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# Studies on Ziegler-Natta Catalysts. Part I. Reaction between Trimethylaluminum and α-Titanium Trichloride

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## Synopsis

The reaction between α-$TiCl_3$ and $AlMe_3$ at 65°C. in the absence of solvent was studied by a method which gives information about the early stages of the reaction. The results obtained give evidence for a sequence of consecutive reactions and show that the first of these is a fast partial alkylation of the α-$TiCl_3$ surface. The mechanism of formation of methane in the last step of the reaction is discussed in detail.

## I. INTRODUCTION

In a preceding paper,[1] a reaction scheme was proposed for the reaction between α-$TiCl_3$ and $Al(CH_3)_3$ in the absence of solvent, and some conclusions concerning the structure of the resulting surface product were presented. In the present paper the initial period of the reaction and the reaction steps leading to the formation of methane are treated in more detail. The earlier propositions have been completed on the basis of more experimental evidence.

## II. INITIAL PERIOD OF REACTION: ALKYLATION OF $TiCl_3$

It was noted earlier that in the first stages of the reaction a rapid extraction of chlorine takes place; this extraction was previously followed by a method[1] which will be called method A throughout this paper. A new method, referred to as method B, more appropriate to the obtention of precise data on the initial period, is described below.

### Experimental

**Materials.** The materials used, α-$TiCl_3$, $Al(CH_3)_3$ and $Al(CD_3)_3$, were prepared as previously described.[1]

**Method B.** A sample of $TiCl_3$ of known BET surface is stored in vessel A of the apparatus represented in Figure 1. The vessel A carries

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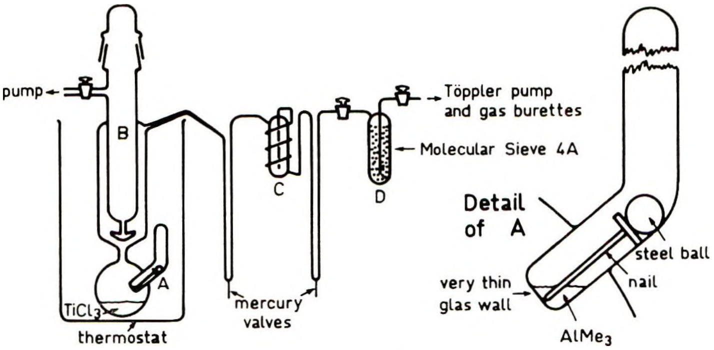


Fig. 1. Apparatus for the study of the reaction between $TiCl_3$ and $AlMe_3$ by method B.

three reservoirs of the type shown at the right, each containing a known quantity of $AlMe_3$.

The reaction space A is thermostatted and separated from the rest of the high vacuum apparatus ($10^{-4}$ mm. Hg) by means of a mercury valve. The reaction starts when one of the $AlMe_3$ reservoirs is opened by the shattering of its thin glass wall. Reservoir B, which is connected to a vacuum pump, is quickly filled with liquid nitrogen when the desired reaction time is attained.

The nitrogen solidifies, and in less than 30 sec. all of the volatile products, $AlMe_3$, $AlMe_2Cl$, and $CH_4$, are condensed on the wall of B. The mercury valves are opened, and the volatile products are allowed to escape, the temperature of B being gradually raised to 65°C. and collected in two traps immersed in liquid nitrogen, the aluminum compounds in trap C, and methane in trap D on Linde 4A molecular sieves. The mercury valves are closed when all products condensed on B have been removed.

The apparatus is provided with three parallel sets of traps which allow three successive reactions of exactly known duration to be run.

The amounts of methane retained in traps D are measured manometrically after the traps have been brought to room temperature. The aluminum compounds trapped in C are collected in small tubes, weighed, and analyzed for $CH_3$ and chlorine. The nonvolatile reaction product remaining after the third run is hydrolyzed, and the amount of hydrolysis gas is measured.

It is worth mentioning that Linde 4A molecular sieves, cooled by liquid nitrogen, adsorb methane very quickly, leaving a residual pressure of only $10^{-1}$ mm. Hg.

## Results

Two reactions between $\alpha$-$TiCl_3$ and $Al(CH_3)_3$ have been run at 65°C. in the absence of any other compound. Each run consists in three successive steps of various duration. The results are given in Table I.

The symbols used in Table I are defined as follows: $Ti_{surf.}$ is the number of milligram-atoms of Ti in the surface layer (the area occupied by one

TABLE I

Stoichiometry of the $\alpha$-$TiCl_3$–$AlMe_3$ Reaction, Initial Period, 65°C., Method B

| | RB18 | | | RB19 | | |
|---|---|---|---|---|---|---|
| | Step 1 | Step 2 | Step 3 | Step 1 | Step 2 | Step 3 |
| Surface $TiCl_3$, m.$^2$ | 139 | | | 158 | | |
| $Ti_{surf.}$, mg.-atoms | 1.36 | | | 1.55 | | |
| $Cl_{surf.}$, mg.-atoms | 2.04 | | | 2.32 | | |
| Partial reaction time, sec. | 155 | 416 | 1180 | 66 | 291 | 825 |
| Total time, sec. | 155 | 571 | 1751 | 66 | 357 | 1182 |
| $Cl_v$, mg.-atoms | 0.670 | 0.127 | 0.129 | 0.760 | 0.171 | 0.144 |
| $Cl_v/Al_f$ | 1.59 | 0.93 | 0.83 | 1.81 | 1.07 | 0.77 |
| $\Sigma Cl_v/\Sigma Al_f$ | 1.59 | 1.43 | 1.30 | 1.81 | 1.61 | 1.40 |
| $(C_R + C_D)/Cl_v$ | 0.73 | 1.54 | 1.62 | 0.67 | 1.22 | 1.43 |
| $\Sigma(C_R + C_D)/\Sigma Al_f$ | 1.16 | 2.20 | 2.11 | 1.21 | 1.96 | 2.00 |
| $Cl_v/Ti_{surf.}$ | 0.49 | 0.10 | 0.10 | 0.49 | 0.11 | 0.11 |
| $\Sigma Cl_v/Ti_{surf.}$ | 0.49 | 0.59 | 0.69 | 0.49 | 0.60 | 0.70 |

$TiCl_3$ unit in the surface being estimated at 16.3 A.$^2$);[2,3] $Cl_{surf.}$ is the number of milligram-atoms of Cl in the outermost chlorine layer; $Cl_v$ is the number of milligram-atoms of Cl found in the volatile aluminum compounds for each step; $Al_f$ is the number of milligram-atoms of Al fixed in the nonvolatile product after each step calculated from weight and composition of in- and out-going aluminumalkyls; $C_R + C_D$ is the number of millimoles of methane formed in the course of each step; $\Sigma Cl_v$, $\Sigma Al_f$, $\Sigma(C_R + C_D)$ denote the sum of $Cl_v$, $Al_f$, and $(C_R + C_D)$, respectively, from the start of the reaction to the end of the step.

Some of the data contained in Table I are graphically represented in Figures 2–4.

A close examination of these data reveals a number of interesting facts.

(*1*) The ratios $Cl_v/Al_f$, $\Sigma Cl_v/\Sigma Al_f$ change as a function of time (Fig. 2).

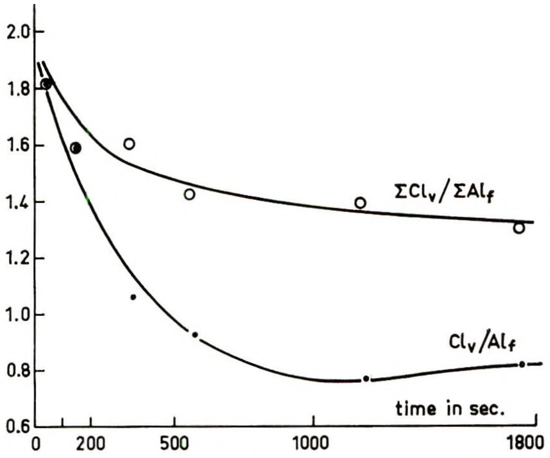


Fig. 2. Ratios $Cl_v/Al_f$ and $\Sigma Cl_v/\Sigma Al_f$ as a function of time.

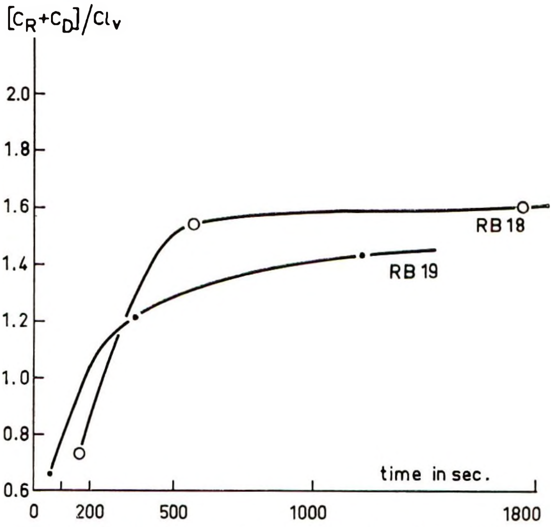


Fig. 3. Ratio ($C_R$ + $C_D$)/$Cl_v$ as a function of time.

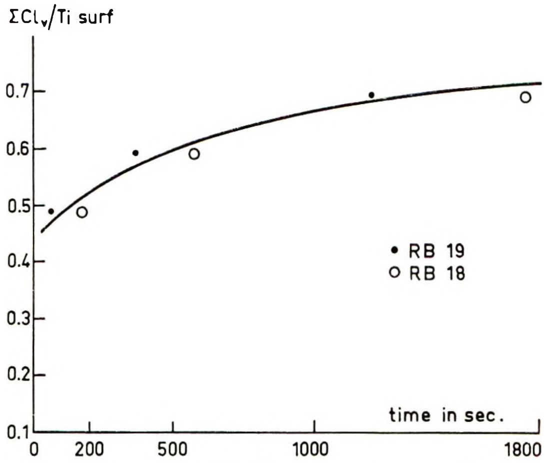


Fig. 4. The ratio $\Sigma Cl_v/Ti_{surf.}$ as a function of time.

The stoichiometry of the reaction at any one time is variable and depends on the degree of advancement. $Cl_v/Al_f$ is greater than 1 at the beginning, drops below 1, and climbs again. $\Sigma Cl_v/\Sigma Al_f$ drops steadily with time but remains greater than 1.

(*2*) The variation of the stoichiometry is also shown by Figure 3 ($C_R$ + $C_D$)/$Cl_v$ is 0.6–0.7 after the first step to become 1.4–1.6 after the third. The ratio $\Sigma(C_R + C_D)/\Sigma Al_f$ also rises quickly from 1.16–1.21 in the first step to about 2 and more in the subsequent ones.

(*3*) Figure 4 shows that the amount of chlorine, $Cl_v$, extracted in the first step of short contact time is great in comparison with the amounts extracted in the subsequent steps of much longer duration. In fact, in less than 1 min., approximately the limit of measurement attainable by the technique used, 1 Cl for 2 Ti surface atoms, is removed. A comparison with Figure 2 shows that in the early moments of the reaction, when chlorine is removed fast, the ratio $Cl_v/Al_f$ is greater than 1, i.e., more chlorine is removed than aluminum fixed. In later stages of the reaction, $Cl_v/Al_f$ is close to 1. This shows that the removal of chlorine preceeds the fixation of aluminum.

## Discussion

The $\alpha$-$TiCl_3$ used is in the form of flat leaflets, more or less hexagonal, as shown by Figure 5, which is an electron micrograph of a carbon replica. The general morphology of crystals from various preparations is always the same; also a photograph published by other workers strongly resembles the one given here.[4]

The largest faces are formed by the 001 basal planes in which only chlorine atoms lie in the outermost layers (cf. Fig. 6). The diagonal lengths of these crystal faces are in the order of $2 \times 10^4$ A. The thickness of the crystals is always small and may be estimated to be $5 \times 10^2$ A. from electron micrographs, which show crystals perpendicularly erected. Assuming a perfectly hexagonal form the surface ratio of the lateral face to the basal face may be evaluated to be $5 \times 10^{-2}$, and the same value represents in good approximation the ratio of the number of chlorine atoms on the lateral face to chlorine atoms on the basal face. By using this ratio, the number of milligram-atoms of chlorine contained in the lateral faces may be calculated. It amounts to 0.10 and 0.12 for experiments RB18 and RB19 (Table I). As the values of $Cl_v$ obtained in the first step of the same

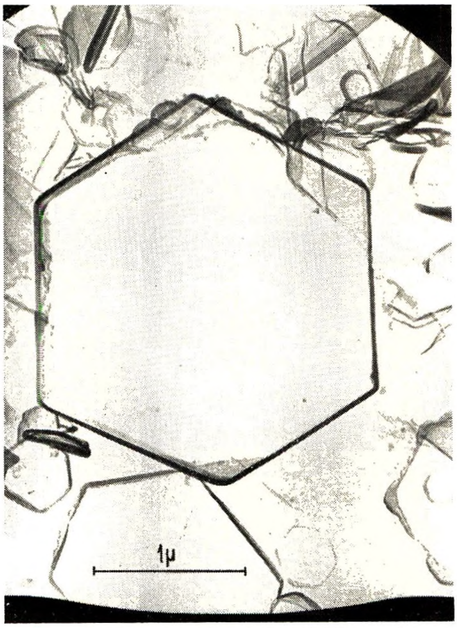


Fig. 5. Electron micrograph of an $\alpha$-$TiCl_3$ carbon replica.

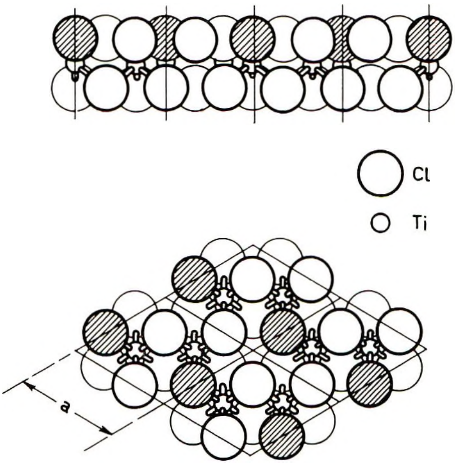


Fig. 6. Crystal structure of $\alpha$-$TiCl_3$ according to Natta et al.[2,3] The shadowed circles represent the chlorine atoms that are quickly exchanged in the early stage of the reaction.

experiments, are much greater (0.67 and 0.76), one may assume that the chlorine extraction measured by $Cl_v$ is mainly related to the 001 planes. It is well known that $\alpha$-$TiCl_3$ has a layer structure in which each titanium layer lies between two chlorine layers, one of which forms the outermost layer of the crystal. This therefore contains three chlorine atoms for two titanium atoms in the middle layer. Because the $Cl_v/Ti_{surf.}$ ratio after the short initial step is close to 0.5 (i.e., one chlorine removed for two titaniums of the middle layer), it must be concluded that the initial quick reaction removes one chlorine atom out of three from the outermost layer. Now, it must be emphasized that, due to the coordination number six of the titanium and the structure of $TiCl_3$, each chlorine atom of $\alpha$-$TiCl_3$ is connected to two titanium atoms. The chlorine atoms extracted in the early stage of the reaction between $\alpha$-$TiCl_3$ and $AlMe_3$, may then be positioned as shown in Figure 6, in which the reactive chlorine atoms are represented by shadowed circles placed in a regular way for symmetry reasons.

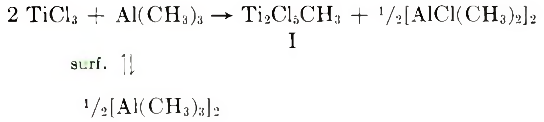
On the other hand, the results presented here confirm perfectly the earlier proposition[1] that the overall reaction must operate by means of a sequence of consecutive reaction steps; indeed, Figures 2 and 3 show that the overall stoichiometry changes as a function of time in a very marked way. Now it is seen from Figure 2 and Table I that the ratio $\Sigma Cl_v/\Sigma Al_f$ decreases with time, and that the ratio $\Sigma(C_R + C_D)/\Sigma Al_f$ increases with time. The reaction sequence must therefore be: extraction of chlorine from $TiCl_3$, fixation of aluminum from $AlMe_3$ in the solid phase, formation of methane. Because only $TiCl_3$ and $AlMe_3$ are present, the extraction of the chlorine atoms from $TiCl_3$, which are recovered as $AlMe_2Cl$, must correspond to the exchange reaction:

$$TiCl_3 + Al(CH_3)_3 \rightarrow TiCl_2CH_3 + AlCl(CH_3)_2 \quad (1)$$

This step is very fast in the early stage of the reaction, one chlorine atom out of three being removed from the outermost chlorine layer in a very short time. The product formed at this point may be visualized as on Figure 6, in which the shadowed circles represent new methyl groups.

It may be worth while to point out that (*a*) each methyl group is linked to two titanium atoms on the 001 plane (it is not necessarily true for the other faces); (*b*) this reaction affects the whole $TiCl_3$ surface, modifying it in an irreversible way and thus excluding valid comparison between pure $\alpha$-$TiCl_3$ and catalyst surface on the basis, for instance, of adsorption measurements; (*c*) the reproducibility of the $Cl_v/Al_f$ ratio obtained in the first step excludes the possibility that impurities (e.g., adsorbed $TiCl_4$) play an important role in the reaction.

Finally, the value of the ratio $Cl_v/Ti_{surf.}$ at the end of the rapid initial period must be explained. This value being close to $^1/_2$, the reaction may be written as shown in eq. (2).



$$\begin{array}{l} 2\,\mathrm{TiCl_3} + \mathrm{Al(CH_3)_3} \rightarrow \underset{\mathrm{I}}{\mathrm{Ti_2Cl_5CH_3}} + {}^1/_2[\mathrm{AlCl(CH_3)_2}]_2 \\ \qquad \text{surf.}\ \upharpoonleft\!\downharpoonright \\ \quad {}^1/_2[\mathrm{Al(CH_3)_3}]_2 \end{array} \qquad (2)$$

This expression takes into account the fact that each chlorine atom of $TiCl_3$ is coordinated to two titanium atoms. Substitution of one chlorine atom by a $CH_3$ group will therefore alter the charge distribution of two titanium atoms. This might render the substitution of a second chlorine atom more difficult.

A tentative explanation may also be offered in terms of the proposal of Klemm and Krose[5] that at not too low temperatures the $Ti^{+3}$ ions in $TiCl_3$ are in equilibrium with $Ti^{+4}$ and $Ti^{+2}$:

$$2\,\mathrm{TiCl_3} \rightleftharpoons \mathrm{TiCl_4 \cdot TiCl_2} \qquad (3)$$

One kind of titanium ions may be assumed to be more reactive towards $Al(CH_3)_3$ than the other, and hence product I would contain a titanium halide moiety of low reactivity towards $Al(CH_3)_3$:

$$\mathrm{Ti_2Cl_5CH_3} \leftrightarrows \mathrm{TiCl_3CH_3 \cdot TiCl_2} \qquad (4)$$

## III. FIXATION OF ALUMINUM IN THE NONVOLATILE PHASE

The fixation of aluminum was established earlier, and the corresponding reaction may be written for stoichiometric reasons as follows[1,6]

$$\mathrm{TiCl_2CH_3} + \mathrm{Al(CH_3)_3} \rightarrow [\mathrm{TiCl_2Al(CH_3)_4}] \qquad (5)$$

This reaction is also supported by the results recently published by Miotto[7] and related to experiments of long duration, followed step by step.

## IV. FORMATION OF METHANE

### Results

The earlier investigation[1,6] of the reactions leading to the formation of methane and the fixation of hydrocarbon groups in the nonvolatile product, which will be called surface compound, has led us to propose the following steps:

$$[TiCl_2Al(CH_3)_4] \rightarrow CH_4 + [TiCl_2AlC_3H_8] \qquad (6)$$

$$[TiCl_2AlC_3H_8] \rightarrow CH_4 + [TiCl_2AlC_2H_4] \qquad (7)$$

in which the formulas in brackets must be taken as empirical formulas. The experimental results in the literature[6,7] suggest that reaction (7) is not complete or that side reactions occur.

The experiments presented in this paper were aimed at a better understanding of the mechanism by which methane is formed. This question is important with respect to the nature of the carbon groups in the final nonvolatile product. Useful information was obtained from reactions involving $Al(CD_3)_3$. The distribution of H and D in reagents and volatile products was established by means of mass spectrometry. The spectra were analyzed in terms of the cracking patterns of deuterated methanes obtained by Moher, Dibeler, and Quinn.[8]

Three reactions were analyzed in which known mixtures of $Al(CH_3)_3$ and $Al(CD_3)_3$ were reacted with $TiCl_3$ at 65°C. for 20 min. The composition of the mixtures and the composition of the methane formed are given in Table II.

It is seen at once that the concentration of $CH_2D_2$ in the gas evolved during the reaction is very small and comparable to the concentration of $CHD_2$ and $CH_2D$ in the reacting $AlMe_3$. One may conclude that no H–D exchange takes place between the individual methyl groups prior to the

TABLE II
Reactions with a Mixture of $Al(CH_3)_3$ and $Al(CD_3)_3$, Method A.

| | Reaction 1 | Reaction 2 | Reaction 3 |
|---|---|---|---|
| Composition of $AlMe_3$ (molar ratio of $CX_3$ groups) | | | |
| $CH_3$ | 0.525 | 0.245 | 0.103 |
| $CH_2D$ | 0.006 | 0.004 | 0.000 |
| $CHD_2$ | 0.025 | 0.053 | 0.064 |
| $CD_3$ | 0.447 | 0.696 | 0.833 |
| Methane of reaction (molar ratio) | | | |
| $CH_4$ | 0.395 | 0.110 | 0.033 |
| $CH_3D$ | 0.129 | 0.121 | 0.065 |
| $CH_2D_2$ | 0.038 | 0.045 | 0.034 |
| $CHD_3$ | 0.321 | 0.328 | 0.280 |
| $CD_4$ | 0.117 | 0.396 | 0.588 |
| Degree of advancement (calculated on methyl groups) | <0.20 | <0.20 | <0.15 |
| $CH_3D + CH_4/CHD_3 + CD_4$ | 1.2 | 0.32 | 0.11 |
| $CH_3/CD_3$ in $AlMe_3$ | 1.17 | 0.35 | 0.12 |
| $CH_4/CH_3D$ | 3.06 | 0.91 | 0.51 |
| $CHD_3/CD_4$ | 2.75 | 0.83 | 0.47 |
| H/D in $AlMe_3$ | 1.15 | 0.36 | 0.14 |
| $[\alpha_{H/D}]$ mean | 2.53 | 2.41 | 3.50 |

formation of methane. Such exchange would lead to a statistical distribution in which $CH_2D$ and $CHD_2$ groups would be predominant. On reaction these groups would give an important proportion of $CH_2D_2$.

The absence of significant amounts of $CH_2D_2$, moreover, clearly indicates that methane is formed by combination of a saturated methyl group ($CX_3$) and a hydrogen atom and not from a $CX_2$, CX, or C fragment possibly present as intermediate or reaction product.

In the lower part of Table II various ratios are given, which have been calculated without taking into account the contributions of $CH_2D$ and $CHD_2$ groups in $CH_3D$ and $CHD_3$ formation. The first one is the ratio of methane formed from $CH_3$ to methane formed from $CD_3$. Its value corresponds closely to the ratio $CH_3/CD_3$ in the starting $AlMe_3$. It appears thus that methane is formed at the same rate whether $CH_3$ or $CD_3$ are the parent groups.

The ratios $CH_4/CH_3D$ and $CHD_3/CD_4$, when compared in any one of the three experiments are found to be about equal. This means that for a given proportion H/D in the reactant mixture, methyl groups, whether $CH_3$ or $CD_3$, add H and D in an approximately constant proportion. The ratios $CH_4/CH_3D$ and $CHD_3/CD_4$ would be equal to H/D if the addition of the hydrogen atom were statistical. In fact, a methyl group $CH_3$ or $CD_3$ prefers to add H rather than D. This preference may be expressed in terms of an isotopic constant $[a_{H/D}]$ calculated from the expressions

$$CH_4/CH_3D = [a_{H/D}]\ (H/D)$$

and

$$CHD_3/CD_4 = [a_{H/D}]\ (H/D)$$

One may calculate by means of the constants $[a_{H/D}]$ the composition of methane formed from the parent groups $CH_2D$ and $CHD_2$ (Table III).

