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Chemically Induced Dynamic Nuclear Polarization and the Mechanism of the Reaction of Et_3Al with CCl_4 in the Presence of Transition Metal Complexes

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Abstract—Integral effects of chemically induced ^1H and ^{13}C nuclear polarization are reported for the reaction of Et_3Al with CCl_4 catalyzed by $Pd(acac)_2$, $Cu(acac)_2$, and Cp_2TiCl_2; for the reaction of $(n\text{-}C_8H_{17})_3Al$ with CCl_4 in the absence of a catalyst and in the presence of $Ni(acac)_2$; and for the reaction of the cyclic organoaluminum compound 1-ethyl-3-butylaluminacyclopentane with CCl_4 in the presence of $Pd(acac)_2$. A scheme of the catalytic cycle of this reaction predicting the formation of both radical and nonradical products is derived from the observed chemically induced dynamic nuclear polarization (CIDNP) effects and from data on the products of the reaction between Et_3Al and CCl_4 in the presence of $Pd(acac)_2$. According to the results of qualitative analysis of the CIDNP effects, the reactions of the trialkylalanes and the cyclic organoaluminum compound with CCl_4 in the presence of various metal complexes proceeded via similar mechanisms.

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Organoaluminum compounds find wide use in chemistry. In particular, they are employed as cocatalysts in various industrially important processes. Complete reaction mechanisms with allowance made for the possible participation of free-radical intermediates should be known for the purposeful formation of these systems. Conventional methods are of little use in the elucidation of free-radical routes in reactions involving organoaluminum compounds. Therefore, it seems interesting to study chemically induced dynamic nuclear polarization (CIDNP) effects in homogeneous catalytic reactions of organoaluminum compounds with halomethanes in the presence of transition metal complexes.

Historically, attention to reactions of organoaluminum compounds with halomethanes in the presence of transition metal complexes was due to the ability of organoaluminum compounds to initiate the free-radical polymerization of vinyl monomers at the initial stage [1]. The initiation ceases at the second stage, which occurs with an induction period [2]. Later it was found by the ^1H CIDNP method that the initial stage of the reaction of Et_3Al with CCl_4 catalyzed by $Ni(acac)_2$ is accompanied by the formation of ethyl and trichloromethyl radicals, whose diffusion pairs show integral polarization effects [3]. A comparison of the CIDNP effects in this catalytic reaction and in the thermal reaction of Et_3Al with CCl_4 in the absence of a catalyst [4] made it possible to suggest a probable scheme of radical formation involving transition metal complexes. Investigation of the second stage of the reaction between the organoaluminum compounds and halomethanes in the presence of transition metal complexes and salts showed that these reaction systems activate inert C–C and C–H bonds in saturated hydrocarbons under mild conditions. Isomerization and dimerization reactions and skeletal transformations of the starting hydrocarbons with the cleavage of these bonds occur under these conditions [5].

We earlier considered the ^1H CIDNP effects in the reaction between Et_3Al and CCl_4 catalyzed by $Ni(acac)_2$ [3]. In the present work, the initial stage of this reaction in the presence of $Pd(acac)_2$ was studied by the ^1H and ^{13}C CIDNP methods and the influence of several other transition metal complexes on the CIDNP effects was considered.

EXPERIMENTAL

A 1 M solution of commercial 98% Et_3Al in cyclohexane-d_{12} was used. The starting CCl_4 was predried over P_2O_5 and distilled.

To observe CIDNP, a 1 M solution of Et_3Al in cyclohexane-d_{12} containing 2–4 mg of $Pd(acac)_2$ was placed in a 5-mm NMR tube in an argon atmosphere. Before this, the NMR spectrum of the starting solution was recorded. Next, a certain amount of a CCl_4 solution was syringed at room temperature into the tube, which was

Chemical shifts and signs of polarization of the products of the reaction between $(C_2H_5)_3Al$ (1 M, 0.4 ml) and CCl_4 (1.0 : 1.5) in the presence of $Pd(acac)_2$ (~2 mg) in C_6D_{12} at room temperature

Products	Product yields*, %	Group	^{1}H NMR		^{13}C NMR	
			δ, ppm	CIDNP sign**	δ, ppm	CIDNP sign**
$(CH_3CH_2)_3Al$		CH_2	0.37(q)	–	0.71	–
		CH_3	1.09(t)	–	8.78	–
CCl_4				–	96.57	–
$(CH_3CH_2)_2AlCl$		CH_2	1.10(t)	–	7.80	–
		CH_3	0.25(q)	–	2.92	–
$CH_3–CH_3$	48		0.84(s)	–	6.96	–
$CH_2=CH_2$	52		5.32(s)	–	122.85	–
$CHCl_3$	7		7.18(s)	*E*	77.45	*A*
$CH_3CH_2CCl_3$	8	CCl_3		–	101.52	*A*
		CH_2	2.67(q)	*A*	49.52	*E*
C_2Cl_6	10	CCl_3		–	106.1	*E*
$CCl_2=CCl_2$	3			–		–

