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Formation and Properties of Ziegler Systems Based on Nickel Bis(dimethylglyoxime) in Catalysis of Hydrogenation Reactions

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Abstract—The effect of the nature of the acidoligand in the nickel precursor on the activity of Ziegler systems in hydrogenation of alkenes was characterized qualitatively. The key steps of the reaction of nickel bis (dimethylglyoximate) with triethylaluminum determined by the methods of IR, NMR, and ESR spectroscopy include the reaction between $AlEt_3$ and the OH group of the dimethylglyoximate ligand, formation of the product of C-alkylation as a result of addition of $AlEt_3$ to the C=N bond, and the reduction of Ni(II) to Ni(0) complexes. The absence of nickel clusters and a low concentration of coordinatively unsaturated Ni(0) complexes is the most probable reason of low catalytic activity of the studied system in hydrogenation catalysis.

Keywords: Ziegler systems, nickel, hydrogenation, mechanism of formation

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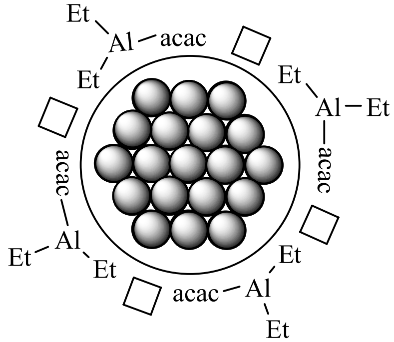
Ziegler systems consisting of transition metal complexes and organoaluminum compounds are one of the most important groups of industrial catalysts not only for oligo- and polymerization of lower alkenes [1–3] but also for hydrogenation [3, 4]. For example, relatively cheap Ziegler catalysts based on Co and Ni compounds are used for the synthesis of hydrogenated styrene block-copolymers, whose production approaches 200000 tons per year [5]. In spite of industrial use of these metal complex catalysts, there is a necessity for further investigation of the Ziegler systems for a purposeful control of the processes of formation of catalytically active species and a design of more effective catalysts. According to [3, 4], nowadays fundamental problems of investigation of the Ziegler hydrogenation catalysts are determination of the influence of the conditions of formation on the catalytic properties, especially on the activity and stability of the catalysts; investigation of the reactions between the precursors based on transition metal compounds and the components of the cocatalyst; compositional and structural nature of the catalytically active compounds; mechanisms of catalytic hydrogenation.

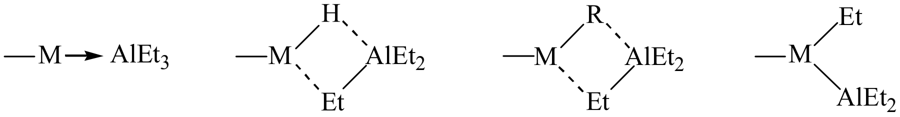
Most researchers agree that the reaction of VIII group metal acetylacetonates with trialkylaluminum gives nanoclusters predominantly of 1.5–3.5 nm diameter [4, 6–8]. In [7–10] the model of nanoparticles was suggested according to which the formed by a redox process AlR_2(acac) was adsorbed on the surface of nanoclusters thus increasing their stability to aggregation:



(□) denotes free space.

Note that up to now the question of the nature of nanoclusters stabilizers in Ziegler systems has no unequivocal experimental proof. Taking into account the poisoning effect of excess AlR_3 on the turnover frequency in hydrogenation of alkenes, as stabilizers of nanoclusters along with AlR_2(acac) trialkylaluminum is also postulated, whose reaction with the transition metal atoms under the conditions of hydrogenation catalysis can result in the formation of surface compounds of the types [7] (Scheme 1).

Scheme 1.



Stabilization of nanoclusters with alkoxy aluminum derivatives, which can be formed in the presence of traces of oxygen and/or water due to high reactivity of organoaluminum compounds, cannot be ruled out, either [11]. Experimental support of the hypotheses on the nature of stabilizing effect of the catalytically active species will provide a solution of the problem of Ziegler systems stability under the conditions of hydrogenation catalysis.