Therefore the amount of $CH_2D_2$ found in the gas of reaction is doubtless due to parent mixed alkyls of the type $CH_2D$ and $CHD_2$ and not to a H–D exchange prior to reaction.

On the other hand, no isotope effect was found for $C^{14}$-labeled $Al(CH_3)_3$, whereas a very important effect was found for $H^3$-labeled $Al(CH_3)_3$, confirming that the determining step of the reaction is the C–H bond rupture.

Some of the conclusions drawn are also confirmed by the following exchange experiments. The nonvolatile products of three reactions between $TiCl_3$ and $Al(CH_3)_3$ of different and rather short reaction times are exchanged with $Al(CD_3)_3$ and the methane formed during and after exchange is analyzed (Table IV).

TABLE III

Deuterated Methanes Coming from $CH_2D$ and $CHD_2$ Groups Present in $AlMe_3$

| | | | |
|---|---|---|---|
| $CH_3D$ | 0.004 | 0.003 | 0.000 |
| $CH_2D_2$ | 0.020 | 0.038 | 0.045 |
| $CHD_3$ | 0.007 | 0.016 | 0.019 |

TABLE IV
Methane Formed from $TiCl_3$–$AlMe_3$ Catalysts during and after Contact with $Al(CD_3)_3$

| Reaction temp./time | 65°C./120 min. | 65°C./60 min. | 65°C./30 min. |
|---|---|---|---|
| Exchange temp./time | 20°C./80 min. | 20°C./60 min. | 20°C./80 min. |
| Methane | | | |
| $CH_4$ | 0.035 | 0.018 | 0.042 |
| $CH_3D$ | 0.000 | 0.000 | 0.018 |
| $CH_2D_2$ | 0.000 | 0.000 | 0.000 |
| $CHD_3$ | 0.895 | 0.940 | 0.834 |
| $CD_4$ | 0.070 | 0.043 | 0.107 |

The absence of $CH_2D_2$ and the high proportion of $CD_3H$ show that the only reaction taking place under these conditions is abstraction of H atoms contained in the surface product, and combination with the $CD_3$ groups either present as exchanged groups in the surface compounds[1] or belonging to the excess $Al(CD_3)_3$. The $CD_4$ formed may be attributed to a further reaction of $TiCl_3$ with $Al(CD_3)_3$.

## Discussion

That the formation of methane does not involve "free" radicals was demonstrated by running the α-$TiCl_3$ + $AlMe_3$ reaction in the presence of $CCl_4$.[9] In these experiments, which are similar to those of Eden and Feilchenfeld,[10] who used ethylaluminum compounds, no methyl chloride was found.

The α-$TiCl_3$–$AlMe_3$ system is particularly suited for this critical experiment as the absence of a β-hydrogen atom must favor the reaction with $CCl_4$ rather than hydrogen abstraction from a hydrocarbon group.[11]

Our results therefore confirm the conclusions of other workers[10,12,13] that the reaction of hydrocarbon formation does not necessarily involve an actually free-radical mechanism.

An actually free-radical mechanism may probably be involved for reactions taking place in solutions,[14–18] but it seems highly probable that the intermediates formed in heterogeneous reactions must be very different from what is generally understood under the term free radicals. In the case of the $TiCl_3$–$AlMe_3$ system studied here, one could consider the methane formation as due to an intramolecular reaction of the unstable compound $[TiCl_2Al(CH_3)_4]$.

On the other hand, our experiments show clearly that no H–D exchange takes place in the course of the reaction, and that methane is formed by a reaction in which one complete methyl group abstracts one hydrogen atom from another hydrocarbon group.

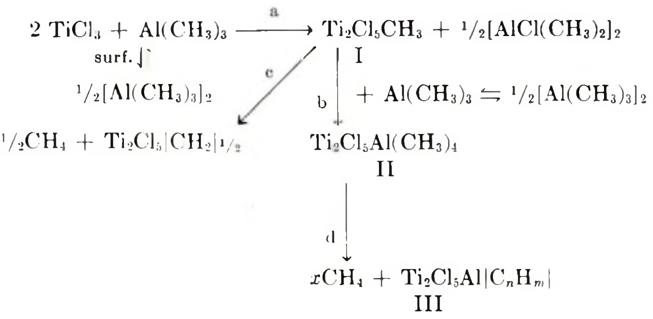
Our results reveal an important primary isotope effect corresponding to a $k_H/k_D$ ratio roughly equal to 2.8 ± 0.4. The existence of an isotope effect proves that a carbon–hydrogen bond is broken in the rate-controlling step of the reaction. It must also be pointed out that the value found is considerably smaller than the values obtained for reactions between methyl radicals and various substances.[19,20]

These values of $k_H/k_D$ lie between 5.2 and 9.9 for reaction at 120°C. and would be greater at 65°C., the temperature used in our experiments. Moreover, our value is also smaller than the maximal value of about 5.5 which has been calculated for a reaction giving a linear transition state with relatively weak C—H bond and assuming that the transmission coefficient, the rate of translation across the energy barrier, and the vibrations other than the C—H vibration involved in the reaction have no influence.[21-23]

Unfortunately, as is generally the case for low $k_H/k_D$ values, it is impossible to determine to what factor the discrepancy is due.

## V. CONCLUSIONS

The results published above confirm our earlier conclusions[1] and allow us to refine and complete the general scheme of the reaction [eqs. (8)].



$$\begin{tikzcd}
2\,TiCl_3 + Al(CH_3)_3 \arrow[r, "a"] \arrow[d, shift left, "surf."] & Ti_2Cl_5CH_3 + {}^1/_2[AlCl(CH_3)_2]_2 \arrow[dl, "c"'] \arrow[dd, "b"', "\mathrm{I}\quad + Al(CH_3)_3 \rightleftharpoons {}^1/_2[Al(CH_3)_3]_2"] \\
{}^1/_2[Al(CH_3)_3]_2 \arrow[u, shift left] & \\
{}^1/_2CH_4 + Ti_2Cl_5[CH_2]_{1/2} & \underset{\mathrm{II}}{Ti_2Cl_5Al(CH_3)_4} \arrow[d, "d"'] \\
& \underset{\mathrm{III}}{xCH_4 + Ti_2Cl_5Al[C_nH_m]}
\end{tikzcd} \qquad (8)$$

The initial reaction step is the fast Cl–CH$_3$ exchange involving one chlorine atom for every two surface titanium atoms. After that, the exchange reaction may continue but for reasons of reactivity at much smaller rates. This reaction certainly takes place on the predominant 001 planes of the $\alpha$-TiCl$_3$ crystals and probably also on the other crystal faces. A different reaction scheme may, however, apply to the latter.

The existence of reaction c of eq. (8) is proved by the fact that, during experiments characterized by a short time of contact between TiCl$_3$ and AlMe$_3$ and a long decomposition time of the reaction product, the ratio Cl$_v$/Al$_f$ and CH$_4$/Al$_f$ are greater than in those experiments where AlMe$_3$ is always in contact with the nonvolatile product. Finally, reaction d of eq. (8) involves the abstraction of one hydrogen atom from a hydrocarbon group by a complete methyl group. Reaction d goes through a rate-determining step in which a C–H bond is broken. The comhosition of product III depends on reaction time and temperature, so that III is represented here by an empirical formula. A subsequent paper[24] gives information on product III.

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## Résumé

La réaction entre α-$TiCl_3$ et $AlMe_3$, en l'absence de solvant et à 65°C, a été étudiée par une technique permettant de suivre les premiers moments de réaction. L'étude permet de proposer un schéma réactionnel en plusieurs étapes, de détailler la première étape, qui consiste en une alkylation ménagée de la surface de α-$TiCl_3$, ainsi que de préciser le méchanisme de la formation du méthane, dernière étape de la réaction.

## Zusammenfassung

Die Reaktion zwischen α-$TiCl_3$ und $AlMe_3$ wurde bei 65°C in Abwesenheit von Lösungsmitteln untersucht. Eine genaue Messmethode gestattet, über den Reaktionsverlauf im Anfangsstadium Aussagen zu machen. Die Ergebnisse lassen auf einen Reaktionsmechanismus schliessen, in welchem der erste Schritt eine partielle Alkylierung der α-$TiCl_3$ Oberfläche bewirkt. Die Bildung von Methan in der letzten Reaktionsstufe wird in Einzelheiten besprochen.

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# Studies on Ziegler-Natta Catalysts. Part II. Reactions between α- or β-$TiCl_3$ and $AlMe_3$, $AlMe_2Cl$, or $AlEt_3$ at Various Temperatures

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## Synopsis

The following reactions, carried out in the absence of solvents, has been studied: α-$TiCl_3$ + $Al(CH_3)_3$ at 20°C., β-$TiCl_3$ + $Al(CH_3)_3$ at 65°C., α-$TiCl_3$ + $Al(CH_3)_2Cl$ at 20 and 65°C., and α-$TiCl_3$ + $Al(C_2H_5)_3$ between 30 and 65°C. It appears that a general reaction mechanism, such as discussed in the preceding paper of this series, applies to all these reactions between $TiCl_3$ and aluminum alkyls. The differences in overall stoichiometry between some of these systems may be linked to differences in stability of the intermediate Ti—C bonds. In the case of α-$TiCl_3$ + $Al(CH_3)_2Cl$, alkylation is probably accompanied by fixation of the $AlCH_3Cl_2$ on the nonvolatile product.

## I. INTRODUCTION

Part I of this series of papers[1] concerned the reaction between α-$TiCl_3$ and $Al(CH_3)_3$, run at 65°C. In this paper results on three related catalyst systems are presented: α-$TiCl_3$ and $Al(CH_3)_3$ at 20°C., β-$TiCl_3$ and $Al(CH_3)_3$ at 65°C. and α-$TiCl_3$ and $AlMe_2Cl$ at 20 and 65°C. Some results and comments on the reaction between α-$TiCl_3$ and $AlEt_3$ are also given.

## II. EXPERIMENTAL

The general experimental technique, called method A, has been described earlier.[2] In some cases the initial period of the reaction has been followed by the more elaborate method B.[1] The preparation of most of the reagents has been described.[2] $AlCl(CH_3)_2$ was obtained by heating $Al(CH_3)_3$ and $AlCl_3$, the latter being in small excess over the stoichiometric quantity, in a sealed tube at 60°C. The product was freed from $AlCl_2CH_3$ by complex formation with NaCl.

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## III. REACTION BETWEEN $\alpha$-TiCl$_3$ AND Al(CH$_3$)$_3$ AT 20°C.

Two reactions were run at 20°C. in the absence of any solvent and followed by method A. The temperature was kept at 20°C. in all steps except the last of the second run (65°C.). The results are summarized in Table I.

TABLE I

Reaction of $\alpha$-TiCl$_3$ + Al(CH$_3$)$_3$, 20°C., Method A

| | RB4 | RB13 | | | |
|---|---|---|---|---|---|
| | Step 1 | Step 1 | Step 2 | Step 3 | Step 4 |
| Step temperature, °C. | 20 | 20 | 20 | 20 | 65 |
| Surface $\alpha$-TiCl$_3$, m.$^2$ | 243 | 172 | | | |
| Ti$_{surf.}$ | 2.37 | 1.68 | | | |
| Cl$_{surf.}$ | 3.55 | 2.52 | | | |
| Partial reaction time, sec. | 1140 | 1200 | 1200 | 5400 | 1200 |
| Total time, sec. | 1140 | 1200 | 2400 | 7800 | 9000 |
| Cl$_v$ | 1.08 | 0.784 | 0.181 | 0.091 | 0.155 |
| Cl$_v$/Al$_f$ | 1.96 | 1.56 | 1.12 | (2.5) | 0.97 |
| $\Sigma$Cl$_v$/$\Sigma$Al$_f$ | 1.96 | 1.56 | 1.46 | (1.51) | 1.41 |
| (C$_R$ + C$_D$)/Cl$_v$ | 0.65 | 0.89 | 1.3 | 2.0 | 1.8 |
| $\Sigma$(C$_R$ + C$_R$)/$\Sigma$Al$_f$ | 1.28 | 1.38 | 1.44 | (1.60) | 1.64 |
| Cl$_v$/Ti$_{surf.}$ | 0.46 | 0.47 | 0.11 | 0.05 | 0.09 |
| $\Sigma$Cl$_v$/Ti$_{surf.}$ | 0.46 | 0.47 | 0.57 | 0.63 | 0.72 |

The symbols in Table I have been defined in the preceding paper.[1] The values in parentheses appear to be too high, probably because of experimental error.

It is clear that the reaction at 20°C. presents the same general features as the reaction at 65°C.:[1] decrease of the Cl$_v$/Al$_f$ and $\Sigma$Cl$_v$/$\Sigma$Al$_f$ ratios, increase of the (C$_R$ + C$_D$)/Cl$_v$ and $\Sigma$(C$_R$ + C$_D$)/$\Sigma$Al$_f$ ratios. It follows that the general reaction scheme applies to both temperatures. More particularly, it may be seen from the results of experiments RB13 and RB4 that chlorine is removed rapidly even at 20°C. until a Cl$_v$/Ti$_{surf.}$ ratio of approximately 0.5 is reached. This is compatible with our conclusion that the first step in the reaction sequence is a fast exchange reaction between TiCl$_3$ and Al(CH$_3$)$_3$.

## IV. REACTION BETWEEN $\beta$-TiCl$_3$ AND Al[CH$_3$]$_3$ AT 65°C.

The $\beta$-TiCl$_3$ was prepared by reaction between TiCl$_4$ and H$_2$ in a silent discharge according to the method of Gutmann, Nowotny, and Ofner,[3] in which the gaseous ratio of TiCl$_4$ and H$_2$ is adjusted to give TiCl$_3$ and not TiCl$_2$. The brown product obtained has a large specific surface ($\sim$ 155 m.$^2$/g.). Its general morphology cannot be observed even by electron microscopy. The electron micrographs show only a very fine powder without structure (cf. also Korotkov and Li[4]).

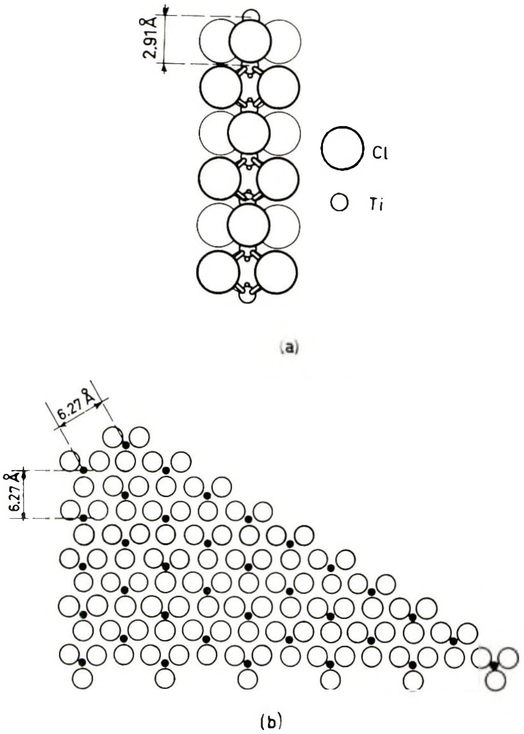


Fig. 1. (*a*) Stereochemical model of the stack which characterizes the β-modification of $TiCl_3$ according to Natta et al.[5] (*b*) Top view of a face perpendicular to the c axis, showing the structure of the most probable faces parallel to the c axis.

The crystalline structure of β-$TiCl_3$ was studied by Natta and coworkers,[5,6] and their results were confirmed by Cras[7] working on better crystallized samples.

β-$TiCl_3$ has a fiber-shaped structure. $TiCl_3$ units are piled up in stacks parallel to the main axis *c* of the crystal The titanium atoms situated along the *c* axis are octahedrically coordinated to six chlorine atoms belonging to the same stack. The stacks are linked only by van der Waals forces acting between chlorine atoms of neighboring rows. It seems reasonable, therefore, that the crystal grows mainly along the *c* axis using the coordination energy and that the faces parallel to the *c* axis are more developed than the faces perpendicular to the same axis. Our discussion is based on the assumption that the faces perpendicular to the *c* axis give a negligible contribution to the total surface.

Now, it may be seen from Figure 1 that for any crystal face parallel to the *c* axis the distance between the titanium atoms is 2.91 A. along the *c* axis and 6.27 A. in the direction perpendicular to the axis.

Therefore, whatever the face considered and provided that every titanium atom is bound to three chlorine atoms, the external surface corresponding to one titanium atom may be evaluated at 18.25 $A.^2$

TABLE II
Reaction of $\beta$-$TiCl_3$ + $Al(CH_3)_3$, 65°C., Method B

| | RB24 | | |
|---|---|---|---|
| | Step 1 | Step 2 | Step 3 |
| Step temperature, °C. | 65 | 65 | 65 |
| Surface $\beta$-$TiCl_3$, m.$^2$ | 195 | | |
| $Ti_{surf.}$ | 1, 77 | | |
| Partial reaction time, sec. | 63 | 294 | 903 |
| Total time, sec. | 63 | 357 | 1260 |
| $Cl_v$ | 0.938 | 0.427 | 0.525 |
| $Cl_v/Al_f$ | 1.19 | 1.18 | 1.29 |
| $\Sigma Cl_v/\Sigma Al_f$ | 1.19 | 1.19 | 1.22 |
| $(C_R + C_D)/Cl_v$ | 1.13 | 1.55 | 1.00 |
| $\Sigma(C_R + C_D)/\Sigma Al_f$ | 1.34 | 1.50 | 1.45 |
| $Cl_v/Ti_{surf.}$ | 0.53 | 0.24 | 0.30 |
| $\Sigma Cl_v/Ti_{surf.}$ | 0.53 | 0.77 | 1.07 |

As in the case of the $\alpha$-$TiCl_3$, the volatile compounds after reaction contain only methane, chlorodimethylaluminum and an excess of trimethylaluminum. Because the values of $Cl_v/Al_f$ and $\Sigma(C_R + C_D)/\Sigma Al_f$ are of the same order in both cases, the same general reaction scheme may be applied.[1,2]

However, in contrast to the $\alpha$-$TiCl_3$ + $Al(CH_3)_3$ reaction, no significant variation of the ratio $Cl_v/Al_f$ is observed as a function of time. Nevertheless it is highly probable in the case of the $\beta$-$TiCl_3$ too, the reaction takes place by a multi-step sequence in which the first step is the exchange (alkylating) reaction followed by the fixation of trimethylaluminum on the alkylated site. This view is supported by the fractional value of the ratios $Cl_v/Al_f$ observed which could be hardly explained by another mechanism.

Just as for $\alpha$-$TiCl_3$, a very rapid extraction of chlorine takes place with $\beta$-$TiCl_3$ in the first moments of the reaction, and this fast exchange reaction affects again one chlorine atom for two titanium atoms close to the surface ($Cl_v/Ti_{surf.}$ ratio = 0.50).

The explanation given for the $\alpha$-$TiCl_3$ systems also applied here since every chlorine atom in the surface may be considered as belonging to two titanium atoms.

## V. REACTION BETWEEN $\alpha$-$TiCl_3$ AND $Al(CH_3)_2Cl$ AT 20 AND 65°C.

The results of two experiments are summarized in Table III.

An important characteristic of these reactions is that the Cl/Al ratios are exactly the same in the $Al(CH_3)_2Cl$ reactant and the volatile aluminum compound recovered after the reactions, even when the amount of $Al(CH_3)_2Cl$ is small in comparison to the chlorine present on the $\alpha$-$TiCl_3$ surface. However, the reaction may not be described as a chemisorption. In fact, methane and higher hydrocarbons are formed in comparatively high quantities, and the infrared spectra of $\beta$-$TiCl_3$ + $Al(CH_3)_2Cl$ systems show the

TABLE III
Reaction between $\alpha$-$TiCl_3$ and $Al(CH_3)_2Cl$, Method A

| | RB6 | RB17 | | |
|---|---|---|---|---|
| | Step 1 | Step 1 | Step 2 | Step 3 |
| Step temperature, °C. | 20 | 65 | 65 | 65 |
| Surface $\alpha$-$TiCl_3$, m.$^2$ | 210 | 105 | | |
| $Ti_{surf.}$ | 2.06 | 1.02 | | |
| Partial reaction time, sec. | 1800 | 1800 | 3600 | 5400 |
| Total reaction time, sec. | 1800 | 1800 | 5400 | 10800 |
| $Al(CH_3)_2Cl$ fixed, mg. atom | 0.78 | 0.33 | 0.06 | 0.08 |
| $\Sigma Al(CH_3)_2Cl$ fixed, mg.-atom | 0.78 | 0.33 | 0.39 | 0.47 |
| $Al(CH_3)_2Cl$ fixed/$Ti_{surf.}$ | 0.37 | 0.32 | 0.06 | 0.08 |
| $\Sigma Al(CH_3)_2Cl$ fixed/$Ti_{surf.}$ | 0.37 | 0.32 | 0.38 | 0.46 |
| $(C_R + C_D)$, mmole | | | | |
| $CH_4$ | 0.078 | | | |
| $C_n (n > 1)$ | 0.104 | | | |

presence of $AlCH_3Cl_2$.[8] Moreover, the volatile products of the reaction contain small amounts of $TiCl_3CH_3$, especially when the reaction is carried out at low temperature and stopped quickly. This compound is easily recognized because of its strong color. It is known that methane, ethane, and higher hydrocarbons are formed in considerable amounts during the decomposition of pure $TiCl_3CH_3$ in solution[9] and also during the decomposition of a mixture of $TiCl_3CH_3$ and trimethyl- or chlorodimethylaluminum[10] between 20 and 65°C. These facts lead one to assume that the first step in the reaction is a rapid exchange of Cl for $CH_3$.

The $TiCl_3CH_3$ formed partially decomposes, giving methane and higher hydrocarbons. The other product of the reaction, $AlCH_3Cl_2$, would be strongly associated with $TlCl_3$ and might not be recovered by evaporation under vacuum. Such an effect is highly probable since Ziegler and coworkers have described several strongly associated products obtained from inorganic salts and chlorine containing aluminum compounds.[11,12]

The proposed reaction scheme is as given in eqs. (1)–(4):

$$2TiCl_{3\,surface} + Al(CH_3)_2Cl \rightarrow Ti_2Cl_5CH_3 + AlCH_3Cl_2 \tag{1}$$

$$Ti_2Cl_5CH_3 \rightleftharpoons TiCl_2\cdot TiCl_3CH_3 \tag{2}$$

$$TiCl_3CH_3 \rightarrow \text{decomposition products } (CH_4 + \text{higher hydrocarbons} + TiCl_3) \tag{3}$$

$$TiCl_3 + AlCH_3Cl_2 \rightarrow \text{nonvolatile complex} \tag{4}$$

The formation of $TiCl_3CH_3$ tends to support the internal redox reaction:[13]

$$2Ti^{+3} \rightleftharpoons Ti^{+2} + Ti^{+4}$$

on the basis of which we gave already a tentative explanation for the $Cl_v/Ti_{surf.}$ ratios of 0.5 observed in the fast exchange reaction between $TiCl_3$ and $Al(CH_3)_3$.[1]

That the formation of $TiCl_3CH_3$ could be due to $TiCl_4$, present as an impurity, is hard to believe since the values of the ratios $Cl_v/Ti_{surf.}$ of the rapid first exchange reaction are reproducible.

Comparison of the value of ($C_R + C_D$), taking into account the presence of hydrocarbons higher than methane, and the amount of $Al(CH_3)_2Cl$ used shows that reaction (3) is incomplete and leaves on the surface some $Ti—CH_3$ bonds.

## VI. REACTION BETWEEN α-$TiCl_3$ AND $Al(C_2H_5)_3$

The reaction was followed by means of method A, however slightly modified because of the low vapor pressure of $Al(C_2H_5)_3$ as compared with that of $Al(CH_3)_3$. In order to recover the volatile products of the reaction it appeared necessary to increase the temperature; 85°C. was found satisfactory. The most important results are summarized in Table IV.

