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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE STRUCTURE OF CERTAIN PRODUCTS OF THE INTERACTION OF ALUMINUM ALKYLS WITH TITANIUM(IV) DERIVATIVES

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Recently we reported ([1]) on the electron paramagnetic resonance spectra of the products of the interaction of triisobutylaluminum with dicyclopentadienyltitanium dichloride. Further investigation made it possible to generalize the observed regularities to other compounds and to draw certain conclusions about the structure of the reaction products. The interaction of aluminum alkyls and aluminum aryls was studied: $Al(C_2H_5)_3$; $Al(C_6H_5)_3$; $Al(iso\text{-}C_3H_7)_3$; $Al(CH_3)_3$; $Al(iso\text{-}C_4H_9)_3$; $Al(C_2H_5)_2Cl$ with titanium(IV) derivatives: $(C_5H_5)_2TiCl_2$; $(C_5H_5)_2TiBr_2$; $(C_5H_5)_2TiJ_2$.

Fig. 1

At a reagent ratio of $1:1$ in toluene solution, very similar E.P.R. signals were obtained in all cases, with a g-factor equal to 1.975. At low reagent concentrations (less than $1 \cdot 10^{-3}$ M/l) the signals have a characteristic form (Fig. 1), which can be explained by the presence of unresolved hyperfine structure. Study of the E.P.R. spectra at other Al/Ti ratios showed that all aluminum alkyls and aluminum aryls can be divided into two groups. With increasing Al/Ti ratio, in the case of $Al(CH_3)_3$, $Al(C_6H_5)_3$, and $AlCl(C_2H_5)_2$, signals I (Fig. 1) change little, whereas in the case of $Al(C_2H_5)_3$, $Al(iso\text{-}C_3H_7)_3$, and $Al(iso\text{-}C_4H_9)_3$, new signals are formed with well-resolved hyperfine structure. In these latter systems, when $Al:Ti$ is varied from $1:1$ to $\sim 20:1$, signal I (Fig. 1) is transformed into signal II (Fig. 2a), which is a doublet with a g-factor equal to 1.985. When the $Al:Ti$ ratio is increased to $\sim 50:1$ and higher, signal II undergoes further change into signal III, with a g-factor of 1.988, consisting of eight components (Fig. 3a). The form of signals II and III does not depend on the nature of the

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Fig. 2

Figure 2: Fig. 2

alkyl for the aluminum alkyls of the second group, nor on the nature of the halogen atom for the titanium halides.

The transition I → II → III was observed both when the concentration of AlR_3 was increased at constant concentration of $(C_5H_5)_2TiCl_2$, and when the concentration of $(C_5H_5)_2TiCl_2$ was decreased at constant concentration of the aluminum alkyl. This influence of the reagent ratio made it natural to suppose that the aluminum alkyls contain some identical additives, the amounts of which, as the Al : Ti ratio increases, become comparable with the amounts of the titanium derivative and which form new complexes with them.

Such additives may be hydrides, which, as is known, are readily formed in the preparation of $Al(C_2H_5)_3$, $Al(iso\text{-}C_3H_7)_3$, and $Al(iso\text{-}C_4H_9)_3$, and are absent in the cases of $Al(CH_3)_3$ and $Al(C_6H_5)_3$.

To test this hypothesis, $AlH(iso\text{-}C_4H_9)_2$ was synthesized and its interaction with $(C_5H_5)_2TiCl_2$ was studied. At an Al : Ti ratio equal to 1, a type-I signal was again observed, but already at ratios of 2 : 1 and 3 : 1 signals II and III were obtained. This leaves no doubt as to the participation of aluminum hydrides in the formation of the complexes responsible for signals II and III. The doublet II can then be explained by splitting at the hydrogen atom in a complex containing one molecule of $AlH(iso\text{-}C_4H_9)_2$.

Signal III is more complex. As can be seen from Fig. 3a, it consists of 6 lines of approximately equal intensity and two lines with an intensity 3–4 times smaller.

As we have already indicated ([1]), this hyperfine structure may be explained by the distribution of the spin density of the unpaired electron between the Al atom and two H atoms. This now finds a natural explanation in the fact that the molecule of the reaction product contains two H atoms from two molecules of aluminum hydride.

Further confirmation of the participation of hydride hydrogen in the complexes formed was provided by experiments with deuterated diisobutylaluminum hydride of composition $AlD[CH_2CD(CH_3)_2]_2$. The ESR spectra of the products of reaction of this compound with $(C_5H_5)_2TiCl_2$, corresponding to signals II and III, are shown in Figs. 2b and 3b. It can be seen that replacement of hydrogen by deuterium leads to an almost complete disappearance of the hyperfine structure in both cases.

Fig. 2

The nuclear moment of the D atom is 3.2 times smaller than the nuclear moment of the proton, and the number of lines in the case of D should be greater because of the difference in the spins of the H and D nuclei (for H, $I = \frac{1}{2}$; for D,

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$I = 1$). This should lead to a blurring of the hyperfine structure, which is indeed observed experimentally.

On the basis of these and literature data, some conclusions may be drawn about the structure of the complexes formed.

