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# THE DECOMPOSITION OF TRIETHYLALUMINIUM BY TITANIUM CHLORIDES

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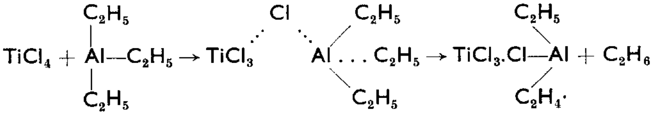
**Abstract**—It is shown that in the decomposition of triethylaluminium and diethylaluminium halide by titanium chlorides no free ethyl radicals are liberated. Instead ethane is evolved through intramolecular abstraction of hydrogen by one ethyl group from a neighbouring ethyl group. The molecule then rearranges to give a $C_4H_9\dot{A}lCl$ radical which in conjunction with the titanium chloride appears to catalyse the polymerization of α-olefines.

THE reaction between triethylaluminium and titanium tetrachloride to form "Ziegler" catalysts is accompanied by the evolution of gases. Their appearance is generally explained[1–10] by applying the mechanism originally proposed by Gilman and Jones[11] for the case of monoalkylmetals and monoalkylmetal chlorides:

$$TiCl_4 + RMe \rightarrow MeCl + TiCl_3 + R\cdot \qquad (1)$$

When more than one alkyl group is attached to the metal this reaction is not supported by experimental evidence. In this case the radical is not liberated and cannot later on recombine, disproportionate or abstract hydrogen from the solvent as has been postulated.[1–10] Instead, the alkyl group is stabilized within the molecule by hydrogen abstraction from another alkyl group attached to the same metal:[12]



$$TiCl_4 + \overset{C_2H_5}{\underset{C_2H_5}{Al}}\!-\!C_2H_5 \rightarrow TiCl_3 \overset{Cl}{\cdots} \overset{C_2H_5}{\underset{C_2H_5}{Al}}\ldots C_2H_5 \rightarrow TiCl_3.Cl\!-\!\overset{C_2H_5}{\underset{C_2H_4\cdot}{Al}} + C_2H_6 \qquad (2)$$

I

## EXPERIMENTAL

(1) Triethylaluminium or diethylaluminium bromide were allowed to react with titanium tri- and tetrachloride in the presence of carbon tetrachloride and gas samples were taken before the mixture had time to "explode".[13] The analysis is given in Table 1. It will be noted that little ethyl chloride was formed.

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(2) The reaction between triethylaluminium and titanium tetrachloride was carried out in the presence of n-heptane. Neither the amount nor the composition of the gas evolved were different from that liberated in the absence of n-heptane.[12]

(3) Triethylaluminium and titanium chlorides were allowed to react for 50 hr in the absence of a solvent and the gas evolved was analysed (Table 2). It will be noted that the ratio butane:ethane in gas depended strongly on the ratio triethylaluminium:titanium tetrachloride used.

(4) Triethylaluminium and titanium tetrachloride were allowed to react in the absence of a solvent. After 3, 60 and 220 min respectively the gas evolved was pumped out and analysed (Table 3). Only small amounts of butanes were evolved in the first 3 min but later on the ratio butane:ethane increased considerably.

(5) Triethylaluminium and titanium tetrachloride were allowed to react in the presence of carbon tetrachloride for 4 min at 0°C and the carbon tetrachloride was quickly pumped off together with the evolved gas. The residue was then decomposed with water. The gaseous product consisted of 91·1 % ethane, 7·1 % n-butane and 1·8 % isobutane. It must be remembered that in this case the unreacted excess of triethylaluminium was decomposed together with the reaction product. The ethane in the gas originated therefore only in part from the decomposition of the reaction product. No ethyl chloride could be detected.

TABLE 1. COMPOSITION OF GAS EVOLVED BY REACTION IN CARBON TETRACHLORIDE

| Reaction | $Al(C_2H_5)_3 + TiCl_4$ | $Al(C_2H_5)_3 + TiCl_3$ | $Al(C_2H_5)_2Br + TiCl_4$ |
|---|---|---|---|
| Ratio Al:Ti | 2 | 0·9 | 2 |
| Gas Composition mole % | | | |
| ethane | 84 | 99 | 99 |
| butanes | 9 | traces | 1 |
| ethyl chloride | 7 | traces | 0 |

TABLE 2. RATIO OF BUTANE:ETHANE IN GAS EVOLVED ON REACTING TRIETHYLALUMINIUM AND TITANIUM CHLORIDES

| Titanium chloride | $TiCl_4$ | | | | | | $TiCl_3$ | $TiCl_2$ |
|---|---|---|---|---|---|---|---|---|
| Al:Ti | 9·1 | 3·1 | 0·97 | 0·84 | 0·22 | 0·125 | *a* | *a* |
| $C_4H_{10}:C_2H_6$ | 0·05 | 0·00 | 0·15 | 0·14 | 0·28 | 0·28 | 0·03 | 0·05 |

[a] in the experiments with $TiCl_3$ and $TiCl_2$, the triethylaluminium was in excess relative to the surface of the crystals.