TABLE IV

Reaction between α-$TiCl_3$ and $Al(C_2H_5)_3$ at Various Temperatures, Method A

| | Reaction 112 | Reaction 106 | Reaction 105 | Reaction 103 |
|---|---|---|---|---|
| Reaction temp., °C. | 30 | 35 | 65 | 65 |
| Reaction time, min. | 11200 | 5590 | 60 | 135 |
| Recovery temp., °C. | 85 | 85 | 85 | 85 |
| Recovery time, min. | 120 | 180 | 180 | ~120 |
| $Cl_v/Al_f$ | 3.12 | 2.05 | 1.00 | 0.90 |
| $(C_i - C_v)/Al_f$ | 4.86 | 4.30 | 4.09 | 3.22 |
| $(C_R + C_D)/(C_i - C_v)$ | 0.50 | 0.50 | 0.41 | 0.37 |
| $C_H/Al_f$ | 0.90 | 0.81 | 1.17 | 0.77 |
| Volatile phase | | | | |
| Cl/Al | 0.75 | 0.98 | 1.00 | 0.87 |
| $C_2H_5/Al$ | 2.26 | 2.02 | 2.50 | 2.32 |

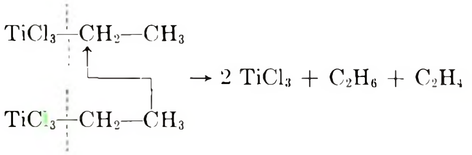
The symbols appearing in Table IV are defined as follows: $C_i$ denotes the number of millimoles of $C_2H_5$ in the reactant $Al(C_2H_5)_3$; $C_v$ is the number of millimoles of $C_2H_5$ in the volatile aluminum compounds recovered after the reaction; $C_R + C_D$ is the number of millimoles of hydrocarbon formed during the reaction and recovery period; $C_H$ is the number of millimoles of hydrocarbon formed on hydrolysis of the nonvolatile reaction product.

Unfortunately, the surface of the α-$TiCl_3$ samples was not measured. Neither were the hydrocarbon mixtures $C_R$, $C_D$, and $C_H$ quantitatively analyzed. It was proved that no ethylene was present in the gases $C_R$ and $C_D$, which were essentially ethane. However, the presence of traces of polyethylene in the nonvolatile phase after hydrolysis points to the formation of ethylene in the reaction. $C_i$ and $C_v$ were recovered as pure ethane on hydrolysis of the aluminum compounds. It may be concluded from Table IV that the aluminum alkyls present in the volatile phase after reaction consist of practically pure $AlCl(C_2H_5)_2$, all of the initially added $Al(C_2H_5)_3$ having reacted. That no $AlCl_2C_2H_5$ is recovered does not mean that this compound is not formed. It may be absent for various reasons: too low vapor pressure to be recovered by pumping, strong adsorption on the $TiCl_3$ surface, or disproportionation into $AlClEt_2$ and $AlCl_3$ at 85°C. in vacuum.

The formation of $AlCl(C_2H_5)_2$ and the values of the $Cl_v/Al_f$ ratios much greater than one suggest strongly that a mechanism similar to that proposed[1] for $Al(CH_3)_3$ is operating.

$$\begin{tikzcd} 2TiCl_{3surf.} + Al(CH_2H_5)_3 \arrow[r, "a"] \arrow[d, shift left, "b"] & \underset{\text{I}}{Ti_2Cl_5C_2H_5} + {}^1/_2[AlCl(C_2H_5)_2]_2 \arrow[d, "c"] \\ {}^1/_2[Al(C_2H_5)_3]_2 \arrow[u, shift left] & \text{decomposition products} \end{tikzcd} \tag{5}$$

It is highly probable that product I is unstable between 20 and 85°C. and that the decomposition step c of eq. (5) follows the mechanism proposed by de Vries for $TiCl_3C_2H_5$:[9]



$$\begin{matrix} TiCl_3 \vdots CH_2—CH_3 \\ TiCl_3 \vdots CH_2—CH_3 \end{matrix} \rightarrow 2\ TiCl_3 + C_2H_6 + C_2H_4 \tag{6}$$

Step c of reaction (5) seems to be important at low temperature, but at 65°C. the fixation of aluminum appears to be predominant. Indeed the ratio $Cl_v/Al_f$ decreases from 3.12 to about 1 when the reaction temperature increases from 20 to 65°C. Therefore the following reaction must occur:

$$\begin{tikzcd} Ti_2Cl_5C_2H_5 \arrow[d, "d"'] & \\ \underset{\text{II}}{Ti_2Cl_5Al(C_2H_5)_4} & + Al(C_2H_5)_3 \rightleftharpoons {}^1/_2[Al(C_2H_5)_3]_2 \end{tikzcd} \tag{7}$$

Product II decomposes, giving ethane for nearly half of the ethyl groups involved in the reaction $[(C_R + C_D)/(C_i\text{-}C_v) \simeq 0.5]$.

The difference in stoichiometry between the $\alpha$-$TiCl_3$–$Al(CH_3)_3$ and the $\alpha$-$TiCl_3$–$Al(C_2H_5)_3$ systems may be easily explained on the basis of the decomposition rate of the Ti—C bond, which is much greater for Ti—$C_2H_5$ than for Ti—$CH_3$.

In the $\alpha$-$TiCl_3$-$Al(CH_3)_3$ system step c of eq. (5) is slow,[9] and a reaction similar to step d of eq. (7) takes place for practically all the methyltitanium sites previously formed. It follows that the ratios $Cl_v/Al_f$ and $(C_i\text{-}C_v)/Al_f$ for reactions of long duration will be always close to 1 and 4.[2] With $Al(C_2H_5)_3$ on the contrary, the relative rates of steps c and d will be variable and will depend strongly on the reaction conditions (concentration, temperature, etc.) giving different $Cl_v/Al_f$ and $(C_i\text{-}C_v)/Al_f$ ratios, as shown in Table IV.

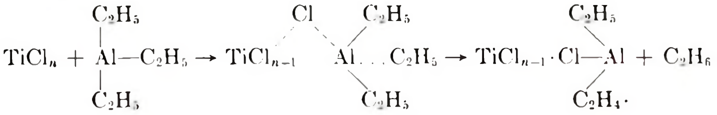
Another consequence of this situation is the following. With $Al(CH_3)_3$ the alkylated sites formed in reaction a react almost completely according to reaction (7) so that the sites become covered. A further reaction on the titanium chloride substrate then becomes impossible and the reaction is stopped, giving $AlCl(CH_3)_2$ and leaving an excess of $Al(CH_3)_3$. On the contrary, with $Al(C_2H_5)_3$ the decomposition reaction of the Ti-$C_2H_5$ bonds formed leaves a clean titanium chloride surface which undergoes further alkylation.

With a given quantity of $TiCl_3$ more $Al(C_2H_5)_3$ will react than $Al(CH_3)_3$, and the reduction of titanium will also be more extensive in the former case.[14]

Also, the composition of the surface compound will depend more strongly on the conditions of preparation. For instance, at low Al/Ti ratios in the reactant mixture, the conversion of $Al(C_2H_5)_3$ may be complete and the clean titanium chloride surface regenerated by the decomposition of the unstable Ti—C bonds may now be attacked by $AlCl(C_2H_5)_2$ formed in the alkylation reaction.

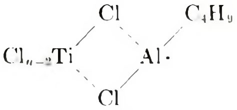
Finally it is worthwhile to point out that the decomposition of the Ti—$C_2H_5$ bonds results in the formation of chlorine vacancies on the surface. It has been shown[15,16] and it has been postulated[17–20] that the accessibility of titanium atoms, brought about by such vacancies, is a necessary condition for obtaining an active polymerization site.

One may therefore assume that those alkylating reactants which form unstable Ti—C bonds produce active sites of different kinds, and therefore, of different activities and different stereospecificity. The results and conclusions exposed above are difficult to reconcile with the mechanism proposed by Eden and Feilchenfeld.[21] According to these authors, the first step in the reaction between $TiCl_3$ and $Al(C_2H_5)_3$ may be represented as shown in eq. (8).



III

Now product III is supposed to undergo an internal rearrangement and the final catalytically active compound would be IV:



IV

This mechanism is unable to explain our stoichiometric results, especially the ratios $Cl_v/Al_f$ and the ratios $(C_i-C_v)/Al_f$ found. If the Eden and Feilchenfeld mechanism were valid, the ratios $Cl_v/Al_f$ would be equal to 0 and the ratios $(C_i-C_v)/Al_f$ would be equal to 3. We found for similar conditions (room temperature and high Al/Ti ratio), respectively, 3.12 and 4.68 at 30°C. and 2.05 and 4.30 at 35°C.

Our results show also that the alkylating reaction takes place even at low temperature and seems to be very rapid. Therefore the concept of adsorption of the alkylaluminum on the $TiCl_3$ surface is inadequate to describe the actual situation.[22,23]

## VII. CONCLUSIONS

The reactions between α- or β-$TiCl_3$ and trialkylaluminum such as $Al(CH_3)_3$ and $Al(C_2H_5)_3$ seem to obey the following general mechanism: (*1*) a rapid exchange reaction in which one chlorine atom for every two titanium atoms in the surface of $TiCl_3$ is replaced by an alkyl group from $AlR_3$; (*2*) the titaniumalkyl compound either decomposes or adds a trialkylaluminum molecule and gives a product of general formula $Ti_2Cl_5AlR_4$; (*3*) this product is unstable and decomposes, giving hydrocarbons and a nonvolatile surface product.

The comparison between the experiments with $Al(CH_3)_3$ and those with $Al(C_2H_5)_3$ shows that the decomposition of the Ti—C bond is relatively more rapid to the addition of aluminumalkyl with $Al(C_2H_5)_3$ than with $Al(CH_3)_3$.

Finally, this addition reaction is relatively more rapid to the exchange reaction with β-$TiCl_3$ than with α-$TiCl_3$.

In the case of $Al(CH_3)_2Cl$ the results obtained indicate that, after a first exchange reaction, the dichloromethylaluminum formed is adsorbed on the $TiCl_3$ surface shielding it for further reaction.

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## Résumé

Les réactions suivantes ont été étudiées en absence de solvant: α-$TiCl_3$ + $Al(CH_3)_3$ à 20°C, β-$TiCl_3$ + $Al(CH_3)_3$ à 65°C, α-$TiCl_3$ + $AlCl(CH_3)_2$ à 20 et 65°C et α-$TiCl_3$ + $Al(C_2H_5)_3$ entre 30 et 65°C. Les réactions entre $TiCl_3$ et trialkylaluminum peuvent être représentées par un schéma unique, les divergences s'expliquant par les différences de stabilité des liaisons Ti-$CH_3$ et Ti-$C_2H_5$. Ce schéma est celui déjà proposé pour la réaction α-$TiCl_3$ + $Al(CH_3)_3$ à 65°C. Dans le cas du système α-$TiCl_3$ + $AlCl(CH_3)_2$ il est montré que la réaction consiste en une alkylation de la surface de $TiCl_3$ probablement avec fixation du $AlCl_2CH_3$ formé.

## Zusammenfassung

Folgende Reaktionen wurden in Abwesenheit von Lösungsmittel untersucht α-$TiCl_3$ + $Al(CH_3)_3$ bei 20°C, β-$TiCl_3$ + $Al(CH_3)_3$ bei 65°C, α-$TiCl_3$ + $Al(CH_3)_2$ Cl bei 20 und 65°C. und α-$TiCl_3$ + $Al(C_2H_5)_3$ zwischen 30 und 65°C. Für diese Reaktionen gilt ein allgemeines Reaktionsschema das in der vorgehender Arbeit ausführlich entwickelt wurde. Unterschiede in der Gesammtstoechiometrie zwischen den verschiedenen Systemen werden auf Unterschiede der Stabilität der intermediären Ti—C Bindungen zurückgeführt. Im Falle der Reaktion α-$TiCl_3$ + $Al(CH_3)_2Cl$ muss wahrscheinlich eine Fixierung von $AlCH_3Cl_2$ im festen Reaktionsprodukt, in Betrachtung genommen werden.

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# Studies on Ziegler-Natta Catalysts. Part III. Composition of the Nonvolatile Product of the Reaction between Titanium Trichloride and Trimethylaluminum or Dimethylaluminum Chloride

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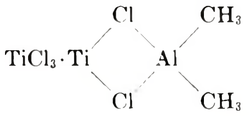
## Synopsis

The surface product formed in the reaction between $TiCl_3$ and $Al(CH_3)_3$ has been studied. Stoichiometric data, $CH_3/CD_3$ exchange, and infrared spectra permit the conclusion that the surface product is essentially a compound having the formula



A model structure is proposed for this compound, valid for the 001 face of α-$TiCl_3$. In it the titanium and chlorine atoms maintain the positions which they occupy in the α-$TiCl_3$ lattice. One of the methyl groups protrudes from the surface whereas the other occupies the chlorine vacancy created during the reaction in the chlorine surface layer. A different sterism of the methyl groups is compatible with the experimental result that half of the methyl groups are very easily exchanged whereas the other half are not touched by the exchanging agent. According to this model it has to be assumed that the titanium atoms in the 001 plane, by far the largest face of the α-$TiCl_3$ crystal, are not accessible. A similar model, leading to equivalence conclusions is proposed for β-$TiCl_3$. The infrared spectra of $Al(CH_3)_3$, $Al(CD_3)_3$, $AlCl(CH_3)_2$, $AlCl(CD_3)_2$, $AlCl_2CH_3$, $AlCl_2CD_3$, $TiCl_3CH_3$, $TiCl_3CD_3$, $Hg(CD_3)_2$, and $Zn(CD_3)_2$ are discussed. Spectra of surface products formed on interaction of some of these compounds with $TiCl_3$ are given.

## I. INTRODUCTION

In parts I and II of this series it was shown that a general mechanism applies to the reactions between $TiCl_3$ and aluminum alkyls. In a first fast reaction step chlorine atoms in the surface are exchanged for alkyl groups. Consecutively, the alkylated surface reacts with aluminum alkyl, giving an alkane and a nonvolatile surface product. The elemental composition of

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this surface product, though depending on reaction conditions, may be fixed between rather narrow limits. Because the $TiCl_3$ surface becomes catalytically active in olefin polymerization after reaction with aluminum alkyl, all information on the chemical species contained in the surface product is highly desirable. This paper brings such information based on stoichiometric data, $CH_3/CD_3$ exchange, and infrared spectra.

## II. MATERIALS

The preparation of most of the reagents has already been described.[1-3] $AlMeCl_2$ was prepared by heating $AlMe_3$ with an excess of $AlCl_3$ in a sealed tube at 60°C. The product sublimes easily under gentle heating in vacuum forming nice large crystals.

$Zn(CD_3)_2$ was prepared by heating $Hg(CD_3)_2$ with an excess of zinc in a sealed tube. $TiCl_3Me$ was prepared by reaction under vacuum of $TiCl_4$ with $ZnMe_2$ in paraffin oil. A small excess of $ZnMe_2$ over the stoichiometric ratio $Zn/Ti = 0.5$ was used. The product of reaction was freed from $TiCl_2Me_2$ by distillation.

## II. STOICHIOMETRIC STUDIES

The composition of the nonvolatile surface product formed in the reaction between $\alpha$-$TiCl_3$ and $Al(CH_3)_3$ has already been discussed.[1] It was concluded that the surface product contained aluminum, carbon, and hydrogen in a ratio close to 1:2:4.

No simple meaningful structural formula could be given for the surface product. It was proved that approximately half of the carbon contained in it was present as methyl groups and the remaining part as hydrocarbon fragments, such as C, CH, $CH_2$, and $CH_3$ groups and also species having C-C links, the average composition of which was CH by difference. These poorly definable species are formed in a complicated reaction in which methane is produced from a methyl group and a hydrogen atom belonging to a hydrocarbon fragment ($CH_3$, $CH_2$, CH) present in the surface.[2] The nature and the amounts of the various products depend on reaction conditions, mainly temperature and reaction time.

Since all of the experiments that will be presented in this paper, which were aimed at elucidating the composition and structure of the surface product, were performed under mild conditions, i.e., at temperatures at or below 65°C., it seems more correct to limit the stoichiometric data to those earlier experiments that were run at 65°C. These results are summarized in Table I. The experimental procedure called method A, has been described.[1]

The symbols used in Table I are defined as follows: $Cl_v$ is the number of milligram-atoms of chlorine found in the volatile aluminum compounds at the end of the reaction; $Al_f$ is the number of milligram-atoms of aluminum fixed in the nonvolatile product at the end of the reaction. $C_i$-$C_v$ is the difference, expressed in milligram-atoms, between the carbon contained in

TABLE I

Stoichiometry of the Reaction between α-$TiCl_3$ and $Al(CH_3)_3$

| | Run 101 | Run 99 | Run 120 | Run 122 | Run 96 | Run RA5 | Mean values |
|---|---|---|---|---|---|---|---|
| Reaction time, min. | 120 | 120 | 120 | 120 | 150 | 300 | |
| Reaction temp., °C. | 65 | 65 | 65 | 65 | 65 | 65 | |
| Decomposition time, min. | 60 | 120 | 120 | 6000 | 4000 | 60 | |
| Decomposition temp., °C. | 65 | 65 | 65 | 65 | 20 | 65 | |
| $Cl_v/Al_f$ | 0.98 | 1.04 | 0.97 | 1.18 | 1.05 | 1.12 | 1.0 |
| $(C_i - C_v)/Al_f$ | 4.0 | 4.0 | 4.0 | 4.2 | 4.0 | 4.1 | 4.0 |
| $(C_R + C_D)/Al_f$ | 1.72 | 1.59 | 1.71 | 1.94 | 1.72 | 1.61 | 1.70 |
| $C_h/Al_f$ | 2.27 | 2.09 | 2.30 | 1.59 | 2.29 | 1.72 | 2.05 |
| $CDH_3/C_h$ | — | — | 0.805 | 0.758 | | | |

the sample of $Al(CH_3)_3$, which is put in reaction, and that contained in the volatile aluminum compounds at the end of the reaction. (This quantity represents the carbon which has reacted and is either fixed in the nonvolatile product or set free as methane.) $C_R + C_D$ is the number of millimoles of methane formed in the course of the reaction from time zero to the end of the reaction; $C_h$ is the number of milligram-atoms of carbon recovered as methane on hydrolysis, with $H_2O$ or $D_2O$, of the nonvolatile product, at the end of the reaction; $CDH_3$ is the number of millimoles of $CDH_3$ found on hydrolysis with $D_2O$ of the nonvolatile product.

The ratio Al:C:H derived from the mean values of Table I becomes now 1:2. 3:5. 2, and the overall reaction, discussed in Part I of this series,[2] can be written as follows:

$$2TiCl_{3\text{surf.}} + [Al(CH_3)_3]_2 \rightarrow {}^1/_2[Al(CH_3)_2Cl]_2 + 1.7\ CH_4 + Ti_2Cl_5AlC_{2.3}H_{5.2} \quad (1)$$

Defining $C_{n-h}$ as the carbon which is not recovered on hydrolysis, the surface product may be represented by:

$$Ti_2Cl_5Al[C_h]_{2.05}[C_{n-h}]_{0.25}H_{5.2}$$

The ratio Ti/Al = 2/1 applies strictly only to the initial period of the reaction during which a quick removal of one chlorine atom for two titanium atoms in the surface is followed by the fixation of one aluminum atom. A further slow chlorine removal, accompanied by fixation of aluminum, takes place tending to decrease the ratio Ti/Al as the reaction goes on. The formula given above is therefore a good approximation only when the reaction time does not exceed a few hours. It should also be kept in mind that it applies to reactions run at temperatures not exceeding 65°C. At higher temperatures more methane is produced in the reaction, and the C/H ratio of the nonvolatile product is lowered appreciably.

A similar composition of the surface product was obtained by Miotto,[4] who used multistep reactions and long total reaction times to establish the stoichiometry. The ratio Al:C:H = 1:2. 5:6 given by this author differs nevertheless only slightly from our value.

## IV. EXCHANGE STUDIES

It has already been shown[1] that 45% of the hydrolyzable carbon may be exchanged for $CD_3$ when $Al(CD_3)_3$ is added to the nonvolatile product of the reaction between $TiCl_3$ and $Al(CH_3)_3$. This exchange reaction was used in order to obtain more information concerning the carbon-containing groups present in the surface product.

The nonvolatile product from a $TiCl_3$–$Al(CH_3)_3$ reaction was exchanged twice with an excess of $Al(CD_3)_3$ and divided into two parts of which one was hydrolyzed with $H_2O$ and the other with $D_2O$. The molar composition of the methane of hydrolysis is given in Table II.

TABLE II

Composition of the Methane Obtained on Hydrolysis of an Exchanged Reaction Product[a]

| Methane of hydrolysis | $H_2O$ | $D_2O$ |
|---|---|---|
| $CD_4$ | 0.010 | 0.442 |
| $CHD_3$ | 0.448 | 0.029 |
| $CH_2D_2$ | 0.010 | 0.065 |
| $CH_3D$ | 0.033 | 0.442 |
| $CH_4$ | 0.498 | 0.021 |

[a] Reaction temperature and time, 65°C./60 min.; decomposition temperature and time, 65°C./160 min.; exchange temperature and time, 20°C./30 min.

Assuming that a $CD_3$ group gives $CHD_3$ on hydrolysis with $H_2O$ and that a $CH_3$ group gives $CH_3D$ on hydrolysis with $D_2O$, one sees that 45% of the hydrolyzed carbon was present as exchangeable methyl groups and 44% as nonexchangeable groups. The surface product contains as many exchangeable methyl groups as nonexchangeable methyl groups. The proportion of $CH_4$ in the $H_2O$ hydrolysis is somewhat larger than that of nonexchangeable $CH_3$ groups. The difference can be attributed to the presence of $CH_2$, CH, and C groups in the reaction product, all of which give $CH_4$ on hydrolysis with $H_2O$. It seems safe to assume that an exchangeable $CH_3$ group of the surface compound gives only $CH_3D$ on hydrolysis with $D_2O$, as does $CH_3$ in $Al(CH_3)_3$. These have to be thought of as linked to Al in view of the great facility with which aluminum alkyls exchange alkyl groups. The infrared spectrum of the surface compound shows in fact that exchangeable and also nonexchangeable methyl groups are mainly or exclusively linked to aluminum. This makes the proposed mechanism of hydrolysis applicable to both kinds of groups.

The mixture of trimethyl aluminum recovered after exchange never contains more than 2–10% Cl with respect to Al fixed in the surface product. This means that the surface product has no exchangeable chlorine. It is probable that a further unimportant reaction takes place between $TiCl_3$ and $Al(CD_3)_3$, releasing Cl from the $TiCl_3$.

# V. INFRARED SPECTROSCOPIC INVESTIGATION OF THE SURFACE PRODUCTS

## Apparatus

The cells used throughout this work are of the type depicted on Figure 1. The cell body is made of Pyrex glass and carries a number of breakseals allowing successive manipulations on the vacuum line. The cell is melted off and transferred to the spectrometer when a spectrum is wanted. The windows, 2.5 cm. in diameter, are glued on with Ciba Araldite Adhesive 103. NaCl, KBr, and Irtran (Kodak) were used as window materials. After completion of the experiment the windows can be removed by dipping the cell in chloroform. A Perkin-Elmer Model 21 double-beam instrument calibrated in wavelengths was used.

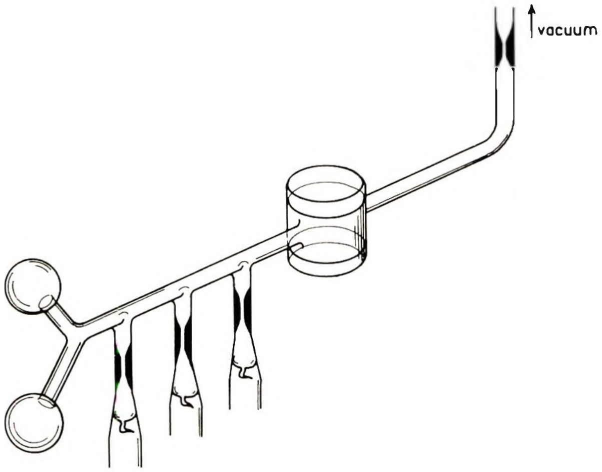


Fig. 1. Infrared cell.

## Method

### *Spectra of the Organometallic Compounds*

Small amounts of volatile compounds were distilled into one of the small bulbs. The cell was put in front of the entrance slit of the spectrophotometer in such a way that contact of the liquid with the windows was avoided. The cell path was chosen empirically, depending on the vapor pressure of the compound so as to give convenient band intensities.