As a result of an X-ray structural analysis, Natta et al. ([2]) concluded that the product of the reaction of $Al(C_2H_5)_3$ with $(C_5H_5)_2TiCl_2$ is a compound with the structure

$$\begin{matrix} C_5H_5\backslash \\ C_5H_5/ \end{matrix} \; Ti \left(\begin{matrix} Cl \\ Cl \end{matrix} \right) Al \; \begin{matrix} /C_2H_5 \\ \backslash C_2H_5 \end{matrix} \qquad \text{(A)}$$

in which 2 chlorine atoms play the role of bridging bonds between titanium and aluminum. Such a compound contains an unpaired electron ([3]) and, apparently, is responsible for the signal I observed by us. A similar compound is evidently also obtained in the interaction of $AlH(iso\text{-}C_4H_9)_2$ with $(C_5H_5)_2TiCl_2$ at a component ratio of 1 : 1, since hydrogen evolution is then observed and the composition of the compound formed, its visible spectrum, and its ESR spectrum correspond to compound A.

With further addition of $AlH(iso\text{-}C_4H_9)_2$, no evolution of gases occurs, but the ESR spectrum and the color of the solution change. This can be expla–

by the following reactions of complex A:

$$1) \quad (C_5H_5)_2Ti \begin{matrix} Cl \\ \\ Cl \end{matrix} Al(iso\text{-}C_4H_9)_2 \rightleftarrows (C_5H_5)_2TiCl + Al(iso\text{-}C_4H_9)_2Cl \qquad \text{(B)}$$

$$2) \quad (C_5H_5)_2TiCl + AlH(iso\text{-}C_4H_9)_2 \rightleftarrows (C_5H_5)_2Ti \begin{matrix} H \\ \\ Cl \end{matrix} Al(iso\text{-}C_4H_9)_2.$$

Compound B contains hydrogen instead of chlorine in the bridging bond; cleavage at this bond also leads to the formation of a doublet in signal II. Further substitution by a similar mechanism will lead to the formation of a compound with two bridging bonds through H atoms,

$$(C_5H_5)_2Ti \begin{matrix} H \\ \\ H \end{matrix} Al(iso\text{-}C_4H_9)_2, \qquad \text{(C)}$$

which is responsible for signal III.

The observed shift of the g-factor from I to III indicates that the character of the orbital on which the unpaired electron is located changes. Apparently, in

this transition the spin density of the unpaired electron on the aluminum atom increases.

The reactions forming complexes B and C are equilibrium reactions, since the addition of an excess of $Al(C_2H_5)_2Cl$ leads to the reverse transition of signal III into signal II.

It is possible that similar products are formed in the case of insoluble systems $AlR_3 + TiCl_4$, where the absence of hyperfine structure in the observed e.p.r. spectrum ([4]) did not make it possible to draw a conclusion about the structure of the complexes.

For these systems one may assume the formation of the structure:

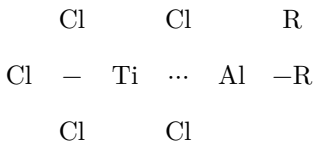

Fig. 3

However, in this case compounds of this type play the role of intermediate products, since their dissociation into AlR_2Cl and $TiCl_3$, which precipitates, evidently proceeds practically completely. This is in agreement with the fact that in the system $Al(iso\text{-}C_4H_9)_3$—$TiCl_4$ the e.p.r. signal, visible at room temperature, gradually disappears.

Of great interest is the elucidation of the catalytic activity of the observed complexes. We have found that solutions of complexes corresponding to signals I, II, III polymerize ethylene with the formation of polyethylene. During polymerization the e.p.r. spectra of the solution change in accordance with the transition III $\rightarrow$ II $\rightarrow$ I. Further study of this interesting fact may make it possible to approach the mechanism of initiation of catalytic polymerization.

Experimental Part

$Al(CH_3)_3$ was prepared by prolonged boiling of CH_3I with an alloy of Al (40%) and Mg (60%), followed by purification of the product by double distillation in vacuum (m.p. 15°). $Al(C_6H_5)_3$ and $Al(iso\text{-}C_3H_7)_3$ were prepared via organomercury compounds according to the scheme:

$$RBr \xrightarrow{NaHg} R_2Hg \xrightarrow{Al} R_3Al.$$

Purification of $Al(C_6H_5)_3$ was carried out by double recrystallization from xylene (m.p. 235°). Purification of $Al(iso\text{-}C_3H_7)_3$ was carried out by double distillation in vacuum (b.p. 40–42°/1 mm). $AlH(iso\text{-}C_4H_9)_2$ and $AlD(iso\text{-}C_4H_8D)_2$ were prepared by heating $Al(iso\text{-}C_4H_9)_3$ and $Al[CH_2CD(CH_3)_2]_3$ at 140° for 2 h,

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with removal by pumping of the isobutylene formed; the products were purified by double distillation in vacuum (b.p. 118°/1 mm). $(C_5H_5)_2TiCl_2$ was obtained according to the scheme

$$C_5H_6 \xrightarrow{Na} NaC_5H_5 \xrightarrow{TiCl_4} TiR_2Cl_2$$

and was purified by recrystallization from chloroform and toluene. Diethylaluminum chloride was obtained by the reaction

$$2AlR_3 + AlCl_3 \rightarrow 3AlR_2Cl$$

and was purified by distillation in vacuum (b.p. 96°/1 mm).

Experimental procedure. All operations with aluminum alkyls were carried out in a special box under an atmosphere of argon purified from traces of moisture and oxygen.

The absorption spectra of the components in the visible region were recorded on an SF-4 spectrophotometer. Electron paramagnetic resonance spectra were recorded on an EPR-2 IKhF spectrometer with high-frequency modulation of the magnetic field.

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