

**MICROHETEROGENEOUS CATALYTIC SYSTEM Ni(0)<sub>coll</sub>-Ni(I)-Ni(II)  
FOR LOW-PRESSURE POLYMERIZATION OF BUTADIENE. III.\***

**ELECTRIC CONDUCTIVITY OF BIMETALLIC COMPLEXES  
AND PARAMAGNETISM**

R. PŘIKRYL, A. TKÁČ and A. STAŠKO

*Institute of Chemical Physics,  
Slovak Institute of Technology, Bratislava*

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Character of active centres of a three-component catalytic system Ni(acac)<sub>2</sub>-BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> for low-pressure butadiene polymerization was studied making use of parallel changes in electric conductivity and number of paramagnetic particles in the reduction of Ni(II) to Ni(I) and colloidal nickel. In correlation with analysis of IR spectra, new experimental technique of studying EPR signals as well as electric conductivity in one measuring cell, confirmed formation of metallic complexes of the types Ni-B, Ni-Al, B-Ni-B, B-Ni-Al. Symmetric metallic complexes exhibit a considerably reduced electric conductivity in a nonpolar medium. In the ternary system of highest catalytic effect, minimum conductivity has been observed, the number of paramagnetic colloidal nickel particles being maximum, which excludes ionic character of active centres.

The infrared spectra studies<sup>1</sup> of reaction products of the three-component catalyst system [Ni(acac)<sub>2</sub>, BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, where acac denotes acetylacetonate] for low-pressure polymerization of butadiene suggested formation of bi- and trimetallic organocomplexes of type Ni-B, Ni-Al, Ni(0)-Al(III), B(III)-Al(III) or possibly B(III)-Ni(I)-Al(III). The complexes in which the nickel atom presents itself as Ni(I) are paramagnetic<sup>2</sup> due to the unpaired 3d<sup>9</sup> electron, and yield the EPR signal of  $g = 2.05$ . The decomposition of complexes, in which Ni(0) under some excess of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> is the centre metal, leads to the formation of colloidal nickel Ni(0)<sub>coll</sub> which produces ferromagnetic domains and renders a broad singlet of  $g = 2.2$ . In this paper, an experimental method for parallel studying EPR signals and electric conductivity in nonpolar solvents in one measuring cell has been worked out in order to determine the part of conducting or paramagnetic components during the formation of catalytic active centres. This method has added to a deeper knowledge of the kinetics of the catalyst synthesis and particularly to the characterization of electric properties of organometallic complexes assumed on the basis of the IR spectra analysis.

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## EXPERIMENTAL

*Reagents.* The reagents used and preparation of samples have been described in our papers<sup>1,2</sup>. Toluene for the preparation of solutions for the conductivity measurements was freed of thiophene and moisture, while all the measurements were carried out in the atmosphere of dry nitrogen additionally purified from traces of oxygen.

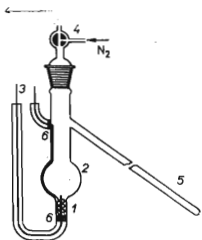


FIG. 1

Combined Cell for Measuring Electric Conductivity and EPR Signals

1 Conductivity cell with electrodes (platinum wire placed in the centre of a platinum coil), 2 part of the vessel in which mixing of components ("titration") is carried out, 3 direct-current voltage supply, 4 three-way glass ground stopcock with inert gas inlet, 5 quartz cell for EPR spectra measurement, 6 electrode seals.

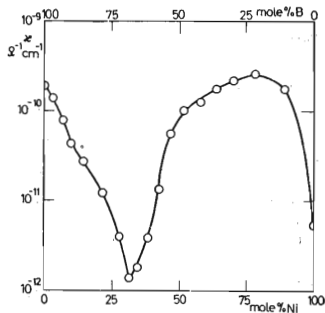


FIG. 2

Plot of Direct-Current Conductivity against Mole Fraction of Nickel Acetylacetonate or Boron Trifluoride Etherate during Gradual Mixing of Both Components at 20°C

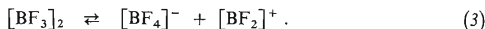
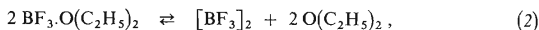
*Electric conductivity and EPR spectroscopy.* In order to measure electric conductivity as well as EPR signals of the same sample simultaneously (about 1 ml), a device made of glass (Fig. 1) was developed. Platinum coil with a platinum wire placed in its centre provided electrodes of the resistance vessel of capacity  $10^{-2} \text{ cm}^{-1}$ . The vessel closed with a three-way stopcock is connected with the EPR cell, its internal diameter being 4 mm. So far the titration measurements were carried out, the samples were briefly agitated in the vessel by ultrasonics at 20°C on adding the reacting components. The conductivity was calculated from value of the electric resistance measured after one minute on applying direct-current voltage of 100 V. The resistance was measured by teraohmmeter Tesla BM 283. The conductivity was determined with a limiting relative error of max. 10%, reproducibility of the measurements was  $\pm 3\%$ . By leaning the vessel, the sample under study was poured into the EPR cell and the whole assembly was inserted into the spectrometer resonance cavity.

