MICROHETEROGENEOUS CATALYTIC SYSTEM $Ni^0_{colloid}$–Ni^I–Ni^{II} FOR LOW-PRESSURE POLYMERIZATION OF BUTADIENE. I.

REDOX EQUILIBRIA AS STUDIED BY ELECTRON PARAMAGNETIC RESONANCE IN SYSTEM $Ni(acac)_2$–$BF_3.O(C_2H_5)_2$–AlR_3^*

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Molar Ni/Al ratio, alkylation capacity, and temperature determine equilibrium between various redox forms of nickel during reduction of nickel acetylacetonate in nonpolar solvents by alkyl-aluminium. The reduction in presence of boron trifluoride etherate predominantly leads to the formation of colloidal nickel, and the catalytic system for butadiene polymerization is of micro-heterogeneous character. By using the EPR spectra, a relative amount of the nickel colloid can be determined on the basis of ferromagnetic resonance ($g = 2\cdot2$, line width $\Delta H_{1/2} = 500$—600 Oe) in contrast to Ni^I, where the unpaired $3d^9$ electron provides a singlet of $g = 2\cdot05$ and line width $\Delta H_{1/2} = 35$ Oe. For the molar Al/Ni ratios being higher than unity, the Ni—O bond is homo-lytically splitted to produce free radical from the ligand, to which the septet having $g = 2\cdot004_3$ belongs.

In absence of moisture traces, acetylacetonates of transition metals are readily soluble in non-polar solvents, being thus often used as starting components of homogeneous catalytic systems for low-pressure polymerization of dienes. Catalytic activity varies with kind and oxidation degree of the transition metal[1-5]. Binary systems on reduction of Co^{III} and Ni^{II} acetylacetonates with diethylaluminium chloride[6] were applied to the catalysis of propylene oxide and 1,4-*cis* polybutadiene of the mean molecular weight[7].

For the production of 1,4-*cis*-polybutadiene of the JSR type, having high molecular weight, a three-component catalyst was developed, in which, beside nickel acetylacetonate and alkyl-aluminium in terms of a reducing agent, the boron trifluoride complexes are present[8-11]. In the patent literature[8] and studies of Ueda and coworkers[12], nickel is reported to be responsible for the 1,4-*cis* orientation, while compounds of boron trifluoride which together with aluminium condition the catalytic activity, for the increase of the molecular weight.

In the three-component system Ni–B–Al, mutual ratio of individual components consider-ably changes catalytic activity and ultimate molecular weight of 1,4-*cis*-polybutadiene, whereas microstructure of the polymer is in this case affected only little.** The structure of active centre, kinetics of Ni^{II} reduction with alkyl metal, and elementary stages of the stereoregulating mechan-ism have not been elucidated so far. Arnett and Mendelsoln[13] assume homolytical splitting of the bond between metal and oxygen of appropriate Mn^{III} and Fe^{III} acetonates by autooxidation,

free radical of the ligand being produced simultaneously, to be an elementary step during the catalytic action. Theory of the formation of cyclic peroxidic free radical during reduction of a central atom in the transition metal of acetylacetonates was on the basis of kinetic studies further developed by Bamford and Lind[14]. The existence of free radicals, due to the electron transfer, was not in these studies experimentally confirmed and neither radical-ionic equilibria were examined. In a series of papers we shall pay our attention to the study of these problems by using electron paramagnetic resonance (EPR), infrared spectroscopy, and electric conductivity methods together with the investigation of the kinetics of low-pressure butadiene polymerization.

The study of ternary catalytic system Ni–B–Al which is of microheterogeneous character completes our previous papers devoted to elucidation of the structure of active centres in the heterogeneous Ziegler–Natta catalytic system during the polymerization of isoprene[15] as well as in the homogeneous catalytic system $CuCl_2$–cyclohexylamine during the polymerisation of 2,6-xylenol[16].

