

AN NMR AND ESR- INVESTIGATION OF THE CATALYTIC SYSTEM $\text{Ni}(\text{acac})_2$, C_3H_4 , $(i\text{-Bu})_3\text{Al}$ FOR THE POLYMERIZATION OF PROPADIENE

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(Received June 23, 1980)

Summary

The formation of an active propadiene polymerization catalyst in the system $\text{Ni}(\text{acac})_2$, C_3H_4 , $(i\text{-Bu})_3\text{Al}$ was studied by means of ^1H NMR and ESR spectroscopy. At low temperature two types of nickel(I) complexes could be trapped, probably intermediates in the formation of the catalyst, which is proposed to be a tetrahedrally or octahedrally coordinated paramagnetic Ni(II) complex.

Introduction

In Ziegler-Natta catalysts the structures of the active components are still obscure [1]. Only indirect structural evidence is available and only the structures of less active similar complexes are known [2]. The fact that the most active catalysts are heterogeneous makes structural studies more difficult.

For the propadiene polymerization a homogeneous, very active nickel acetylacetonate-based catalyst [3] is used, which is as active as a catalyst based on NiCl_2 or NiBr_2 [4]. By means of infrared spectroscopy [4, 5] and kinetic measurements [5, 6], indirect information could be obtained about the structure of the catalytically active species.

Infrared spectroscopy [4] showed that in the reaction of $\text{Ni}(\text{acac})_2$ + C_3H_4 with $(i\text{-Bu})_3\text{Al}$, the formation of $\text{Al}(\text{acac})_3$ is observed up to $\text{Al}/\text{Ni} = 2/3$ and that of $(i\text{-Bu})_2\text{Al}(\text{acac})$ up to $\text{Al}/\text{Ni} = 2$. The last compound is an indifferent by-product of the catalyst formation [6]. The $i\text{-Bu}$ -groups exchanged for the acac -group are simultaneously released as isobutene, and no isobutane is detected. For $\text{Al}/\text{Ni} \leq 2$, bis- π -allylnickel may possibly be formed [4]. Kinetic measurements [6] showed that for $\text{Al}/\text{Ni} > 2$ a bimetallic Ni-Al complex is formed. Because π -allylnickel complexes have low IR extinctions, NMR experiments were performed to elucidate the struc-

ture of both complexes at $Al/Ni \leq 2$ and $Al/Ni > 2$. As the NMR experiments did not give the expected results, possibly because of paramagnetic nickel species, ESR measurements were also performed.

Experimental

The reactions were carried out as described previously [4]. The solvents used were benzene, toluene, D6-benzene, and D8-toluene. For NMR, the Ni concentration was about 0.2 molar; for ESR, Ni concentrations of 0.2 and 0.02 molar were used.

The NMR spectra were recorded on a 60 Mc Varian Em 360 NMR spectrometer and on a 100 Mc Varian XL-100 NMR spectrometer. Tetramethylsilane was used as internal standard. The ESR spectra were recorded on a X-band Varian-E ESR spectrometer.

Results and discussion

NMR results

In Table 1 the NMR absorptions of the pure compounds and of the catalyst mixtures are shown. These results confirm the conclusions from IR spectroscopy [4]. At $Al/Ni \leq 2$ we detected $Al(acac)_3$, at $Al/Ni > 2$, $(i-Bu)_2Al(acac)$ and isobutene are present and a smaller amount of isobutane*. Furthermore it was found, in accordance with Kroll and Naegele [10], that $Al(acac)_3$ and $(i-Bu)_3Al$ react rapidly with each other, forming $(i-Bu)_2Al(acac)$. At a ratio $i-Bu/acac < 2$, $Al(acac)_3$ and $(i-Bu)_2Al(acac)$ were observed and for $i-Bu/acac > 2$, $(i-Bu)_2Al(acac)$ and $(i-Bu)_3Al$. With large quantities of $(i-Bu)_3Al$ (e.g. $i-Bu/acac = 10$) added to $Al(acac)_3$ or $Ni(acac)_2$ the NMR spectrum showed new absorptions, which are probably due to a reaction product of the $i-Bu$ -group with the $acac$ -group, see refs. 10 and 11