## RESULTS AND DISCUSSION

Electric properties were studied in toluene solutions during the catalyst synthesis, while conductivity of pure solvent amounted to  $10^{-14} - 10^{-15} \Omega^{-1} \text{ cm}^{-1}$ . 5% solutions of starting components  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and dimer<sup>3</sup>  $[\text{Al}(\text{C}_2\text{H}_5)_3]_2$  have a  $10^2$  times greater conductivity of  $2 - 3 \cdot 10^{-10} \Omega^{-1} \text{ cm}^{-1}$ , similarly as equally concentrated  $\text{Ni}(\text{acac})_2$  solution producing a trimer<sup>4</sup> under these conditions. This enhanced conductivity may be partially accounted for the dissociation of triethyl aluminium dimer<sup>5</sup>



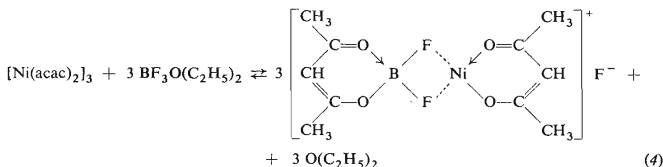
and in case of boron trifluoride etherate, which from about 10% is dissociated to dimer and free ether<sup>6</sup>, for the decomposition of  $[\text{BF}_3]_2$  according to



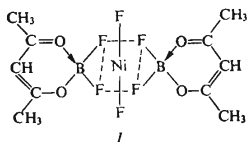
Binary mixtures  $\text{Ni}(\text{acac})_2 + \text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ,  $\text{Ni}(\text{acac})_2 + \text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 + \text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{Ni}(\text{acac})_2 +$  butadiene, and three-component system  $\text{Ni}(\text{acac})_2 - \text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 - \text{Al}(\text{C}_2\text{H}_5)_3$  were prepared over a wide range of molar ratios. Attention has been paid particularly to molar ratio  $\text{Ni} : \text{B} : \text{Al} = 1 : 6.5 : 6$  for which the highest catalytic activity was observed. With all the samples, also intensity of appropriate EPR signals was determined simultaneously with measuring the electric conductivity.

*Mixture Ni(acac)<sub>2</sub> + BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>*

Addition of a relatively small amount of the toluene solution of  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  to  $\text{Ni}(\text{acac})_2$  solution immediately provides increase of electric conductivity (Fig. 2), which will virtually be kept on constant value until the molar  $\text{Ni}/\text{B} = 1$  ratio is reached. Further increase of the quantity of boron trifluoride etherate leads to the decrease in conductivity of  $4 \cdot 10^{-10} \Omega^{-1} \text{ cm}^{-1}$  till it attains a minimum of  $2 \cdot 10^{-12} \Omega^{-1} \text{ cm}^{-1}$  for the molar ratio  $\text{Ni}/\text{B} = 1 : 2$ . By exceeding the "point of equivalence", the  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  surplus increases conductivity to a value corresponding to the 5% toluene solution of pure boron trifluoride etherate. During mixing, no reduction of Ni(II) takes place and the system behaves as diamagnetic from the viewpoint of EPR. When considering results of the IR spectra analysis<sup>1</sup> which pointed out gradual exchange of two acetylacetonate ligands of Ni(I) for F, ether being simultaneously evolved, the conductivity changes can be interpreted in the region of the molar ratio  $\text{Ni}/\text{B} = 1$  by formation of partially dissociated conducting "asymmetric"



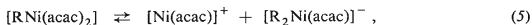
bimetallic complex according to (4). For the molar ratio Ni/B = 1 : 2, a complete exchange of Ni(II) ligand for fluorine atom is achieved, while undissociated coordinated symmetric complex *I* with Ni(II) which has a minimum conductivity is produced:



The data achieved by studying IR spectra of the reaction products responsible for the formation of the complex considered are thus becoming complete.