EXPERIMENTAL

Reagents. Nickel acetylacetonate[17] (Kaučuk, Kralupy) was dried at 24°C and 10^{-1} Torr for one hour, in special cases, it was dehydrated at 110°C and 10^{-3} Torr for a period of two hours; triethylaluminium and triisobutylaluminium (Chemische Werke, Bergkamen). Toluene and benzene R.G. were freed of thiophene by washing with sulphuric acid, sodium hydroxide solution, and water and dried with use of molecular sieves; middle runnings were used after rectification on a 90 plate column under nitrogen atmosphere. Binary and ternary mixtures were prepared in the inert nitrogen atmosphere in thermostated vessels under magnetic stirring (procedure *A*), or they were produced directly in a measuring cell using ultrasonic generator in terms of an agitator (procedure *B*).

EPR Spectra Measurements. Spectrometer Varian E-3 of modulation 100 kHz was used. The cells of diameter 4 mm were closed by a three-way stopcock so that the measurements could be carried out in absence of oxygen and moisture traces. Position of bands (*g*-factor) and number of unpaired spins were found by using values of the "pitch" standards as well as of the α,α-diphenyl-β-picrylhydrazyl ones. The EPR spectra were taken within +100 to −150°C, while the inert gas was passed though a quartz Dewar tube placed in the resonance cavity and thermostated within ±2°C (Variable temperature accessory-Varian). A simulated EPR spectrum was produced by means of Spectrosystem 100 Varian.

RESULTS

Binary Systems Ni–Al, Ni–B, B–Al

On mixing toluene, benzene, or hexane nickel acetylacetonate (*I*) solutions 2% with the triethylaluminium ones, original green colour of the solutions is changed into the dark-brown one and the EPR signals are not observed until the molar ratio Al/Ni = 1 is exceeded. On further addition of the reducing agent, three different types of paramagnetic particles are produced, whose EPR signals differ in their *g*-factor, spectral width, and hyperfine structure of lines as well as in their reactivity against oxygen and water.

In the first stage of the reduction with triethylaluminium, a septet with binomial ratio of line intensities 1 : 6 : 15 : 20 : 15 : 6 : 1 with $g = 2·0043 \pm 0·0004$ and coupling constant 10 Oe (Fig. 1*a*) is produced. Further amount of the alkyl metal leads to a new grouping of the spectrum,
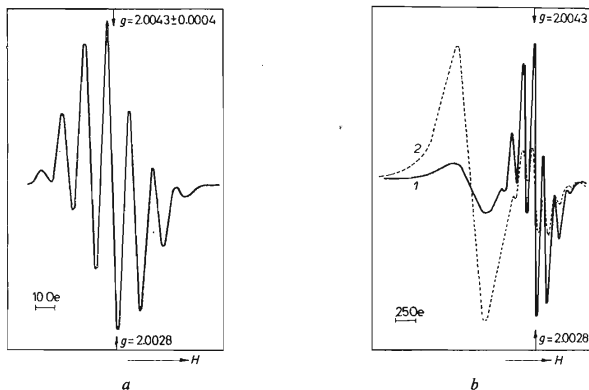
FIG. 1

EPR Spectrum of Free Radical and Ni^I During Reduction of Ni(acac)$_2$ with Triethylaluminium at 23°C

Sample preparation by procedure *B*, acetylacetonate dried at 30°C and 10^{-1} Torr. Molar Al/Ni ratio *a* 3, *b* 5 (*1*), and 7 (*2*).
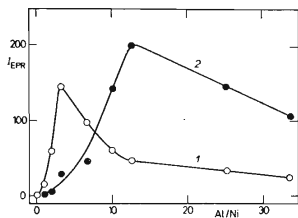

FIG. 2

Plot of EPR Signal Intensity of Free Radical (*1*) and Ni^I (*2*) against Molar Al/Ni Ratio during Reduction of Ni(acac)$_2$ with Triethylaluminium at 23°C
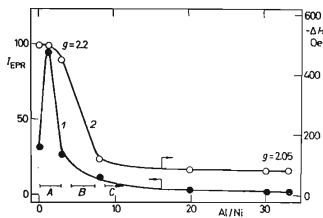
Sample preparation by procedure *A*.

