AN INVESTIGATION OF THE CATALYTIC SYSTEMS $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, C_3H_4 , $(\text{iBu})_3\text{Al}$ FOR THE POLYMERIZATION OF PROPADIENE

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Summary

In the catalytic systems $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$, C_3H_4 , $(\text{iBu})_3\text{Al}$, the active catalyst is formed *via* exchange of acac for iBu groups. From kinetic measurements it follows that $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ give the same catalyst with a polymerization rate constant $k_p = 29 \pm 3 \text{ min}^{-1}$ at relatively high Al/Co ratios (≥ 30). At low Al/Co ratios (≤ 0.05) a less active catalyst is formed with a polymerization rate constant $k_p = 3.6 \pm 0.4 \text{ min}^{-1}$, possibly due to the acac groups remaining in the catalytically active complex. The kinetic results show that the highly active cobalt catalyst is formed *via* an equilibrium with $(\text{iBu})_3\text{Al}$ which indicates that the active catalyst complex is bimetallic.

Introduction

During the last ten years there has been much research on the mechanism and kinetics of the polymerization of conjugated diolefins with homogeneous Ziegler-Natta catalysts [1]. Less research has been done on the polymerization of cumulated diolefins. The first were studies by Baker [2] and by Havinga [3]. Otsuka [4] showed that π -allyl nickel complexes are catalysts for the propadiene polymerization. Van den Enk and van der Ploeg [5] found that catalytic systems based on a transition metal, propadiene, and tri-isobutylaluminium, are even better catalysts. Van Ommen *et al.* [6] showed that bis- π -allylnickel, which itself is already a catalyst, can be activated by tri-isobutylaluminium to the same activity as the $\text{Ni}(\text{acac})_2$ -based catalyst. The highest activity for the propadiene polymerization was observed for the analogous system based on cobaltdiacetylacetonate [7].

Cobaltacetylacetonate can be obtained as a Co^{II} and as a Co^{III} compound. It is of interest to know if the lowest valence state gives the highest activity, as normally found for titanium containing Ziegler catalysts [1].

To reach a better understanding of the catalytically active species in the cobalt catalyst, two kinds of experiments were performed:

(i) Infrared investigations to obtain more information about the formation and structure of the catalytically-active cobalt species.

(ii) Rate measurements to compare the Co^{II} and Co^{III} catalysts and to obtain an insight into the mechanisms of the catalyst formation and of the polymerization of propadiene.

Experimental

Materials

The $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ (Baker) used in this work are purified by sublimation at 190°C . The tri-isobutylaluminium (Schuchardt, purity 93 - 95%) is used without further purification. The toluene (Merck, pro analysis) is dried on molecular sieves (Union Carbide, 13X) and degassed and saturated with purified nitrogen. The nitrogen used is freed from oxygen with a B.T.S. catalyst (BASF) and dried with molecular sieve 13X. The O_2 and H_2O contents are less than 1 p.p.m. each. Propadiene (L'air liquide, purity 99%) is freed from O_2 and H_2O by bubbling through tri-isobutylaluminium.

Procedures

The method used for the infrared measurements has been described earlier [6]. The polymerizations are performed in the same way as described by van den Enk and van der Ploeg [5].

The kinetic measurements are carried out in a glass reactor which is dried at 120°C and assembled while still hot. The reactor is evacuated and filled with purified propadiene. The $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$ solutions in toluene are injected *via* a serum cap and saturated with propadiene. Then the tri-isobutylaluminium is injected with a micro syringe (accuracy about 0.1 μl). The polymerization started at once and is followed by measuring, with a gas buret containing a teflon plunger with a mercury seal [8], the amount of propadiene consumed as a function of time.

The determination of the rate of dissolution of propadiene showed us that there was no limitation from this side. The Hatta number is $\sqrt{k_r D}/k_{\text{solv}} \cong 10^{-4}$ (k_r = reaction rate constant, D = diffusion constant of propadiene in benzene and toluene, and k_{solv} = rate constant of dissolution [9]). This number must be larger than 0.3 for the dissolution process to influence the reaction rate. The solubility of propadiene in toluene at -3.5°C was found to be 4 ± 0.4 mole l^{-1} .

