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KINETICS AND MECHANISM OF THE INTERACTION OF ALUMINUM ALKYLS WITH TITANIUM HALIDES

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Recently, in a number of studies [1–3] it was shown that, upon the interaction of aluminum alkyls with dicyclopentadienyltitanium dichloride, soluble products are formed that are capable of catalyzing the polymerization of ethylene. In our preceding paper [4] we gave data on the structure of the final paramagnetic complexes formed as a result of the reaction. Although polymerization of ethylene does occur in the presence of these complexes, their activity is considerably lower than the activity of the reacting system, such as, for example, $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$. Thus, the most active particles are formed and disappear in the course of reduction of Ti^{4+}. It was therefore of considerable interest to elucidate the detailed mechanism of the interaction of aluminum alkyls with titanium halides, with determination of the structure of the species participating in the reduction process. In the present work we give results on the interaction of $(C_5H_5)_2TiCl_2$ with $Al(C_2H_5)_3$, $Al(CH_3)_3$, and $Al(C_2H_5)_2Cl$, and we attempt to construct a mechanism of the process by summarizing our own and literature data.

I. Reaction of $(C_5H_5)_2TiCl_2$ **with** $Al(C_2H_5)_3$**.** In this reaction, which proceeds very rapidly, titanium is reduced with formation of a blue complex according to the scheme

$$(C_5H_5)_2TiCl_2 + Al(C_2H_5)_3 \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)_2\,(IV) + \tfrac{1}{2}C_2H_6 + \tfrac{1}{2}C_2H_4.$$

Ethane is formed in an amount corresponding to one half of the $(C_5H_5)_2TiCl_2$ taken, which formally corresponds to disproportionation of ethyl groups. Ethylene is always obtained in smaller quantity than ethane; formation of butane is not observed. Aluminum alkyls react analogously with $TiCl_4$. The difference is that in this case Ti is reduced to lower valence states than 3+; therefore, at not very large Al:Ti ratios, alkane is obtained in an amount equal to one half relative to the Al taken, and not to the Ti, as in the case of $(C_5H_5)_2TiCl_2$. The reduced yield of ethylene compared with ethane is usually explained by partial

Fig. 1

Figure 1: Fig. 1

polymerization of ethylene. We found that, upon decomposition of the reaction products of $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_3$ with water, butane is obtained (about 20% relative to the $(C_5H_5)_2TiCl_2Al$ taken), which can formally be explained merely as a single insertion of ethylene into the Me—C bond during the reduction process.

II. Reaction of $(C_5H_5)_2TiCl_2$ **with** $Al(CH_3)_3$**.** In this case, when toluene solutions of the reagents are mixed, reduction of titanium proceeds slowly, and a blue complex of type IV is not formed. When the reaction is carried out in the presence of ethylene, a rapid color change from red to blue is observed; methane is evolved and ethylene is absorbed. It turned out that the blue complex formed in this reaction can be isolated by distillation. Analysis of the resulting crystals, the visible spectrum, and the electron paramagnetic resonance spectrum show that the product has a structure analogous to IV, and the composition $(CH_3)_2AlCl \cdot (C_5H_5)_2TiCl$. It was found that other α-olefins as well—propylene, butylene-1, amylene-1—react in a similar manner. In contrast to ethylene, of which there is absorbed

considerably greater than one mole per mole of titanium taken; in the case of the other α-olefins cited, absorption occurs approximately in an equimolecular ratio. After decomposition with water of the reaction products obtained in the presence of propylene, a noticeable amount of butane was isolated; and upon decomposition with water of the reaction products obtained in the presence of ethylene, propane and butane are obtained. Thus, in this case also the reaction proceeds in accordance with the formal scheme of disproportionation of alkyl groups, but first insertion of the olefin into the Me—C bond occurs, with formation of an alkyl capable of disproportionation, and the new olefins formed in the course of disproportionation again insert into the Me—C bond.

