

MICROHETEROGENEOUS CATALYTIC SYSTEM Ni(0)<sub>col</sub>-Ni(I)-Ni(II)  
FOR LOW-PRESSURE POLYMERIZATION OF BUTADIENE. II.\*  
AN INFRARED STUDY OF THE MECHANISM OF REDUCTION

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Reactions leading to the formation of active centers in a three component microheterogeneous catalytic system containing nickel(II)acetylacetonate-trifluoroboron etherate-triethylaluminium are described on the basis of infrared spectra interpretation. This catalytic system is suitable for low pressure polymerization of butadiene. The acetylacetonate ligand attached to Ni(II) can be changed for an alkyl group on triethylaluminium if the ratio of Al/Ni in the mixture containing metalalkyl and acetylacetonate does not exceed the value of one. At higher ratio (Al/Ni > 1) Ni(II) is reduced to Ni(I) forming paramagnetic bimetallic complexes [NiR—AlR<sub>3</sub>]. In the mixtures of Ni(acac)<sub>2</sub> with BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> the acetylacetonate ligand is exchanged for halogen, the process being accompanied by the evolution of ether; the reaction quantitatively produces NiF<sub>2</sub> at the molar ratio B/Ni = 2. Subsequent alkylation of NiF<sub>2</sub> leads to the formation of NiR<sub>2</sub> intermediate which is further reduced by triethylaluminium to colloid nickel. Colloid nickel is a carrier of organometallic complexes containing catalytically active centre. The structure of paramagnetic species formed in the process of reduction is discussed on the basis of EPR spectra.

We have shown<sup>1</sup> that three different types of paramagnetic species are formed during the reduction of nickel(II) acetylacetonate by triethyl- and triisobutylaluminium resp. Their concentration varies from 10<sup>-5</sup>–10<sup>-6</sup> mol l<sup>-1</sup> which is too low to facilitate their detection by infrared spectroscopy. As the EPR signals have characterized sufficiently individual paramagnetic intermediates of the reaction as well as relative changes of different redox forms Ni(0)<sub>col</sub>, Ni(I) and Ni(II) resp., subsequent infrared analysis of final reaction products may help to elucidate the reaction mechanism.

#### EXPERIMENTAL

Chemicals, their preparation and purity have already been described<sup>1</sup>. The solutions were stored under an argon atmosphere; the mixing was done in a magnetically stirred and thermostated jacketed vessel fitted with a three way tap. Infrared spectra of individual pure components and their different mixtures resp. were examined in 4-7% toluene solutions. The spectra were taken on a double beam Zeiss UR 10 spectrometer using NaCl and KBr cells of 0.1 and 0.09 mm path-

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length resp. The cells were flushed with dried and deoxygenated nitrogen prior to filling. The solutions were transferred into the cells under the stream of an inert gas. The concentration of storage solutions was: Ni(acac)<sub>2</sub> 0.15 mol/l, BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> 0.54 mol/l, Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> 0.49 mol/l.