Spectra were also taken of the nonvolatile methylaluminum dichloride. Crystals were introduced into the cell under vacuum. The cell attachments were made very small in order to permit heating of the complete cell to about 65°C. There was always some condensation on the window leading to strong deterioration of the NaCl when this was used as window material.

### *Spectra of the Surface Products*

**$\alpha$-TiCl$_3$ Systems.** The cell is provided with a sealed-in tungsten filament for the preparation of $\alpha$-TiCl$_3$ *in situ*. A mixture of TiCl$_4$ vapor and hydrogen is admitted and the filament is brought to glow intermittently. The windows are about 2.5 cm. apart and are cooled with an air stream in order to avoid cracking under thermal stress. A film of purple $\alpha$-TiCl$_3$ is obtained, covering the windows and the cell wall. This film is reacted with the vapor of the aluminum alkyl. Spectra are always taken after removal of all volatile material.

**$\beta$-TiCl$_3$ Systems.** In these experiments cells with a path length of 1–1.2 cm. are used. Aluminum foil is applied to the windows serving as electrodes for a high voltage-high frequency discharge. A mixture of TiCl$_4$ vapor and hydrogen is admitted. The windows are cooled by an air stream, and the discharge is turned on and off for short periods of time (a few seconds). A brown film deposits on the window and on the cell wall. The reaction is stopped when the windows appear opaque in strong light. It is worth mentioning that the windows do not undergo damage during the preparation of the TiCl$_3$ films.

**TiCl$_4$ Systems.** In these experiments a cell provided with two inlets is used. Two nitrogen streams, one carrying TiCl$_4$ and the other Al(CH$_3$)$_3$, merge in the cell. The whole apparatus is mounted in front of the spectrophotometer.

The spectrum of the solid reaction product which deposits in the cell is taken at various time intervals and varying flow ratios of the reactants.

## Results

### *Spectra of the Reagents*

**Titanium Trichloride.** Two weak, broad bands are found at 23.3 and 24.8 $\mu$ (Fig. 4). Depending on the thickness of the layer and also on the quality of the surface of the windows, scattering occurs up to about 5 $\mu$.

**Organometallic Compounds.** In the course of this work the spectra were taken over the range of 2–25 $\mu$ for Al(CH$_3$)$_3$, Al(CH$_3$)$_2$Cl, Al(CD$_3$)$_3$, Al(CD$_3$)$_2$Cl, Hg(CD$_3$)$_2$, Zn(CD$_3$)$_2$ (Fig. 2), TiCl$_3$CH$_3$, and TiCl$_3$CD$_3$ (Fig. 3); and over the range at 2–15 $\mu$ for AlCH$_3$Cl$_2$ and AlCD$_3$Cl$_2$.

The spectra of the methylaluminum compounds have been interpreted by Hoffmann[5] and more recently by Gray,[6] who included the deutero compounds. We prefer the assignments of Gray, given in Table III, because the interpretation of the spectra of the surface products is more satisfactory on this basis. It may be recalled that the methylaluminum compounds are dimeric and that chlorine occupies the bridge positions in the chloro derivatives.

**Trimethylaluminum.** Our spectra of Al(CD$_3$)$_3$ and of catalyst TiCl$_3$–Al(CD$_3$)$_3$ are somewhat difficult to reconcile with Gray's interpretation as far as the methyl deformation bands are concerned.

TABLE III
Infrared Spectra of Aluminum Compound[a]

| | $Al(CH_3)_3$ | | | $Al(CD_3)_3$ | | | $Al(CH_3)_2Cl$ | | | $Al(CD_3)_2Cl$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | cm.$^{-1}$ | $\mu$ | Intensity | cm.$^{-1}$ | $\mu$ | Intensity | cm.$^{-1}$ | $\mu$ | Intensity | cm.$^{-1}$ | $\mu$ | Intensity |
| $CX_3$ asymm. deformation | 1445 | 6.92 | vw | 1140 | 8.75 | vw | 1440 | 6.95 | vw | | 9.65[b] | w |
| | | | | | 9.65[b] | w | | | | | | |
| $CX_3$-bridge symm. deform. | 1255 | 8.00 | m | 1036 | 9.65 | m | | | | | | |
| | | | | | 10.45[b] | vs | | | | | | |
| $CX_3$-Al symm. deform. | 1208 | 8.30 | s | 955 | 10.48 | s | 1212 | 8.25 | s | 957 | 10.45 | s |
| | | | | | 10.45[b] | vs | | | | | | |
| Al-C stretching as/as $B_{1u}\nu_8$ | 772 | 12.95 | s | 677 | 14.78 | s | 720 | 13.90 | vs | 664 | 15.10 | s |
| $CX_3$-Al rocking | 700 | 14.30 | vs | 579 | 17.30 | vs | 700 | 14.30 | | 583 | 17.15 | vs |
| Al-C stretching s/as $B_{3u}\nu_{16}$ | 616 | 16.22 | m | 570 | 17.55 | | 585 | 17.10 | m | 530 | 18.88 | w |
| $CX_3$-bridge rocking | 572 | 17.50 | s | 472 | 21.20 | vs | | | | | | |
| bridge stretching $B_{3u}\nu_{17}$ | 480 | 20.80 | m | 435 | 23.00 | m | 310 | 32.20 | m | 307 | 32.60 | s |

[a] Unless otherwise noted, assignments according to Gray.[6]

[b] Assignments made in this paper.

Asymmetric methyl deformation, symmetric bridge-methyl deformation and symmetric outer methyl deformation occur at 6.92, 8, and 8.3 $\mu$, respectively, in $Al(CH_3)_3$. Gray assigns these fundamentals in $Al(CD_3)_3$ to bands lying at 8.75, 9.65, and 10.48 $\mu$. The shifts $\nu_H/\nu_D$ observed are:

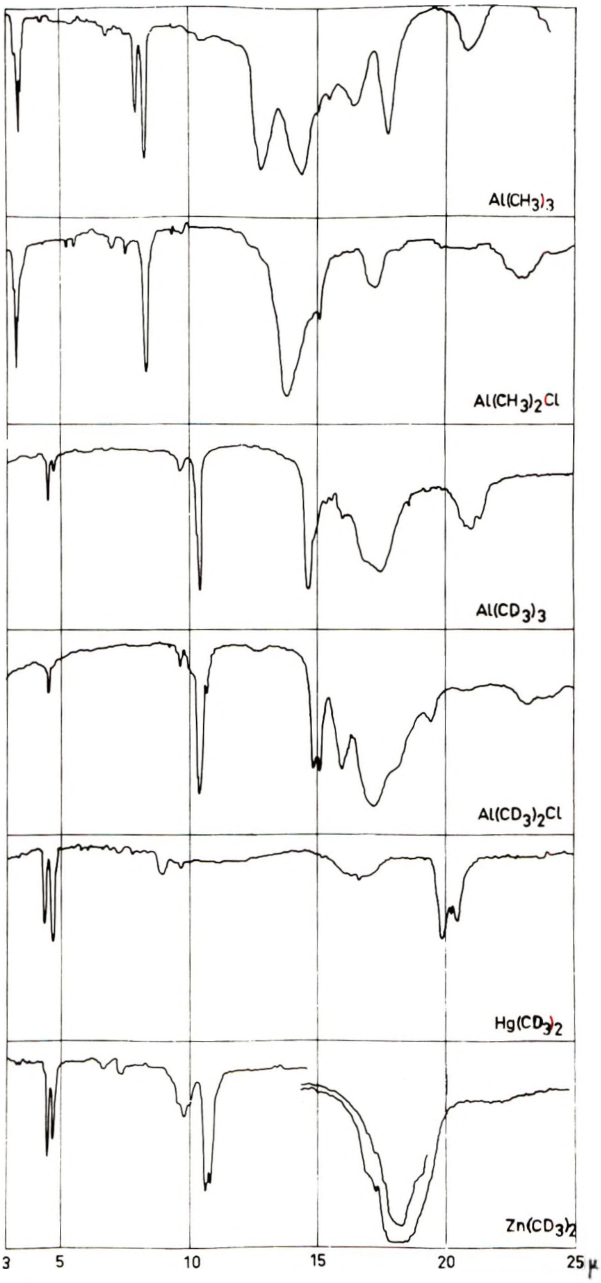


Fig. 2. Spectra of organometallic compounds taken in the vapor phase.

1.26, 1.21, and 1.27. The first of these seems low for the asymmetric methyl deformation. The change in dipole moment in a molecule $CH_3X$ induced by the asymmetric deformation is not in the direction of the bond C—X. X will therefore not much influence the frequency, and an isotope shift close to 1.41 for the pure H-D effect may be expected. The value found in the systems $CH_3Cl/CD_3Cl$, $CH_3Br/CD_3Br$, and $CH_3I/CD_3I$ is 1.38.[7] We find a value 1.33 in $Hg(CH_3)_2/Hg(CD_3)_2$ and 1.43 in $Zn(CH_3)_2/Zn(CD_3)_2$. A shift of 1.21 seems also small for the symmetric bridge methyl deformation whereas 1.27 for the outer methyl deformation appears to be in the right order of magnitude. The symmetric methyl deformation shows shifts of 1.29 in $Hg(CH_3)_2/Hg(CD_3)_2$, 1.28 in $Zn(CH_3)_2/Zn(CD_3)_2$, and 1.32 in $CH_3Cl/CD_3Cl$, $CH_3Br/CD_3Br$, and $CH_3I/CD_3I$.

Our spectrum of $Al(CD_3)_3$ differs from that of Gray in this region. The 8.75 μ band is absent, the 9.65 μ band is weak, and the 10.45 band is very strong. We find it better to ascribe asymmetric methyl deformation to 9.65 μ ($\nu_H/\nu_D$ = 1.395) and to consider the 10.45 μ band as due to symmetric deformation. This band then contains both kinds of methyl groups, bridge and outer methyls.

Further evidence for this assignment is the presence of the 9.65 μ band in $Al(CD_3)_2Cl$. If it has to do with the methyl bridges it should not be present in this spectrum.

This question will be discussed further when the catalyst spectra are considered. It should be noted here that in some spectra of $Al(CD_3)_3$ we observed a weak shoulder to the 10.45 band at 10.65 μ and a weak band at 16 μ which is not observed by Gray.

**Association of $Al(CD_3)_3$.** The comparison of the spectra of $Al(CH_3)_3$ and $Al(CD_3)_3$ in the methyl deformation region reveals differences that could be readily explained assuming that $Al(CD_3)_3$ is monomeric. Indeed, in $Al(CH_3)_3$ the symmetric methyl deformation gives two bands, 8 μ for the bridge methyl and 8.3 μ for the outer methyl, with a relative intensity of 1 to 2. $Al(CD_3)_3$ has only one strong band in the corresponding region at 10.45 μ. The 9.65 μ band, which we consider to be due to the asymmetric deformation, is weak and not comparable in intensity with the 10.45 band.

It seemed, therefore, worthwhile to study the cryoscopic behavior of $Al(CD_3)_3$. Benzene was used as solvent. Prior to use it was distilled from $AlEt_3$ and only the middle fraction was taken. The cell provided with a Beckmann thermometer and a magnetic stirrer was connected to a vacuum

TABLE IV
Association Factors for $Al(CD_3)_3$ in Benzene Solution

| Molarity of solute expressed as monomers $m_w$ | Melting point lowering $\Delta T$, °C. | Molarity of solute $m_t$ | Association factor $R$ |
|---|---|---|---|
| 0.1493 | 0.375 | 0.0728 | 2.05 |
| 0.2664 | 0.700 | 0.1355 | 1.97 |
| 0.4568 | 1.220 | 0.2347 | 1.95 |

line. A known amount of benzene (about 25 cm.[3]) and small known amounts of $Al(CD_3)_3$ (200–300 mg.) were subsequently distilled into it. No evidence of reaction was noted. The working formula given by Pitzer and Gutowsky[8] was used. Table IV gives the experimental data and results.

The results show that $Al(CD_3)_3$ is dimeric even in dilute solution.

**Dimethylaluminum Chloride.** The spectrum of $Al(CH_3)_2Cl$ is in rather good agreement with the spectra of this compound that have already been published.[5,6,9] The band at 23 $\mu$ (435 cm.$^{-1}$) has been discussed in some length by Gray[6] and was attributed by him to the presence of $Al(CH_3)Cl_2$.

Slight differences exist between our spectrum of $Al(CD_3)_2Cl$ and the data of Gray. Our spectrum contains a shoulder at 10.66 and a strong band at 16 $\mu$. These bands may, however, be due to an impurity. The 10.66 $\mu$ absorption can be caused by traces of the dichloro compound. The latter is also responsible for the 23.2 (430 cm.$^{-1}$) band according to Gray.

**Methylaluminum Dichloride.** The spectra of $AlCH_3Cl_2$ and $AlCD_3Cl_2$ were taken in the region 2–15 $\mu$. Some of the bands in the NaCl spectrum are due to complex formation.[10] This can be avoided by using windows of Irtran, an inert material having good transparency between 2 and 13 $\mu$. The complete spectrum of $AlCH_3Cl_2$ free of bands due to complex formation has been obtained by Groenewege[9] in hydrocarbon solution.

We observed the following bands (in $\mu$): $AlCH_3Cl_2$ in NaCl: 7.0 (vw), 7.9 (w), 8.3 (m), 8.5 (m), 11.6 (s), 12.5 (s), and 14.15 (s); $AlCH_3Cl_2$ in Irtran: 7.0 (vw), 7.9 (w), 8.3 (m), 11.7 (s), 12.5 (s); $AlCD_3Cl_2$ in Irtran: 10.45 (m), 12.5 (m).

The 8.5 $\mu$ band has to be attributed to the complex since it is absent in the Irtran spectrum. The spectrum of $AlCD_3Cl_2$ in NaCl has probably a corresponding band at 10.7 $\mu$ which shows up in the spectrum of the $TiCl_3$–$Al(CD_3)_2Cl$ system when this is taken with NaCl windows.

**Mercurydimethyl and Zincdimethyl.** We find it worthwhile to include the spectra of the deuterated compounds, which, in our knowledge, have not been published elsewhere. Using the assignments of Gutowsky[11] we tentatively interpret the spectra as summarized in Table V.

TABLE V

Infrared Spectra of Dimethylmercury and Dimethylzinc

| | Band, $\mu$ | | | Band, $\mu$ | | |
|---|---|---|---|---|---|---|
| | $Hg(CH_3)_2$ | $Hg(CD_3)_2$ | $\nu_H/\nu_D$ | $Zn(CH_3)_2$ | $Zn(CD_3)_2$ | $\nu_H/\nu_D$ |
| Asymm. methyl deformation | 6.78 | 9.0 | 1.33 | 6.9 | 9.9 (?) | 1.43 (?) |
| Symm. methyl deformation | 8.3 | 10.7 | 1.29 | 8.43 | 10.8 | 1.28 |
| Methyl rocking | 12.9 | 16.5 | 1.28 | 14.15 | 18.2 | 1.28 |
| Metal-carbon stretching | 18.2 | 19.9 | 1.09 | 16.25 | 17.2 | 1.06 |

TABLE VI

Spectra of $TiCl_3CH_3$ and $TiCl_3CD_3$, Vapor Phase

| | $TiCl_3CH_3$ | | | $TiCl_3CD_3$ | | | |
|---|---|---|---|---|---|---|---|
| Vibrations | $\mu$ | cm.$^{-1}$ | Intensity | $\mu$ | cm.$^{-1}$ | Intensity | $\nu_H/\nu_D$ |
| $CX_3$ asymm. deform. | | Not observed | | | Not observed | | |
| $CX_3$ symm. deform. | 7.34 | 1362 | w | 10.04 | 995 | w | 1.37 |
| Ti—C stretching | 18.75 | 533 | s | 19.30 | 518 | vs | 1.03 |
| Ti—Cl asymm. stretch. | 20.10 | 498 | s | 20.50 | 488 | s | |
| $CX_3$ rocking | 21.94 | 456 | s | Expected <400 | | | |
| Ti—Cl symm. stretch | Expected <400 | | | Expected <400 | | | |

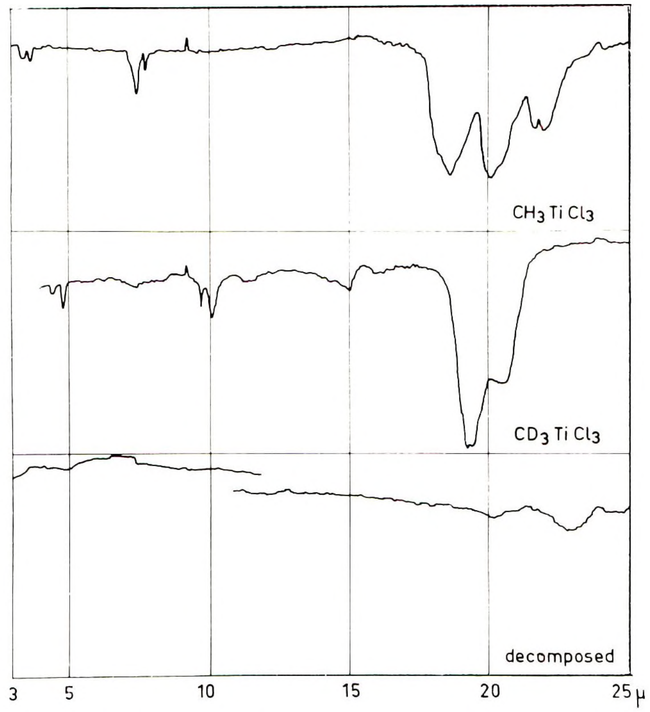


Fig. 3. Spectra of $TiCl_3CH_3$, $TiCl_3CD_3$, and of the solid product of decomposition.

**Methyltitanium Trichloride.** Spectra of this compound have been reported by Groenewege,[9] by Karapinka, Smith, and Carrick,[12] and by Gray.[6] The interpretations given by these authors differ considerably from one another, the main difficulty being the assignment of the Ti-C stretching mode. Our spectrum of $TiCl_3CD_3$ permits to settle the controversy. The spectra are reproduced in Figure 3 and the assignments are given in Table VI.

The assignment of Ti-C stretching to the 533 cm.$^{-1}$ band is arrived at in the following way. The spectrum of $TiCl_3CH_3$ consists of three very strong bands in the KBr region: 533, 498, and 456 cm.$^{-1}$. In the spectrum of $TiCl_3CD_3$ only two bands are found: 518 and 488 cm.$^{-1}$. The 456 cm.$^{-1}$ band cannot be Ti-C stretching, since an acceptable shift, $\nu_H/\nu_D$ between 1 and 1.1, would give a band between 456 and 415 cm.$^{-1}$ on deuteration. The 456 cm.$^{-1}$ band must be attributed to $CH_3$ rocking and may be expected for the deuterated compound to occur around 330 cm.$^{-1}$ if one accepts a shift constant of approximately 1.40 for this mode. A very weak band at 355 cm.$^{-1}$ was noticed by Gray in the spectrum of $TiCl_3CD_3$.[6]

Of the two bands left, 533 cm.$^{-1}$ and 498 cm.$^{-1}$, one has to be attributed to Ti-C stretching and the other to Ti-Cl asymmetric stretching. The latter should be retained at approximately the same frequency in the $TiCl_3CD_3$ spectrum. We assign therefore the 498 cm.$^{-1}$ band to Ti-Cl asymmetric stretching (488 cm.$^{-1}$ in $TiCl_3CD_3$), and by exclusion the 533 cm.$^{-1}$ band becomes Ti-C stretching. Gray[6] and Groenewege[9] have both attributed the 498 cm.$^{-1}$ band to an impurity. The degenerate asymmetric Ti-Cl stretching of $TiCl_4$ occurs exactly at this position. $TiCl_4$ could either be present as an impurity in the sample or formed by the decomposition of $TiCl_3CH_3$. We are sure, however, that our samples contained very little if no $TiCl_4$, and that almost no decomposition occurred while the spectra were taken. The cell body was painted in black in order to avoid photochemical decomposition. The spectra were taken quickly and could be taken four times without change in intensity of any of the bands. The fourth spectrum showed the appearance of weak broad bands at 23.3 and 24.8 $\mu$ which we have observed in the spectra of $\beta$-$TiCl_3$ and also in the spectra of the solid reaction product obtained when $TiCl_3CH_3$ is exposed to ultraviolet light.

The spectra contain only one significant band for each compound in the methyl deformation region: 1362 cm.$^{-1}$ for $TiCl_3CH_3$ and 995 cm.$^{-1}$ for $TiCl_3CD_3$. Of the two deformations, asymmetric and symmetric, the latter should be the stronger, and the above band positions are assigned to it. Groenewege made the same assignment earlier, and he drew the attention to the anomalously high value of this frequency with respect to the correlation of Sheppard[13] between the $CH_3$ deformation frequency and the electronegativity of the metal atom. Also the isotopic shift $\nu_H/\nu_D = 1.37$, which we observe, appears unusually high. Both facts may be due to the transition metal nature of titanium.

The weak bands at 7.6 $\mu$ (1320 cm.$^{-1}$) in the spectrum of $TiCl_3CH_3$ and 9.6 $\mu$ (1042 cm.$^{-1}$) in that of $TiCl_3CD_3$ are attributed to methane. $CH_4$ has an intense band at 1306 cm.$^{-1}$. The corresponding band of $CD_4$ comes at 995 cm.$^{-1}$ and would be covered by the deformation band of $TiCl_3CD_3$. The very weak band at 1042 cm.$^{-1}$ could be due to small amounts of $CD_3H$. Methane, the main gaseous decomposition product of methyltitanium trichloride, is very likely to be formed under the experimental conditions used in obtaining the spectra.

### *Spectra of the Surface Products*

**$\alpha$-$TiCl_3$ Systems.** The spectra of the surface products obtained by reaction of aluminum alkyls on $\alpha$-$TiCl_3$ contain only very weak bands. They are qualitatively the same as the much more intense spectra obtained with $\beta$-$TiCl_3$. Conclusions reached for $\beta$-$TiCl_3$ systems may therefore be applied to the $\alpha$-$TiCl_3$ systems.

The difference in band intensity is certainly due to the much smaller surface of $\alpha$-$TiCl_3$ as compared with $\beta$-$TiCl_3$.[3] That the surface compound is chemically the same in both cases was already shown by our results on the stoichiometry of the catalyst-forming reactions.[2,3]

**$\beta$-$TiCl_3$ Systems.** Typical spectra are reproduced in Figure 4.

*$TiCl_3$ + $Al(CH_3)_3$.* Most of the bands may be interpreted easily by analogy with the spectra of $Al(CH_3)_3$ and $Al(CH_3)_2Cl$: 6.85 $\mu$ is asymmetric

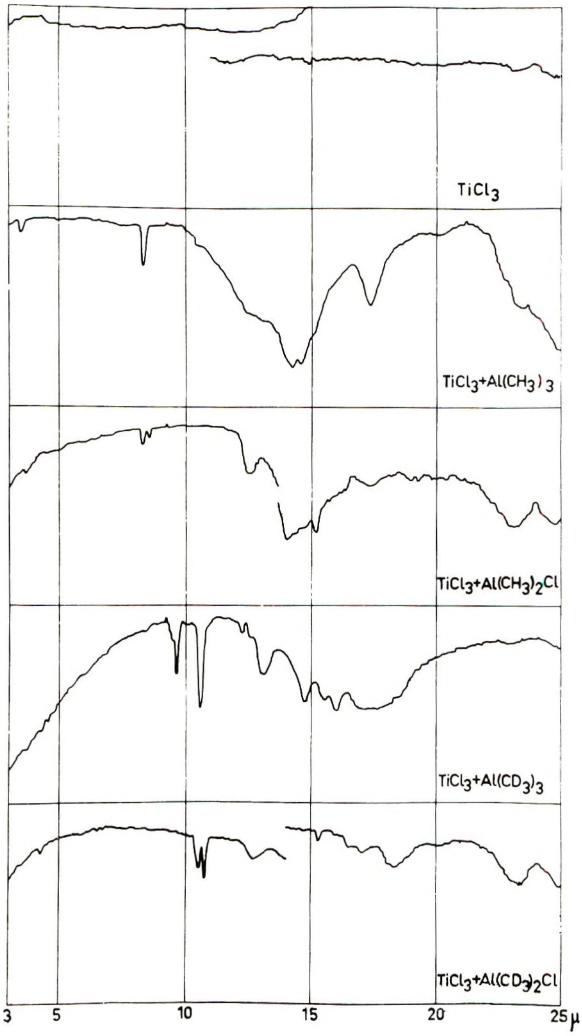


Fig. 4. Spectra of surface products.

methyl deformation and 8.3 μ is symmetric outer methyl deformation. A broad band covers the region 12–16 μ and shows a well-resolved maximum at 14.10 μ. This is clearly equivalent to the 14.3 μ band of $Al(CH_3)_3$ and $Al(CH_3)_2Cl$, outer methyl rocking. In some of the spectra additional structure is found with a maximum at 13 μ. This probably corresponds to the 12.95 μ band of $Al(CH_3)_3$ assigned to asymmetric Al-C stretching. The 17.3 μ band may be compared with the 17 μ band in $Al(CH_3)_2Cl$ for symmetrical Al-C stretching.