Fig. 1. Kinetics of the reaction of $Al(C_2H_5)_2Cl$ with $(C_5H_5)_2TiCl_2$ in benzene at 28°. Change with time of the concentration C of complex III (1), $\lg C_0/C$ (2), and $C^{1/2}$ (3) (C was determined from the optical density at $\lambda = 455$ mμ)

In cyclohexane, the reaction of ethylene absorption with simultaneous reduction of the red complex proceeds several times more slowly than in toluene.

III. **Reaction of** $(C_5H_5)_2TiCl_2$ **with** $Al(C_2H_5)_2Cl$.* Reduction in this case proceeds at a measurable rate. It is convenient to study the kinetics of the reaction by the change in the visible spectra observed in the work of Breslow and co-workers ([1,3]). In these studies it was shown that the reaction proceeds according to the scheme:

$$2(C_5H_5)_2TiCl_2 + [(C_2H_5)_2AlCl]_2 \rightleftharpoons 2(C_5H_5)_2TiCl_2 \cdot (C_2H_5)_2AlCl \quad (II),$$

Fig. 2

Figure 2: Fig. 2

$$\mathrm{II} \rightleftharpoons (C_5H_5)_2C_2H_5TiCl \cdot C_2H_5AlCl_2 \quad (\mathrm{III}),$$

$$\mathrm{III} \longrightarrow (C_5H_5)_2TiCl \cdot C_2H_5AlCl_2 \quad (\mathrm{IV}).$$

The slow stage of the reaction is the conversion of complex III into complex IV, accompanied by a change in color from red to blue.

As is seen from Fig. 1, the reaction follows order 1/2, which holds up to 70-80% conversion. Thereafter the order changes, passing into first order. Breslow and Long (^{3}) observed only first order of the reaction. It is possible that this is connected with the lower concentrations of the initial $(C_5H_5)_2TiCl_2$ with which these authors worked. The rate constant $k_{1/2}$ depends only weakly on the concentration of $Al(C_2H_5)_2Cl$ (Fig. 2). When $[Al(C_2H_5)_2Cl]$ is increased 30-fold, $k_{1/2}$ changes by only a factor of 2.

At lower concentrations of $(C_5H_5)_2TiCl_2$, when the reaction order with respect to III approaches first order, the reaction rate over a very wide range does not depend at all on the concentration of $Al(C_2H_5)_2Cl$.

Fig. 2

The rate constants measured in the interval 25-47° are:

$$k_{1/2}\ (\text{in benzene}) = 5.25 \cdot 10^6 \cdot \exp(-15700/RT)\ \mathrm{mol}^{1/2} \cdot \mathrm{l}^{-1/2} \cdot \mathrm{sec}^{-1};$$

$$k_{1/2}\ (\text{in methylcyclohexane}) = 1.58 \cdot 10^{11} \cdot \exp(-22200/RT)\ \mathrm{mol}^{1/2} \cdot \mathrm{l}^{-1/2} \cdot \mathrm{sec}^{-1}.$$

Mechanism of the Reaction

The experimental data presented refute the concept of a free-radical mechanism for the reduction of titanium halides by alkyaluminum compounds. Indeed, if ethane and ethylene were products of disproportionation of free radicals, the formation of butane, as a product of their recombination, should have been observed at the same time. In addition, ethyl radicals would have had to abstract H from the solvent, at least from one such

[*] The study of the kinetics of this reaction was begun jointly with E. W. Randall and L. E. Sutton in Oxford.

as toluene. However, the amount of ethane corresponds exactly to the disproportionation process. In the system $TiCl_4$—$Al(iso\text{-}C_4H_9)_3$ it was shown that the yield of isobutane does not decrease upon addition of free-radical acceptors, for example anthracene. The radical mechanism is also contradicted by data on the reaction of $Al(CH_3)_3$ with $(C_5H_5)_2TiCl_2$, which proceeds slowly in the absence of olefins, a fact difficult to explain from the standpoint of a radical scheme.