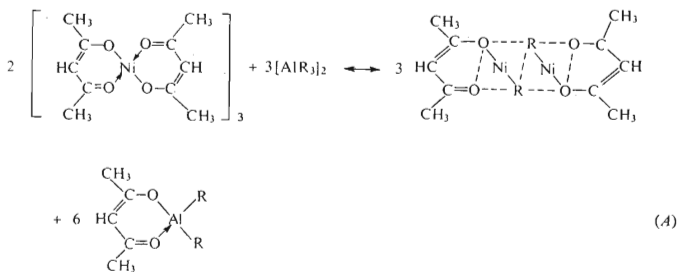
## RESULTS AND DISCUSSION

The infrared spectra of acetylacetonates of various metals (Ni, Al, Cu, B) are generally characterized by a pronounced shift of valence vibrations of chelate coordinated carbonyl groups C=O into the region of 1570–1600 cm<sup>-1</sup> (ref.<sup>2-5</sup>). The spectrum of Ni(acac)<sub>2</sub> exhibits C=O vibrations at 1600 cm<sup>-1</sup>, C–H deformational vibrations in CH<sub>3</sub> groups are seen at 1480, 1410 and 1360 cm<sup>-1</sup>, and C–O valence vibrations at 1265 and 1200 cm<sup>-1</sup>. The 1025 and 930 cm<sup>-1</sup> bands correspond to C–C valence vibrations whereas the 700 cm<sup>-1</sup> absorption is due to the C–H rocking vibrations. The position of bands between 600–700 cm<sup>-1</sup> is a specific one for the skelet consisting of central metal ion — ligand. The absorption at 400 cm<sup>-1</sup> is typical for Ni–O vibrations. The band at 1540 cm<sup>-1</sup> characterizes trimer [Ni(acac)<sub>2</sub>]<sub>3</sub>. The most intense bands of this trimer are practically identical with the absorption bands of other metal acetylacetonates e.g. copper<sup>3</sup> at 1550, lead<sup>4</sup> at 1516, aluminium<sup>5</sup> at 1548 cm<sup>-1</sup>. Those acetylacetonates where the central metal is fully coordinated with acetylacetonate ligand show absorptions at 1540 ± 5 cm<sup>-1</sup> and a 1025 ± 5, 930 ± 7 cm<sup>-1</sup> doublet. If, however, one or more ligands are replaced by halogen, as e.g. in the case of (acac)BF<sub>2</sub> molecule<sup>6</sup>, the intensity of the 1540 cm<sup>-1</sup> absorption decreases, a typical band at 930 cm<sup>-1</sup> disappears, whereas the absorption at 1580 cm<sup>-1</sup> corresponding to metal coordinated carbonyl group remains unchanged. The decrease in intensity of absorption in the region of 1250–1290 cm<sup>-1</sup> is also connected with the removal of one ligand. An intense band with two maxima at 1230 and 1190 cm<sup>-1</sup> due to the valence vibration B–F<sup>7</sup> dominates the spectrum of boron trifluoride etherate. The spectrum of boron trifluoride in the absence of ether contains these valence vibrations in positions 1200 and 1240 cm<sup>-1</sup> resp. The absorption at 1030 cm<sup>-1</sup> in the etherate spectrum is in connection with C–O–C vibrations. Its position is slightly shifted towards lower frequencies when compared with non-bonded ether 1120 cm<sup>-1</sup><sup>8</sup>. The three bands at 880, 830 and 770 cm<sup>-1</sup> resp. are typical skeletal vibrations of the BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> molecule. The decomposition of associate is accompanied by the disappearance of these absorption bands. An intense band from 720 to 580 cm<sup>-1</sup> which is due to Al–C bond valence vibration is a common absorption seen in infrared spectra of alkylaluminates<sup>9-12</sup>. The NMR studies of nonbranched alkylaluminium derivatives performed by Ramey and coworkers<sup>13</sup> confirmed a dimer structure<sup>9</sup> of [AlR<sub>3</sub>]<sub>2</sub>. This intense band is reduced from the original four or more lines to one band when the dimer diminishes. This simple band corresponds to asymmetrical valence vibrations. The quantitative structural changes of triethylaluminium in various mixtures during the process of reduction can be followed on the basis of the 990 cm<sup>-1</sup> band changes.