The broad strong band, which is seen on Figure 4 to set in at 22 μ is doubtful. Some of our spectra did not show such strong absorption in this region. In some of the spectra weak additional bands are found at 8.5, 9.7, and 11.3 μ.

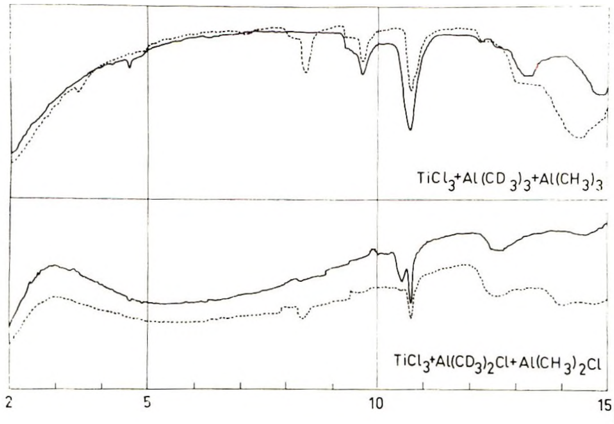


Fig. 5. $CD_3/CH_3$ exchange: (——) the $TiCl_3$–$Al(CD_3)_3$ and $TiCl_3$–$Al(CD_3)_2Cl$ systems; (– –) after exchange with $Al(CH_3)_3$ and $Al(CH_3)_2Cl$.

Obviously absent in the spectrum are the bands of $Al(CH_3)_3$ at 8.0, 17.5, and 20.8 $\mu$, that have to do with the bridging methyl groups.

The spectrum taken as a whole bears close resemblance to the $Al(CH_3)_2Cl$ spectrum. The most likely structure of the aluminum alkyl part of the surface product which gives rise to the spectrum seems to be a monomeric $Al(CH_3)_2$ unit, the aluminum atom of which is coordinated to chlorine atoms of the $TiCl_3$ surface.

*$TiCl_3$ + $Al(CD_3)_3$.* The 9.65 $\mu$ band is present in the parent $Al(CD_3)_3$ and in $Al(CD_3)_2Cl$ and is attributed to $CD_3$ asymmetric deformation for reasons given above. Whereas the 8.3 $\mu$ band for symmetric outer methyl deformation in $Al(CH_3)_3$ is preserved at the same wavelength in the $TiCl_3$–$Al(CH_3)_3$ spectrum, a shift is found for the corresponding band in this case: from 10.45 $\mu$ in $Al(CD_3)_3$ to 10.65 $\mu$. This fits with the idea that the 10.45 $\mu$ band in $Al(CD_3)_3$ contains both bridge and outermethyl deformation. The shift of this band to 10.65 $\mu$ has, then, the same meaning as the disappearance of the 8 $\mu$ band in the $TiCl_3$–$Al(CH_3)_3$ system and is due to the absence of bridging methyl groups.

The 14.75 $\mu$ peak of the broad band which covers the region 14–19 $\mu$ has probably the same origin as the 14.78 $\mu$ band in $Al(CD_3)_3$, i.e., Al-C asymmetric stretching. The maximum of the broad band lies around 17.25 $\mu$. This is again the outer methyl rocking which falls at 17.3 $\mu$ in $Al(CD_3)_3$ and at 17.15 $\mu$ in $Al(CD_3)_2Cl$. It corresponds to the maximum at 14.10 $\mu$ in the $TiCl_3$–$Al(CH_3)_3$ system.

Clearly absent is the 21.2 $\mu$ band of the parent $Al(CD_3)_3$ assigned to $CD_3$ bridge rocking. This is further good evidence for the absence of bridging $CD_3$ groups in the $TiCl_3$–$Al(CD_3)_3$ system.

Additional weak bands for which we have no interpretation are found at 13.1, 15.5, and 16 $\mu$. The first two possibly correspond to the weak 9.7 and 11.3 $\mu$ bands found in the $TiCl_3$–$Al(CH_3)_3$ system giving the same $\nu_H/\nu_D$

value. It is again clear that the longer wavelength part of the spectrum is very similar to the $Al(CD_3)_2Cl$ spectrum. A structure identical to that proposed for the $TiCl_3$–$Al(CH_3)_3$ product may therefore be admitted.

*$CH_3/CD_3$ Exchange in $TiCl_3$–$AlMe_3$ Systems.* That some of the methyl groups in the surface product undergo exchange can be confirmed easily by infrared spectra. Figure 5 shows the spectral changes which a $TiCl_3$–$Al(CD_3)_3$ product has undergone after a contact of about 2 hr. with excess $Al(CH_3)_3$. In fact, the same shifts are obtained to the same extent after much shorter contact times, indicating that the exchange is a fast reaction.

The biggest change occurs for the $CD_3$ deformation band at 10.65 $\mu$. Its intensity is greatly reduced, and a corresponding $CH_3$ band is formed at 8.3 $\mu$. This is clear evidence that the methyl groups undergoing exchange are bound to aluminum. Apparently, the 9.65 $\mu$ band undergoes little if no decrease, which is in contradiction with our interpretation of this band as outer $CD_3$ deformation. This band is, however, rather weak and the background line not being well defined and constant, the quantitative comparison before and after exchange is difficult. The appearance of a very weak band at 6.95 $\mu$ is in accord with a small decrease of the 9.65 band. The 14.75 $\mu$ maximum is shifted to 14.30 $\mu$, again good evidence that Al-$CD_3$ is changed to Al-$CH_3$. On exchange of a $TiCl_3$–$Al(CH_3)_3$ product with Al-$(CD_3)_3$ the same changes are found to occur in the reverse sense. It is probable that only the methyl groups exchange and not the aluminum atom. First of all, not all methyl groups exchange, and secondly the 10.65–8.3 $\mu$ shift is also observed on exchange with $Zn(CH_3)_2$, indicating that the aluminum atom is retained.

*$TiCl_3$ + $Al(CH_3)_2Cl$.* This spectrum shows two weak bands in the Al-$CH_3$ deformation region at 8.3 and 8.5 $\mu$, strong bands at 12.5 and 14 $\mu$, medium at 17.2 and 23.2 $\mu$. Of these, the 8.3, 14, 17.2, and 23.2 $\mu$ bands are present in the spectrum of the parent compound $Al(CH_3)_2Cl$. The remaining bands are present in the spectrum of $AlCH_3Cl_2$ when taken in NaCl.

In the whole a close resemblance is found between the spectrum of this system and that of $Al(CH_3)_2Cl$.

*$TiCl_3$ + $Al(CD_3)_2Cl$.* The spectrum, with bands at 10.5 (w), 10.7 (w), 12.7 (m), 15.2 (s), 18.2 (s), and 23.3 (w) $\mu$ is similar to the previous one. Taken with Irtran windows it contains only one band, at 10.5 $\mu$, in the methyl deformation region. The 10.7 $\mu$ band is therefore indicative of the presence of $Al(CD_3)Cl_2$. It is impossible to decide whether this compound is only trapped by the NaCl window or whether it is also retained by the $TiCl_3$ in a strong chemisorption.

On exchange of the catalyst with $Al(CH_3)_2Cl$ the 10.5 $\mu$ band shifts to the 8.3 $\mu$ position, whereas the 10.7 $\mu$ band remains unchanged (Fig. 5). The conclusions derived from the spectra of the product, obtained in the reaction of dimethylchloroaluminum and $TiCl_3$, are that methyldichloroaluminum is formed in this reaction and that the surface product must be very similar to that obtained in the reaction between $TiCl_3$ and trimethylaluminum.

*$TiCl_4$ + Trimethylaluminum.* In view of the fact that the concentration

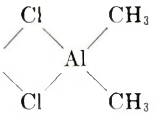
of catalyst obtained from $TiCl_3$ is limited by the surface and therefore small it seemed worth while to investigate the reaction product of $TiCl_4$ and trimethylaluminum, which should because of its high concentration be better observable by infrared.

The experimental difficulties, amongst others the obtention of reproducible and known flow rates of reagents, are very great and a thorough study of this system was not undertaken. It seems that better experimental techniques have been used by Gray et al.[14] The spectra obtained show indeed strong absorption bands all of which are, however, also observable with $TiCl_3$ catalysts. As main result these experiments reveal the similarity of the final reaction products.

### Conclusions Derived from the Infrared Spectroscopic Study

(*1*) All of the bands contained in the spectra of the surface products can be attributed to vibrations of methyl groups bound to aluminum.

(*2*) The absence of bands characteristic of bridge methyl groups and the close resemblance of the spectra to that of $AlClMe_2$ indicates that the aluminum alkyl part of the surface product has only outer methyl groups. The structure I appears, therefore, to be a plausible one



I

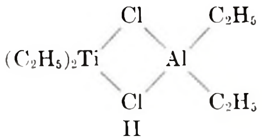
(*3*) No evidence is found for the existence of Ti-C bonds. This conclusion is based on comparison with the spectrum of $TiCl_3CH_3$.

## VI. DISCUSSION AND CONCLUSIONS

The empirical formula, $Ti_2Cl_5Al[C_h]_{2.05}[C_{n-h}]_{0.25}H_{5.2}$, of the nonvolatile surface product formed in the reaction between $\alpha$-$TiCl_3$ and $Al(CH_3)_3$ was derived from stoichiometric data only. The infrared and exchange studies show that the surface product contains methyl groups linked to aluminum. Such groups give $CH_3D$ on hydrolysis with $D_2O$ and the amount of $CH_3D$ present in the methane of hydrolysis is therefore a measure of their concentration in the surface product, 80% according to the data of run 120 of Table I. The methyl groups consist of exchangeable and nonexchangeable ones in equal amounts. This information on the structure of the surface product may be expressed by the following formula:

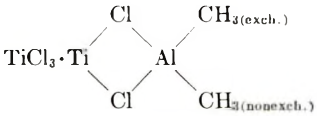
$$Ti_2Cl_5Al[CH_{3\text{exch.}}]_{0.82}[CH_{3n-\text{exch.}}]_{0.82}$$
$$[C_{h\text{residual}}]_{0.41}[C_{n-h}]_{0.25}[H_{\text{residual}}]_{0.28}$$

This formula may be compared with the structure (II) proposed by Natta et al.[15-17] for the product of the reaction between dicyclopentadienyltitanium dichloride and triethylaluminum.



II

The surface product of the $TiCl_3$–$Al(CH_3)_3$ reaction contains Al and $CH_3$ in a ratio close to 1:2. We propose as its predominant constituent a compound III with a structure similar to that above:



III

A plausible stereochemical model can be given for this compound. We assume that the titanium and chlorine atoms occupy the same positions as in the α-$TiCl_3$ crystal and that the aluminum atom and the methyl groups have the same relative position as in trimethylaluminum and related aluminum compounds. The model is drawn in perspective in Figure 6.

The chlorine atoms having their centers in $Cl_1$ and $Cl_2$, belong to the upper external layer of a α-$TiCl_3$ crystal. $C_1$ and $C_2$, the centers of the methyl groups, lie in a plane Ti-Al-$C_1$-$C_2$, perpendicular to the plane Ti-$Cl_1$-Al-$Cl_2$. $Cl_1$ and $Cl_2$ are located respectively behind and before the Ti-Al-$C_1$-$C_2$ plane.

Now the question is whether the $C_2$ methyl groups can be accommodated in the hole left by a chlorine atom, closest neighbor to $Cl_1$ and $Cl_2$, that has been removed in the course of the reaction. In deciding this one meets with the difficulty as to what dimensions to give to the methyl group. Pauling[25] has discussed the van der Waals radius of the methyl group and assigned it

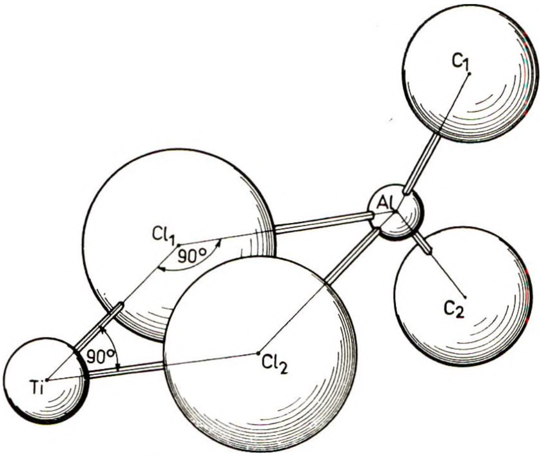


Fig. 6. Perspective drawing of the surface compound. Only those chlorine atoms that take part in the formation of the Ti–Cl–Al bridges are shown.

TABLE VII

Stereochemical Data on some Titanium and Aluminum Compounds

| Compound | | Distance, A. | Angle |
|---|---|---|---|
| α-TiCl$_3$[a] | Ti—Cl distance | 2.55 | |
| | Cl—Cl—Cl angle (Cl in the same layer and neighbors) | | 60° |
| | Cl—Ti—Cl angle (Cl in the same layer and neighbors) | | 90° |
| $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$[b] | Ti—Cl (bridge) | 2.5 | |
| | Al—Cl (bridge) | 2.5 | |
| | Al—C (out of bridge) | 2.0 | |
| | Cl—Ti—Cl (bridge) angle | | 90° |
| | Cl—Al—Cl (bridge) angle | | 90° |
| | Ti—Cl—Al (bridge) angle | | 90° |
| $[Al(CH_3)_3]_2$[c] | Al—C (bridge) | 2.23–2.34 | |
| | Al—C (out of bridge) | 1.99–2.00 | |
| | Al—C—Al (bridge) angle | | 70° |
| | C—Al—C (bridge) angle | | 110° |
| | C—Al—C (out of bridge) | | 124 |
| $[AlCl(CH_3)_2]_2$[d] | Al—Cl (bridge) | 2.31 | |
| | Al—C (out of bridge) | 1.85–2.00 | |
| | Cl—Al—Cl (bridge) angle | | 89 ± 4° |
| | C—Al—C (out of bridge) angle | | 120–135° |
| $(AlCl_2CH_3)_2$[e] | Al—Cl (bridge) | 2.25 | |
| | Al—Cl (out of bridge) | 1.93 | |
| | Al—C (out of bridge) | 2.05 | |
| | Cl—Al—Cl (bridge) angle | | 88.9° |
| | Cl—Al—C (out of bridge) angle | | 124.5° |
| | Al—Cl—Al (bridge) angle | | 91.1° |
| | Cl—Al—C (bridge-out of bridge) angle | | 105.8° |
| Radii[f] | Ionic $Cl^-$ | 1.81 | |
| | Ionic $Ti^{+3}$ | 0.69 | |
| | Ionic $Al^{+3}$ | 0.50 | |
| Present model | Ti—Cl (bridge) | 2.55 | |
| | Al—Cl (bridge) | 2.55 | |
| | Cl—Ti—Cl (bridge) angle | | 90° |
| | Cl—Al—Cl (bridge) angle | | 90° |
| | Ti—Cl—Al (bridge) angle | | 90° |
| | Al—C (out of bridge) | 2.00 | |
| | C—Al—C (out of bridge) angle | | 126° |
| Radii (present model) | Ionic $Ti^{+3}$ | 0.69 | |
| | Ionic $Cl^-$ | 1.81 | |
| | $CH_3$ group | 1.81 | |

[a] Data of Natta et al.[18,19]

[b] Data of Natta et al.[15-17]

[c] Data of Lewis and Rundle.[20]

[d] Data of Brockway and Davidson.[21]

[e] Data of Allegra et al.[22]

[f] Data of Wells[23] and Hush and Pryce.[24]

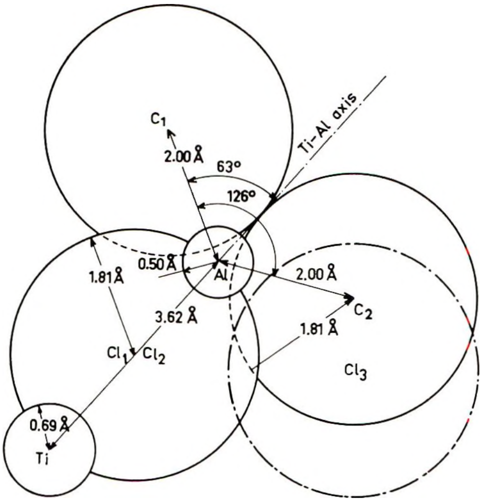


Fig. 7. Scale drawing of the $\alpha$-$TiCl_3$ surface compound showing that the methyl (or methylene) group fits in the chlorine vacancy.

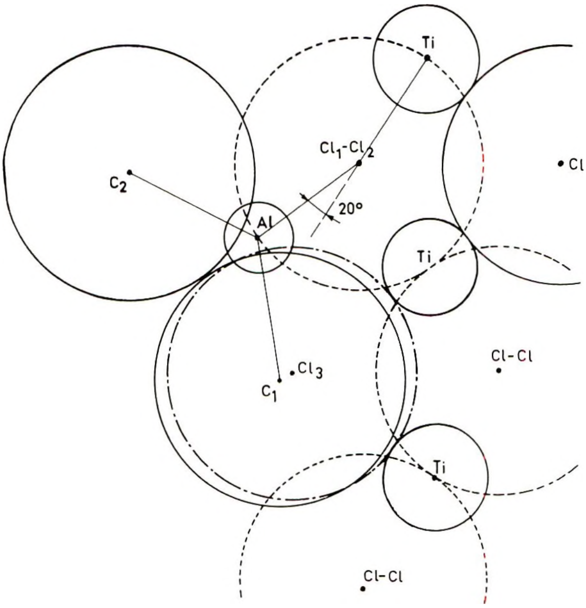


Fig. 8. Scale drawing of the $\beta$-$TiCl_3$ surface compound cut along the Ti-Al-$C_1$-$C_2$ plane.

2 A. The effective radius, however, depends on the direction in space. In the case of $Al(CH_3)_3$,[20] the outer methyl groups are at a C-C distance of about 3.4 A., considerably less than the value expected on the basis of the van der Waals radius. Using a Stuart model for $CH_3$ and a $TiCl_3$ lattice on scale one finds that the methyl group fits easily in a chlorine vacancy. In

the absence of a theoretically sound value for the dimensions of the methyl group we shall therefore in drawing a stereochemical model give it the radius of $Cl^-$, i.e., 1.81 A.

Using the values of bond lengths, bond angles and radii given in the lower part of Table VII that are equal to or very close to experimental values obtained on related compounds, it is possible to draw Figure 7. The chlorine vacancy is represented by a dotted circle, the center of which, $Cl_3$, lies in the plane Ti—Al—$C_1C_2$. The figure, drawn to scale, shows that the $C_2$ methyl group fits very easily in the chlorine vacancy.

The proposed structure is in good agreement with the observed infrared spectra. These contain bands due to outer methyl vibrations and no bands characteristic of bridge methyl vibrations. The model also explains why half of the methyl groups are easily exchanged for $CD_3$ whereas the other half do not undergo exchange: the $C_1$ methyl group is easily accessible to any exchanging agent whereas the $C_2$ methyl group is shielded by the surrounding chlorine atoms of the upper layer of the $TiCl_3$ crystal.

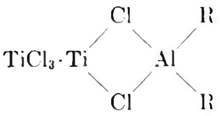
It should be remembered that the reaction product covers almost the entire surface of the $\alpha$-$TiCl_3$ crystal. If now the proposed structure represents accurately the predominant surface compound, the conclusion is reached that, with methyl groups filling the chlorine vacancies, the surface titanium atoms in the 001 plane are not accessible.

The model remains valid also for higher alkyls. It is easily seen that, e.g., in the case of ethyl, no steric strain results when the methylene groups are kept in the fixed positions $C_1$ and $C_2$.

For the $\beta$-$TiCl_3$ systems, a similar model may be accepted. We assume that the most developed faces of the $\beta$-$TiCl_3$ crystals are the faces parallel to the *c* axis of the titanium atoms.[3] From the crystallographic data on $\beta$-$TiCl_3$ given by Natta et al.[18,19] and the bond lengths, angles, and radii of Table VII it is possible to build the model of Figure 8. In this case the methyl groups cannot fit in the chlorine vacancy without imparting strain on the molecule. It is necessary to bend the Ti—Cl—Al bonds by an angle of 20° and the aluminum atom lies now outside the Cl—Ti—Cl plane. Again an interesting feature of this model is that the $\beta$-$TiCl_3$ system has no titanium atoms accessible from the main crystal faces, those parallel to the c axis.

The results and conclusions that are presented in this and the foregoing papers enable us to draw a picture of the alterations undergone by the $TiCl_3$ surface in the reaction with aluminum alkyls. The virgin surface of $TiCl_3$ whether $\alpha$ or $\beta$, is essentially composed of chlorine atoms. Titanium atoms in an external position are found only in the less developed faces: the lateral faces of the $\alpha$-$TiCl_3$ leaflets and the tops of the $\beta$-$TiCl_3$ stacks, or at surface defects.

In a first fast reaction step, in which surface chlorine atoms are exchanged for alkyl groups, half of the titanium atoms closest to the surface become alkylated. The alkylated surface gives rise to two parallel reactions. The most important of these, a further reaction with aluminum alkyl, leads to the formation of a surface compound



The structure of this compound may be imagined to be such that one R group, or part of one R group, occupies now the position of the surface chlorine that was removed in the very first reaction. No surface vacancies are therefore created, and the titanium atoms have not become any more accessible from the outside than they were before. This model strictly applies only to the main crystal faces. The formation of the same surface compound on the less developed faces will not change appreciably the accessibility of external titanium atoms.

The Ti—C bond being inherently unstable, the alkylated surface may however, also undergo decomposition prior to the reaction with aluminum alkyl. In this case a vacancy is formed in the surface and a titanium atom becomes accessible from the outside. This reaction will not be important when R does not have a β-H atom, for instance when R is methyl or neopentyl.[26] It will, however, occur readily for instance when R is ethyl. This will eventually give rise to accessible titanium atoms in the main crystal faces such as exist on edges, defects and less developed faces.

With this description of the $TiCl_3$ surface after its reaction with aluminumalkyl in mind we arrive now at the crucial and much debated question: what makes this surface an active polymerization catalyst? The conclusions arrived at here, and the results obtained in an electron micrographic study of the $TiCl_3$–$AlMe_3$ catalyst[27] permit a partial answer. The comparison of electron micrographs, taken before and after polymerization, show that active sites exist only at those places where titanium atoms are accessible. This is an essential condition for polymerization to occur. The aluminum-containing compound which covers the surface is certainly not catalytically active in its most abundant form, that is on the well-developed crystal faces where it is completely surrounded by chlorine atoms. This is the reason why we have used the terms "nonvolatile product," "surface product," and "surface compound," and why we have avoided the work "catalyst" throughout this paper.

Experiments aimed at a better understanding of the intimate mechanism of polymerization will be presented in subsequent papers of this series.