The pressure is kept constant at 1 atm and the temperature at $-3.5 \pm 0.1^\circ\text{C}$. The heat of polymerization is very large and therefore it is difficult to control the temperature of the reactor at room temperature. At -3.5°C the cooling devices used made a heat transfer possible at a rate which enabled us to control the temperature in the reactor during the polymerization within 0.1°C . The reaction orders are determined by using different concentrations of cobalt and aluminium. The total reaction volume is 5 ml,

the total reaction time amounts to 90 min. The polymer is isolated in the way described by van den Enk and van der Ploeg [5] and is characterized by means of infrared spectroscopy.

Results and discussion

(a) *Infrared investigation of the catalyst*

When $(iBu)_3Al$ is added to $Co(acac)_2$ or $Co(acac)_3$, metallic cobalt, isobutene, and isobutane are formed. Depending on the Al/Co ratio, the formation of $Al(acac)_3$ (1 288 (s) 930 (s) 490 (s) cm^{-1}) for $Al/Co^{II} \leq 2/3$ or $Al/Co^{III} \leq 1$, and of $(iBu)_2Al(acac)$ (1 294 (s) 935 (s) 500 (w) cm^{-1}) for $Al/Co^{II} > 2/3$ or $Al/Co^{III} > 1$ was observed from their characteristic infrared vibrations. This is in accordance with the observations of Kroll and Naegle [10].

For $Co(acac)_3$ this is the same as found by Pasynkiewicz [11] using Me_3Al and by us in the case of $Ni(acac)_2$ [6]. From the measurements of Pasynkiewicz [11] and Tamai [12] it became clear that $Co(acac)_3$ (1 288 - 466 cm^{-1}) is first reduced by aluminium alkyls to $Co(acac)_2$ (1 260 - 425 cm^{-1}) before all the acac groups are exchanged.

In the presence of propadiene the same phenomena are observed for $Co(acac)_2$ and 3 as for $Ni(acac)_2$ [6]. The Al compounds react in the same way as described above in the absence of C_3H_4 . From the spectra it follows that C_3H_4 reacts; its specific absorptions (1 945 (s) 835 (s) cm^{-1}) disappear and vinylidene absorptions (1 625 (s) 890 (s) cm^{-1}) appear. This also happens for a ratio of $C_3H_4/Co = 2$ or 3. Compensation of $Al(acac)_3$ respectively $(iBu)_2Al(acac)$ shows only the vinylidene absorptions. After evaporation of the solvent and re-resolution, the vinylidene group was still present, while in the evaporated benzene or toluene only isobutene could be detected. A possible explanation for the observed phenomena is that the hydride group is kept in the Co-complex and forms a σ -allyl group by insertion of the C_3H_4 [13]. π -allyl absorptions are not detected, possibly due to their low intensity. A similar insertion is found for C_4H_6 in the Co-Cl bond of $CoCl(PPh_3)_3$ [16]. Also, the formation of Co-H complexes [14] *via* β -H abstraction [15] in Co- iBu complexes is known. For instance $CoH_3(PPh_3)_3$ [17] can be formed from $Co(acac)_2$ or 3 provided PPh_3 is present as a stabilizing base. Probably, in our case, the C_3H_4 has the same function, followed by its insertion which gives an even more stable complex. All reactions are carried out under N_2 . From the literature [18] it is known that in the presence of PPh_3 , nitrogen complexes are formed. In the presence of C_3H_4 , however, no absorptions of bound N_2 are present, so in this case a N_2 complex is not formed.

(b) *Preliminary polymerization experiments and polymer characterization*

In Table 1 and Fig. 6 one can see that for the polymerization to take place there is no minimum Al/Co ratio larger than 0.01, in contrast to what

TABLE 1

Polypropadiene obtained with different Co(acac)₂-(iBu)₃Al ratios

Exp.	Co(acac) ₂ (mole l ⁻¹)	Co:Al:C ₃ H ₄ (initial)	T (°C) (reaction temp.)	Reaction time (h)	Solvent	Type polymer (polypropadiene)	m.pt. (°C) DTA* m.p.**,**	Crystallinity
I	0.04	2:1:60	40-60	2	toluene	1,2,1,2	- 95	+
II	0.02	5:1:60	40-60	2	benzene	1,2,1,2	95 { 94-105 } 112 { 127 }	+
III	0.002	1:1:600	40-60	2	toluene	1,2,1,2	112 { 119-123 } 126 }	+
IV	0.002	2:1:4800	-10	2	toluene	1,2,1,2	116 { 123-126 } 126 }	+
V	0.002	2:1:3600	0	16	toluene	1,2,1,2	126 { 123-126 } 126 }	+

*Differential thermal analysis.