Bis- π -allylnickel, σ -allylnickel and 1,2,1,2-polypropadiene were not detected. It was most surprising that it was impossible to detect either any nickel complex or the compound formed from the propadiene added. The reaction between bis- π -allylnickel and $(i-Bu)_3Al$ [5] showed a dependence on the Al/Ni ratio. At $Al/Ni = 2/3$ some bis- π -allylnickel was still present. At $Al/Ni = 2$ the bis- π -allylnickel absorptions disappeared completely and no other absorptions except those from $(i-Bu)_3Al$, isobutene and isobutane could be detected. In this case it also was impossible to detect which nickel complex was formed.

*This was also present in blank experiments and is possibly due to the reaction of $(i-Bu)_3Al$ with impurities or OH-groups of the glass tube.

The starting material $\text{Ni}(\text{acac})_2$ dissolved in benzene or toluene gave no NMR (^1H or ^{13}C) spectrum either. Even up to + or - 80 ppm relative to tetramethylsilane no signals were observed, in contrast with results reported in ref. 11a. Magnetic susceptibility measurements showed that this complex is paramagnetic [12]. As the nickel-catalyst complexes did not give ^1H NMR spectra either, it is likely that they are paramagnetic too.

To make sure that we were able to measure the ^1H NMR spectra of paramagnetic compounds with our equipment, we tried $\text{Co}(\text{acac})_2 \cdot 2 \text{ pyr}$. This complex showed broad signals at -3 ppm, +10 ppm and 23 ppm, unlike those found by Eaton [11a].

ESR results and discussion

In earlier measurements [6] no ESR absorptions were detected between 0 °C and 25 °C. If the preparation of the catalyst mixture was not performed with enough care, or if $\text{Ni}(\text{acac})_2$ and $(i\text{-Bu})_3\text{Al}$ are added together in the absence of propadiene, a broad signal near $g = 2.2$ ($\Delta H_{p-p} = 2500$ Gauss) (see Fig. 1) is found, which is probably due to finely divided nickel metal [13] as a decomposition product. At room temperature no ESR signal is detected, which may be due to line broadening. Thus we attempted to detect the paramagnetic Ni complex by performing measurements at low temperature on a glassy solution. At -160 °C ESR absorptions were indeed observed. The results at different Ni and Al concentrations, reaction times and temperatures are presented in Table 2. $\text{Ni}(\text{acac})_2$ in toluene did not show an ESR spectrum even at -160 °C.

As shown earlier [4] at ratios $\text{Al}/\text{Ni} \leq 2$ a yellow C_1 complex is formed, which does not give a measurable ESR signal, even when the complex is prepared at room temperature and measured at temperatures between 25 °C and -160 °C.

Preparing the C_1 complex at low temperature (-80 °C) makes no difference. To prove that the complexes still contain Ni we decomposed them by raising the temperature or adding air. In agreement with earlier observations [4] a large ESR absorption at $g = 2.2$ was found ($\Delta H_{p-p} = 2500$ gauss) (see Fig. 1 spectrum 2). The same was found for the reaction between $\text{Ni}(\text{acac})_2$ in $(i\text{-Bu})_3\text{Al}$ without propadiene (see spectrum 1). The yellow C_1 complex must be paramagnetic, because otherwise we could have measured the NMR spectrum (see Table 1).

At Al/Ni ratios above 2, the red C_2 complex is formed at room temperature which gives no measurable ESR absorption at 21 °C, nor could an NMR spectrum be measured. If we used bis- π -allylnickel instead of $\text{Ni}(\text{acac})_2$ no measurable NMR spectrum is present either. Measuring the C_2 complex at low temperature (between -80 °C and -160 °C), signals at $g = 2.18$ and $g = 2.06$ are detected. The signal found at $g = 2.18$ is less broad than the signal at $g = 2.2$ from the decomposed complexes (see spectrum 3).