With the aforesaid in mind, an important problem of the Ziegler catalysis is establishing of the influence of the nature of acidoligand in the precursor of the transition metal complex on the catalytic properties. Formation of complexes (nanoclusters) active in hydrogenation in the Ziegler type systems is connected with substitution by alkyl groups of ligands, which are covalently or coordinatively bound with the transition metal. Therefore, a decrease of activity of these systems with the increase of stability of the starting transition metal complexes can be expected [3]. However, taking into account various functions of a cocatalyst, the nature of acidoligand in the precursor (MX_n) may affect not only the rate of reduction but also the stabilization of the formed particles (complexes) with organoaluminum compounds and, hence, their catalytic properties. Most studied as the precursors in the Ziegler systems are acetylacetonates and 2-ethylhexanates of transition metals [3–10]. Here we present the results of investigation of catalytic properties and the reaction between the components of the catalytic system on the basis of triethylaluminum and nickel bis(dimethylglyoximate) [$Ni(dmg)_2$]. The choice of the latter as a precursor was due to the presence in the acidoligand various heteroatoms (O, N) capable of complexation with the transition metal, and its diimine structure.

$Ni(dmg)_2$ is poorly soluble in organic solvents, but the addition of triethylaluminum to the suspension of $Ni(dmg)_2$ in benzene leads to homogenization of the system in the course of 1–2 min with the formation of a dark-red solution and evolution of gaseous products. In spite of these visual changes, hydrogenation of styrene in the presence of catalytic system $Ni(dmg)_2$–$n$$AlEt_3$ at 30°C occurs with a long inductive period (~2 h) indicative of a low rate of transformation of the nickel precursor to the catalytically active species under mild conditions. The average activity of the system $Ni(dmg)_2$–$AlEt_3$ ([Al] : [Ni] = 5) in hydrogenation of styrene does not exceed 0.08 min^{-1}. The maximum catalytic activity in hydrogenation of cyclohexene was 0.03 min^{-1}, which is much worse than the activity of the Ziegler systems based on nickel bis(acetylacetonate) for which the turnover frequency in hydrogenation of terminal alkenes reached 140 min^{-1}. At the increase of the temperature to 50 and 70°C the inductive period was shortened and the catalytic activity increased 2 and 8 times respectively. A characteristic feature of the Ziegler systems in hydrogenation catalysis is the extremal shape of the dependence of specific catalytic activity on the ratio [Al] : [M] when trialkylaluminum is used as a cocatalyst [3, 7, 8]. For the system $Ni(dmg)_2$–$n$$AlEt_3$, the ratio of the components at which the activity is maximal ([Al] : [Ni] ≈ 15) is 3–4 times higher than at the use of $Ni(acac)_2$ as a precursor under the same conditions (Fig. 1).

The results of investigation of the effect of the nature of nickel precursors on the activity of catalytic systems NiX_2–$AlEt_3$ in hydrogenation of cyclohexene are presented in the Table. According to the table, there is a reverse dependence between the catalytic activity of systems NiX_2–$AlEt_3$ [X = acetylacetonate (**I**), *o*-aminophenolate (**II**), salicylaldoximate (**III**), 8-oxyquinolate (**IV**), and dimethylglyoximate (**V**)] and the constants of stability of the nickel complexes. With the increase of the constant of stability the turnover number decreases by more than three orders of magnitude. The effect of thermodynamic and kinetic stability of transition metal compounds on the hydrogenation activity of the Ziegler type catalysts was first established in [12].

To evaluate the validity of the hypotheses on such a strong effect of the nature of acidoligand on quantitative characteristics of Ziegler systems in hydrogenation catalysis, we have studied the model system $Ni(dmg)_2$–$AlEt_3$ using spectral methods.

A characteristic absorption band of $Ni(dmg)_2$ in the IR spectrum is the ν(C=N) band at 1568 cm^{-1} [13]. In the spectrum of $Ni(dmg)_2$ intense bands of stretching vibrations of the N–O bond (ν_{as} 1238 cm^{-1}, ν_s 1098 cm^{-1}) are also present. The bands of stretching and deformational vibrations of the bridging O–H groups (ν_s 3200 cm^{-1}; δ 1785 cm^{-1}) in the dimethylglyoximate ligand $Ni(dmg)_2$ have low intensity.