* The yields are in percent relative to the initial Et_3Al.
** *A* is positive polymerization, and *E* is negative polarization (hyphen means the absence of polarization).

mounted directly in the spectrometer sensor. The ^{1}H and ^{13}C NMR spectra were recorded during the vigorous reaction on a JEOL FX-90Q spectrometer operating at 89.5 MHz (^{1}H) and 22.5 MHz (^{13}C).

For the analysis of the reaction products, the reaction was carried out in an argon atmosphere in a three-necked flask fitted with a magnetic stirrer, a dropping funnel, and a reflux condenser. A 1.2 M solution (5 ml) of Et_3Al (6 mmol) in hexane was introduced into the flask, which contained $Pd(acac)_2$ (9 mg, 0.5 mol % relative to Et_3Al) and was connected to a gas meter. To prevent the onset of the second stage of the reaction, a solution (1.6 ml) of CCl_4 in hexane (1 : 2) was added dropwise at ^{13}C over 10 min to the resulting dark solution, and then 0.5 ml of CCl_4 (5.1 mmol) was added; that is, the total amount of CCl_4 added was 10.6 mmol. During the reaction, 121 ml (under normal conditions) of a gas evolved, which is 0.9 mol per mole of Et_3Al. The gas consisted of ethane (48%) and ethylene (52%). The initial hydrolysis stage was carried out under cooling, and then the hydrolysis was brought to the end at room temperature by adding 10% HCl. During the hydrolysis, 250 ml of a gas (1.85 mole per mole of triethylamine) was collected, which contained 97.4% ethane and 2.6% ethylene. The organic layer separated in a separatory funnel from the aqueous phase was dried with $MgSO_4$ and was analyzed by GC/MS.

The reaction products were analyzed using a Chrom-5 chromatograph equipped with a capillary column (25 m in length, 5% SE-30 phase) and a QCMS-QP2010 Plus GC/MS system (Shimadzu) with an SPB-1 column (Supelco, 30 m × 0.25 mm × 0.2 μm, 5% phenyl/95% methyl silicone phase). The NBS library (United States), containing 75000 mass spectra, was used to identify the compounds.

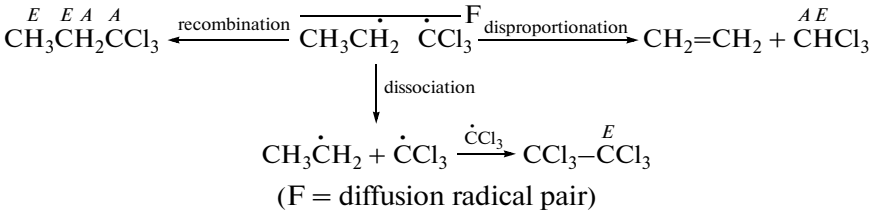
RESULTS AND DISCUSSION

The exothermic reaction of Et_3Al with CCl_4 catalyzed by $Pd(acac)_2$ proceeds vigorously and is accompanied by the evolution of gaseous products. An induction period is observed before the second, nonradical stage. Its duration depends on the temperature and on the concentration of the reactants, which makes it possible to study the initial stage until the second stage starts [5].

The interaction of a 1 M solution of Et_3Al in cyclohexane with CCl_4 (1 : 1.5–3.0) at room temperature yields Et_2AlCl, ethane, ethylene, chloroform, hexachloroethane, and trichloropropane. When the reaction is carried out directly in the cell of the NMR spectrometer, the spectra exhibit integral CIDNP effects for ^{1}H and ^{13}C. The signs of nuclear polarization, chemical shifts (δ), and signals assignments are presented in the table. The ^{1}H and ^{13}C NMR signals were assigned based on published data and by comparisons with the spectra of authentic samples.

The ^{1}H NMR spectra of the starting solution of Et_3Al, the reaction mixture under the reaction conditions, and the reaction products are shown in Fig. 1.