On preparing the red C_2 complex at low temperature -80 °C, unexpected results were obtained. Measuring the ESR spectrum at -160 °C we found two absorptions, a small one at $g = 2.49$ and one at $g = 2.06$ (see

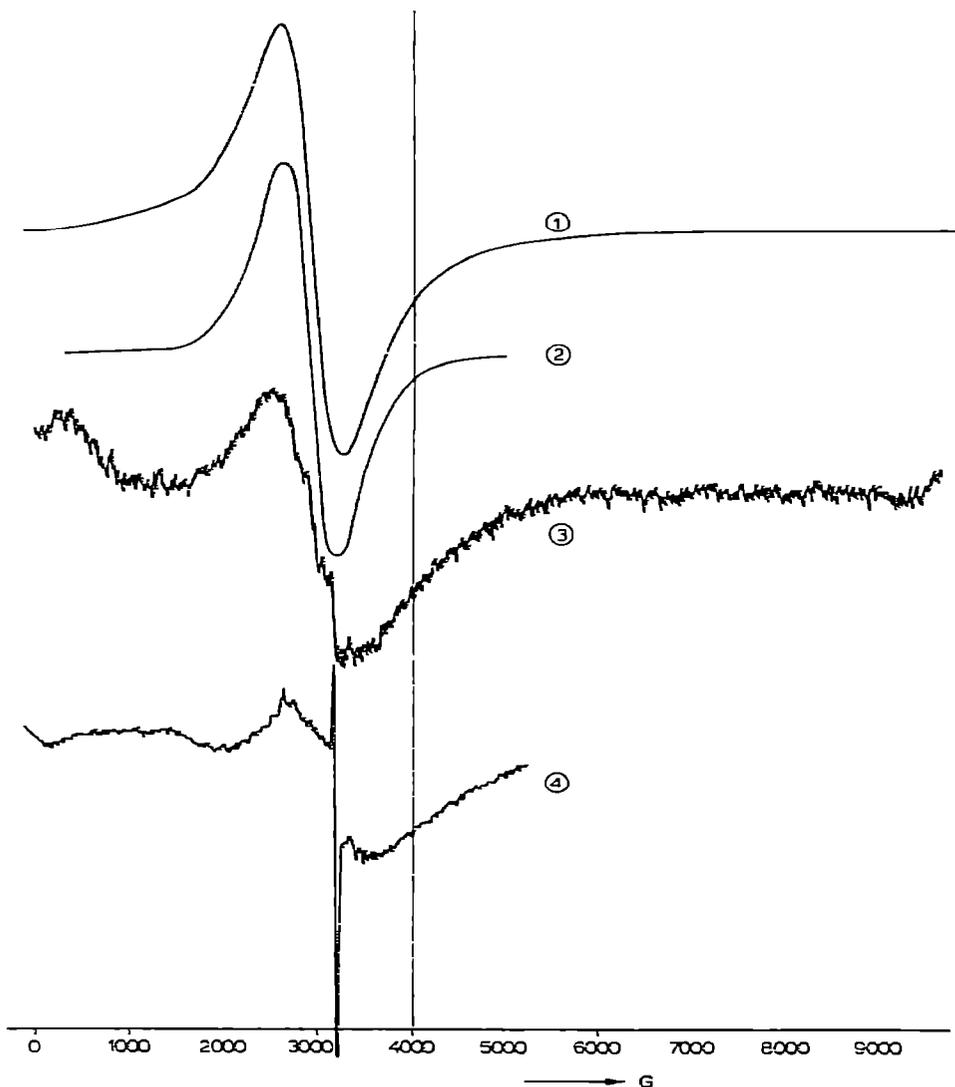


Fig. 1. ESR adsorptions in the reaction mixtures of the catalyst system $\text{Ni}(\text{acac})_2$, C_3H_4 , $(i\text{-Bu})_3\text{Al}$. Spectrum 1: Reaction product between $\text{Ni}(\text{acac})_2$ and $(i\text{-Bu})_3\text{Al}$ = 1:8; reaction at 25°C ; $C_{\text{Ni}} = 0.2 \text{ mol l}^{-1}$, receiver gain: 4×10^2 . Spectrum 2: Decomposition of the catalyst complex after 2 days, $\text{Ni}(\text{acac})_2$: C_3H_4 : $(i\text{-Bu})_3\text{Al}$ = 1:6:10 at 25°C , $C_{\text{Ni}} = 0.2 \text{ mol l}^{-1}$; receiver gain: 2.5×10^2 . Spectrum 3: Reaction product of $\text{Ni}(\text{acac})_2$, C_3H_4 : $(i\text{-Bu})_3\text{Al}$ = 1:60:20; reaction at 21°C , spectrum at -160°C , $C_{\text{Ni}} = 0.02 \text{ mol l}^{-1}$, receiver gain: 10^4 . Spectrum 4: Reaction product of $\text{Ni}(\text{acac})_2$: C_3H_4 : $(i\text{-Bu})_3\text{Al}$ = 1.6:20; reaction at -80°C , spectrum at -160°C ; $C_{\text{Ni}} = 0.02 \text{ mol l}^{-1}$; receiver gain: 10^3 .