FIG. 3

Reduction of Ni(acac)$_2$ with Triisobutylaluminium at 23°C

Sample preparation by procedure *B*. *1* Change in the EPR signal intensity, *2* change in the *g*-factor value expressed by shifting the centre of symmetry from that of the standard. (ΔH in Oe). Region: *A* Ni$^0_{colloid}$, *B* Ni$^0_{colloid}$ + Ni^I + (acac)·, *C* Ni^I.

the intensity decrease of the septet being accompanied by a formation of the singlet having $g = 2.05$, of spectral width $\Delta H_{1/2} = 35$ Oe (Fig. 1b). The plot of intensity of both signals against the Al/Ni molar ratio is presented in Fig. 2. On exceeding ratio 15 , linear decrease of the singlet intensity is connected with gradual dilution. If instead triethylaluminium the hexane solution of triisobutylaluminium is applied to the reduction, new broad line of $\Delta H_{1/2} = 500$ to 600 Oe and $g = 2.2$ is observed before the molar ratio equal to unity is achieved. The maximum of signal intensity is observed with the molar ratio· Al/Ni $= 2$. Further amount of the reducing agent decreases the signal intensity and free radical signal having $g = 2.004_3$ is observed. For higher ratios (>8), the most distinct spectrum band is the singlet with $g = 2.05$ (Fig. 3 and 4).

The broad signal of $g = 2.2$ observed during the reduction with triisobutylaluminium may be observed even in the reduction with triethylaluminum, provided that crystalline I loses its constitution water prior to the dissolution, and the experiments are carried out entirely in absence of moisture traces troughout the system. Thus, already at low triethylaluminium concentrations a broad line of $g = 2.2$ (Fig. 5) is produced. Further rise of the reducing agent concentration provides septet of $g = 2.004_3$ near the singlet having $g = 2.05$ in the EPR spectrum. Considerably broad signals of 4.000 Oe can be observed, even when a trace amount of finely powdered nickel metal is dispersed in an inert carrier — calcium carbonate (compare with[18]). If the mixtures are prepared under equilibrium (according to procedure A) and at the temperature of reduction being 23°C, maximum intensity of the free radical septet having $g = 2.004_3$ is attained for the molar Al/Ni ratio equal to 5, whereas by using nonequilibrium procedure B (by local surplus of the reducing
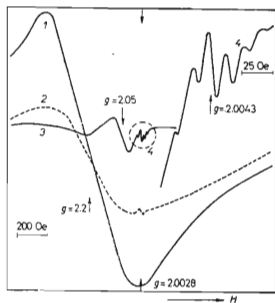
FIG. 4

EPR Spectra Belonging to Colloidal Nickel, Ni^I, and Free Radical during Reduction of Ni(acac)$_2$ with Triisobutylaluminium at 23°C

Sample preparation by procedure A. Molar Al/Ni ratio: 1 1, 2 3, 3 8, 4 amplified signal of the septet.
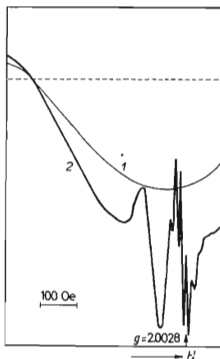
FIG. 5

EPR Spectra of Colloidal Nickel, Ni^I, and Free Radical from Ligand, Obtained in the Reduction of Anhydrous Ni(acac)$_2$ with Triethylaluminium at 23°C in Absence of Moisture Traces

Sample preparation by procedure A. Molar Al/Ni ratio: 1 1/2·2, 2 3.

agent) for the ratio amounting to 3. If the reduction is carried out at 0°C, paramagnetic particles characterized by signal $g = 2.05$ are preferentially produced; if, however, the system is completely free of water traces, this type of particle is produced in a small amount only (Fig. 6). The septet intensity of free radical decreases irreversibly with time and is more efficient, the higher is the temperature of the process (Fig. 7a), while intensity of the singlet $g = 2.05$ in the inert medium moderately increases with temperature (Fig. 7b). The signals were measured also at low temperature down to $-150°C$, a splitting of the signal being not observed with any line.

Increasing the klystron microwave power the signals of $g = 2.05$ and $g = 2.2$ which, in contrast to the septet having $g = 2.004_3$, cannot be saturated.