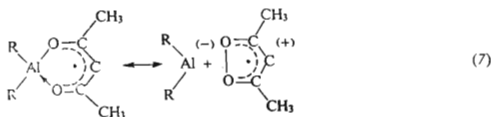
#### Mixture Ni(acac)<sub>2</sub> + Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

Infrared spectra analysis<sup>1</sup> of the products of reaction between Ni(acac)<sub>2</sub> and triethyl aluminium pointed out that up to molar ratio Ni/Al = 1, original structures of the nickel acetylacetonate trimer and triethyl aluminium dimer are disturbed. In this process, acetylacetonate ligand on the nickel atom is exchanged for the aluminium alkyl group. In spite of the fact that the system does not yield the EPR signals, the process is connected with the increase of conductivity, as can be seen from Fig. 3. The dimers produced can be partially dissociated according to equations



The maximum conductivity is observed with molar ratio Al/Ni ≈ 4 : 1, consequently under conditions when also maximum intensity of the EPR signal-septet of  $g = 2.004_3$  is being observed. The signal was assigned to the free ligand radical<sup>2</sup> bound to the aluminium atom after a homolytic breaking of the Ni—O bond. A simultaneous product of the reduction is diamagnetic associate of two paramagnetic NiR molecules with

compensated antiparallel spins of two  $3d^9$  electrons  $RNi \uparrow \downarrow NiR$ . A fairly high conductivity could be under these conditions explained by the dissociation of the radical according to (7).



This dissociation provides a cyclic peroxide presumed by Banford<sup>7</sup> and Arnett<sup>8</sup> on the basis of kinetic measurements in the reduction of transition metals, with the exception that positive ion-radical must be considered.

We have pointed out that under excess of triethyl aluminium, diamagnetic dimer  $RNi \uparrow \downarrow NiR$  decomposes into paramagnetic bimetallic complex<sup>1</sup> of type II which provides the EPR

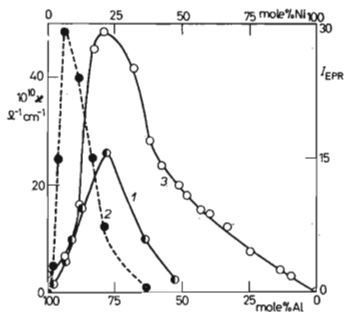
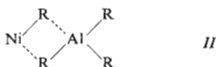


FIG. 3

Plot of Direct-Current Conductivity 3 and Intensity of EPR Signals 1, 2 against Mole Fractions of Triethyl Aluminium or Nickel Acetylacetonate during Gradual Mixing of Both Components at 20°C

EPR signals: free radical from acetylacetonate ligand with  $g = 2.004_3$  (1), and from paramagnetic Ni(I) particles of  $g = 2.05$  (2).

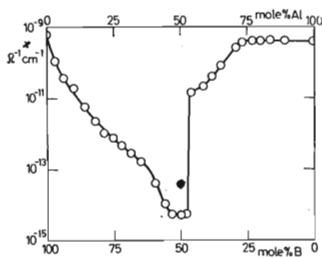


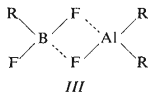
FIG. 4

Plot of Direct-Current Conductivity against Mole Fraction of Boron Trifluoride Etherate or Triethyl Aluminium during Gradual Mixing of Both Components at 20°C

singlet with  $g = 2.05$ . The maximum of this signal is observed for the molar ratio  $\text{Al}/\text{Ni} = 6 : 1$ , *i.e.* under a condition, when  $\text{Ni}(\text{I})$  placed in the centre is completely coordinated  $[\text{NiR}]_2[\text{AlR}_3]_4$ . Under this condition, minimum conductivity in the system is observed. The conductivity decreases together with extinction of the EPR septet, while free radical is under the triethyl aluminium excess changed into inactive nonconducting alcoxaluminates.

#### Mixture $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2 + \text{Al}(\text{C}_2\text{H}_5)_3$

The plot of conductivity against molar B/Al ratio (Fig. 4) has a shape of typical titration curve with a sharp flexure for molar ratio  $\text{Al}/\text{B} = 1$ . The original conductivity of boron trifluoride etherate decreases during stepwise addition of triethyl aluminium and attains a minimum for equimolar ratio  $\text{Al}/\text{B} = 1$ . The conductivity decreases by as much as 5 orders of magnitude from value  $8 \cdot 10^{-10}$  down to  $7 \cdot 10^{-15} \Omega^{-1} \text{cm}^{-1}$



Infrared spectra analysis under these conditions showed that bimetallic complexes of type III, analogous to the Ziegler-Natta complex<sup>9-11</sup>, may be assumed. Also in this case, similarly as in the formation of bimetallic Ni-B and Ni-Al complexes, it appeared that entirely coordinated systems are virtually nonconducting. Excess of triethyl aluminium causes enhanced conductivity, the conductivity of original pure  $\text{Al}(\text{C}_2\text{H}_5)_3$  component being attained at the same time.