spectrum 4) which could be g_2 and g_1 of a Ni(I) species according to literature [13]. The intensities of these absorptions depend on the concentrations of $(i\text{-Bu})_3\text{Al}$, $\text{Ni}(\text{acac})_2$ and on the Ni/Al ratio, temperature and time.

TABLE 2

ESR absorptions in the reaction mixture; of the catalyst system $\text{Ni}(\text{acac})_2$, C_3H_4 , $(i\text{-Bu})_3\text{Al}$ at different temperatures

[Ni] (mol l ⁻¹)	$\text{Ni}(\text{acac})_2 \cdot \text{C}_3\text{H}_4 \cdot$ $(i\text{-Bu})_3\text{Al}$	T_r (°C)	Time (min)	T_{sp} (°C)	Ni^+ (g_{\perp})	Ni^+ (g_{\parallel})	Ni^+ (g_{iso})	Ni metal	Ni^{2+}
0.2	1 — —			25/—160	no absorptions				
0.2	1 0 4	-80	10	25/—160				2.24	
0.2	1.3 2	-80	10/20	25/—160	no absorptions				
0.2	1.6 20		5	-160/—80		2.06			2.18
			21	21	no absorptions				
0.2	1.3 4	-80		-160/—100	2.46	2.06			
				0/ 25		2.06	2.09		
			8	-160	2.51	2.08			
			days	25			2.09		
0.02	1.30 4	-80		-160	2.49	2.06			
extra added $\text{Ni}(\text{acac})_2$ at	1.30 1,3	-80		-160	no absorptions				
0.02	1.30 4	-80		-160				2.24	
0.02	1.60 20	-80		-150	2.47	2.06			
				-25	no absorptions				
				-160	2.47	2.06			
			24 h	25	no absorptions				
			36	25				2.19	
			days						
0.02	1.30-100	-80	10	-160	2.47	2.06			
			100	-21	no absorptions				
			135	-160	2.49	2.06			
			36	+21	no absorptions				
			days						

T_r = temperature of reaction, T_{sp} = temperature of measurement

With increasing concentration of $(i\text{-Bu})_3\text{Al}$ and/or $\text{Ni}(\text{acac})_2$ the signal intensity increases if $\text{Al}/\text{Ni} > 2$. Adding enough $\text{Ni}(\text{acac})_2$ to the reaction mixture so that Al/Ni becomes < 2 causes the $\text{Ni}(\text{I})$ signals to disappear, which means that the formation is reversible. The intensity of the signal decreases with reaction time and also when the temperature is raised. At room temperature a spectrum could only be recorded at high $\text{Ni}(\text{acac})_2$ concentration (0.2 m). The temperature at which the reaction takes place also influences the intensity of the signal. Only an extremely small signal is observed if the preparation is performed at room temperature.

Another striking observation is that the anisotropic signal at -160°C ($g_{\perp} = 2.06$, $g_{\parallel} = 2.49$) changes into an isotropic one with $g = 2.09$ at -96°C . This cannot be due to the same complex because then an average g -value of 2.20 would have been expected.

A possible explanation of these observations is that in the reaction between $\text{Ni}(\text{acac})_2$, C_3H_4 and $(i\text{-Bu})_3\text{Al}$ at low temperature, an intermediate $\text{Ni}(\text{I})$ complex is formed and frozen in, giving an anisotropic ESR spectrum.

with $g_1 = 2.49$, $g_1 = 2.06$. At -96°C , the melting point of toluene, a different Ni(I) complex with $g = 2.09$ is formed. This may be due to the coordination of an extra C_3H_4 molecule. With time and at higher temperatures this Ni(I) complex disappears. At room temperature a Ni(II) complex is formed which can be detected at -160°C at $g = 2.18$ [14].