FIG. 6

Plot of EPR Signal Intensity Corrected for Width of Line against Molar Al/Ni Ratio during Reduction of Ni(acac)$_2$ with Triethylaluminium under Various Conditions

1—4 Reduction of commonly dried sample, 5—7 of anhydrous sample at 24°C (1, 2, 5—7) or 0° (3, 4), respectively. The curves 1, 3, 5 belong to free radical from the ligand, 2, 4, 6 to paramagnetic particles of Ni^I, and (7) to colloidal nickel.
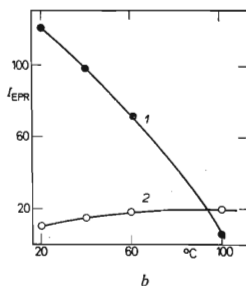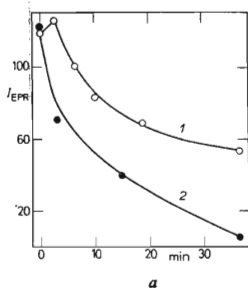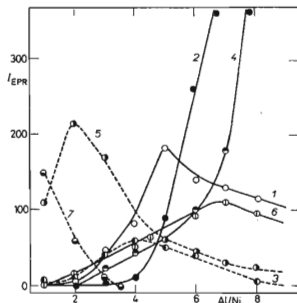

FIG. 7

Reduction of Ni(acac)$_2$ with Triethylaluminium

a Course of the EPR signal intensity of free radical from the ligand: 1 40°C, 2 60°C (the samples cooled down to 23°C on heating); b temperature dependence of signal intensity: 1 Free radical, 2 paramagnetic Ni^I particles (the sample was gradually brought from the room temperature of 23°C to 100°C within 10 minutes). Sample preparation by procedure B.

Ternary System Ni–B–Al

An effective catalytic system for the stereoregulating polymerization of butadiene can be established, if a defined quantity of boron trifluoride etherate is added to the mixture of I with alkylaluminium. On exceeding the molar ratio B/Ni = 1, green voluminous precipitate is deposited from the toluene solution in presence of the excess of boron trifluoride etherate, no EPR signals being observed over a wide concentration range. The EPR signal is produced neither in a mixture of boron trifluoride etherate with alkylaluminium.

In the EPR spectra of ternary catalytic active mixtures, broad signal of colloidal nickel of $g = 2\cdot2$ is dominating, on which singlet with $g = 2\cdot05$ Fig. 8 is superimposed. Signal $g = 2\cdot2$, which for the molar ratio Al/Ni = 5 attains a minimum, while intensity of the signal $g = 2\cdot05$ is maximum, decreases for the constant ratio Al/B = 0·95 with the increasing content of alkyl metal with respect to the I being reduced. If constant ratio Al/Ni = 6 is maintained, the amount of colloidal nickel linearly increases with the rising content of boron trifluoride etherate, until the number of resonating particles, approximately equal to the number of nickel atoms present in the system prior to reduction (Fig. 9), is attained. The EPR signal is under this condition quantitatively localized in the deposited solid phase. The course of sedimentation may be followed from the decrease in intensity of the EPR signal with time since the sample has been homogenized by ultrasonics before inserting into the resonator cavity (Fig. 10). Deposition of nickel in terms of a sedimenting solid phase does not occur, if the catalytic system is prepared in presence of 10% solution of butadiene in toluene and the latter is present in a 20—30 fold molar excess in relation to I. The system is apparently homogeneous and presence of butadiene will change the structure of the EPR signal observed under equal conditions in absence of the monomer, provided that no polymerization takes place (Fig. 11). Unsplitted superimposed signals having $g = 2\cdot05$ and free radical of $g = 2\cdot004_3$ can be observed on a broad signal of colloidal nickel, and even a new band at $g = 2\cdot1$ appears.
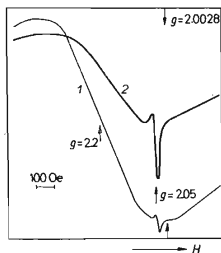

Fig. 8

EPR Signals in Ternary Microheterogeneous Catalytic Systems $Ni(acac)_2$–BF_3.O. $.(C_2H_5)_2$–$Al(C_2H_5)_3$.