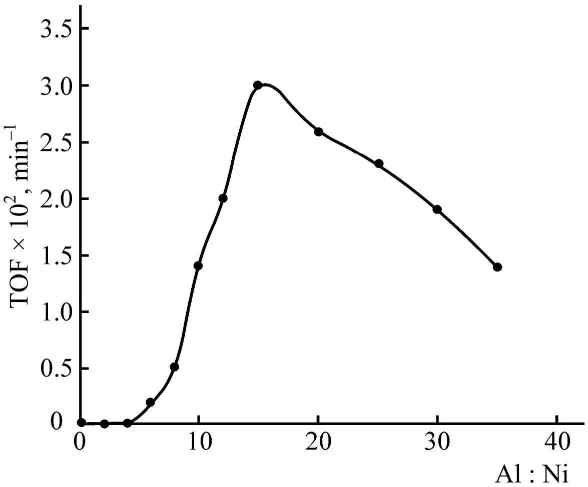
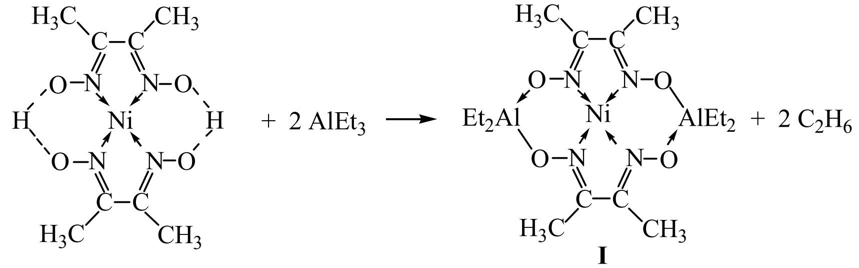


Fig. 1. Effect of the ratio $AlEt_3$: $Ni(dmg)_2$ on the catalytic activity of the system $Ni(dmg)_2$–$nAlEt_3$ in hydrogenation of cyclohexene. Conditions of the reaction: 30°C, $p(H_2)$ = 2 at, volume of solution 18 mL, solvent – benzene, [Ni] = 1.4×10^{-2} mol/L; [Al] : [Ni] = 15.

Upon the reaction of suspension of $Ni(dmg)_2$ in benzene with triethylaluminum ([Al] : [Ni] = 2) under argon the reaction system becomes homogeneous. The process is followed by evolution of a gas in the amount of 1.9 mol/mol Ni, which consists mainly of ethane (98%) and traces of ethylene and butene-1. In the IR spectrum of the system $Ni(dmg)_2$–$2AlEt_3$ taken after 20 min from the beginning of the reaction the band ν(C=N) at 1568 cm^{-1} is shifted to higher frequencies by 25 cm^{-1} and the band at 1785 cm^{-1} corresponding to deformational vibrations of the bridging O-H groups of $Ni(dmg)_2$ is lacking (Fig. 2). These changes as well as the data of volumetry are indicative of the predominant reaction between $AlEt_3$ and the bridging hydroxy groups of the dimethylglyoximate ligand:

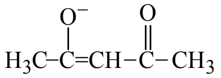
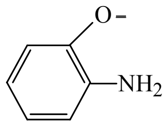
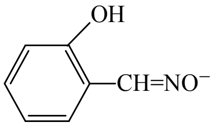
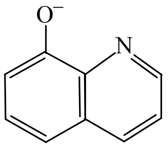
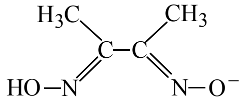


I

(1)

The absorption band ν(C=N) in free oximes usually appears at 1685–1650 cm^{-1} although its position depends on the strain in the ring [13]. The band at 1593 cm^{-1} in the spectrum of the system $Ni(dmg)_2$–$2AlEt_3$ we assigned to the stretching vibrations of the C=N bond in complex **I**. Its intensity depends on the molar ratio of the components. When [Al] : [Ni] is increased from 2 to 5, its intensity is decreased by an

Effect of acidoligand on the turnover frequency in hydrogenation of cyclohexene in the catalytic system NiX_2–$AlEt_3$[a]

Parameter	I	II	III	IV	V
X	 $H_3C-\overset{O^-}{\overset{\vert}{C}}=CH-\overset{O}{\overset{\Vert}{C}}-CH_3$				
TOF, min^{-1}	120	25	15	3	0.03[b]
pK[c]	10.77	11.41	–	21.38	24.64

[a] Reaction conditions: 30°C, $p(H_2)$ = 2 at, volume of solution 18 mL, solvent – benzene, [Ni] = 1.4×10^{-2} mol/L; [Al] : [Ni] = 6. [b] [Al] : [Ni] = 15. [c] pK = –log K (K is an instability constant).