When Et_3Al reacts with CCl_4 in cyclohexane in the absence of a catalyst, ^{1}H and ^{13}C CIDNP appear in the geminal singlet radical pair of the ethyl and trichloromethyl radicals [4] formed in one elementary event. A comparison between the thermal and catalytic processes shows that the catalytic reaction is accompanied by the inversion of polarization signs of the chloroform and trichloropropane nuclei. The inversion can be due to a change in the multiplicity of the radical pair. Therefore, it can be assumed that, in the catalytic reaction, integral nuclear polarization appears in the diffusion pair of the ethyl and trichloromethyl radi-



Scheme 1.

cals. The recombination of this pair yields trichloropropane (Scheme 1).

Polarized chloroform and ethylene result from the intracellular disproportionation of this pair. Probably, polarized hexachloroethane is the product of radical pair dissociation followed by the recombination of two trichloromethyl radicals.

The observed signs of ^1H and ^{13}C CIDNP are indicated in Scheme 1. They coincide with those predicted using the Captain rules for strong magnetic fields [6].

The addition of styrene as an efficient free-radical scavenger to the reaction mixture suppresses the polarization effects. This confirms the assumption about CIDNP generation in diffusion radical pairs. Thus, all CIDNP effects observed for both protons and carbon nuclei are well explained in terms of the diffusion pair of the ethyl and trichloromethyl radicals and their subsequent transformations.

Let us consider a possible route for the formation of the ethyl and trichloromethyl radicals in the catalytic process. According to published data, the interaction of Et_3Al with $Pd(acac)_2$ results in the reduction of the latter [7]. When the amounts of Et_3Al and $Pd(acac)_2$ (Al/Pd < 2) are comparable, the following ligand exchange occurs:

$$Et_3Al + Pd(acac)_2 \longrightarrow Et_2Al(acac) + EtPd(acac).$$

When Et_3Al is in excess, the reaction yields diethylpalladium:

$$Pd(acac)_2 + 2AlEt_3 \longrightarrow 2Et_2Al(acac) + PdEt_2.$$

In the case of a large excess of Et_3Al (Al/Pd > 10), the reaction occurs instantly and the resulting $PdEt_2$ is unstable and decomposes readily to Pd(0) and gaseous products (ethane and ethylene). It can be assumed that part of the $PdEt_2$ decomposes homolytically to form the ethyl radical:

$$PdEt_2 \longrightarrow Pd(0) + C_2H_6 + C_2H_4 + CH_3\dot{C}H_2.$$

Pd(0) is aggregated and precipitates as a black colloid. In our case, we can assume that Pd(0) atoms react with CCl_4:

$$Pd(0) + CCl_4 \longrightarrow PdCl + \dot{C}Cl_3.$$

This assumption is verified by the existence of the Kharasch reaction [8] between an organomagnesium compound RMgX and an organic halide catalyzed by transition metal salts, which generates intermediate radicals and yields products of the R–R type:

$$M(0) + R'Hal \longrightarrow MHal + \dot{R}'.$$

Next, PdCl again reacts with excess Et_3Al:

$$PdCl + Et_3Al \longrightarrow PdEt + Et_2AlCl.$$

Based on experimental evidence and literature data, the formation of the major products and radical intermediates in the reaction of Et_3Al with CCl_4 in the presence of Pd^{2+} can be presented as the following catalytic cycle (Scheme 2).

This mechanism of the reaction between Et_3Al and CCl_4 in the presence of the Pd complexes coincides with the scheme proposed previously for the reaction of Et_3Al with CCl_4 catalyzed by $Ni(acac)_2$ [9]. Therefore, the mechanisms of the reactions of $Pd(acac)_2$ and $Ni(acac)_2$ with Et_3Al are very similar, and this is in agreement with the literature [7].

Since the free-radical polymerization of vinyl chloride is efficiently initiated by reaction systems involving Et_3Al and CCl_4 in the presence of the titanium and copper compounds [1, 10], we verified the existence of CIDNP effects in this reaction catalyzed by $Cu(acac)_2$ and Cp_2TiCl_2. A vigorous reaction occurred in both cases, which was accompanied by emission from the hydrogen nuclei of chloroform. After the reaction, the