**Melting point microscope.

Fig. 1. Infrared spectrum of 1,2,1,2-polypropadiene. $C_{Co} = 22 \times 10^{-4} \text{ mole l}^{-1}$, $Al/Co = 5$, $T = -3.5^\circ\text{C}$.

was found for nickel [7], where Al/Ni must be larger than 2. Neither the separate reactants of the catalyst system, nor combinations of $Co(acac)_2$ or 3 and $(iBu)_3Al$, are capable of polymerizing the propadiene added. Obviously, the presence of propadiene during the catalyst formation is essential. This is in agreement with the observations of van den Enk and van der Ploeg [5, 7].

There is no solvent effect if we change from toluene to benzene. The polymers obtained from either the Co or the Ni system have the same structure, melting point and crystallinity. The structures of the polymers are determined from their infrared spectra (see Fig. 1) and they contain only the 1,2,1,2-structural element [7, 19].

1,2,1,2-polypropadiene

From product analysis we found that aside from the polymer no oligomers were formed.

(c) Rate measurements

Figure 2, giving representative experimental results, shows that the rate of polymerization is constant for a period of at least 60 min. Only at very low $Co(acac)_3$ concentrations is the initial rate very high, but after 5 - 10 min it decreases to a constant value (see Fig. 3), after 60 min a small further decrease in rate is observed.

For $Co(acac)_2$ the same results were obtained. The amount of propadiene taken up in the first 10 min (extrapolating the rate between 10 and 60 min to $t = 0$) corresponds with the amount of propadiene (about 15 ml) expected to dissolve in the 0.2 ml of tri-isobutylaluminium added. For the rate, when plotted as a function of the concentrations of the catalyst compo-

Fig. 2. The volume of C_3H_4 consumed as a function of time: $C_{Co}^{III} = 28.4 \times 10^{-4}$ mole l^{-1} ; $C_{Al} = 1.600 \times 10^{-4}$ mole l^{-1} , $T = -3.5^\circ C$.

Fig. 3. The volume of C_3H_4 consumed as a function of time: $C_{Co}^{III} = 1.6 \times 10^{-4}$ mole l^{-1} ; $C_{Al} = 1.600 \times 10^{-4}$ mole l^{-1} , $T = -3.5^\circ C$.

Fig. 4. The rate of the C_3H_4 polymerization as a function of Co^{II} and Co^{III} concentration. $C_{Al} = 1600 \times 10^{-4} \text{ mole l}^{-1}$, $T = -3.5^\circ C$. $\circ$ for Co^{II} and $\times$ for Co^{III} .

nents, the slope of the straight line measured between 10 and 60 min was used.

If these rates are plotted for constant and relatively high ($1600 \times 10^{-4} \text{ mol l}^{-1}$) $(iBu)_3Al$ concentrations as a function of the concentration of Co^{II} and Co^{III} (see Fig. 4), a first order dependence on cobalt is found, and Co^{II} and Co^{III} give almost identical rates at the same concentrations. The slopes of the two lines are, respectively, $31 \pm 3 \text{ min}^{-1}$ for Co^{II} and $27 \pm 3 \text{ min}^{-1}$ for Co^{III} . These values were calculated with a least-squares method and both have an uncertainty of 10%. Within the experimental accuracy, the rate constants for Co^{II} and Co^{III} are equal in the measured concentration range. From this we conclude that Co^{II} and Co^{III} give the same catalyst when larger amounts of $(iBu)_3Al$ are present, as it is improbable that catalysts with Co present in different valencies would give the same rate of polymerization.

From the plot of the polymerization rate (see Fig. 5) as a function of the $(iBu)_3Al$ concentration at relatively low ($22 \times 10^{-4} \text{ mole l}^{-1}$) but constant Co^{III} concentration, we find that there is a decreasing dependence on the $(iBu)_3Al$ concentration. At high Al concentrations, the order in $(iBu)_3Al$ becomes zero. This can be explained by the formation of the active catalyst *via* an equilibrium between Co- and Al-containing species.