On the other hand, a number of data indicate the possibility of an ionic mechanism. As we have seen, the reduction of $(C_5H_5)_2TiCl_2$ by diethylaluminum chloride proceeds in benzene with a lower activation energy than in methylcyclohexane. The reaction of $(C_5H_5)_2TiCl_2$ with $Al(CH_3)_3$ in the presence of olefins in toluene proceeds considerably faster than in cyclohexane. This may be connected with a decrease in the ability toward ion formation on going from benzene and toluene to methylcyclohexane and hexane. The kinetic order $^1/_2$ in the case of the reaction of $(C_5H_5)_2TiCl_2$ with $(C_2H_5)_2AlCl$ can hardly be explained in any other way than by equilibrium dissociation into ions of complex III, which is confirmed by a considerable increase in electrical conductivity upon its formation (^{5}). We believe that the kinetic data for this reaction can be explained by the following mechanism:

0) $[Al(C_2H_5)_2Cl]_2 \rightleftarrows Al(C_2H_5)_2^+ + Al(C_2H_5)_2Cl_2^-$
1) $2(C_5H_5)_2TiCl_2 + [Al(C_2H_5)_2Cl]_2 \rightleftarrows 2(C_5H_5)_2TiCl_2 \cdot Al(C_2H_5)_2Cl$ (II)
2) $\mathrm{II} \rightleftarrows (C_5H_5)_2Ti(C_2H_5)Cl \cdot Al(C_2H_5)Cl_2$ (III)*
3) $\mathrm{III} \rightleftarrows (C_5H_5)_2TiC_2H_5^+ + Al(C_2H_5)Cl_3^-$
4) $(C_5H_5)_2TiC_2H_5^+ + Al(C_2H_5)_2Cl_2^- \rightarrow (C_5H_5)_2Ti(C_2H_5)_2 + Al(C_2H_5)_2Cl_2$
4′) $(C_5H_5)_2Ti(C_2H_5)_2 + Al(C_2H_5)_2^+ \rightarrow (C_5H_5)_2TiC_2H_5^+ + Al(C_2H_5)_3$
5) $(C_5H_5)_2Ti(C_2H_5)_2 \rightarrow (C_5H_5)_2Ti + C_2H_6 + C_2H_4$
6) $(C_2H_5)_2Ti + \mathrm{II} \rightarrow (C_5H_5)_2TiCl + (C_5H_5)_2TiCl_2Al(C_2H_5)_2$

At comparatively high concentrations of $(C_5H_5)_2TiCl_2$ the reaction rate (v) is determined by stage (5) and, thus, under the condition of a stationary concentration of $(C_5H_5)_2Ti(C_2H_5)_2$,

$$v = k_5[(C_5H_5)_2Ti(C_2H_5)_2] = k_5\frac{k_4[(C_5H_5)_2TiC_2H_5^+][Al(C_2H_5)_2Cl_2^-]}{k_{4'}[Al(C_2H_5)_2^+] + k_5}.$$

At high concentrations of $Al(C_2H_5)_2Cl$, when k_5 may be neglected in comparison with $k_{4'}[Al(C_2H_5)_2^+]$, and taking into account that $[Al(C_2H_5)_2^+] \simeq [Al(C_2H_5)_2Cl_2^-]$, we obtain

$$v = k_5\frac{k_4}{k_{4'}}[(C_5H_5)_2Ti^+C_2H_5].$$

Substituting the value of the concentration of $(C_5H_5)_2TiC_2H_5^+$, determined from equilibrium 3) (taking into account that $[(C_5H_5)_2TiC_2H_5^+] \simeq [Al(C_2H_5)Cl_3^-]$), we obtain:

$$v = k_5 \frac{k_4}{k_{4'}} K_3^{1/2}\,[\mathrm{III}]^{1/2},$$

which explains the reaction order observed experimentally and the independence from the concentration of $Al(C_2H_5)_2Cl$.

