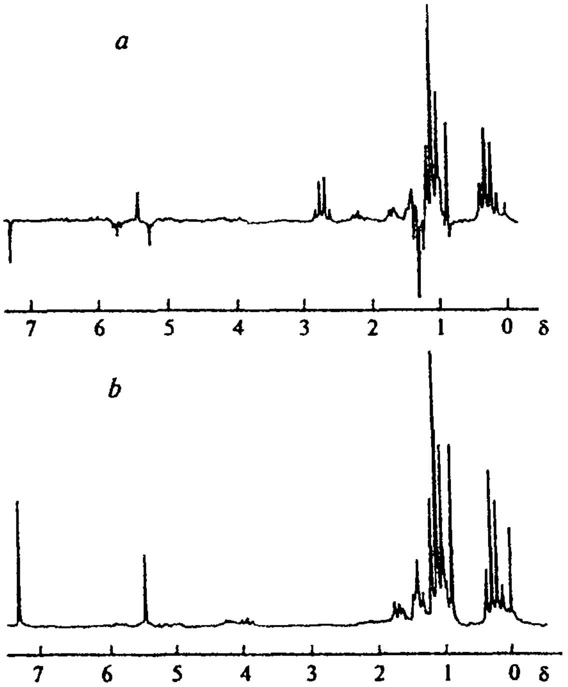


Fig. 1. ^1H NMR spectra (100 MHz, FT) recorded during the reaction of Et_3Al with $CHCl_3$ in cyclohexane-d_{12} in the presence of $Ni(acac)_2$ at room temperature: *a*, 13 s after the addition of chloroform; *b*, at the end of the reaction.

Table 1. Signs of proton polarization in the products of the reaction of Et_3Al with $CHCl_3$ in the presence of $Ni(acac)_2$

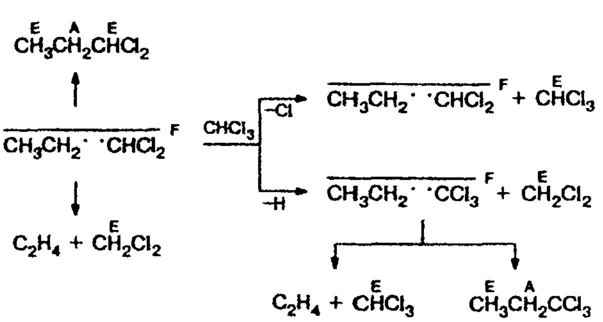
Compound	Group	δ	CIDNP sign*
$CHCl_3$		7.3	E
CH_2Cl_2		5.2	E
C_2H_4		5.4	—
C_2H_6		0.86	—
$CH_3CH_2CCl_3$	CH_3	1.3	E
	CH_2	2.1	A
$CH_3CH_2CHCl_2$	CH_3	1.3	E
	CH_2	2.1	A
	CH	5.6	E

* E is the emission, and A is the absorption of the signal.

and they almost disappeared at the end of the reaction. After the end of the process, the spectrum of the reaction mixture exhibits signals of organoaluminum compounds (OAC), the starting chloroform, ethane, and ethylene (Fig. 1, *b*). Thus, it can be concluded that, as in the case with CCl_4, the radical route of the reaction of Et_3Al with $CHCl_3$ is a side process.

By analogy to the reaction with CCl_4, the appearance of CIDNP in the products of the reaction of Et_3Al with $CHCl_3$ can be explained by the sequence of transformations of the diffusional radical pair (RP) of the ethyl and dichloromethyl radicals (RPs-1) presented in Scheme 1.

Scheme 1



(F is the radical pair with noncorrelated spins, and E and A are the emission and the absorption of the signal)

The assumption about diffusional RPs is confirmed by the complete suppression of CIDNP effects when styrene was added, which is, in this case, a radical trap. Disproportionation and recombination of RPs-1 afford polarized methylene dichloride and 1,1-dichloropropane, respectively. The polarization of the starting chloroform can be explained by the fact that the dichloromethyl radical in the diffusional RP-1 eliminates the Cl atom from the molecule of the starting chloroform, transforming it into polarized chloroform, *i.e.*, the following exchange occurs:

$$\overline{Et^{\cdot}\ {}^{\cdot}CH^{*}Cl_2}^{\,F} + CHCl_3 \longrightarrow \overline{Et^{\cdot}\ {}^{\cdot}CHCl_2}^{\,F} + CH^{*}Cl_3\,.$$

The formation of 1,1,1-trichloropropane can probably be explained also by the exchange of the dichloromethyl radical with the chloroform molecule, but with the elimination of a hydrogen atom. Polarized 1,1,1-trichloropropane is the product of the recombination of the newly formed RP of the ethyl and trichloromethyl radicals (see Scheme 1).