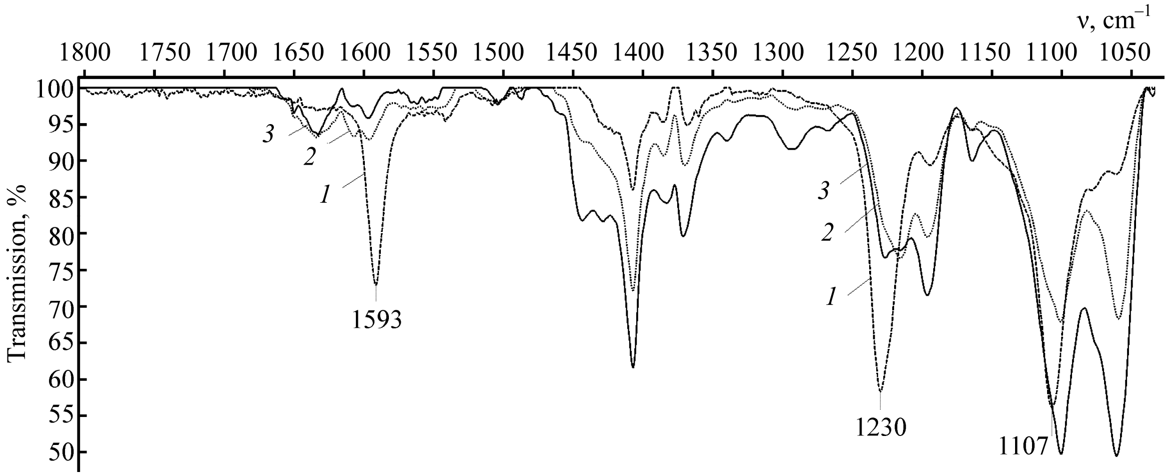


Fig. 2. IR spectra of the system Ni(dmg)$_2$–nAlEt$_3$ in benzene for the ratio [Al] : [Ni] = (*1*) 2; (*2*) 5; and (*3*) 10.

order of magnitude, and for 10-fold excess of AlEt$_3$, 12 times (Fig. 2, curves *2, 3*). Along with this, a new band appears at 1633 cm^{-1}, which apparently belongs to ν(C=N) absorption band in the product of AlEt$_3$ addition to one double bond C=N. This assumption is based on published data, according to which the ν(C=N) band of the isolated C=N bond in Ph–N=C·(CH$_3$)–C(CH$_3$)(Et)–N(AlEt$_2$)Ph is shifted to high frequencies by 25 cm^{-1} (from 1635 to 1660 cm^{-1}) relative to the starting diimine Ph–N=C(CH$_3$)–C(CH$_3$)=N–Ph [14]. Taking all this into account the observed decrease of intensity of the band at 1593 cm^{-1} with the increase of the [Al] : [Ni] ratio ([Al] : [Ni] > 2) is indicative of a partial addition of AlEt$_3$ to the C=N bond. Additional information about the products of the reaction of the components of the catalytic system Ni(dmg)$_2$–nAlEt$_3$ was obtained from the analysis of the ^{1}H and ^{13}C NMR spectra.

In the ^{1}H NMR spectrum of the system Ni(dmg)$_2$–2AlEt$_3$ the signals of free triethylaluminum (δ, ppm: 0.41, q, J = 8.2 Hz, AlC$\underline{H}_2$CH$_3$; δ 1.22 t, J = 8.2 Hz, AlCH$_2$C$\underline{H}_3$) are practically lacking. This is an indication of a nearly quantitative transformation of AlEt$_3$ (Fig. 3). Most intense are the signals at 0.55 ppm (q, J = 8.2 Hz) and 1.67 ppm (t, J = 8.2 Hz) in the ratio 2 : 3 belonging to the protons of the ethyl group at the aluminum atom, as well as a singlet at 1.48 ppm. The downfield shift of the signals of CH$_3$ (Δ = 0.45 ppm) and CH$_2$ (Δ = 0.14 ppm) relative to free AlEt$_3$ is indicative of the fact that the aluminum atom is bound to a more electronegative element. For example, in Al(acac)Et$_2$, the protons of the methylene and methyl groups resonate at δ 0.45 ppm (q, J = 8.2 Hz, C$\underline{H}_2$) and δ 1.47 ppm (t, J = 8.2 Hz, C$\underline{H}_3$) respectively [7]. From this, it can be concluded that the signals at 0.55 and 1.67 ppm correspond to the protons of the ethyl group of the O–AlEt$_2$ fragment. The singlet at δ 1.48 ppm having the same intensity as the signal at 1.67 ppm was assigned to the methyl group protons CH$_3$C=N in the acidoligand of the nickel complex. The analysis of the ^{1}H NMR spectroscopy data is consistent with the results of IR monitoring of the system Ni(dmg)$_2$–2AlEt$_3$ and confirms the formation of complex **I** in the reaction of Ni(dmg)$_2$ with two moles of AlEt$_3$ according to scheme (1).