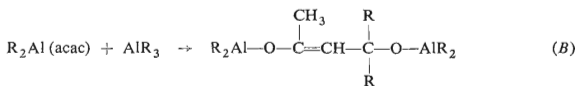
### *Changes in Infrared Spectra of Binary Mixtures with Different Molar Ratio Ni/Al*

It follows from the absorption bands intensity changes of both reacting components [Ni(acac)<sub>2</sub>]<sub>3</sub> and [Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (Fig. 1) that the formation of the original trimer structure of acetylacetonate and the dimer structure of triethylaluminium is suppressed till the molar ratio Ni/Al = 1; in the former case the intensity of the bands at 1265 and 930 cm<sup>-1</sup> decreases, in the latter case the 990 cm<sup>-1</sup> band intensity

is lowered. The position of absorption bands due to C=O valence vibrations of acetylacetonate ligand ( $1600-1580\text{ cm}^{-1}$ ) suggests that the chelate structure is preserved till the molar ratio  $\text{Ni}/\text{Al} = 1:3$ . No band due to free non-coordinated carbonyl groups which should appear at  $1720\text{ cm}^{-1}$  is seen in the spectrum. Judging from C—O valence vibrations (disappearance of  $1265\text{ cm}^{-1}$  band) it may be concluded that the chelate structure of  $\text{Ni}(\text{acac})_2$  diminishes, whereas new bands appear in the spectrum which are characteristic for a chelate ligand bonded to aluminium ( $1280\text{ cm}^{-1} \pm \pm 7\text{ cm}^{-1}$ ). The intensity of bands at  $800-820\text{ cm}^{-1}$  corresponding to Al—O valence vibrations increases with the increasing concentration of triethylaluminium. This signifies that the the  $\text{R}_2\text{Al}-\text{O}-\text{C}$  structure predominates in the system. This process is reflected in the infrared spectrum in which the valence vibrations bands of  $\text{R}_2\text{Al}-\text{C}$  ( $990\text{ cm}^{-1}$ ) diminish. The spectral changes can be accounted for by the transfer of acetylacetonate ligand from central Ni(II) ion to Al(III); this causes the decrease in the number of Ni—O and Al—C bonds and the increase of Ni—C and Al—O bonds. At molar ratio  $\text{Ni}/\text{Al} = 1$  the efficiency of this process is 50%, whereas at higher ratio then  $\text{Al}/\text{Ni} = 1:3$  the acetylacetonate ligand is completely bonded to the aluminium atom. These experimental facts suggest that up to the ratio  $\text{Al}/\text{Ni} = 1$  the system will not exhibit paramagnetic properties in the EPR spectra<sup>1</sup>. The alkyl group bonded to aluminium is only exchanged for the nickel bonded ligand the process causing, at the same time, the disappearance of both  $[\text{Ni}(\text{acac}_2)]_3$  trimer and  $[\text{AlR}_2]_2$  dimer.



At the great excess of alkylaluminium the chelate structure is suppressed, the process being accompanied by the formation of alkoxyaluminates probably *via* the reaction



The formation of paramagnetic particles indicated by EPR spectroscopy<sup>1</sup> when the molar ratio Al/Ni > 1 could be explained by interpreting the reaction mechanisms suggested on the basis of infrared spectral studies. The excess of triethylaluminium reduces nickel(II) acetylacetonate forming Ni(I) with unpaired 3d<sup>9</sup> electron and a free ligand radical which appears as a septet in the EPR spectrum ( $g = 2.004$ ):

When there is only a slight excess of alkylaluminium, the NiR associates forming a diamagnetic dimer [NiR]<sub>2</sub> which decomposes at higher concentrations of triethylaluminium giving paramagnetic Ni-Al complex, to which a singlet ( $g = 2.05$ ) can be assigned. It is assumed that in reaction (D) free coordination places are solvated by solvent molecules.

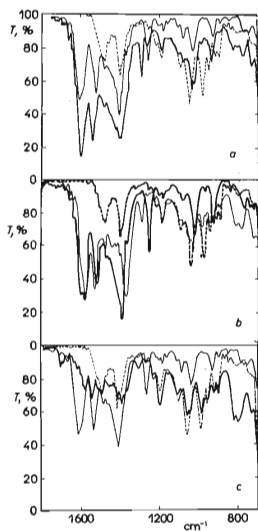


FIG. 1

Spectra of the Reaction Mixture of Nickel(II) Acetylacetonate with Triethylaluminium at the Molar Ratio Ni/Al 1:1 (a), 1:3 (b), 1:9 (c)

Toluene solutions: — mixture (5%), — nickel(II) acetylacetonate (5%), ..... triethylaluminium (5%).