Let us consider the possible route of the formation of radicals in the reactions under study. The $Ni(acac)_2$—Et_3Al catalytic system has been studied in detail in many works. In particular, it has been shown[2] that the nickel complex is rapidly reduced by a high excess of OAC (as in our case):

$$Et_3Al + Ni(acac)_2 \longrightarrow EtNi(acac) + Et_2Al(acac),$$

$$EtNi(acac) + Et_3Al \longrightarrow NiEt_2 + Et_2Al(acac),$$

$$NiEt_2 \longrightarrow Ni^0 + C_2H_6 + C_2H_4 + {}^{\cdot}CH_2Me.$$

The $NiEt_2$ formed decomposes, due to its instability, to Ni^0 and gaseous products (ethane, ethylene). It could be expected that a minor portion of the nickel dialkyl compound would decompose homolytically to form the ethyl radical. At a high excess of OAC, Ni^0 is present in the reaction mixture mainly as colloidal nickel, which then reacts, most likely, with CCl$_4$ to form the $^\cdot$CCl$_3$ radical.

$$Ni^0 + CCl_4 \longrightarrow NiCl + {}^\cdot CCl_3$$

This stage has been found in the Kharasch reaction,[4] *i.e.*, the interaction of Grignard's reagent RMgX with organic halides in the presence of catalytic amounts of transition metal salts, resulting in the formation of the R—R product.

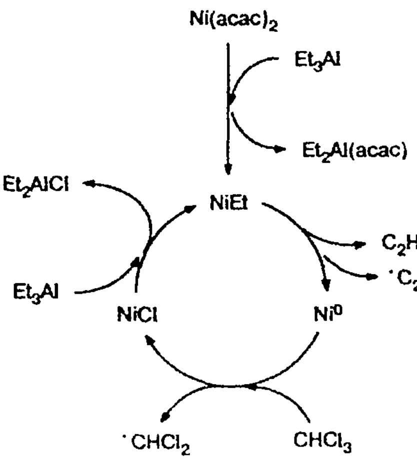
$$M^0 + R'Hal_4 \longrightarrow MHal + {}^\cdot R'$$

At the last stage, NiCl is alkylated by the starting Et$_3$Al.

$$NiCl + Et_3Al \longrightarrow Et_2AlCl + NiEt$$

Therefore, the formation of the main products and radical intermediates in the catalytic reactions of Et$_3$Al with CCl$_4$ and with CHCl$_3$ can be presented as the catalytic cycle shown in Scheme 2.

Scheme 2



In this scheme, the ethyl and dichloromethyl radicals appear at different stages of the cycle and, hence, can form a diffusional RP only at random collisions in the solution. CIDNP effects appear in these RPs.

The catalytic cycle for the reaction of Et$_3$Al with CCl$_4$, which has been studied in the previous report,[1] can be presented in the same manner, replacing chloroform by CCl$_4$ and the $^\cdot$CHCl$_2$ radical by $^\cdot$CCl$_3$ in Scheme 2.

The possible direct interaction of the alkylnickel compound NiEt with polyhalomethane with a one-electron transfer and formation of a singlet RP

$$NiEt + CCl_4 \longrightarrow NiCl + \overline{Et^\cdot \ {}^\cdot CCl_3}^{\,S}$$

should be ruled out, because the expected signs of polarization in the products of transformation of this RP contradict the experimental signs.

Experimental

A 1—2 *M* solution of triethylaluminum (92.8%) in cyclohexane or hexane was used. Chloroform was dried with CaCl$_2$ and distilled. Cyclohexane-d$_{12}$ with a content of admixtures of 0.1% (degree of deterioration 99.5%) was used for recording ^{1}H NMR and CIDNP spectra.

1,1,1-Trichloropropane and 1,1-dichloropropane were identified by comparison of their spectra with those of authentic samples.

For the detection of CIDNP, the reactions were carried out directly in the field of an NMR spectrometer at room temperature. Chloroform was added by a syringe to a solution of Et$_3$Al containing a known amount of Ni(acac)$_2$ in a 5-mm tube in the detector of the spectrometer. ^{1}H NMR spectra were detected on Tesla BS-467 (60 MHz, CW) and Tesla BS-567A (100 MHz, FT) spectrometers.

Gases evolved during the reaction were analyzed on an Agat gas chromatograph (column 6.8 m × 4 mm, *n*-hexadecane (25%) on zeolite S-22, 40—60 mesh, ~20 °C, a katharometer as the detector, hydrogen as the gas carrier). *n*-Butane was used as the reference gas.

For analysis of gaseous products, the reaction was carried out in a three-necked flask with a magnetic stirrer, a dropping funnel, and a reflux condenser in an argon atmosphere. A 2 *M* solution (5.1 mL) of Et$_3$Al (10.2 mmol) in hexane was added to a flask containing 28 mg of Ni(acac)$_2$ (1 mol.% relative to Et$_3$Al). The flask was attached to a gas volumeter. A mixture of 1.6 mL of CHCl$_3$ (20 mmol) and 5 mL of hexane was added dropwise (to avoid overheating) to the resulting dark solution. A gas (100 mL under standard conditions, 0.44 mole per mole of Et$_3$Al) consisting of ethane (73%) and ethylene (27%) evolved during the reaction.

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