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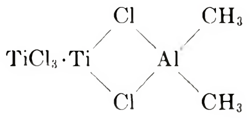
## Résumé

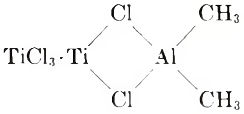
Le produit formé par la réaction entre $Al(CH_3)_3$ et $TiCl_3$ à la surface du $TiCl_3$ a été étudié. L'étude stoechiométrique de la réaction, les réactions d'échange des groupes hydrocarbonés et leur hydrolyse, ainsi que l'étude par spectroscopie infra-rouge font admettre la présence prépondérante d'un composé dont la formule est



Un modèle stéréochimique de ce composé est proposé, qui est adapté aux faces 00.1 du $\alpha$-$TiCl_3$, de loin les plus développées. Dans ce modèle, les atomes de titane et de chlore occupent les mêmes positions que dans le réseau cristallin du $\alpha$-$TiCl_3$ pur. Les deux groupes méthyles sont stériquement différents. L'un d'eux sort nettement de la surface tandis que l'autre occupe le trou laissé par un atome de chlore enlevé pendant la réaction. Ceci est en accord avec le fait expérimental que seulement la moitié des groupes méthyles est échangeable au contact de $Al(CD_3)_3$. La structure est telle que les atomes de titane de la face 001 sont inaccessibles. Un modèle similaire est proposé pour le $\beta$-$TiCl_3$, conduisant à des conclusions semblables. Les spectres IR de $Al(CH_3)_3$, $Al(CD_3)_3$, $AlCl(CH_3)_2$, $AlCl(CD_3)_2$, $AlCl_2CH_3$, $AlCl_2CD_3$, $TiCl_3CH_3$, $TiCl_3CD_3$, $Zn(CD_3)_2$ et $Hg(CD_3)_2$ et ceux des produits de surface obtenus par réaction de certains de ces composés sur $TiCl_3$ sont donnés.

## Zusammenfassung

An der Oberfläche von $TiCl_3$ entsteht bei der Reaktion mit $Al(CH_3)_3$ ein nicht flüchtiges Reaktionsprodukt. Mit Hilfe von stoechiometrischen Daten, $CH_3/CD_3$ Austausch und infrarot Spektren schliessen wir auf das Vorhandensein einer Oberflächenverbindung folgender Struktur:



Für $\alpha$-$TiCl_3$ schlagen wir ein Modell vor, in dem die Titan- und Chloratome die gleichen Positionen wie im $TiCl_3$-Gitter einnehmen. Die zwei Methylgruppen der Oberflächenverbindung sind sterisch verschieden. Eine ragt aus der Oberfläche heraus, die andere nimmt die bei der Reaktion entstehende Chlorlücke ein. Dieses Modell steht in Einklang mit dem experimentellen Befund, dass die Hälfte der Methylgruppen leicht austauschbar ist. Anhand dieses Modells muss angenommen werden, dass die Titanatome in der 001 Kristallfläche (diese Kristallfläche bildet fast ausschliesslich die Oberfläche von $\alpha$-$TiCl_3$) nicht zugänglich sind. Ein Modell, das zu ähnlichen Schlüssen führt, wird für $\beta$-$TiCl_3$ vorgeschlagen. Die infrarot Spektren von $Al(CH_3)_3$, $Al(CD_3)_3$ $AlCl(CH_3)_2$, $AlCl(CD_3)_2$, $AlCl_2CH_3$, $AlCl_2CD_3$, $TiCl_3CH_3$, $TiCl_3CD_3$, $Hg(CD_3)_2$ und $Zn(CD_3)_2$ werden besprochen, sowie die infrarot Spektren von Reaktionsprodukten, die bei der Einwirkung einiger dieser Substanzen auf $TiCl_3$ entstehen.

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# Studies on Ziegler-Natta Catalysts. Part IV. Chemical Nature of the Active Site

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## Synopsis

The determination of the number of sites active in the polymerization of ethylene on the surface of α-$TiCl_3$–$Al(CH_3)_3$ dry catalysts leads to the conclusion that this number is small in comparison to the total surface of the catalyst. Qualitatively this conclusion is also reached by two other independent methods. Infrared spectra of the catalyst before and after polymerization do not show a change in the type of bonds present in the surface. Electron microscopy proves that no active sites are formed on the basal plane of the α-$TiCl_3$ which constitutes 95% of the total surface. The results strongly favor the lateral faces of α-$TiCl_3$ as the preferred location of active centers. The lateral faces contain chlorine vacancies and incompletely coordinated titanium atoms. This must then be the essential conditions for the formation of active centers. The propagation of the polymer chain has been repeatedly shown to follow an insertion mechanism. The active site, therefore, necessarily contains a metal–carbon bond. The study of catalysts derived from $TiCl_3CH_3$ leads to the conclusion that a Ti—C bond on titanium of incomplete coordination is the active species in these cases. The alkylation of surface titanium atoms was proven to be an intermediate step in the catalyst formation from $TiCl_3$ and $AlR_3$. Survival of titanium–alkyl bonds on the lateral faces, where titanium atoms are incompletely coordinated explains best, in the light of our data, the activity of Ziegler-Natta catalysts. Coordination of aluminum alkyl compounds in or around the active center probably complicates the structure of the active centers.

## INTRODUCTION

In the previous papers of this series[1-3] the reactions between α- or β-$TiCl_3$ and $Al(CH_3)_3$ or $Al(CH_3)_2Cl$ or $Al(C_2H_5)_3$ have been discussed at length. These reactions are limited to the surface of $TiCl_3$ and lead to products that are catalytically active in the polymerization of α-olefins. The following picture of the alteration undergone by the α-$TiCl_3$ surface in its reaction with $Al(CH_3)_3$, which with minor modifications applies also to the other systems, may be given.

The main reaction product is a compound $TiCl_3 \cdot TiCl_2Al(CH_3)_2$ (I). This compound covers completely the 001 faces of the α-$TiCl_3$ crystals, with half ot its methyl groups occupying vacancies created by the removal of Cl atoms during the reaction. This compound may also exist on the

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structurally different and less developed faces of the crystal: the lateral faces and the faces of the growth spirals. There is, however, no experimental proof for the existence of compound I in these locations. Compound I is formed by a sequence of reactions of which only the first is clearly understood. This is an alkylation of the surface leading to a compound that is adequately described by the formula $TiCl_3TiCl_2CH_3$ (II). Compound II reacts further with $AlMe_3$, finally giving compound I. Due to the inherent instability of the Ti—C bond, however, II may decompose by itself along a parallel pathway. The net result of this reaction is the formation of a chlorine vacancy. The experimental results substantiate the existence of this reaction. The values of the ratio of aluminum atoms fixed to chlorine removed is less than one. The effect is particularly pronounced when $AlEt_3$ is used. This is in agreement with the proposed reaction scheme because it is known that the Ti—$C_2H_5$ bond is by far less stable than the Ti—$CH_3$ bond and will therefore more readily decompose by itself. A third possibility which may not be overlooked when describing the $TiCl_3$ surface after its reaction with $Al(CH_3)_3$ is that under certain conditions the intermediately formed Ti—C bond could be present as such in the final reaction product. Conditions for this to occur would be that the Ti—C bond be stabilized in itself and also towards its further reaction with $Al(CH_3)_3$. A Ti—C bond could possibly be more stable when the titanium atom has a low coordination number. This condition is fulfilled on the lateral faces of $\alpha$-$TiCl_3$ where the titanium atoms do not possess their coordination number 6. Anyway the absence of bands characteristic of Ti—$CH_3$ in the infrared spectra of the reaction product indicates that if these groups exist, their concentration must be extremely small compared to the concentration of compound I in the surface.

With this description of the catalyst surface in mind we shall now proceed to a discussion of which of the species described have to be considered as being a constituent part of the active site. For this it is important to have an idea of the number of active sites present in the catalyst. Knowing the number and comparing it to the concentrations of the various species present might permit one to close in on the species actually involved.

Since the infrared spectrum of the dry catalyst is readily observable it is obvious that comparison of spectra before and after polymerization may help in ascertaining the nature of the active site.

Electron-microscope work[4] has shown that an accessible titanium atom is an essential constituent of the active site in bimetallic catalysts. It is therefore desirable to gain deeper insight into the mode of action of those catalytic systems that contain titanium as the only metal. Experimental results pertaining to this problem shall be presented.

We shall try to pour all these data into a consistent picture of the active site of Ziegler-Natta catalysts as far as its chemical constituents goes. The geometry of the active site and also other factors responsible for stereoregulation will be considered in part V of this series.[5]

## COUNTING OF ACTIVE POLYMERIZATION SITES

It is generally assumed that hydrocarbon groups of the catalytically active sites participate in the initiation of polymerization and that they form the dead end of the polymeric chain. Support for this hypothesis comes from the experiments of Natta et al.[6] with $\alpha$-$TiCl_3$–$Al(^{14}C_2H_5)_3$-labeled catalyst. Also Phillips and Carrick,[7] using a catalyst formed by reaction between $AlBr_3$, $Sn(C_6H_5)_4$ and a vanadium halide, found one phenyl group per polyethylene molecule. The hypothesis is also very well supported by the results obtained by Chien[8,9] with a soluble bis(cyclopentadienyl)titanium dichloride–dimethylaluminum chloride catalyst.

It seems, therefore, safe to assume that the number of hydrocarbon groups transferred from the catalyst to the polymer represents the number of active sites or its upper limit if secondary reactions take place. Of these, exchange between growing chain and aluminum alkyl in solution is avoided in our experiments, since ethylene is polymerized from the gas phase in the absence of solvent and excess aluminum alkyl. In an attempt to determine the number of active sites present in our "dry catalysts" we prepared catalysts from $\alpha$-$TiCl_3$ and $Al(^{14}CH_3)_3$, following the technique described earlier.[10] These techniques allow the determination of the total amount of carbon present in the catalyst.

A known amount of ethylene is allowed to polymerize on the catalyst. The polymer–catalyst mixture is then hydrolyzed and the polymer is recovered. It is washed first with aqueous HCl–methanol, next with methanol, and then dried.

The $^{14}C$ content of the polymer is determined by combustion of a weighed sample and the $^{14}CO_2$ activity is counted in an ionization chamber coupled to a Cary Model 32 vibrating reed electrometer (Applied Physics Corpo-

TABLE I
Proportion of Hydrocarbon Groups Transferred from Catalyst to Polymer

| | RA 29 | RA 30 | RA 26 |
|---|---|---|---|
| $\alpha$-$TiCl_3$ + $Al(^{14}CH_3)_3$ reaction time, min. | 90 | 150 | 120 |
| Temperature, °C. | 65 | 65 | 65 |
| Carbon content of the catalyst before polymerization $C_{cat}$, mg.-atom | 0.708 | 1.016 | 3.502 |
| Ethylene polymerized $E_p$, (65°C.) mmole | 28.25 | 47.11 | 780 |
| $^{14}C$ specific activity of the polymer, $\mu$c./mg.-atom of carbon | $1.75 \times 10^{-3}$ | $2.25 \times 10^{-3}$ | $0.53 \times 10^{-3}$ |
| Total activity of the polymer, $\mu$c. | 0.099 | 0.212 | 0.827 |
| Carbon content of the polymer coming from the catalyst, $C_{cp}$ mg.-atom | 0.025 | 0.053 | 0.207 |
| $C_{cp}/C_{cat}$ | 0.035 | 0.052 | 0.059 |
| $E_p/C_{cat}$ | 40 | 44 | 223 |

ration, Monrovia, California). The $^{14}C$ specific activity of the $Al(^{14}CH_3)_3$ sample used amounted to 4.0 $\mu$c./mg.-atom of carbon. The results of three experiments are summarized in Table I.

From this table it follows that the proportion of carbon transferred from the catalyst to the polymer ($C_{cp}/C_{cat}$) is very low and that the ratio $C_{cp}/C_{cat}$ does not change much when the ratio $E_p/C_{cat}$ increases very strongly. The results may be explained in two ways: either only few of the hydrocarbon groups contained in the surface product belong to catalytically active sites, or the ratio of the rate of propagation to the rate of initiation in the polymerization is very high.

Relevant to the first interpretation is that the ratio $C_{cp}/C_{cat}$ is of the same order of magnitude as the ratio of the surface of the lateral faces to the total surface of the $\alpha$-$TiCl_3$ crystals, estimated at about $5 \times 10^{-2}$.[1] This correlation renders new support to the widely accepted view that the active sites are localized mainly on the lateral faces and on faces having the structure of the lateral faces.[4,11-14]

The correlation is, however, only apparently true. The ratio of lateral face to basal plane is calculated for well-developed regular crystals. $\alpha$-$TiCl_3$ catalysts show in reality a great number of surface irregularities, and there is growing evidence that these are particularly rich in active centers. As a consequence, one has to accept that perfectly developed lateral faces are not an all-over active region of polymerization.

As for the second interpretation, assuming that all hydrocarbon groups present in the surface product are potentially active sites, one has to postulate that the propagation at a once initiated center is so fast that only few monomer molecules partake in initiation, the great majority being used up in the propagation of the chain. A very rough calculation on the basis of the data of Table I and assuming first-order initiation and propagation with respect to monomer concentration gives a value $k_p/k_i$ of about $2$-$4 \times 10^4$. This high value makes the second interpretation appear unsound.

## INFRARED STUDY OF THE POLYMERIZATION OF ETHYLENE ON DRY CATALYSTS

Several catalytic systems have been studied by infrared spectroscopy. The spectra of the nonvolatile reaction products (dry catalysts) between $TiCl_3$ and the various aluminum alkyls have been given already.[3]

Spectra have been taken before and after polymerization of a convenient amount of ethylene or propylene on a given sample of a dry catalyst. A quantitative comparison of the spectra before and after polymerization is therefore possible, and any decrease or increase of a band belonging to the dry catalyst is meaningful. It was hoped at the beginning of this work that such changes of intensity would occur during polymerization or that the spectra after polymerization would show new bands indicative of a modification of the dry catalyst. If insertion of monomer occurs on the Al—C

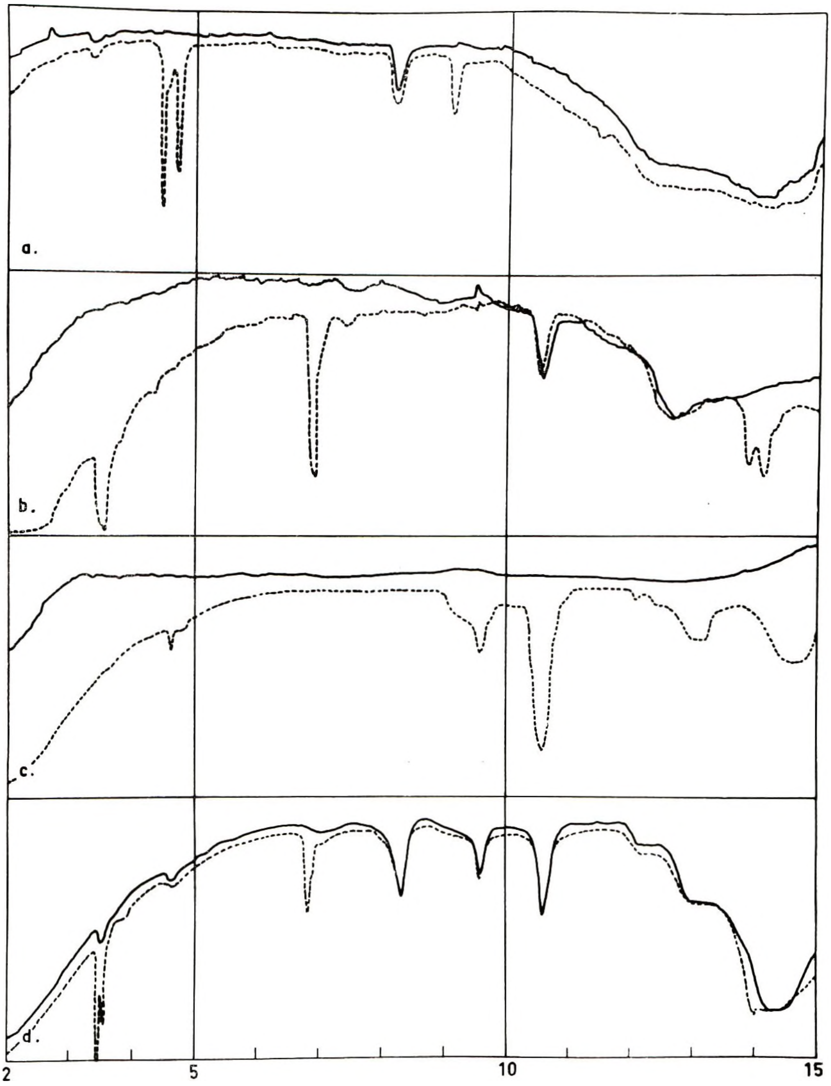


Fig. 1. Spectra of catalysts before and after *in situ* polymerization of ethylene: (*a*) $TiCl_3$ + $Al(CH_3)_3$ (——) and the same after polymeriztion of $C_2D_4$ (- -); (*b*) $TiCl_3$ + $Al(CD_3)_2Cl$ (——) and the same after polymerization of $C_2H_4$ (- -) (spectra taken with Irtran windows); (*c*) $TiCl_3$ (——) and $TiCl_3$ + $Al(CD_3)_3$ (- -); (*d*) The same after exchange with $Al(CH_3)_3$ (——) and after polymerization of $C_2H_4$ (- -).

bond such changes would be observable most easily by polymerizing $C_2D_4$ on a $TiCl_3$–$Al(CH_3)_3$ catalyst, provided that a significant amount of Al—C bonds are active. In this case interesting results would be obtained with $CH_3/CD_3$-exchanged catalysts, showing, e.g., activity of the exchangeable and relatively free $CH_3$ groups.

If polymerization were to lead to Ti—C bonds, which are not found in the spectra of the dry catalysts, these could show up at positions known from $TiCl_3CH_3$, provided again that the concentration of such bonds would be significant.

The spectra of several systems before and after polymerization are given in Figure 1. Spectra of polyethylene $(CH_2)_n$ and $(CD_2)_n$ are given in Figure 3. In all these cases the final spectrum obtained after polymerization is merely the superposition of the spectrum of the dry catalyst as it was before and that of the polyethylene formed on it, and no new bands due to titanium–alkyl bonds arise. The same holds for the spectra taken in the KBr region as well as for systems in which propylene is polymerized. These results are readily explained by assuming that the concentration of the active sites is too small to give an observable change in the spectrum and no direct information as to the nature of the active sites is gained. However, a more specific conclusion imposes itself. Because the surface product $TiCl_3$–$TiCl_2Al(CH_3)_2$ (I) is readily observable in the infrared spectrum due to its high concentration on the surface, it cannot be the active site in its most abundant form, i.e., on the 001 plane. Since, however, we know that only a small percentage of the carbon fixed in the surface partakes in polymerization, one might argue that (I) on the 001 could still be the active site. If only a small percentage of it were active one would not see a change in the infrared spectrum. However, this appears very improbable. The 001 face of the dry catalyst as a regular, repeating composition fully covered as it is with I, one sees therefore no reason why only a small percentage of it would be active. Moreover the unquestionable proof for the inactivity of (I) in the 001 plane comes from the electron-microscopic work which shows the absence of active sites in the 001 plane.

## ELECTRON-MICROSCOPIC STUDY

A safe answer to the question of how big a proportion of the surface groups partakes in polymerization comes from our results obtained with electron microscopy. Electron micrographs show that the polymer is formed spotwise on the α-$TiCl_3$–$Al(CH_3)_3$ dry catalyst.[4] No quantitative measurements are possible with this technique, but an essential qualitative result is that the spots are not statistically distributed on the catalyst surface. If all the sites created by the catalyst-forming reaction, which affects the complete surface of $TiCl_3$, were equally active, a random distribution of spots over the whole surface would be expected. The fact that polymer is found only along the growth spirals and on the lateral faces is a proof that only a small proportion of the hydrocarbon groups retained in the surface product of the reaction $TiCl_3 + Al(CH_3)_3$ are catalytically active. This general conclusion is thus supported by the results of three independent techniques: tracer studies, infrared spectroscopy, and electron microscopy.

## CATALYSTS CONTAINING TITANIUM AS ONLY METAL

### Evidence that the Growing Polymer Chain is Attached to Titanium

The electron-microscopic study of $TiCl_3$–$Al(CH_3)_3$ catalysts has proven that titanium is an essential constituent part of the active site of these bimetallic catalytic systems. In order to understand the role played by the titanium atom in the polymerization step it is therefore desirable to study the mode of action of those catalytic systems that contain titanium as the only metal.

Beerman reported first the synthesis of alkyl titanium halides[15] and their activity as polymerization catalysts. Beerman and Bestian[16] have shown that the active catalyst is formed in the decomposition of solutions of $TiCl_3$-$CH_3$. By measuring the deuterium content of the polymer separated from the reaction mixture after hydrolysis with $D_2O$ they ascertained that the polymerization takes place by insertion of the olefin in a Ti—C bond. Growth on titanium is also the polymerization mechanism accepted by de Vries[17] and Edgecombe.[18] Although this appears the only plausible mechanism and although we do not question the purity of the $TiCl_3Me$ used by the various authors, a rigorous proof that only the titanium is involved asks for the experimental confirmation that the number of active polymerization sites is greater than the number of foreign metal atoms present in the system. In order to get this proof we analyzed very carefully a batch of highly pure $TiCl_3Me$ and determined the number of active sites involved in polymerization by alcoholysis of the polymer–catalyst mixture with $CH_3OD$ and by assaying the number of C—D bonds thus formed in the polymer by means of infrared spectroscopy.

The preparation of the $TiCl_3CH_3$ is performed as follows. A spherical vessel A, equipped with a breakseal B and a magnetic stirrer contains a weighed amount of $TiCl_4$ (almost 60 mmole) diluted in 20 cc. pentane. This vessel A is connected to a vessel C through a G3 sintered glass filter and to a reservoir containing a weighed amount of about 30 mmole of pure dimethylzinc in 250 cc. of pentane. The reservoir is separated from the vessel A by a breakseal D. The whole system is under vacuum and closed. Vessel A is cooled at −78°C., breakseal D is broken, and the pentane solution of dimethylzinc is gently distilled into the vessel A, which is stirred magnetically. The reaction is regulated by cooling or rewarming vessel A. When all of the dimethylzinc has been introduced, the reaction mixture is stirred for 1 hr. and warmed to −20°C. in order to complete the reaction and to dissolve the $TiCl_3CH_3$. The mixture is filtered at −20°C. through the sintered glass filter, cooled in vessel B with liquid nitrogen, and sealed off. By this technique we avoided all contact with air and humidity. The $TiCl_4$ used was the Fluka pure product previously distilled and the dimethylzinc was synthesized in two steps: first $CH_3I$ and cadmium amalgam give dimethylmercury which may be easily purified by distillation; next dimethylmercury is reacted with pure zinc in excess in a sealed tube by progressive heating from 50°C. to 95°C. during 3 days and carefully distilled (m.p. 42°C.).

TABLE II
Impurities Analysis in $TiCl_3CH_3$

| | Impurities, % | | |
|---|---|---|---|
| | $TiCl_4$ reactant | $TiCl_3CH_3$ 1st preparation | $TiCl_3CH_3$ 2nd preparation |
| Zn | $\leq 10^{-2}$ | $\leq 10^{-2}$ | $\leq 10^{-2}$ |
| B, Mg | $< 10^{-3}$ | $< 10^{-2}$ | $< 10^{-3}$ |
| Si, Ca | $< 10^{-3}$ | $< 10^{-2}$ | $< 10^{-3}$ |
| Fe | $< 10^{-3}$ | $< 10^{-2}$ | $< 10^{-3}$ |
| Al | $< 10^{-3}$ | $< 10^{-3}$ | $< 10^{-3}$ |
| Cu | $< 5 \times 10^{-3}$ | $< 10^{-3}$ | $< 5 \times 10^{-3}$ |
| Others | $< 10^{-3}$ | $< 10^{-3}$ | $< 10^{-3}$ |

The assay of foreign metals was done by ultraviolet emission spectroscopy on the solid residues obtained after alcoholysis of $TiCl_3CH_3$ samples, followed by treatment with $HNO_3$ and evaporation of all volatile material.

The conclusions of the analyses of two independent preparations are given in Table II.