At low concentrations of $Al(C_2H_5)_2Cl$, when $k_5 \gg k_4[Al(C_2H_5)_2Cl]$,

$$v = k_4[(C_5H_5)_2TiC_2H_5^+][Al(C_2H_5)_2Cl_2^-] = k_4K_3^{1/2}[\mathrm{III}]^{1/2}[Al(C_2H_5)_2Cl]^{1/2}.$$

Thus, in agreement with experiment, the reaction order with respect to $Al(C_2H_5)_2Cl$ should vary from $^1/_2$ to 0.

At low concentrations of $(C_5H_5)_2TiCl_2$, apparently, equilibrium no longer has time to become established and reaction (3) becomes rate-determining. It is clear that in this case the order with respect to III should be first and the reaction rate should not depend on the concentration of $Al(C_2H_5)_2Cl$ if it is present in excess. However, when the Al/Ti ratio is decreased to 1 : 1, when alkylating ions $Al(C_2H_5)_2Cl_2^-$ are almost absent from the solution, the reaction should slow down sharply. This is indeed observed; moreover, in the work of Breslow and Long (3) it was shown that the reaction assumes zero order. It is possible that in this case the rate-determining stage is reaction (0) and, thus, the overall rate does not depend on the concentration of complex III. In any case, the kinetic zero order and the sharp retardation of the reaction at Al/Ti = 1 refute the suggestion of Breslow and Long that decomposition III $\rightarrow C_2H_5^{\cdot} + (C_5H_5)_2TiCl_2Al(C_2H_5)Cl$ takes place, since in that case the reaction rate could not depend at all on the concentration of excess $Al(C_2H_5)_2Cl$.

Disproportionation of alkyl groups occurs, in our opinion, intramolecularly in $(C_5H_5)_2Ti(C_2H_5)_2$. The assumption that a process of this kind is facile explains the fact that, up to now, diethyl derivatives of titanium have not been obtained, whereas diphenyl and dimethyl derivatives have been synthesized, for which reaction 5 is impossible because of the absence of a β-hydrogen atom.

In a solution of $Al(C_2H_5)_3$, the ion $Al(C_2H_5)_4^-$ has a considerably stronger alkylating action than the ion $Al(C_2H_5)_2Cl_2^-$ in a solution of $Al(C_2H_5)_2Cl$.

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* The kinetics of reaction 2) is complex (3), and it is not a simple intramolecular rearrangement.

This should lead to acceleration of a reaction of type 4 in the case of $Al(C_2H_5)_3$ compared with $Al(C_2H_5)_2Cl$, to an increase in the concentration of $(C_5H_5)_2Ti(C_2H_5)_2$ and, thus, to the rate of the reduction reaction.

The reaction with olefins shows that one of the particles participating in the reaction mechanism must have the ability to add an olefin and to rearrange, forming a longer alkyl radical. Such a particle, in our opinion, is $(C_5H_5)_2Ti^+C_2H_5$. The charge of this particle facilitates the formation of a π-complex with the olefin, which then rearranges into $(C_5H_5)_2Ti^+C_4H_9$. In the absence of a strong alkylating agent (as in the case of diethylaluminum chloride), such a reaction leads to polymerization. With a small amount of ethylene and in the presence of strong alkylating agents, this and the subsequent reactions 4 and 4′ lead to the formation of aluminum alkyls containing butyl groups, as in the case of $Al(C_2H_5)_3$ and $(C_5H_5)_2TiCl_2$, and also propyl and butyl groups, as in the reaction of $(C_5H_5)_2TiCl_2$ with $Al(CH_3)_3$ in the presence of ethylene and propylene.

The proposed mechanism may be extended to the reduction of other titanium halides, and also, in its main features, to halides of other transition elements. Let us note that for reactions of $R \cdot MgX$ with $CoCl_2$ and HgR_2 with VCl_4, where the absence of free radicals was also shown ([6,8]), the formation of MeR_2 as an intermediate particle was assumed ([7,8]).

It may be supposed that the catalytic activity in polymerization reactions is associated with the formation of ions $\cdots MeR^+$ (Me is a transition element, R is alkyl), which are present in solution in the case of homogeneous catalysts and on the surface in the case of heterogeneous catalysts.

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Note: Figure translations are in progress. See original paper for figures.