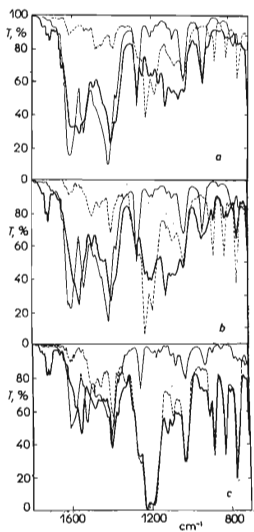
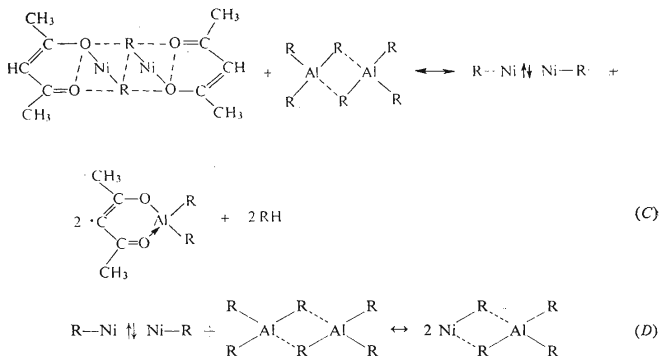


FIG. 2

Spectrum of Reaction Mixture of Nickel(II) Acetylacetonate with Boron Trifluoride Etherate at the Molar Ratio Ni/B 1:1 (a), 1:2 (b), 1:6 (c)

Toluene solutions: — mixture (7%), — nickel(II) acetylacetonate (7%), ..... boron trifluoride etherate (5%).

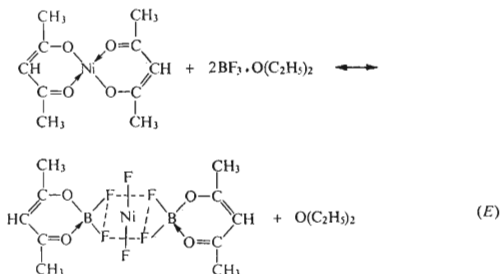


The formation of bimetallic Ni-Al complexes during which ethane evolved was also observed by Witt and Hogan<sup>14</sup> when studying the reduction of Ni(II)-2-ethylhexanoate. As the maximum intensities of the EPR spectra of Ni(I) particles are seen at molar ratio Al/Ni  $\approx$  6 *i.e.* when the electric conductivity of the system is minimal, it can be assumed that the suggested structure of the bimetallic Ni-Al complex is only the simplest one and that the nickel atom is fully coordinated with alkylaluminium NiR<sub>5</sub>AlR<sub>3</sub>. The presence of moisture in the system causes decomposition of such a complex thus precluding farther reduction to colloid nickel<sup>1</sup>. Free ligand radical forms alkoxyaluminates R<sub>2</sub>Al—O—C in the presence of an excess of triethylaluminium whereas in the presence of oxygen traces it reacts to R<sub>2</sub>Al—R'—O—O. peroxi radicals. Bimetallic Ziegler-Natta type complexes containing alkylaluminium with a transition metal have already been described<sup>15</sup>; also mixed bridged alkylaluminium complexes are known<sup>16</sup>.