1 Ni : B : Al = 1 : 1·3 : 1·25; 2 Ni : B : Al= = 1 : 6·3 : 6·20. Sample preparation by procedure A.
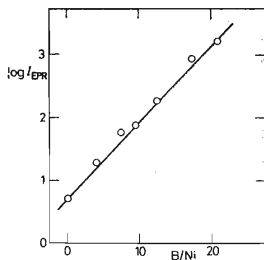

Fig. 9

Change in EPR Signal Intensity Belonging to Colloidal Nickel in Ternary System $Ni(acac)_2$–BF_3.$O(C_2H_5)_2$–$Al(C_2H_5)_3$ with Molar Ratio B/Ni

Ratio Al/Ni = 6. Sample preparation by procedure A.

Effect of Oxygen

The EPR signal of free radical (septet), produced by reduction in an inert atmosphere changes into the singlet on subsequent contamination with dried air oxygen (Fig. 12), while under these conditions, the original intense signal with $g = 2.05$ immediately extinguishes. Colloidal nickel cannot be prepared in presence of oxygen traces. As far as it has been prepared by reduction in ternary Ni–B–Al systems, the intensity of its signal ($g = 2.2$) slightly decreases during subsequent contamination with dried oxygen traces, while singlet ($g = 2.05$) proportionally increases. Larger amount of oxygen removes both signals.

FIG. 10

Decrease of the EPR Signal Intensity of Colloidal Nickel during Reduction of Ni(acac)$_2$ with Triisobutylaluminium at 24°C

The spectrum record made every minute on mixing the sample by ultrasonics.
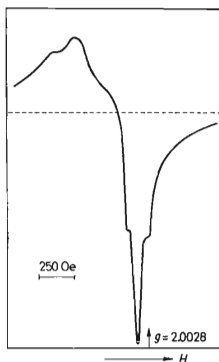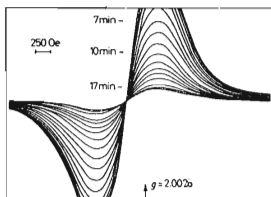

FIG. 11

EPR Signal for Catalytic-Active Ternary System Ni : B : Al = 1 : 6.5 : 6.3 in Presence of Butadiene (10% solution in toluene for ratio Ni(acac)$_2$: butadiene = 1 : 20)

Sample preparation by procedure A.
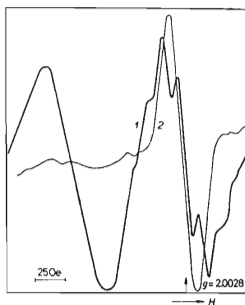

FIG. 12

EPR Signal during Reduction of Ni(acac)$_2$ with Triethylaluminium in Nitrogen Atmosphere at 24°C prior to (1) and on (2) the Contamination with Dried Air Oxygen

Molar ratio Al/Ni = 4.

DISCUSSION

The EPR signals of various paramagnetic particles can be observed in the reduction of nickel acetylacetonate (I) with triethylaluminium only on exceeding the molar ratio $Al/Ni = 1$, even though immediately on contact of both components, structural changes associated with the formation of dark products take place. We suppose that in absence of boron trifluoride etherate, one ligand after distortion of the original trimer structure[18] of I is primarily exchanged with organometal alkyl group. The compound
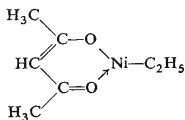
which does not yield EPR signals, is thus produced. It is reduced with surplus of triethylaluminium to produce free radical which provides septet of $g = 2 \cdot 004_3$. The singlet having $g = 2 \cdot 05$ is a product of reduction of Ni^{II} and we assign it to the unpaired $3d^9$ Ni^I electron. Assuming analogy with the mechanism of internal redox reactions in the homolytical breakage of the metal–oxygen bond of acetyl acetonates, studied by Arnett and Mendelsohn[13] as well as by Bamford and Lind[14] on the basis of the kinetic measurements

$$(acac)_n\ Me^{n+} \rightarrow (acac)_{n-1}\ Me^{(n-1)} + (acac) \qquad (A)$$
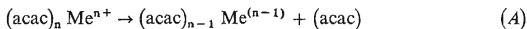
we should observe parallel changes in the intensity of EPR signals of both paramagnetic particles produced in one elementary stage