Note that complex **I** is not the only product of the reaction of Ni(dmg)$_2$ with AlEt$_3$ at [Al] : [Ni] = 2. In the ^{1}H NMR spectrum of the system Ni(dmg)$_2$–2AlEt$_3$, apart from the described above, the signals at 1.35 ppm (t, J = 8.2 Hz, C$\underline{H}_3$) and 0.22 ppm (q, J = 8.2 Hz, C$\underline{H}_2$) were registered in the ratio 3 : 2 (Fig. 3). They suggest the formation of a different fragment Al–Et. The intensity of these signals is ~3 times less than that of the signals of the OAlEt$_2$ fragment of complex **I**.

It is known that AlEt$_3$ can react with imines [15] or diazobutadienes [14, 16] by the donor-acceptor type with the formation of the adduct R$_2$C=NH·AlEt$_3$. In many cases, the reaction is not stopped at this stage but further addition of AlEt$_3$ to the C=N bond takes place with the formation of the product of C-alkylation. The reaction of reduction with imines can be followed also by the formation of alkenes [14, 16]:

$$\mathrm{R'N{=}CR'_2 + AlR_3 \rightleftarrows R_3Al \leftarrow NR'{=}CR'_2,} \quad (2)$$

$$\mathrm{R_3Al \leftarrow NR'{=}CR'_2 \rightarrow R_2AlNR'{-}C(R)R'_2,} \quad (3)$$

$$\mathrm{R_3Al \leftarrow NR'{=}CR'_2 \rightarrow R_2AlNR'{-}C(H)R'_2 + R_{-H}.} \quad (4)$$

For compounds where the AlEt$_2$ group is bound to the nitrogen atom with covalent bond, as well as for

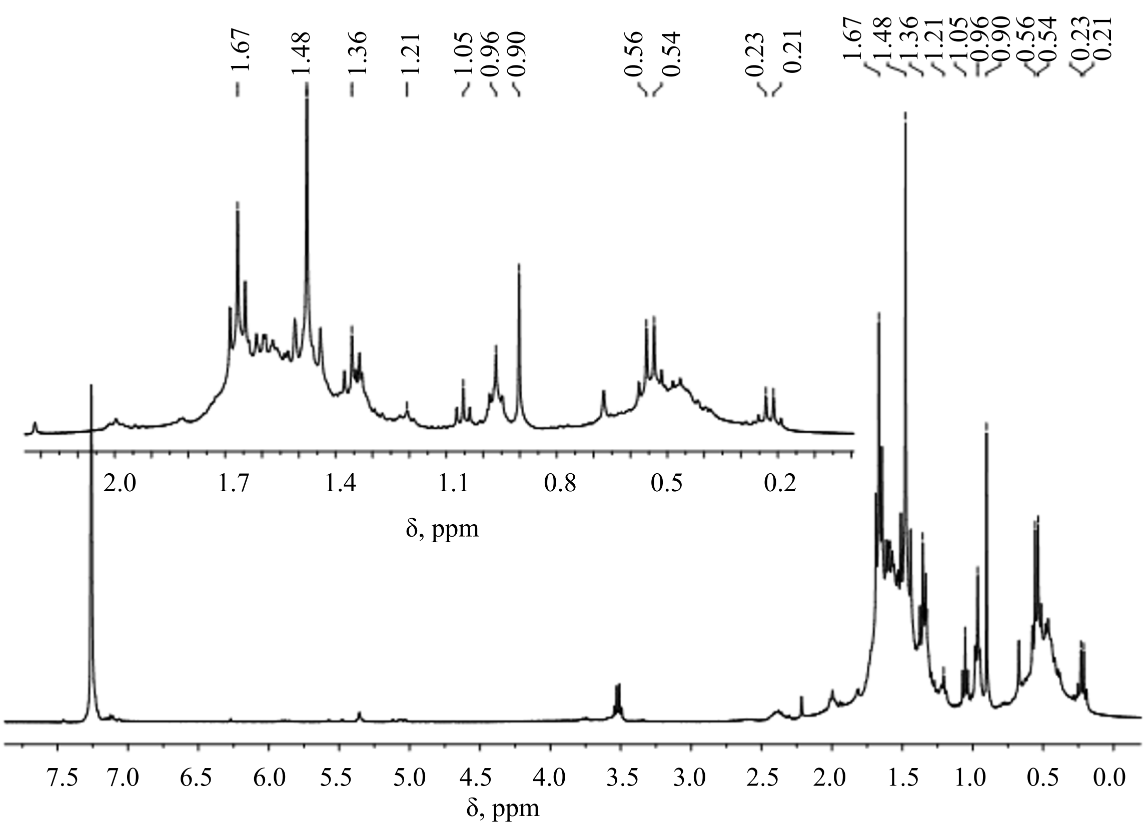


Fig. 3. ^{1}H NMR spectra of Ni(dmg)$_2$–2AlEt$_3$ system in benzene–d_6.