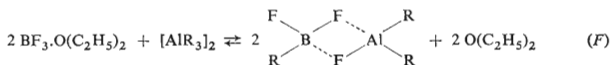
#### *Changes in Infrared Spectra of Binary Ni(acac)<sub>2</sub>-BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> Mixtures with Different Molar Ratio Ni/B*

In Fig. 2 the spectra are compared of nickel(II)acetylacetonate and boron trifluoride etherate solutions resp. with those of their mixture in molar ratio Ni/B = 1. The reaction of the initial components reflects in the infrared spectra; the intensity of B—F valence vibrations bands at 1190 and 1230 cm<sup>-1</sup> substantially decreases whereas new band at 1120 cm<sup>-1</sup> corresponding to valence C—O—C vibrations of nonbonded ether appears. The chelate structure of the ligand remains mostly preserved judging from characteristic bands due to C=O and C—O valence vibrations. The original Ni(acac)<sub>2</sub> reacts, however, forming boron acetylacetonate. A doublet at 1540–1605 cm<sup>-1</sup> forms a new single band absorbing at 1550 cm<sup>-1</sup>. The 1410 cm<sup>-1</sup> band is shifted into the region of 1400 cm<sup>-1</sup> and new bands at 910–950 cm<sup>-1</sup> appear. These absorptions, which are due to valence vibrations of the B—C bond, are typical for the type R<sub>3</sub>B compounds. The acetylacetonate

ligand bonded to nickel is exchanged for halogen at the increasing concentration of  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$



Under these conditions the absorption at  $1720\text{ cm}^{-1}$  corresponding to free carbonyl groups can be observed in the spectra. About 15–20% of the total amount of carbonyls are not bonded in a chelate form. Compounds of the type  $\text{F}_2\text{B}(\text{acac})_2$  can be expected amongst the reaction products. Ether as a polar compound can, to some extent, attack the (acac)-ligand chelate bond. At the molar ratio of  $\text{Ni}/\text{B} = 1 : 2$  the acetylacetonate is no more bonded to the nickel atom but it is attached to boron. Thus the  $\text{NiF}_2$  structure can be expected in the system. Similarly, boron trifluoride etherate in the presence of triethylaluminium will exchange the fluor atom for the alkyl group (Fig. 3). The reaction (F) leads to the formation of a sparingly soluble product; the reaction proceeds quantitatively when the molar ratio  $\text{B}/\text{Al} = 1 : 1$ .



#### *Changes of Infrared Spectra During the Synthesis of Microheterogeneous Ni—B—Al Catalytic System*

When the ratio  $\text{Ni} : \text{B} : \text{Al} = 1 : 6.5 : 6$  an efficient catalytic system is obtained. The system is prepared by adding triethylaluminium into the reaction mixture of  $\text{Ni}(\text{acac})_2 + \text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  ( $\text{Ni}/\text{B} = 1 : 6.5$ ). The resulting spectral changes are apparent from Figs 2c and 4 (spectrum 2). A characteristic valence vibration band at  $1190\text{--}1230\text{ cm}^{-1}$  corresponding to the remaining  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  molecules diminishes whereas a typical chelate structure of acetylacetonate ligand is preserved. At the same time the band at  $1720\text{ cm}^{-1}$  corresponding to free carbonyls disappears. Quite pronounced changes are also seen in the C—O valence vibration region at

1350–1450  $\text{cm}^{-1}$ . New bands appear at 1120 and 800  $\text{cm}^{-1}$ , the former being due to valence vibrations of B—C bond, the latter is caused by Al—F bond vibrations. The intensity of the band at 650  $\text{cm}^{-1}$  typical for metal acetylacetonate bond increases substantially. The position of this absorption depends upon the central metal ion. The particles in the dark-coloured colloid system sediment in the course of time. The infrared spectra of the separated liquid phase and the sediment resp. (Fig. 4) differ in several respects 1600, 1120, 950, 780  $\text{cm}^{-1}$  bands. Whereas the band indicating the presence of free ether dominates in the liquid phase, the spectra of the solid sediment suggest the presence of  $\text{BF}_3$  structure together with acetylacetonate ligand in its chelate form bonded to boron. The most intense band at 950  $\text{cm}^{-1}$  was assigned to  $\text{R}_2\text{B}$  structure. Valence vibrations of Al—O bonds (780  $\text{cm}^{-1}$ ) are also seen in the solid phase. On the basis of the above mentioned data the mechanism of the catalyst synthesis accompanied by the formation of paramagnetic particles with different EPR signals can be suggested. The B—Ni—B complex formed *via* reaction (E) is present in the system when the ratio Ni : B = 1 : 6. The reduction by triethylaluminium proceeds stepwise; in the first step the alkyl group on aluminium is exchanged for fluor according reaction (G).