In Fig. 6 we see that when a relatively high Co^{III} concentration ($1500 \times 10^{-4} \text{ mole l}^{-1}$) is used, the dependence on the Al-concentration is first order in Al over the concentration range used. In this case, the slope gives a polymerization rate constant, $k_p = 3.6 \pm 0.4 \text{ min}^{-1}$. As this is about 8 times smaller than with an excess Al, this means that a different catalyst is probably formed in this case.

(d) Discussion of the kinetic results

From Fig. 5, which gives the rate as a function of the Al concentration, we get the impression that an equilibrium is involved in the formation of the

Fig. 5. The rate of the C_3H_4 polymerization as a function of Al concentration. $C_{Co}^{III} = 22 \times 10^{-4} \text{ mole l}^{-1}$, $T = -3.5^\circ C$.

Fig. 6. The rate of the C_3H_4 polymerization as a function of Al concentration. $C_{Co}^{III} = 1500 \times 10^{-4} \text{ mole l}^{-1}$, $T = -3.5^\circ C$.

active catalyst. From Fig. 5, k_p (polymerization rate constant) and K_A (equilibrium constant) can be calculated if it is assumed that:

(i) the rate of the polymerization is first order in the concentration, C^* , of the active catalyst [18, 19]

$$r_p = k_p C^* \quad (1)$$

(r_p is the rate of polymerization);

(ii) the active catalyst complex is formed *via* an equilibrium between the cobalt component (denoted by Co) and $(iBu)_3Al$ (denoted by Al)

This gives:

Fig. 7. Test of kinetic model (see text).

$$K_A = \frac{C^*}{(Co - C^*)(Al - C^*)} \quad (3)$$

If $Al \gg C^*$ we find:

$$K_A = \frac{C^*}{(Co - C^*)Al} \quad (4)$$

Combination of eqns. (1) and (4) yields

$$1/Al = K_A k_p \frac{Co}{r_p} - K_A \quad (5)$$

Plotting the data according to this equation gives a straight line (see Fig. 7), which justifies our assumptions. A straight line is not obtained, for example, if a second order in Al is assumed. From this we find $K_A = 27 \text{ l mole}^{-1}$ and $k_p = 29 \pm 3 \text{ min}^{-1}$.

With this K_A value we can calculate that in the presence of an excess of Al ($Al/Co \geq 30$) all Co present is converted to C^* . This is in accordance with the observed first order in Co (Fig. 4), with the same rate constant as calculated above. Summarizing:

Co^{III} , k_p from Fig. 5: $29 \pm 3 \text{ min}^{-1}$

Co^{III} , k_p from Fig. 4: $27 \pm 3 \text{ min}^{-1}$

Co^{II} , k_p from Fig. 4: $31 \pm 3 \text{ min}^{-1}$

Within the experimental uncertainty of 10%, these rate constants are equal in the measured concentration ranges.

The experimental results given in Fig. 6 have been obtained under conditions such that the Co^{III}/Al ratio ≥ 20 . If we suppose that the K_A value is the same, it can be calculated that all the Al added is converted to

active catalyst. So a first order in Al is expected, as is indeed observed. But the k_p value is found to be 3.6 min^{-1} , which is quite different from the k_p values found for an excess of Al ($\text{Al/Co} \geq 3$). This is discussed in the next Section.

Discussion of the mechanism of the catalyst formation

Going from low to high Al concentrations, the picture of the catalyst formation is now as follows (see Scheme 1).

When $\text{Co/Al} \geq 20$, $(\text{iBu})_3\text{Al}$ exchanges all its iBu -groups for acac -groups, forming $\text{Al}(\text{acac})_3$ and a Co-complex which still contains acac -groups (Scheme 1, complex A). The Co-complex is stabilized by C_3H_4 under the formation of π - or σ -allyl complexes. This complex is able to polymerize C_3H_4 to 1,2,1,2-polypropadiene with a k_p of $3.6 \pm 0.4 \text{ min}^{-1}$. The equilibrium of the reaction between $\text{Co}(\text{acac})_2$ and $(\text{iBu})_3\text{Al}$ is almost completely to the side of the active complex, in agreement with the observation that the reaction is first order in $(\text{iBu})_3\text{Al}$.