From the results obtained it is not yet clear whether the formation of the Ni(I) complex at low temperature is an intermediate in catalyst formation or only a by-product of the low temperature reaction. The experiment with extra $\text{Ni}(\text{acac})_2$ and the preparation of the catalyst at room temperature suggest that the Ni(I) species measured at low temperature could be an intermediate. If this is the case, this Ni(I) complex is formed by decomposition of the $\text{Ni}(\text{i-Bu})_2$ [4] formed initially. At low temperature this complex reacts more slowly than at room temperature.

It is difficult to imagine a mechanism of catalyst formation in which first the Ni(II) from $\text{Ni}(\text{acac})_2$ is reduced to Ni(I) and then re-oxidized to an unknown Ni(II) complex. It is shown however by [15] that metal atoms behave totally different compared to finely divided metal particles in reactions with olefins. Therefore in the presence of C_3H_4 it might be possible that part of the Ni(II) is reduced via Ni(I) to Ni atoms which can give, *via* oxidative addition, a π - or σ -allylnickel(II) complex [16 - 21].

It is however still possible that at room temperature a σ -allyl Ni complex is formed via Ni-H bonds, as proposed earlier [4].

The detection of a small amount of Ni(I) gives the impression that here also part of the nickel complex is formed *via* reduction. As pointed out in [6], both mechanisms can result in the same Ni complexes. On the basis of the results presented, one cannot decide between these possibilities; probably both are taking place depending on the reaction temperature.

The difference in reactivity between $\text{Ni}(\text{acac})_2$ and $\text{Ni}(\text{acac})_2 + \text{C}_3\text{H}_4$ lies in the possibility that in the former the Ni atoms form metal particles which do not react with C_3H_4 [4]. Only if the C_3H_4 is added directly after $(\text{i-Bu})_3\text{Al}$ can part of the nickel be saved for catalyst formation [4].

In the second case, the presence of C_3H_4 prevents the formation of Ni particles by forming Ni(II) complexes *via* oxidative addition [21]. This Ni(II) complex must then form an octahedral or tetrahedral complex by reaction with $(\text{i-Bu})_3\text{Al}$, which can explain the ESR results.

A Ni(0) complex is excluded because it should not be paramagnetic and thus NMR spectra should be observable, as shown for example by $\text{Ni}(\text{PPh}_3)_2$ [22]. The presence of a Ni(II) square planar complex is ruled out for the same reason.

The fact that at room temperature no paramagnetic complex can be detected may have three causes:

- (i) broadening of the signal due to fast conformational changes,
- (ii) the existence of several Ni(II) complexes with different coordination shells in equilibrium with each other;
- (iii) a large zero field splitting, which has been observed earlier for Ni complexes [14].

If reduction of Ni(II) plays a role in catalyst formation it must be possible to make a nickel catalyst electrochemically for propadiene polymerization. By using Al electrodes we indeed succeeded in preparing nickel and cobalt catalysts for propadiene polymerization [6].

Conclusions

(i) In the catalyst system Ni(acac)₂, C₃H₄, (i-Bu)₃Al, for the polymerization of propadiene, the presence of an (intermediate) Ni(I) complex ($g_1 = 2.49$, $g_1 = 2.06$) is observed by ESR measurements at low temperature (−160 °C).

(ii) At the melting point of toluene (−96 °C) this Ni(I) complex is converted into another Ni(I) complex with $g = 2.09$, possibly due to the coordination of an extra C₃H₄ molecule.

(iii) At room temperature the active C₂ complex is a paramagnetic octahedral or tetrahedral Ni(II) complex, which at −160 °C shows an ESR signal with $g = 2.18$.

(iv) NMR spectra of the active catalyst are not observed because of its paramagnetism.

Acknowledgements

We thank J. M. Visser and M. Perik for measuring the NMR and ESR spectra, respectively, and B. Nieuwenhuijse for his help in the interpretation of the ESR spectra

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