#### Three-component Catalytic System Ni-B-Al

Unless a chemical reaction takes place in the system and two components are only mixed mutually, no distinct maxima or minima can be observed on the conductivity curves. As example of such a course stands here the plot of conductivities against composition of  $\text{Ni}(\text{acac})_2$ -butadiene mixtures (Fig. 5). Effect of butadiene on the conductivity was also followed with Ni + B, Ni + Al, and B + Al systems. The deviations observed were within limiting errors and did not affect the results in any respect. The measurements were carried out in order to check the effect of monomer on electric conductivity in the process of the catalyst synthesis, for the catalyst improves homogeneity of the microheterogeneous catalytic system. In the synthesis, triethyl aluminium is gradually added to the mixture of  $\text{Ni}(\text{acac})_2$  and butadiene together with boron trifluoride etherate, the molar B/Ni ratio being 6.5 : 1. The course of electric conductivity and change in intensity of EPR signals as dependent

on appropriate molar ratios are graphically presented in Fig. 6. Prior to reduction, the bimetallic complex (acac)BF<sub>2</sub>.NiF<sub>2</sub>F<sub>2</sub>B(acac) already described and some excess of unreacted BF<sub>3</sub>.O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> are then present in the system. With the increasing concentration of triethyl aluminium also intensity of the EPR signal of colloidal nickel ( $g = 2.2$ ) linearly increases; the intensity attains maximum for molar ratio Al : (Ni + B)  $\approx 1$ . The maximum of the number of paramagnetic particles is coincident with the minimum of electric conductivity and lies in the concentration region of greatest polymerization activity. The ionic character of active centres can be then excluded. Further increase of conductivity after exceeding the maximum under excess of triethyl aluminium is due to the formation of complex RBF<sub>2</sub>.R<sub>2</sub>AlF after reaction with excess of unreacted BF<sub>3</sub>.O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. Also the effect of dissolution with the low-conducting triethyl aluminium must be considered.

When comparing the Ni + B + Al system with that of Ni + B + Al + butadiene (20%, vol.), it can be seen that presence of monomer does not change shape of the conductivity curve. A relatively little increase of conductivity within 20–40%

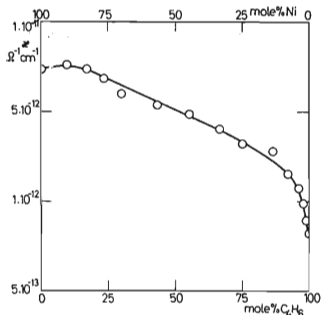


FIG. 5

Plot of Direct-Current Conductivity against Molar Ratio of Nickel Acetylacetonate or Butadiene during Gradual Mixing of Both Components at 20°C

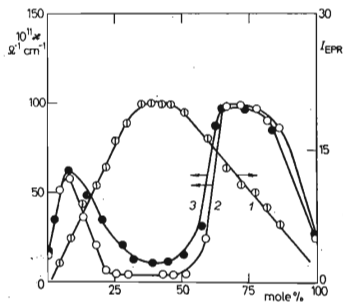


FIG. 6

Plot of EPR Signal Intensity (1) and Direct-Current Conductivity (2, 3) against Mole Fraction of Triethyl Aluminium in Ternary Catalytic System Ni-B-Al under Maintaining Constant Ratio between Nickel Acetylacetonate and Boron Trifluoride Etherate Ni : B = 1 : 6.5

Mole fraction  $n_{Al} = n_{Al} / (n_{Al} + n_B + n_{Ni})$ ;  $n_{Ni} + n_{Al} = \text{const.}$ , 2 Ni : B : Al = 1 : 6.5 : x. 3 Ni : B : Al : butadiene = 1 : 6.5 : x : 30.

of triethyl aluminium in presence of butadiene is due to a better homogeneity of the microheterogeneous catalytic system; at the same time also desaggregation of colloidal nickel particles<sup>2</sup> takes place.

Simultaneous study of electric conductivity and paramagnetic properties of the reaction products in correlation with analysis of IR spectra showed distinct connection between electric properties and structure of bimetallic complexes which share in the formation of catalyst active centre. It is necessary to consider primarily the nonconducting complex which exists in the presence of colloidal nickel. A more detailed description of an active centre will result, as will be shown later, merely from kinetic study of polymerization, *i.e.* by immediate testing of the activity of the system studied under various reaction conditions.

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