$$(acac)\ Ni^{II}\text{-}C_2H_5 \xrightarrow{Al(C_2H_5)_3} Ni^I\text{-}C_2H_5 + (acac). \qquad (B)$$
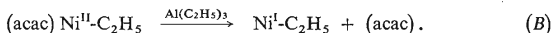
With the increasing triethylaluminium concentration, maximum of the septet of free ligand radical is first observed, and for higher molar Al/Ni ratios only, the maximum of singlet Ni^I. The position of the maximum varies according to choice of experimental conditions (way of agitating, temperature, water and oxygen traces) and according to the alkylation ability of the reducing agent applied. During the very efficient alkylation with triisobutylaluminium or aluminium hydride, or if boron trifluoride etherate is present, a broad line with $g = 2,2$, which is characteristic for ferromagnetic resonance of colloidal nickel, is observed on account of the Ni^I singlet. Colloid particles, if present in sufficient quantity, form aggregates and are gradually deposited, whereby the EPR signal is transferred from the liquid phase to the solid one. Contrary to colloidal nickel, the free radical signal is localized in the liquid

phase. The ferromagnetic resonance in domain regions of the nickel colloid can according to Bagguley[19] appear only when its aggregates are in size larger than 100 Å. At the same time, also the singlet width, which can attain $450-500$ Oe, is connected with the size of the aggregate. At the beginning of reduction $Ni^{II} \rightarrow Ni^I \rightarrow Ni^0_{colloid}$ neither the EPR signal of primary products, nor that of the paramagnetic Ni^I particles can be intercepted. The spectral width of the Ni^I signal is about 5 times greater than that of the septet. Certain amount of paramagnetic Ni^I particles is simultaneously reduced to colloidal nickel whose line is as much as twenty times broader and becomes therefore lost in the record noise at the low concentration of the colloid particles. The fact that paramagnetic Ni—R particles cannot be observed, may be accounted also for the formation of diamagnetic dimers with compensated antiparallel spins:

$$Ni^I \diamondsuit Ni^I$$

with R at top and R at bottom of the bridge.
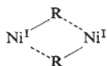
These effects cause mutual shift of both maxima on the curves showing dependence of the intensity of EPR signals against Al/Ni molar ratio.

The septet resonating in the region of free electron with $g = 2.004_3$ having binomial ratio of line intensities, is due to the interaction of the unpaired electron with six equivalent protons. Since an equal septet is observed independently of the aromatic solvent used (benzene, deuterated benzene, toluene, hexane), the idea may be excluded that ion-radicals are produced which form "sandwich" associates similar to those observed by Olivé and Olivé[5] during reduction of vanadyl acetylacetonate. Explanation of the observed signal in terms of the peroxidic radical
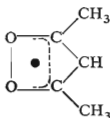
presumed by Bamford and Lind[14] as well as by Arnett and Mendelsoln[13] on breaking the Mn—O bond by redox mechanism during irradiation of manganese acetylacetonate, appears to be an attractive interpretation. The hyperfine structure could be under this assumption explained by interaction of the delocalized oxygen electron with six equivalent protons of two methyl groups. The methyl groups are in β position as related to oxygen, similarly as is the hydrogen atom linked with a double-bond carbon. The hydrogen in question should then manifest itself in the structure of the EPR signal either as a dominating doublet further splitted to a septet, or by splitting of individual septet lines to doublet. The effect was observed neither in the study

of the spectra at $-150°C$. Since an excess of the alkyl metal is necessary $(Al/Ni > 1)$ to break the Ni–O bond and hence to develop the EPR signals, we assume that in the inert atmosphere, radical of the type
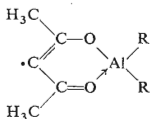
is produced. The radical is resonance-stabilized thus having sufficient length of life at room temperature and being possible to accumulate itself to a concentration of the approximate order of 10^{-5} mol.