When $\text{Al/Co} \geq 3$, all acac -groups are transferred from the cobalt to aluminium and $(\text{iBu})_2\text{Al}(\text{acac})$ is formed as a by-product [6]. It is remarkable that the same activity is found for $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$, which strongly suggests that the catalytically active complex is the same in both cases. In the i.r. spectra we only found absorptions pointing to a σ -allyl group ($1625 - 890 \text{ cm}^{-1}$). This is the same as found for $\text{Ni}(\text{acac})_2$, C_3H_4 , $(\text{iBu})_3\text{Al}$ [6]. It is remarkable that the spectra of the Ni and Co catalyst systems are practically identical. From ref. 11 it is known that reduction of $\text{Co}(\text{acac})_3$ occurs *via* $\text{Co}(\text{acac})_2$. If more $(\text{iBu})_3\text{Al}$ is added, the acac groups are stripped from $\text{Co}(\text{acac})_2$ (see Scheme 1) according to the i.r. spectra, and $(\text{iBu})_2\text{Co}$ is formed as an intermediate *via* β -H abstraction and/or C_3H_4 insertion into a Co-iBu or a Co-H bond. A π - or σ -allyl Co-complex is then formed (Scheme 1 complex B). Börneman [22] states that $\text{Co(II)} (\pi\text{-allyl})_2$ complexes are not stable, and disproportionate to $\text{Co(III)} (\pi\text{-allyl})_3$ and Co(I) species which, in the absence of stabilizing ligands, produces $\text{Co}^{(0)} \downarrow$. In the presence of C_3H_4 , no precipitate is formed. Further, the tris allyl cobalt complex is very unstable, as shown by the fact that above -50°C tris-allyl-cobalt disproportionates [22]. On the contrary our catalyst at -3.5°C must be rather stable, because kinetic measurements show that for at least 90 min no decrease in activity occurs. From these results we conclude that the catalyst complex is a π - or σ -allyl cobalt species which is stabilized by propadiene and/or $(\text{iBu})_3\text{Al}$ [22]. A possible structure explaining all the experimental observations is shown in Scheme 1, complex C*. Cobalt is octahedrally surrounded in a binuclear complex, and activated and perhaps stabilized by $(\text{iBu})_3\text{Al}$. Propadiene also stabilizes the complex and polymerization can proceed by the coordination and insertion of C_3H_4 . The complex also contains $-\text{C}=\text{CH}_2$ groups as shown by the i.r. spectra. The bimetallic active catalyst must be formed *via* an equilibrium, $K_A = 27 \text{ l mole}^{-1}$, as shown

Scheme 1

Al/Co < 2 or 3

A

Al/Co = 2 or 3

Al/Co > 2 or 3

No propadiene present

Propadiene present

These complexes are denoted by B

Scheme 1 (*continued*)

Kinetics give

A possible structure for C^* is

by the kinetic measurements. The higher activity of this bimetallic complex is probably due to the Lewis acidity of $(iBu)_3Al$ [6].

Going from $Al/Co \geq 0.01$ to $Al/Co = 90$, there must be a transition from $k_p = 3.6 \text{ min}^{-1}$ to $k_p = 29 \text{ min}^{-1}$. If this difference is due to acac-groups remaining in the catalyst complex, the differing number of acac-groups in $Co(acac)_2$ compared with $Co(acac)_3$ would lead to a difference in k_p for $Al/Co < 3$. The lower rate for $Co/Al \geq 20$ may also be due to the impossibility of forming a bimetallic complex, because all the $(iBu)_3Al$ has reacted to form $Al(acac)_3$.

This transition in k_p will be the subject of a future publication.

Conclusions

(i) The catalyst in the system $Co(acac)_{2 \text{ or } 3}$, $(iBu)_3Al$ is formed by exchange of acac- for iBu-groups. The Co-iBu or (after release of C_4H_8) Co-H bonds formed in this way are stabilized by propadiene under the formation of a π - or σ -allyl bond.

(ii) At high Al concentrations ($Al/Co > 3$), a highly active, bimetallic, Co-Al catalyst is formed. $k_p = 29 \pm 3 \text{ min}^{-1}$.

(iii) $Co(acac)_{2 \text{ or } 3}$ give the same catalyst in the $Co(acac)_{2 \text{ or } 3}$, C_3H_4 , $(iBu)_3Al$ systems for $Al/Co > 3$.

(iv) At low Al concentrations ($Al/Co < 0.05$) a less active catalyst is formed ($k_p = 3.6 \pm 0.4 \text{ min}^{-1}$), probably due to acac-groups remaining in the catalyst complex or to the impossibility of the formation of a bimetallic catalyst complex.

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