adducts of AlEt$_3$ to nitrogen-containing compounds, the protons of the methylene group are usually shifted upfield with respect to the CH$_2$ group in free AlEt$_3$ to the region 0–0.2 ppm [17, 18]. Therefore, the quartet at 0.22 ppm can belong to the CH$_2$ group either in the N–AlEt$_2$ fragment or in the adduct N·AlEt$_3$. In the ^{13}C NMR spectrum of the system Ni(dmg)$_2$–2AlEt$_3$, along with the signal at 158.2 ppm ($\underline{C}$=N), a signal of low intensity appeared at δ 58.7 ppm, whose position corresponds to a quaternary carbon atom [19]. This fact, as well as the presence in the ^{13}C NMR spectrum along with the methyl carbons (17.7 and 13.5 ppm) the signals at 24.7 and 8.7 ppm, which can be assigned to the carbons of ethyl groups not directly bound to aluminum [δ 24.7 ppm, H$_3$C–*C*H$_2$–C(CH$_3$)–N–AlEt$_2$; δ 8.7 ppm, H$_3\underline{C}$–CH$_2$–C(CH$_3$)–N–AlEt$_2$] allows a conclusion that the reaction of the dimethylglyoximate ligand with AlEt$_3$, as in the case of diazabutadienes, results in reduction of the C=N bond with the formation of the product of C-alkylation. The intensity of the signals increases with the ratio [Al] : [Ni]. Based on this, the signals at 1.35 and 0.22 ppm were assigned to the ethyl fragments at aluminum formed by addition of AlEt$_3$ to the C=N bond:

$$\mathrm{AlEt_3 + –C(CH_3)=N– \rightarrow –C(CH_3)(Et)–N(AlEt_2)–.} \quad (5)$$

Then, the signal at 0.97 ppm (t, J = 6.8 Hz, $C\underline{H}_3$) in the ^{1}H NMR spectrum can be assigned to the methyl group protons [$C\underline{H}_3$CH$_2$–C(CH$_3$)–N–AlEt$_2$]. Unfortunately, the signals of the methylene group protons [CH$_3$C$\underline{H}_2$–C(CH$_3$)–N–AlEt$_2$] cannot be identified because of superposition of multiplets in the region 1.3–1.7 ppm (Fig. 3).

In the ^{1}H NMR spectrum of the system Ni(dmg)$_2$–2AlEt$_3$ the poorly resolved low intensive signals at 0.48 ppm (q, J = 8.3 Hz, C$\underline{H}_2$); 0.28 ppm (q, J = 8.3 Hz, C$\underline{H}_2$) are also present, as well as the signals at 3.52 ppm (q, $^3J_{\mathrm{HH}}$ 7.1 Hz, –Al–OC$\underline{H}_2$CH$_3$) and 1.06 ppm (t, J = 7.1 Hz, –Al–OCH$_2$C$\underline{H}_3$). The latter two signals correspond to the protons of the ethoxy group at aluminum (the result of partial oxidation with traces of oxygen). Their concentration with respect to the ethyl groups of diethylaluminum in complex 1 does not exceed ~7%.

Therefore, IR and NMR analysis of the products of the reaction of the components of the system Ni(dmg)$_2$–2AlEt$_3$ is indicative of two predominant processes: reaction of AlEt$_3$ with OH group of the dimethyl-

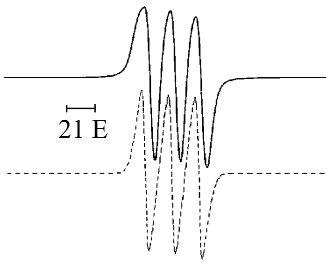


Fig. 4. ESR spectra of the system $Ni(dmg)_2$–$5AlEt_3$ in benzene-d_6 at room temperature.

glyoximate ligand, and addition to the C=N bond. The reaction of $AlEt_3$ with OH group can lead only to the formation of the O–$AlEt_2$ fragment and ethane. However, from the ^1H NMR data, in the reaction system ethylene and butene-1 are also present in trace amounts. The presence of ethylene, whose formation can be considered as a transfer of ethyl group from $AlEt_3$ to nickel with subsequent β-hydride shift, suggests a partial contribution of the redox process between $Ni(dmg)_2$ and $AlEt_3$ even at [Al] : [Ni] = 2. The increase of the yield of gaseous products at [Al] : [Ni] = 5 to 2.2 mol/mol Ni and the fraction of ethylene in gaseous phase points to the increase of contribution of the redox process between the components, whose rate at room temperature is low.