Zinc is the only element present in appreciable trace quantities. Among the other elements detected, boron, magnesium, iron, and aluminum are the ones that might be active in the catalysis. The total concentration of foreign elements is less than $5 \times 10^{-2}\%$. The above conclusions are also reached with the techniques using Eriochrome T[19] and ethylenediaminetetraacetic acid as complexing agent.[20]

Polymerization of ethylene with solutions of $TiCl_3CH_3$ was done in the following way. A sample of 6–7 mmole of $TiCl_3CH_3$ in about 20 cc. of pentane is withdrawn at −20°C. from the stock solution *in vacuo*. The sample is distilled at −20°C. into the polymerization vessel, which is sealed off. The polymerization vessel is equipped with breakseals and with a magnetic stirrer and is maintained at 0°C. Carefully purified

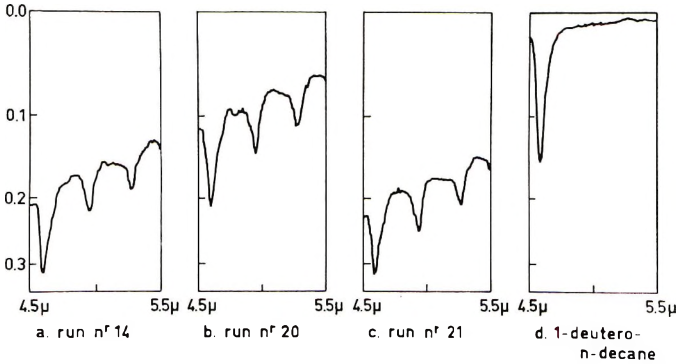


Fig. 2. Spectra of polyethylene obtained with $TiCl_3CH_3$ catalysts, after alcoholysis with $CH_3OD$: (*a, b, c*) C—D stretching region; (*d*) C—D stretching in the reference substance 1-deutero-*n*-decane.

ethylene is introduced in fractions of about 1 mmole until the desired amount is reached. Then, 20–30 cc. of deuterated methanol $CH_3OD$ is distilled into the cooled vessel. This is allowed to warm up slowly and the mixture is alcoholyzed. The polymer is washed with methanol, with aqueous HCl–methanol, and again with methanol and dried under vacuum. The concentration of C—D bonds in the polymer is evaluated by infrared spectroscopy by comparison with 1-deutero-*n*-decane, $CH_3(CH_2)_8CH_2D$, as reference. The reference compound was prepared from 1-bromo-*n*-decane by Grignard reaction followed by deuterolysis with heavy water of 99.5% deuterium content. The spectra reproduced on Figure 2 were taken on KBr disks.

The spectra of the deuterated polymer and of 1-deutero-*n*-decane reveal only one peak in the C—D stretching region, namely, at 4.60–4.61 μ. This position clearly corresponds to 4.62 μ given in the literature for C—D stretching in the $CH_2D$ group.[21,22]

Because the other deuterium-containing groups, —CHD—, —$CD_2$—, and —$CHD_2$, have other stretching frequencies it is safe to assume that only $CH_2D$ groups are incorporated in the polymer chain by alcoholysis. This means that each polymer chain attached at the moment of hydrolysis to the active site becomes marked by one deuterium atom.

Our infrared technique, establishing the nature of the deuterium-containing group, therefore permits an unambiguous counting of the number of polymer chains and appears more reliable for this purpose than the tracer techniques used by other authors.[8,16,23–25] Moreover, no correction must be made for the natural abundance of deuterium ($2 \times 10^{-4}$ D/H). This correction is necessary in techniques that count the total deuterium content. It must also be pointed out that hydrolysis with $D_2O$ of the $TiCl_3$-$CH_3$-polymer mixture introduces deuterium at several positions giving rise to bands at 4.56 and 4.8 μ. The results are summarized in Table III.

We conclude that the number of sites which are still active at the time of alcoholysis is far greater than the total number of impurity atoms present in the system. The metal–C bond in the active site is therefore without question a Ti—C bond.

TABLE III

Number of Active Sites versus Number of Impurities in $TiCl_3CH_3$–Ethylene Systems

| | Run 14 | Run 20 | Run 21 |
|---|---|---|---|
| Initial amount of $TiCl_3CH_3$, mmole | 6.68 | 4.32 | 6.11 |
| $C_2H_4$ polymerized, mmole | 10.6 | 5.0 | 15.6 |
| C-D unit/$C_2H_4$ units in the polymer | $2 \times 10^{-2}$ | $1.9 \times 10^{-2}$ | $1.8 \times 10^{-2}$ |
| Total C-D units, mg.-atom of D | 0.21 | 0.095 | 0.28 |
| Total amount of impurities in initial $TiCl_3CH_3$, mg.-atom | 0.003 | 0.002 | 0.003 |
| Ratio D/impurities | 70 | 47 | 93 |

## Reaction of Ethylene with the $Ti^{+4}$—C Bond

The work of Beerman and Bestian[16] has shown that the activity of solutions of $TiCl_3CH_3$ is linked to the presence of its decomposition products. The exact nature of the active species however is to our knowledge still open to question. The illuminating work of de Vries[17] has shown that a tetravalent alkyltitanium chloride is unstable when the alkyl group carries a $\beta$-hydrogen atom. The same author has also shown that isobutene may be inserted in the Ti—C bond of $TiCl_3CH_3$ with formation of the relatively stable neopentyltitanium trichloride.

$TiCl_3CH_3$ is stable at room temperature. When ethylene is admitted to it polymerization begins, and simultaneously the titaniumalkyl compound decomposes, as is noticeable by the appearance of brown $TiCl_3$. The following experiments given good evidence that the first step is insertion of an ethylene molecule in the $Ti^{+4}$—C bond.

Two reaction mixtures, $TiCl_3CH_3 + C_2D_4$ and $TiCl_3CD_3 + C_2H_4$, were studied qualitatively, and no attempts were made to measure the quantities of reagents and products. The molar ratio of ethylene over titanium compound is estimated to be in the range 1–10. The ratio was higher in the second experiment than in the first. No solvent was used. In both systems an important amount of methane was formed. The reaction $TiCl_3CH_3 + C_2D_4$ yielded methane of composition 60% $CH_3D$ and 40% $CH_4$. The reaction $TiCl_3CD_3 + C_2H_4$ gave 90% $CD_3H$, 2% $CD_2H_2$, and 8% $CD_4$.

These results may be easily understood in terms of intermediate formation of unstable titaniumalkyl compounds having a $\beta$-hydrogen atom[17] as shown in eqs. (1) and (2).

$$TiCl_3CH_3 + C_2D_4 \rightarrow TiCl_3CD_2CD_2CH_3 \qquad (1)$$

$$TiCl_3CD_2CD_2CH_3 + TiCl_3CH_3 \rightarrow CH_3D + \text{hydrocarbon} + 2TiCl_3 \qquad (2)$$

Simultaneous thermal decomposition of methyltitanium trichloride is responsible for the formation of $CH_4$ and $CD_4$ in these experiments. That only a small amount of $CD_4$ was formed in the second experiment may be due to the fact that the pressure of $C_2H_4$ used was higher than that of $C_2D_4$ in the first experiment giving a high yield of $TiCH_2CH_2CD_3$.

As to the nature of the hydrocarbon formed in reaction (2) we believe it to be propylene ($CD_2{=}CD{-}CH_3$), from an examination of the infrared spectrum of the polymer separated from the reaction mixture after hydrolysis with $CH_3OD$ (Fig. 3). The main bands in this spectrum (Fig. 3*a*) are due to polyethylene $(CD_2)_n$ (Fig. 3*c*). The strong band in the C—D bending region at 9.2 $\mu$ is due to $CD_2$ and only part of the weak band at 9.45 $\mu$ belongs to $CD_3$ bending. The concentration of $CD_3$ in the polymer appears thus to be low and probably arises from the hydrolysis of Ti—$(CD_2)_n$—R with $CH_3OD$, giving $CD_3{-}(CD_2)_n{-}R$. R, the alkyl group at the dead end of the chain, is presumably $CH_3$ stemming from $TiCl_3CH_3$. The concentration of $CH_3$ groups in the polymer is, however, important

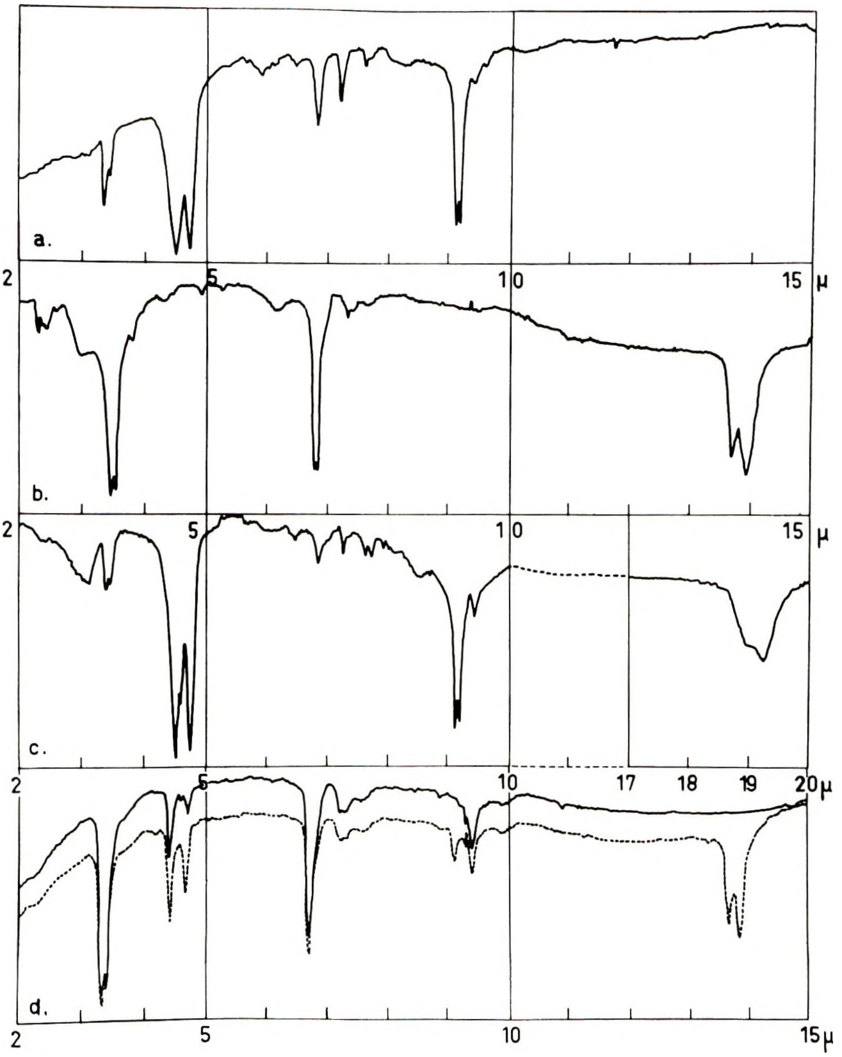


Fig. 3. Spectra of polyethylene: (*a*) polymer obtained from $TiCl_3CH_3 + C_2D_4$ after decomposition with $CH_3OD$; (*b*) linear polyethylene $(CH_2)_n$ obtained with a $TiCl_3$–$Al(CH_3)_3$ catalyst; (*c*) linear polyethylene $(CD_2)_n$ obtained with a $TiCl_3$–Al $(CH_3)_3$ catalyst; (*d*) the system $TiCl_3CD_3 + C_2H_4$ after removal of all volatile products (——) and after continued polymerization of $C_2D_4$ (- -).

and much higher than that of $CD_3$. Indeed the bands seen in the C—H deformation region around 7 μ can only be attributed to $CH_3$. $CH_3$ symmetrical bending in polyethylene comes at 1735 cm.$^{-1}$ (7.26 μ).[26] In $(CH_2)_n$ polyethylene, the 1375 cm.$^{-1}$ peak belongs to a broadened composite band with two other maxima at 1369 and 1353 cm.$^{-1}$ that are due to vibrations of $CH_2$ groups (Fig. 3*b*). In the spectrum of Figure 3a there is only one sharp peak at 1375 cm.$^{-1}$, purely $CH_3$ bending. In the usual polyethylene the intensity of the 1375 cm.$^{-1}$ band is small compared to the 1460 cm.$^{-1}$ band (6.85 μ) which contains $CH_2$ bending and $CH_3$ asymmetrical bending. In this spectrum the two bands are of comparable intensity and this points to $CH_3$ motion as their origin. The intensity of the bands is such that we may conclude the presence of a high concentration of $CH_3$ groups in the polymer. It seems most likely that these are branched $CH_3$ side groups. A high concentration of such groups is readily explained if it is assumed that $CD_2{=}CD{-}CH_3$ is formed in reaction (2). The propylene molecules would then copolymerize with ethylene. In fact, the spectrum in the CH deformation region is very like that of polypropylene.

Equivalent results were obtained when the reaction $TiCl_3CD_3 + C_2H_4$ was run in the infrared cell. For this purpose $TiCl_3CD_3$ was admitted to the cell in such a way that a liquid layer covered one of the windows. When $C_2H_4$ was admitted, a brown deposit formed on the window. The volatile material was removed and the spectrum taken (Fig. 3*d*). It contains an almost vanishing band at 10 μ possibly the $CD_3$ deformation of undecomposed $TiCl_3CD_3$. The other bands are due to hydrocarbon. Except for the bands in the C—D stretching region (4.6–4.9 μ) and in the $CD_3$ deformation region (9.2–9.4 μ) they are due to linear polyethylene $(CH_2)_n$. However, the well resolved 9.4 μ band is again evidence that this polymer must contain $CD_3$ side groups. This band cannot be due to Ti—$CD_3$ asymmetric deformation since it is not observable in the parent $TiCl_3CD_3$ which was only one observable deformation band at 10.04 μ. When $C_2D_4$ was added after the removal of $C_2H_4$, the spectrum represented by the dotted line was obtained. This spectrum has stronger bands in the C—D stretching region and a new band at 9.2 μ, both indicative of linear deuteropolyethylene $(CD_2)_n$. The $CD_3$ deformation band at 9.4 μ is retained without change in intensity. This is additional proof that it belongs to the already formed polymer.

The conclusion from these experiments is that in a primary step one molecule of ethylene becomes inserted in the $Ti^{+4}$—C bond. An unstable titaniumalkyl compound results, which reacts with $TiCl_3CH_3$. It seems therefore unlikely that the polymer formed in the system grows on a tetravalent titanium atom. The active species in this polymerization must be sought among the products formed in the decomposition of the titaniumalkyl compounds. It is possible that it is formed in an exchange reaction

$$TiCl_3 + TiCl_3R \rightarrow TiCl_2R + TiCl_4$$

already proposed by de Vries[17] and later by Edgecombe[18] and that it is a titaniumalkyl compound in which titanium has a valency less than four.

The same conclusion concerning the inactivity of the $Ti^{+4}$—C bond as polymerization catalyst is also reached from experiments with dimethyltitanium dichloride. This product was synthesized from $TiCl^4$ and dimethylzinc in pentane solution with the technique described for $TiCl_3CH_3$. The molar ratio of the reactants was 1/1 in this case. The crude product can be purified by crystallization at low temperature (−80°C.), as reported by Beerman and Bestian.[16]

The crystalline product was analyzed for foreign metals by ultraviolet emission spectroscopy and was found very pure. The main impurities are Zn ($10^{-3}$ g.-atom) and Al, Si, B, Mg, and Cu (maximum $10^{-4}$).

Addition of ethylene at 1 atm. or less to a solution of $TiCl_2(CH_3)_2$ in pentane at 0°C. leads to a quick absorption of 1 mmole of ethylene/mmole of $TiCl_2(CH_3)_2$. Next, formation of 1 mmole of methane, precipitation of a black titanium-containing product, and polymerization of ethylene are observed. After the precipitate has settled down, the supernatant solution is perfectly colorless.

There is no doubt that the observed rapid decomposition of $TiCl_2(CH_3)_2$ at 0°C. is due to a reaction with ethylene, because the starting solution is rather stable at this temperature. No polymer is formed when the experiment is done at $-38$°C. with a perfectly clear solution of $TiCl_2(CH_3)_2$. Polymerization occurs, however, at temperatures as low as $-38$°C. when crystalline, solid $TiCl_2(CH_3)_2$ is present. In this case, the active catalyst is probably a decomposition product on the surface of the crystalline needles. The general conclusions of these experiments as well as those with $TiCl_3CH_3$ are that the $Ti^{+4}$—C bond is able to insert a molecule of monomer (ethylene) and that the product formed is very unstable and decomposes quickly. Therefore a $Ti^{+4}$—C bond is not likely to be the active species in Ziegler-Natta catalysts.

## Growth on Titanium of Valency Less Than Four

In favor of the idea that the polymer is growing on a titanium atom of lower valency is the experimental finding that a dry catalyst prepared from $TiCl_2 + TiCl_3CH_3$ has by far greater activity than that prepared from $TiCl_3 + TiCl_3CH_3$. The activity for polymerization of ethylene of four dry catalysts mentioned in Table IV was compared. $TiCl_2$ was obtained as a black powder by disproportionation of $\alpha$-$TiCl_3$ at 450°C. under vacuum. A weighed quantity of the titanium chloride was brought in contact with the organometallic compound at room temperature. The excess organometallic and all volatile reaction products were removed at 50°C. after a contact time of 10 min. Ethylene was admitted at a pressure of 50 cm. Hg and the rate of polymerization was measured at 50°C. by following the pressure drop at constant volume. Ethylene was readmitted each time

TABLE IV

Comparison of Activity of Dry Catalysts in Polymerization of Ethylene

| Catalyst | Weight $TiCl_n$, g. | Relative rate | Weight of polymer, g. | Yield, % | Polymer m.p., °C. First | Polymer m.p., °C. Next |
|---|---|---|---|---|---|---|
| $TiCl_3 + Al(CH_3)_3$ | 0.77 | 1 | 1.2 | 1.5 | 217 | 126.5 |
| $TiCl_2 + Al(CH_3)_3$ | 0.30 | 2.5 | 2.5 | 8.3 | 217 | 126.5 |
| $TiCl_3 + TiCl_3CH_3$ | 0.77 | >0.1 | 0.2 | 0.3 | 217 | 123 |
| $TiCl_2 + TiCl_3CH_3$ | 0.41 | >12 | 3.1 | 7.6 | 214 | 123 |

the pressure had dropped to 20 cm. Hg until the rate became negligible. The catalyst was then dissolved as well as possible in aqueous HCl. The polymer was dried and weighed. The results are given in Table IV.

The values of the rates given are strictly comparative between each other. They are based on the mean value observed in the first three admissions of ethylene and give an approximate measure of the initial rate at a pressure of 40 cm. Hg. The value 1 was given to the rate observed in the first system and all other rates were recalculated to the same weight of titaniumchloride (0.77 g.). The value given for the $TiCl_2 + TiCl_3CH_3$ catalyst is in fact even below the true value. The pressure drop during the first two admissions of ethylene was too fast to be measured. The yields are expressed as weight of polymer formed to weight of titanium chloride used. The yields cannot be compared to those that would be obtained in a hydrocarbon suspension, as diffusion to the catalyst surface limits the yield. After the end of the runs it is impossible to recover the catalyst completely, this being totally enveloped by polymer. A plausible interpretation of this result is that in the $TiCl_2 + TiCl_3CH_3$ system a redox reaction takes place, eq. (3).

$$TiCl_2 + TiCl_3CH_3 \rightarrow TiCl_3 + TiCl_2CH_3 \quad (3)$$

This would lead to the formation of Ti—$CH_3$ bonds in the catalyst surface. An infrared study of this system could show the presence of methyl groups in the catalyst. Unfortunately, we did not succeed in producing a layer of $TiCl_2$ in the infrared cell. Various methods have been tried without success. The following experiment shows however that the above reaction is indeed a realistic concept. $TiCl_3CH_3$ vapor is introduced in the infrared cell by the technique described earlier.[3] A high-voltage high-frequency discharge is applied, and a brown $TiCl_3$ film is formed. The infrared spectrum of this after removal of all volatile products is identical to that obtained when $TiCl_4$ is reduced with $H_2$ under these conditions and contains no bands characteristic of methyl groups linked to titanium. The brown film is inactive as catalyst when ethylene is admitted. When $TiCl_3CH_3$ is admitted to such a film of brown $TiCl_3$ a very weak band at 7.3 $\mu$ develops, indicating that some methyl groups are retained in the surface. This system does not have a significant activity in polymerization of ethylene.

If, however, a mixture of $TiCl_3CH_3$ and $H_2$ is submitted to the electrical discharge a product is formed whose infrared spectrum has a band at 7.3 $\mu$, doubtless the deformation of $CH_3$ linked to titanium. This brown product now is a very active polymerization catalyst. $C_2D_4$ polymerizes readily on it. The spectrum of the polymerization shows the bands of polydeuteroethylene. Moreover, the intensity of the 7.3 $\mu$ band is greatly reduced, and an additional band is found at 10.14 $\mu$. This band is also present in spectra of $TiCl_3CH_3 + C_2D_4$. We are inclined to ascribe (Ti—)C—C stretching to this band. The presence of the 7.3 $\mu$ band in the catalyst, its decrease on polymerization, and the appearance of the 10.14 μ band are all compatible with reactions (4) and (5).

$$TiCl_3CH_3 + H_2 \rightarrow TiCl_2CH_3 + HCl \quad (4)$$

$$TiCl_2CH_3 + nC_2D_4 \rightarrow TiCl_2(CD_2)_{2n}CH_3 \quad (5)$$

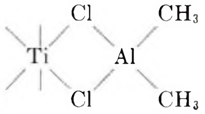
## DISCUSSION

The purpose of this discussion is to clear the essential characteristics of the chemical nature of the active center on the basis of the experimental data that have been presented in this and the preceding papers. Factors of crystal geometry and environment that are held responsible for the stereoregular polymerization on the active center are the subject of the following paper in this series.[5]

Many theories have been advanced concerning the mechanism by which the chain is propagated in Ziegler-Natta catalysis. These theories have been adequately reviewed in their essential lines by Bawn and Ledwith.[27] In a discussion like this it is impossible to study critically each single proposition.

At present agreement is general on the essential nature of the propagation reaction. This is seen as an insertion of the monomer in a metal–carbon bond contained in the catalyst. Proofs for this are numerous and exist for a great variety of catalysts. Essentially they come from two types of experiments. In the one type it is demonstrated that alkyl groups present in the catalyst are found fixed to the polymer chain[6–8,24,25] (also this paper). In the other type of experiments it is shown that on hydrolysis metal carbon bonds are broken[16,17] (also this paper). The experimental evidence for the insertion mechanism is overwhelming and does away with hypotheses invoking a radical mechanism on the surface of the catalyst.

The agreement being quite general on the insertion mechanism, the question arises: what is the metal on which growth occurs? Before discussing this, an important point must be stressed for which again experimental evidence exists. Whatever be the metal in the active site that carries the propagating chain, the transition metal atom plays an essential role in the process of insertion. The results of Carrick et al.[28,29] show that the ethylene/propylene copolymerization ratios depend on the transition metal and not on the metal of the metal organic compound. These results, although they are generally taken as a straightforward indication that the propagating chain grows on titanium, merely prove however that the transition metal atom is a constituent part of the active site. If bimetallic complexes are involved, one could imagine that a change in transition metal affects the other metal–carbon bond, making it more or less reactive. Our results show that the active center obeys the essential condition that it contains an accessible titanium atom.[4,11] Whatever the mechanism that one proposes for the chain growth, it must accommodate a step in which an interaction occurs between the olefin and the accessible titanium atom. Our data on the stoichiometry of the product of the catalyst-forming reaction coupled with the data obtained by exchange studies and infrared spectroscopy clearly establish that the outer layer of the 001 face has the formula $Ti_2Cl_5AlR_2$. This surface compound is a typical bridged bimetallic compound and its structure may be represented by



Situated in the 001 face it does not possess an accessible titanium atom. The total absence of active centers in the 001 face, which is unambiguously established by electron microscopy leads to the conclusion that such bridge compounds cannot be active centers of polymerization when the titanium atom is fully coordinated. Under these circumstances insertion in the Al—C bond, albeit accessible to the olefin, must be excluded as a possible mechanism.

In last analysis, the active site escapes experimental investigation due to the fact that the catalyst surface is extremely complicated and that only a small proportion of it is active. The discussion of the true nature of the active site then becomes a critical evaluation of the two possible types: bimetallic compound or titanium–carbon bond. It seems beyond doubt that both types do function as catalytic species. Bimetallic complexes synthesized by Natta and his collaborators[30] function as catalytic species in solution. On the other hand, catalytic systems containing titanium as only metal are known: $TiCl_3CH_3$[16] or the highly active combination of $TiCl_2$ and $TiCl_3CH_3$ have as active site a titanium–carbon bond. We have reasons to believe that both structures are present in the surface of the $TiCl_3$–aluminum alkyl catalysts which we have studied.