TABLE 3. GAS EVOLVED ON REACTING 1·4 MMOLES $Al(C_2H_5)_3$ WITH 6·3 MMOLES $TiCl_4$ (Al:Ti = 0·22)

| Time (min) | 3 | 60 | 220 |
|---|---|---|---|
| mmoles gas evolved | 0·82 | 1·07 | 0·31 |
| $C_4H_{10}:C_2H_6$ | 0·03 | 0·54 | 0·75 |

## DISCUSSION

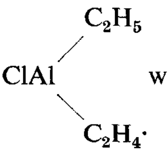
Interpretation of the experimental results showed that titanium chlorides liberated ethane from triethylaluminium without causing ethyl groups to leave the "cage" of the triethylaluminium in the form of a free radical; this conclusion was based on the following observations:

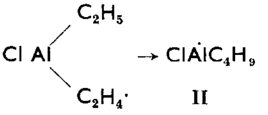
(1) It was shown that the main product of the reaction between $Al(C_2H_5)_3$ and $TiCl_4$ in the presence of carbon tetrachloride is ethane and not ethyl chloride (Table 1). Free ethyl radicals would be expected to be scavenged by $CCl_4$ to give ethyl

chloride. Ethane on the other hand could only be produced by intramolecular reaction as shown in equation (2). Indeed a little ethyl chloride, n-butane and isobutane could be detected. These were due to a subsequent reaction of the primary product (I).[13] It will be noted that the reaction between $Al(C_2H_5)_3$ and $TiCl_3$ in $CCl_4$ gave only ethane because in this case the subsequent reaction occurred much slower and it was possible to collect a gas sample of the pure primary reaction.

(2) Since the presence of heptane solvent had no influence on the reaction, hydrogen was not abstracted from heptane. This is inconsistent with a hypothesis which stipulates free radicals.

(3) Had any free ethyl radicals been liberated they would, in the absence of a solvent, have reacted further to give n-butane, ethane and ethylene (the latter being polymerized). Butane was in fact produced at the lower $Al(C_2H_5)_3:TiCl_4$ ratios but virtually none at the higher. When on the other hand ethylaluminium dichloride was substituted for the triethylaluminium[5] the gas evolved contained a nearly constant proportion of butane whatever the ratio $C_2H_5AlCl_2:TiCl_4$. Obviously the ethyl group of $C_2H_5AlCl_2$, in contrast to that of $Al(C_2H_5)_3$, could not abstract hydrogen by an intramolecular mechanism and had to leave the cage as a free radical.

The reaction between triethylaluminium and titanium chlorides must therefore of necessity pass through the intermediate free radical  $ClAl\begin{matrix}C_2H_5\\C_2H_4\cdot\end{matrix}$ which is probably associated with $TiCl_3$ as shown above (I). This free radical would not be expected to be stable. Indeed it could be shown that its life time was relatively short for it did not abstract chlorine from $CCl_4$. It is suggested that a fast internal rearrangement occurred:

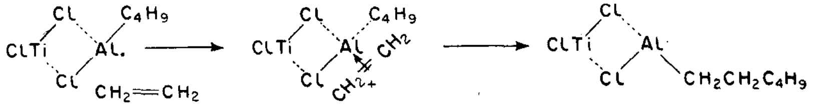


$$Cl\,Al\begin{matrix}C_2H_5\\C_2H_4\cdot\end{matrix} \rightarrow Cl\dot{A}lC_4H_9$$

II

This view is supported by the fact that when sufficient titanium chloride was present to liberate more than one mole alkane per mole triethylaluminium, butane was evolved. As can be seen from Table 3 the proportion of butanes increased with time. During the first phase of the reaction only triethylaluminium was decomposed but later on the decomposition of $Cl\dot{A}lC_4H_9$ became increasingly important.

This difference of behaviour between triethylaluminium and ethylaluminium dichloride towards titanium chlorides is of importance in explaining a probable mode of action of the catalyst. The product (II) for whose existence evidence was given above would be expected to show catalytic properties. The free electron is probably partly stabilized by delocalization through the titanium chloride crystal with which (II) is associated. An ethylene molecule in the neighbourhood of the crystal will be polarized, an electron transferred from its $\pi$ bond through the aluminium to the alkyl group which will dissociate as a carbanion and attach itself to the positive side of the partly bonded ethylene molecule. The process can continue in this way indefinitely:



This mechanism is supported by Adema *et al.*[14] in that for diethylaluminium chloride and titanium tetrachloride the curves of the polymerization rate of ethylene and of the concentration of unpaired electrons (as measured by electron spin resonance) versus time were identical in shape.

It is suggested that the above argument can be generalized: The decomposition of polyalkylmetals or polyalkylmetal halides by heavy metal chlorides takes place through intramolecular abstraction of hydrogen by one alkyl group from another attached to the same metal atom and subsequent liberation of alkane. No free alkyl radical is liberated.

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