With increase of the [Al] : [Ni] ratio the spectral picture is changed. In the ^1H NMR spectrum of the system $Ni(dmg)_2$-$5AlEt_3$ the intensity of signals of complex **I** (0.55 q, 1.67 t and 1.48 s ppm) is considerably decreased; broaden signals of the methylene (δ 0.43 ppm, q, $AlC\underline{H}_2CH_3$) and methyl group (δ 1.29 ppm, t, $AlCH_2C\underline{H}_3$) predominate. Broadening of the signals can be caused by the presence of radicals, inter- or intramolecular exchange or formation of microheterogeneous system. Since no broadening of the other signals is observed the most probable reason for broadening of the signals is inter- or intramolecular exchange of $AlEt_3$ coordinated to nitrogen. In the ^{13}C NMR spectrum of the system $Ni(dmg)_2$–$5AlEt_3$ the intensity of the signals of the product of C-alkylation (58.7, 24.7, 17.7, 13.5, 8.7 ppm) increases. The signals of carbon atoms of the ethyl group at aluminum appear at 8.5 and 0.6 ppm ($AlCH_2\underline{C}H_3$ and $Al\underline{C}H_2CH_3$) respectively.

It is known [3–11] that the reduction of transition metal acetylacetonates with trialkylaluminum gives nanoclusters. In the ESR spectra of the system $Ni(dmg)_2$–$nAlEt_3$ at various ratios of the components, including the excess of $AlEt_3$, the signals of ferromagnetic nickel or complexes of Ni(I) are lacking. Consequently, the reduction of $Ni(dmg)_2$ with triethylaluminum, apparently, leads to the formation of complexes of zero-valence nickel. The ESR spectrum of the system $Ni(dmg)_2$–$nAlEt_3$ shows only low intense signal consisting of three lines with g-factor of 2.026 (Fig. 4). Taking into account that this value is close to that of free electron and the spin of nitrogen atom equal to 1 we suggested that the unshared electron is localized on the nitrogen atom. The shape of the simulated spectrum with localization of electron on one nitrogen atom confirms this assumption.

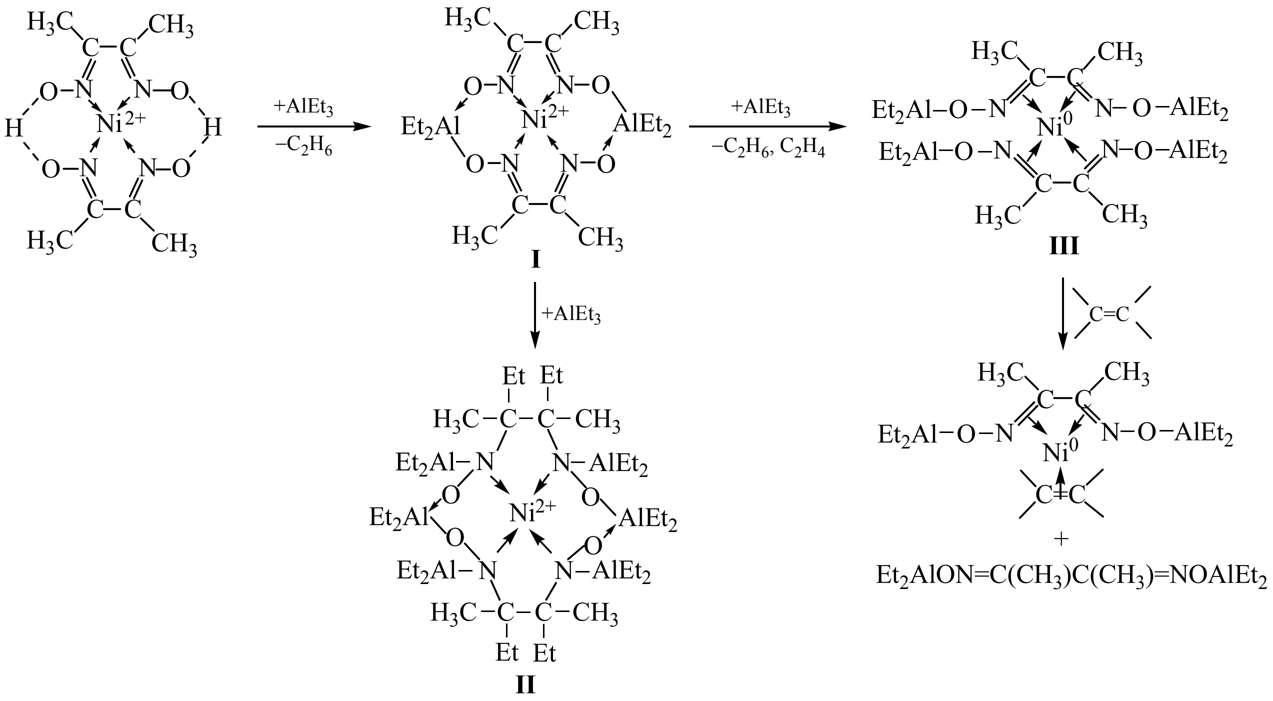
The above analysis of the spectral data allows to suggest the following scheme of the reaction of $Ni(dmg)_2$ with $AlEt_3$. In the first step, triethylaluminum reacts with the bridging OH group of the dimethylglyoximate ligand to give complex **I**. Quantitative proceeding of this process requires consumption of 2 mol of $AlEt_3$/mol Ni without a change in the degree of oxidation of Ni(II). Subsequent transformation of complex **I** with excess $AlEt_3$ depending on the reaction route can lead either to addition of the latter to the C=N double bond (complex **II**) or to reduction of Ni(II) to complexes of Ni(0) (complex **III**) (Scheme 2).