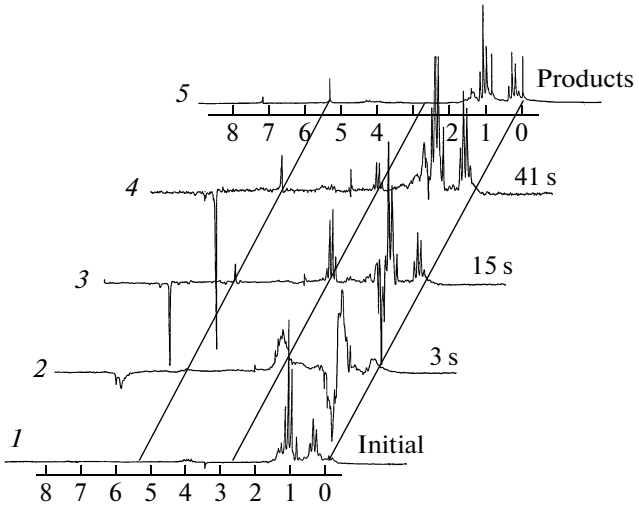
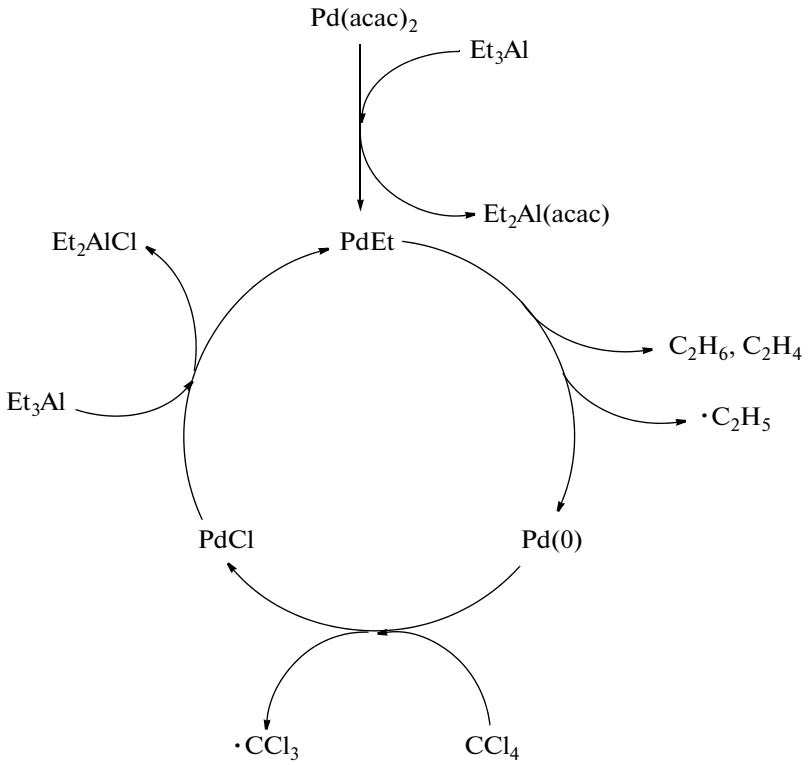


Fig. 1. ^1H CIDNP in the reaction of Et_3Al with CCl_4 in the presence of $Pd(acac)_2$: (*1*) ^1H NMR spectrum of the initial solution of Et_3Al (1 mol/l, 0.4 ml) and $Pd(acac)_2$ (~2 mg) in cyclohexane-d_{12}; (*2–4*) ^1H NMR spectra recorded during the reaction 3, 15, and 41 s after the addition of CCl_4 (0.6 mmol); (*5*) ^1H NMR spectrum of the reaction products.



Scheme 2.