The type  $\text{FAIR}_2$  products are characterized by the 950  $\text{cm}^{-1}$  absorption band. Typical aluminium acetate absorptions at 580–500  $\text{cm}^{-1}$  are not observed. The efficient reduction of the complex takes place immediately after the alkylation, namely at elevated temperature and when trialkyl metal is presented in the excess. The process proceeds in two steps *via* an  $\text{Ni(I)}-\text{R}$  intermediate (EPR signal  $g = 2.05$ ) similarly

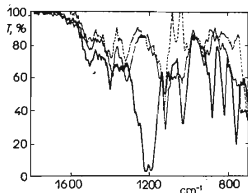


FIG. 3

Spectrum of Reaction Mixture of Boron Trifluoride Etherate with Triethylaluminium in Toluene (7%)

Molar ratio B/Al: — 5 : 1, - - - 1 : 1, ..... 1 : 3.

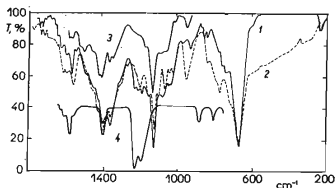
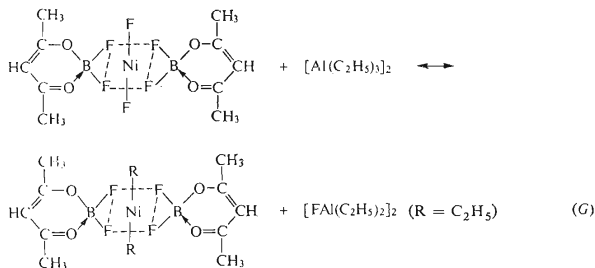


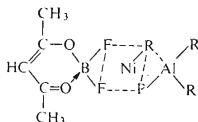
FIG. 4

Spectrum of Individual Phases of the Catalytic System at the Molar Ratio Ni : B : Al = 1 : 6.5 : 6 (toluene solution 7%)

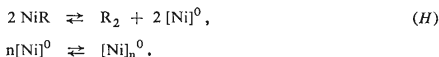
The spectrum of each phase taken after 24 hours' sedimentation. 1 Liquid phase not centrifuged, 2 sediment not centrifuged, 3 liquid phase centrifuged, 4 solid phase centrifuged and dried.



as during the reaction (D). The most plausible structure of the intermediate is following



In the second consecutive step the reduction of the complex results in the elemental nickel [Ni(0)]. The [Ni(0)] atoms agglomerate and are the centra for colloid nickel formation



The remaining  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  present in the catalytic system reacts with the excess of  $\text{Al}(\text{C}_2\text{H}_5)_3$  according reaction (F) thus retarding the rate of complex reduction. Dark particles of colloid nickel exhibit ferromagnetic resonance<sup>1</sup> EPR signal ( $g = 2.2$ ) as soon as their size exceeds 100 Å. As long as the synthesis of catalyst is carried out in the presence of butadiene, the EPR spectra indicate the simultaneous formation of  $\pi$ -complexes<sup>1</sup> between the monomer and the active center. The colloid nickel acts as a carrier of the active complex. On the basis of infrared and EPR spectra resp. it is not possible to define the active complex unambiguously. Neither the study of NMR spectra was successful because the paramagnetism of the system causes resonance line broadening. On the other hand the structure of the active centers may be established more precisely by simultaneous measurements of electric conductivity together with EPR signals correlated with polymerization rates as it will be shown in our next paper.



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