Evidently, the coordinatively saturated complexes of Ni(0) cannot exhibit hydrogenating properties. Under the conditions of hydrogenation catalysis the substitution of nitrogen-containing ligands in the coordination sphere of Ni(0) by a substrate would lead to the formation of complexes of Ni(0) capable of activation of molecular hydrogen and of catalysis in the hydrogenation. The absence of nickel nanoclusters in the system $Ni(dmg)_2$–$AlEt_3$ and a low concentration of coordinatively unsaturated complexes of Ni(0) cause a sharp decrease of the hydrogenating activity of this system relative to the Ziegler catalysts based on the VIII group metal acetylacetonates under mild conditions.

EXPERIMENTAL

Solvents (benzene, toluene) were purified by standard procedures [20], distilled over $LiAlH_4$ on a rectification column, and stored in argon atmosphere in sealed ampules over molecular sieves 4A. Content of water in the solvents measured by Fisher method [21] was ca. 1 mmol/L.

Scheme 2.



Monitoring of the products of the reaction of the components of catalytic systems on the basis of Ni(dmg)$_2$ and AlEt$_3$ in argon atmosphere was performed by the methods of NMR, IR, and ESR spectroscopy. IR spectra of the reaction system placed in a hermetic, flushed with argon, KBr cell with the thickness of the absorbing layer of 0.112 mm were analyzed on a FT-801 spectrometer. ESR spectra were taken on a ESP 70-03 XD/2 spectrometer (KBST), working frequency 9.3 GHz with diphenylpicrylhydrazyl as a standard. ^{1}H, ^{13}C NMR spectra were registered on a DPX 400 Bruker spectrometer.

Synthesis of nickel bis(dimethylglyoximate) Ni(dmg)$_2$ was performed according to [22]. To the solution of nickel diacetate (8.8 g, 0.25 mol) in 200 mL of ethanol dimethylglyoxime (11.6 g; 0.5 mol) in 200 mL of ethanol was added, the mixture was heated on a water bath for 0.5 h, and cooled. The precipitate was filtered off on a Büchner funnel, washed with ethanol, and dried (3 mmHg, 40°C). Yield 13 g (90%).

Ni(II) compounds with 8-oxyquinoline, salicylaldoxime, *o*-aminophenol were prepared similarly.

Hydrogenation procedure. Experiments on hydrogenation of unsaturated compounds were performed in a temperature-controlled vessel with hydrogen excess pressure of 1 atm and vigorous stirring to exclude the reaction in the diffusion region. A pre-evacuated and filled with hydrogen temperature-controlled vessel was successively charged in the flow of hydrogen with Ni(dmg)$_2$ (74.1 mg, 0.25 mmol), benzene (15 mL) and stirred for 30 min to obtain red-dark suspension. To the obtained suspension the substrate (8.7 mmol) and solution of AlEt$_3$ in octane (2 mL) was added varying the ratio [Al] : [Ni] from 2 to 15. The vessel was closed with Teflon stopper with rubber septum for sampling by syringe, excess hydrogen pressure was created and hydrogenation was carried out at vigorous stirring. The reaction was followed manometrically by a decrease of pressure and by GC analysis of the samples. The catalyzate was analyzed on a Chromatek-Crystal 5000.2 chromatograph with flame-ionization detector, capillary column SGE BPX5 30 m, diameter 0.53 mm, and on mass-spectrometer GCMS-QP-2010 Shimadzu.

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