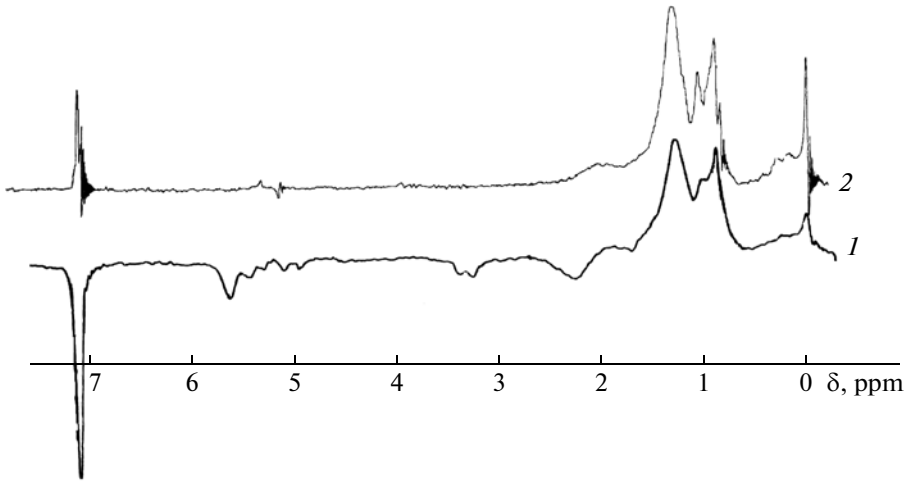
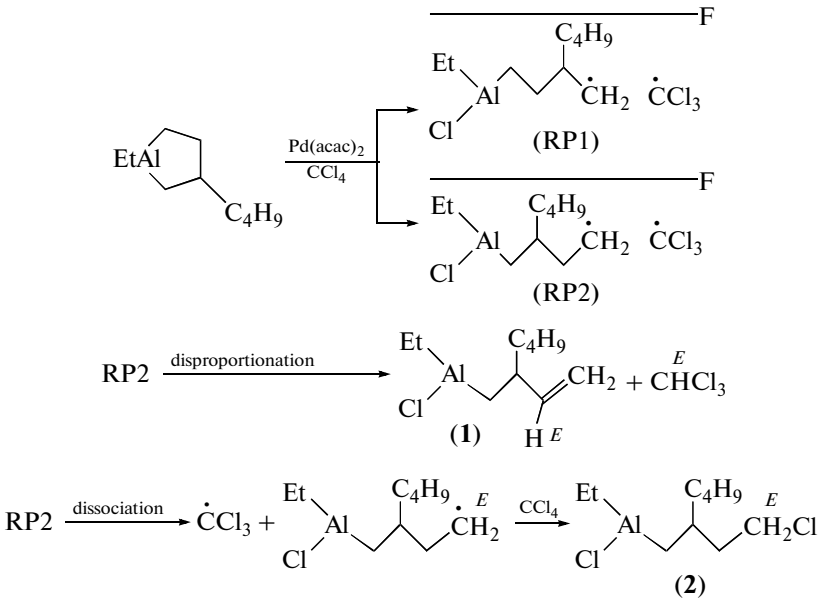


Fig. 2. ^{1}H CIDNP observed in the interaction of a solution of 1-ethyl-3-butylaluminacyclopentane (0.5 ml, 1 mol/l) in C_6D_{12} with (*1*) CCl_4 (0.2 ml) and (*2*) $CHCl_3$ (0.2 ml) at room temperature.

^{1}H NMR spectra of the reaction mixtures contained signals from $CHCl_3$, CH_2Cl_2, $CH_3CH_2CCl_3$, and CH_3CH_2Cl.

The reactions of other abundant trialkylalanes (*i*-Bu_3Al and *i*-Bu_2AlH) with halomethanes were considered earlier [4, 11, 12]. We discovered integral CIDNP effects in the reaction of $(n\text{-}C_8H_{17})_3Al$ with CCl_4, which occurs under thermal and catalytic ($Ni(acac)_2$-catalyzed) conditions. When the process is carried out under the thermal conditions in the absence of a catalyst in cyclohexane-d_{12}, the protons of chloroform and the protons at the double bond of oct-1-ene in the ^{1}H NMR spectra are positively polarized, the multiplet of protons of the $=CH_2$ group ($\delta = 5.73$ ppm) is positively polarized, and the doublet of the $=CH$ group ($\delta = 4.78$ ppm) is negatively polarized. In addition, an unidentified positively polarized singlet at $\delta = 4.63$ ppm is observed. Chloroform emission was observed in the presence of $Ni(acac)_2$.



Scheme 3.

CIDNP effects were also observed in the reaction of CCl_4 with the cyclic organoaluminum compound 1-ethyl-3-butylaluminacyclopentane [13] in the presence of $Pd(acac)_2$ in cyclohexane-d_{12} (Fig. 2). As in other catalytic reactions studied by us, strong emission from chloroform protons was observed in the ^1H NMR spectra in this case, but no polarized signals of the products of the ethyl and trichloromethyl radicals (1,1,1-trichloropropane and ethyl chloride) were observed. Therefore, the ethyl group in the organoaluminum compound is not involved in the reaction of cyclic organoaluminum compounds with CCl_4. The spectra also exhibit broad, negatively polarized signals with chemical shifts of 5.6 and 3.3 ppm, which are likely due to products **1** and **2**, respectively (Scheme 3). This suggests that, in the catalytic reaction of the organoaluminum compounds with CCl_4, the Al–C bond, which is remote from the butyl substituent in the ring, breaks and, accordingly, an RP2 radical pair forms without the formation of an RP1 pair. Only emission from methylene chloride protons was observed in the reaction of 1-ethyl-3-butylaluminacyclopentane with chloroform.

On the whole, our results indicate that the catalytic reactions of trialkylalanes with CCl_4 in the presence of $Cu(acac)_2$ and Cp_2TiCl_2, as well as $Ni(acac)_2$ and $Pd(acac)_2$, in a hydrocarbon solvent occur mainly via the general mechanism presented in Scheme 2.

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