$$\text{(C)}$$
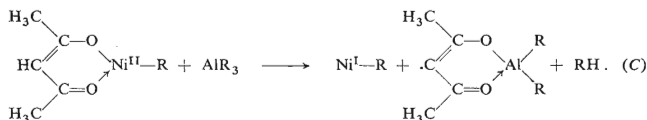
The theoretical EPR spectrum of free radical, achieved with aid of a spectral computer and simulated according to the structure suggested, is identical with the spectrum found experimentally. Gradual extinguishing of this radical both by recombination with further excess of the alkyl metal to produce nonresonating alkoxyaluminates occurs at elevated temperature. The idea of the radical structure suggested is supported by the fact that on contamination of the system with dry air oxygen, the septet is changed into the singlet to produce the oxygen radical, which could not be presumed with the so-called cyclic peroxide:

$$\text{(D)}$$
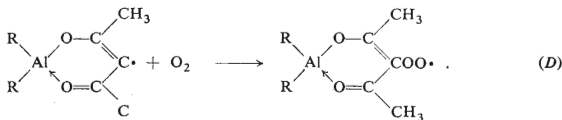
In contrast to the septet, the contamination with traces of air oxygen immediately removes the singlet having $g = 2·05$. The assumption is thus confirmed that the signal is connected with the unpaired $3d^9$ electron of Ni^I which is a reduction product of Ni^{II}. If colloidal nickel in an amount that can be detected with use of the broad line of $g = 2·2$ is present in the system, slight contamination with oxygen does not

remove the Ni^I signal. In terms of an oxidation intermediary product, molecules with Ni^I can be namely produced, due to a partial oxidation of the reactive zero-valent nickel.

The existence of the low level of Ni^I ions taking part in the catalytic reactions, and a high reactivity of the zero-valent nickel were assumed also by other authors[20] on the basis of the kinetic analysis of the synthesis of oligomers from olefines[21,22]. The zero-valent nickel with the paired number of electrons does not yield the EPR signal, unless a colloidal aggregate of at least several domains (approx. 100 Å) in size is produced. As the number of Ni^I spins is $10^{14}/0.3$ ml of the sample, *i.e.* about 10^{-5} mol, also the same level of completely coordinated zero-valent nickel, which cannot be indicated by the EPR method, can be expected. If a relatively large excess of triethylaluminium is present, the colloid particles disintegrate, their solubility improves and signal $g = 2.2$ decreases. Traces of moisture in the solution lower the number of free radicals from the ligand and stabilize the Ni^I particles at the expense of the formation of colloidal nickel. If the reduction is carried out in presence of butadiene, the nickel colloid does not reach particles large enough to be deposited immediately. New signal having $g = 2.1$ is under this condition observed in the system, which can be explained by the formation of π-complexes of butadiene with Ni^I or Ni^0 in the same way as assumed in the catalytic conversion of olefines, the mixture oligomers being thus produced[21,22].

Contrary to triethylaluminium which is dimer, triisobutylaluminium is a monomer[23] and reduces I very strongly to colloidal Ni similarly as also alkyl hydrides do. A considerably more efficient reduction of Ni^{II} to the nickel colloid proceeds in the ternary system in presence of boron fluoride etherate, whereby all Ni^{II} present in the solution are virtually reduced, this being confirmed by the number of resonating particles (approximately 10^{19} spins/0.1 ml solution). In the ternary system, neither formation of the Ni^0BF_3 and $R–Ni^IBF_3$ complexes can be excluded.

By selecting the reaction conditions properly, an equilibrium is established in the system between individual redox-forms of nickel

$$Ni^0_{colloid} \leftrightarrow Ni^0 \leftrightarrow Ni^I \leftrightarrow Ni^{II} \qquad (E)$$
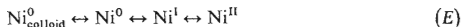
and free radical from the ligand. The catalytic system is of homogeneous character according to what is the ratio of individual forms present. This equilibrium, except for the molar Al/Ni ratio chosen, is heavily affected by temperature, way of mixing the starting components, and by trace amounts of moisture and oxygen. Thus, for example, for the molar ratios Al/Ni = 3, and Al/Ni = 12, the following ratios between individual reduction products become established $Ni^0_{colloid} : Ni^I :$ radical = = 500 : 8 : 1 and 1000 : 500 : 1, respectively. The Ni^I particles are fixed on the surface of the colloidal ones, this leading to the formation of complicated aggregates with active centres of the catalytic system having microheterogeneous character.

Mechanism of the reduction of nickel acetylacetonate by alkyl metals as studied by the EPR method provides a picture of only temporarily stable paramagnetic particles of low concentration level. A complex picture can be provided only on completing the knowledge thus achieved by a parallel study of the reaction mechanism by infrared spectroscopy, electric conductance measurements, and kinetic parameters.

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