Our electron microscopic data reveal that active sites are only found on the lateral faces of the crystals and on the growth spirals which crystallographically may be assimilated to lateral faces. We cannot exclude that the rims, the border lines between 001 and lateral face, are also active, or that they in fact present the only active region of the catalyst. This idea has already been favored by Cram and Kopecky.[31] On the rims one can easily visualize the bridge compound having now an accessible titanium atom. One may postulate a rather facile exchange between chlorine atoms in the bridge and outer alkyl groups in these locations. Indeed, whereas chlorine atoms in the basal plane are all coordinated to two titanium atoms, part of the chlorine atoms belonging to the lateral faces are coordinated to only one titanium atom and are therefore more mobile. The concept of a bimetallic site can therefore be retained as a possible catalytic mechanism. The sort of mechanisms proposed by Natta and collaborators[30] and also by Sinn and Patat[32] and also the mechanism proposed by Uelzmann[33] involving an ionic complex are plausible descriptions of the catalytic mechanism on such bimetallic sites. The combination of Ti and Al would be extremely favorable for olefin activation and polymerization.

The alternative mechanism by which the olefin is inserted in a Ti–alkyl bond[34] present in the catalytic surface now requires attention. A complete theory of this mechanism has been elaborated by Cossee.[35] Cossee's theoretical considerations of the stability of a titanium alkyl at the surface of $TiCl_3$ where the titanium has a low coordination number is very relevant to the $TiCl_3$–$AlR_3$ system. The study of the catalyst-forming reaction between $TiCl_3$ and aluminum alkyl has proven that the first step is a replacement of Cl atoms by alkyl groups. The alkylated surface reacts further with aluminum alky leading to the fixation of aluminum and alkyl groups in the surface. What are the chances that titanium alkyl bonds survive further attack by aluminum alkyl and remain as such in the final catalyst? There is to our knowledge no direct experimental proof for the presence of Ti–alkyl bonds in the $TiCl_3$–$AlMe_3$ catalyst. If such bonds constitute the active centers, their number would amount approximately to $10^{-2}$ of that of the total titanium surface atoms and hence they would escape any direct experimental attack such as infrared spectroscopy. The fact that the active sites are so few in this catalyst may be explained by the survival of Ti—R bonds on the lateral faces, where the titanium atoms are not fully coordinated. According to Carrick et al.,[36] a decrease in the valency of titanium increases the stability of the Ti—C bond, and the calculations of Arlman[37] favor the lateral faces as the catalytically active region.

The high catalytic activity for ethylene polymerization of the system $TiCl_2 + TiCl_3CH_3$, which formally is equivalent to the alkylated surface of $TiCl_3$ or to the intermediate $Ti_2Cl_5CH_3$ that is formed in the reaction between $TiCl_3$ and $Al(CH_3)_3$, gives strong support to the Cossee mechanism.

Growth on a reactive titanium–carbon bond explains best in the light of our data the high reactivity of Ziegler-Natta catalysts. The titanium atom needs to have a chlorine vacancy through which the Ti—C bond becomes accessible to the olefinic double bond. These are the essentials of the active site proposed by Cossee. Such sites are to be found on the lateral faces and on the growth spirals of the $TiCl_3$ crystals after its reaction with an alkylating metal organic compound. However, this is only the essential nature of these sites. It is indeed illogical to ignore the presence of the alkylating organometallic or its reaction products in some form on or in the immediate neighborhood of the active site. The coordination of aluminum compounds, for instance, to the Ti—Cl structures of the lateral faces, must certainly exist and may lead to a partial or total coverage of the Cossee-Arlman site. It is in terms of the steric crowding of this active site that we shall try in the next and last paper of this series[5] to discuss the activity and stereospecificity of Ziegler-Natta catalysts.

Our opinion is that it is dangerous to defend the occurrence of a unique type of active center in the broad class of Ziegler-Natta catalysts. The great differences in stereoregulating power observed when different alkylating agents are used in conjuncture with a given $TiCl_3$[38] cannot be satisfactorily explained solely by steric inversions due to exchange reactions in which the growing chain takes part. Also, the acceptance of, for instance, a simple Cossee site of general application does not explain the notorious low activity of $TiCl_3$–zinc alkyl catalysts as compared to $TiCl_3$–aluminum alkyl catalysts. That the nature of the active center depends to some extent on the alkylating agent seems beyond doubt. We assume that even in a given catalyst combination several types of centers, mono- as well as bimetallic, may be at work concurrently.

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## Résumé

La détermination du nombre de sites actifs dans le catalyseur formé à partir de $\alpha$-$TiCl_3$ et $Al(CH_3)_3$ démontre que ce nombre est petit par rapport à la surface totale du catalyseur. Ce résultat est confirmé par l'étude des spectres infra-rouges de catalyseurs avant et après polymérisation. Les photos obtenues par microscopie électronique démontrent très nettement l'absence de centres actifs de polymérisation sur les plans de base 001 qui constituent 95% de la surface totale. Les centres actifs sont formés exclusivement sur les faces latérales. La structure de ces faces est caractérisée par des défauts d'atomes de chlore et par une coordination inférieure à six des atomes de titane. La condition de structure essentielle à laquelle doit répondre tout site actif paraît être celle-là. Il a été démontré à plusieurs reprises que la propagation de la chaîne sur les catalyseurs Ziegler-Natta se fait par un mécanisme d'insertion de l'oléfine dans une liaison métal-carbone. L'étude de catalyseurs monométalliques obtenus à partir de $TiCl_3$-$CH_3$ a démontré que la liaison Ti—C d'un titanium alcoyl dans lequel le titanium est incomplètement coordonné, constitue l'entité active de ces catalyseurs. Dans la formation de catalyseurs à partir de $TiCl_3$ et $AlR_3$, l'alcoylation des atomes de titane de surface constitue un état intermédiaire. L'activité des catalyseurs Ziegler-Natta serait d'après nos résultats imputable à l'existence sur les faces latérales du $TiCl_3$ de liaisons titanium-alcoyl ainsi qu'au fait de la coordination incomplète des atomes de titane. La structure des centres actifs est probablement compliquée par la coordination des dérivés aluminium alcoyls avec la surface environnante.

## Zusammenfassung

Die Zahl der aktiven Zentren in Katalysatoren, die aus $\alpha TiCl_3$ und $AlR_3$ hergestellt werden, ist gering im Vergleich zu der Gesamtoberfläche. Dieser Befund erklärt, warum IR-Spektren der Katalysatoren vor und nach der Polymerisation von Olefinen gleich sind. Den deutlichsten Hinweis darauf, dass in diesen Katalysatorsystemen nur ein sehr geringer Anteil der Oberfläche aktiv ist, liefert die Elektronenmikroskopie. Die Bilder zeigen keine Polymeren auf der 001-Fläche, die etwa 95% derGesamtoberfläche darstellt. Aktive Zentren kommen lediglich auf den Seitenflächen vor, wo wegen der Existenz von Chlorlücken niedrig koordinierte Titanatome vorhanden sind. Es ist von vielen Seiten bewiesen worden, dass der Wachstumsschritt dieser Polymerisation eine Einschiebung des Monomeren in die Metall-Kohlenstoffbindung ist. Die katalytische Wirksamkeit von Systemen, die sich von $TiCl_3CH_3$ ableiten und nut Titan enthalten, muss uf die Bildung einer Bindung zwischen Kohlenstoff und niedrig koordiniertem Titan zurückgeführt werden. Bei der Reaktion von $TiCl_3$ mit $AlR_3$ werden Ti-Atome an der Oberfläche primär alkyliert. Während in der 001-Fläche die Ti—C—Bildung durch weitere Reaktion mit $AlR_3$ wahrscheinlich wieder gelöst wird, nehmen wir aufgrund unserer Befunde an, dass in den Seitenflächen Titanalkyle überleben und die aktiven Zentren darstellen. Man muss aber berücksichtigen, dass Aluminiumalkylderivate an diesen Stellen koordiniert zur Oberfläche vorliegen und bei der Polymerisation durchaus eine Rolle spielen können.

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# Studies on Ziegler-Natta Catalysts. Part V. Stereospecificity of the Active Center

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## Synopsis

Experimental results on Ziegler-Natta catalysts, based on observations made with the electron microscope, and a qualitative comparison of the stereospecificity of various catalyst combinations are given. The polymerization of olefin in these experiments is performed in the gas phase on dry catalysts in the absence of solvent or excess aluminium alkyl. The crystallographic structure of the lateral faces of $\alpha$-$TiCl_3$ is established by electron microscopy and electron diffraction. The electron micrographs of $\alpha$-$TiCl_3$-$AlMe_3$ catalysts show that the active centers, which are revealed by the dotwise formation of polymer, are located along the growth spirals, on lateral faces, and on surface defects. These regions of the surface are the only regions in which the surface titanium atoms are incompletely coordinated. The presence of chlorine vacancies and exposed titanium atoms is therefore an essential condition for the formation of active centers. However, the number of active centers is small in comparison to the number of incompletely coordinated titanium atoms, and hence it is concluded that the normally occurring $\alpha$-$TiCl_3$ sites with one vacancy do not yield active centers on reaction with aluminum alkyl. It is proposed that the reaction with aluminum alkyl on such sites leads ultimately to a bimetallic complex which fills the original vacancy on the titanium atom. That the complexation is reversible and that the deblocked alkylated site, which is of the type proposed by Cossee, is an active center is not excluded. Such a center would, however, give atactic polymer. Similar complex formation on a $TiCl_3$ site having originally two vacancies would leave one vacancy on the titanium atom. This is believed to be the center of stereospecific polymerization. A model of this active center and a mechanism of polymer growth on it are proposed.

## INTRODUCTION

Since Natta's original discovery of the stereoregulating effect of Ziegler catalysts many efforts have been aimed at the elucidation of the factors responsible for stereoregulation. In our experimental work we have touched a number of catalytic systems that are based on $TiCl_3$ ($\alpha$ and $\beta$) or $TiCl_2$ and the following organometallic compounds: $Al(CH_3)_3$, $AlCl(CH_3)_2$, $Al(C_2H_5)_3$, $TiCl_3CH_3$ and $Zn(CH_3)_2$. The study of these catalysts[1-3] has yielded information on the chemical species contained in the surface. We reached the conclusion that a reactive titanium-alkyl bond constitutes

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the essential nature of the active center of olefin polymerization.[4] However, it appears difficult to explain on this basis, which probably permits an adequate description of the systems $TiCl_3$ + $TiCl_3CH_3$ and $TiCl_2$ + $TiCl_3CH_3$, the sum of observations concerning the marked differences in activity and the spread in stereoregulating power of the various catalytic systems. This paper brings a contribution to the study of this interesting phenomenon. The discussion is guided mainly by observations made by electron microscopy and to some extent by measurements of tacticity of polypropylene samples obtained on various catalysts.

## ELECTRON-MICROSCOPIC STUDY OF POLYMERIZATION

### Experimental Technique

The method of carbon replicas was used throughout. The apparatus which permits the obtention of samples in a form such that carbon replicas may be made is shown in Figure 1. The whole apparatus is evacuated to start with. Ethylene or propylene is stored in vessel F. The apparatus is filled with nitrogen which is purified by passing it through aluminumtriethyl and subsequently through traps cooled by liquid air. The nitrogen pressure is maintained at slightly above atmospheric pressure. Breakseal C is broken with a metal rod which glides smoothly in rubber tube D. The

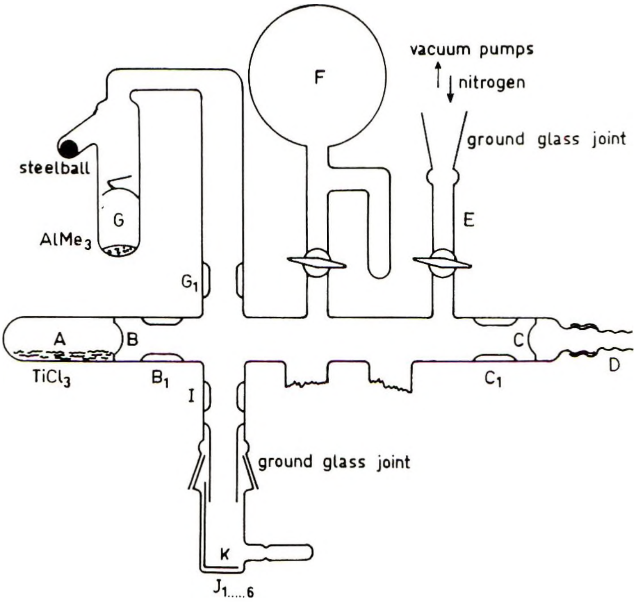


Fig. 1. Apparatus for the obtention of catalyst samples in a form suitable for replication: (A) $TiCl_3$; (B), (C) glass breakseals; (D) rubber tube; (F) olefin; (G) trimethyl aluminum ($J_1 \ldots_6$) six tubes for catalyst sample preparation; (K) copper disk; ($B_1$), ($C_1$), ($G_1$) sealing positions.

rod carries a spoon at its end with which, after breaking seal B, small quantities of $TiCl_3$ from A can be dropped into the six tubes J. Each tube J has a flat bottom and contains a thin copper disk K welded to a tungsten wire. The rod is taken back to its original position at C and the apparatus is sealed off at $B_1$ and $C_1$. Some of the tubes J, containing $TiCl_3$ at this stage, are sealed off at I under vacuum. Trimethylaluminum stored in G is admitted to the remaining samples of $TiCl_3$, recovered in G after a chosen time, and removed by sealing at $G_1$. Olefin is admitted from F, and the remaining tubes J are removed one after the other after given times of polymerization. The tube J is then introduced in a vacuum-bell fitted with a mechanical device which allows opening of the ground glass joint under vacuum and its closing after carbon has been deposited on the sample. When this is done the tube is removed and opened in a nitrogen atmosphere. Disk K is dipped in a benzene–methanol mixture and the catalyst is dissolved. The replica is washed with a solution of aqueous HCl in methanol. The carbon replicas were usually observed in a FM 100 Philips electron microscope.

## Results

Electron micrographs of α-$TiCl_3$ are shown in Figures 2 and 3. They show more or less regular hexagonal leaflets. The large 001 faces generally lie in the plane of the photographs. Some of the smaller crystals stand upright or are inclined and their thickness may be estimated. Some lateral faces do not seem to be perpendicular to the 001 plane. The large crystal of Figure 2 has oblique faces on at least three sides. The 001 faces do not exhibit structural details. After a smooth attack by traces of humidity,

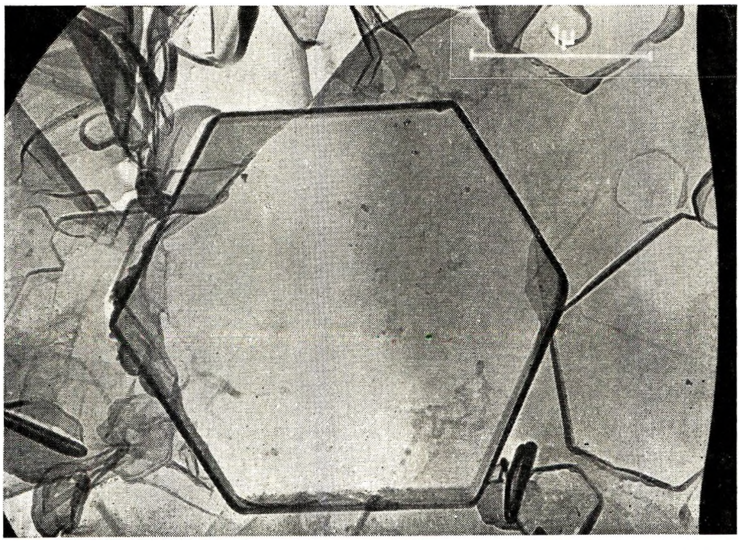


Fig. 2. α-$TiCl_3$, electron micrograph before reaction. Specially regular crystal. 40,000×
Carbon replica.

however, spirals are revealed (Fig. 4). The origins of the spirals are located close to the centers of the hexagonal crystals. At their beginning the spirals are circular and after a few turns they become polygonalized and parallel to the edges of the crystals. It is clear that these spirals are growth spirals which are due to a commonly operating mechanism of crystal growth. They must be present on pure α-$TiCl_3$ but invisible before the attack by traces of humidity. Very surprisingly, α-$TiCl_3$ crystals that have reacted with aluminum-trimethyl appear identical in the electron microscope to

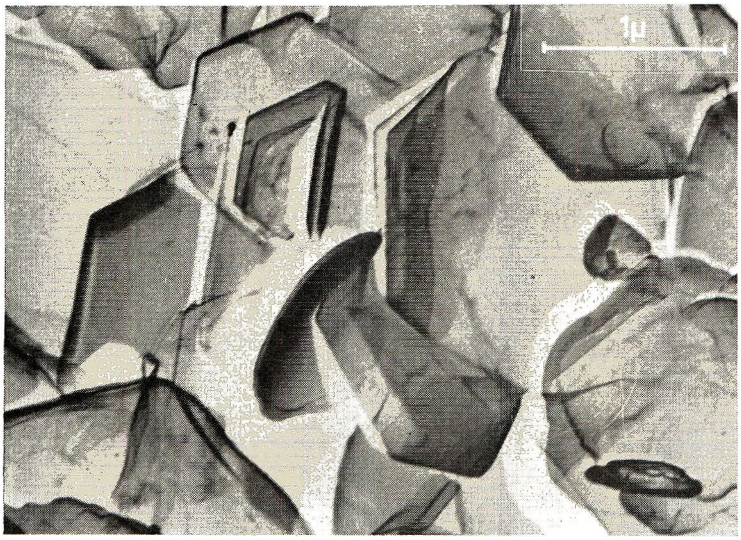


Fig. 3. α-$TiCl_3$, before reaction. Some crystals are seen upright and present their lateral faces. 36,000×. Carbon replica.

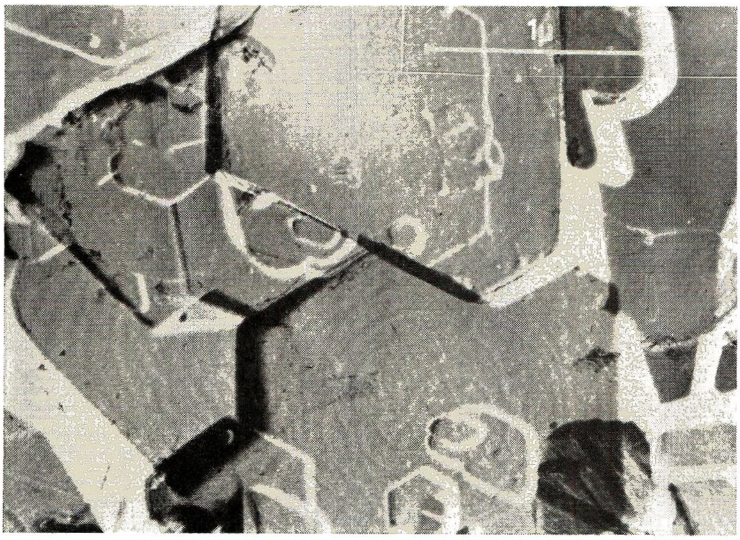


Fig. 4. α-$TiCl_3$ crystals, after a smooth attack by humidity. 46,000×. Carbon replica.

unreacted ones. This fact is, however, easily explained because the only change due to the surface compound, which fully covers the 001 face[3] is a protruding methyl group. In Figures 5–7 replicas obtained after polymerization of propylene are shown. Propylene is a very convenient monomer because it does not polymerize too quickly. Also, the carbon replicas can be freed from adhering polymer by washing them with solvents of polypropylene. These three pictures which were already published pre-

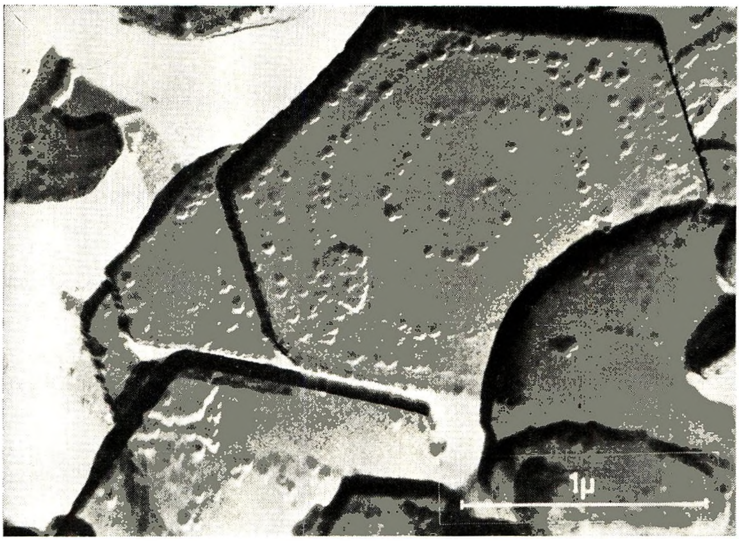


Fig. 5. α-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of propylene. 50,000×. Carbon replica.

Fig. 6. α-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of propylene. 50,000×. Carbon replica.

viously[5] show a great number of dots, undoubtedly the traces of growing polypropylene. The dots are mainly localized on spirals which in all their characteristics correspond to the growth spirals revealed by chemical attack on α-$TiCl_3$ crystals.

In addition a great concentration of growing polymer is found on the perturbed region of the crystal shown in Figure 6. This region must have a great number of surface defects.

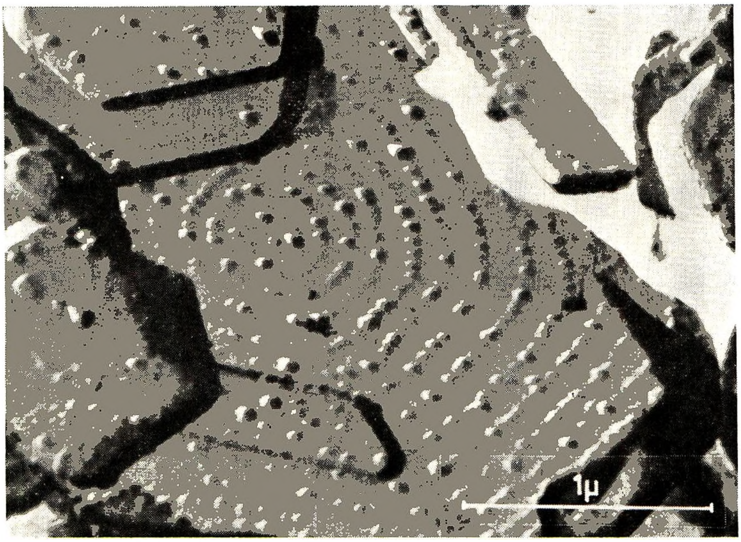


Fig. 7. α-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of propylene. 50,000×. Carbon replica.

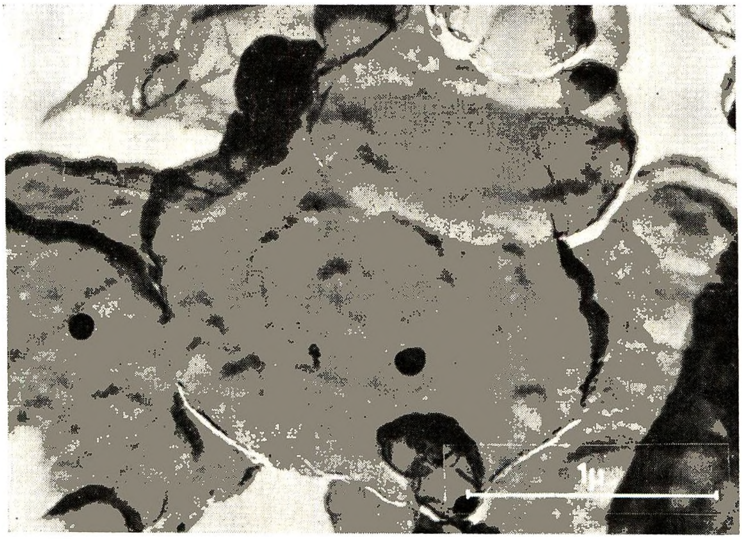


Fig. 8. α-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of ethylene, 50,000×. Carbon replica.

It is somewhat more difficult to judge whether the lateral faces are rich in polymerization sites or whether only the rims are active. In Figures 5 and 6 the rims appear especially loaded with polymer. Very probably this is due to a great concentration of polymerization centers in the lateral faces which causes the overlapping of polymer on the rims. There is no doubt that active polymerization centers are located along the growth spirals, on lateral faces and on surface defects. Moreover, it is obvious from a study

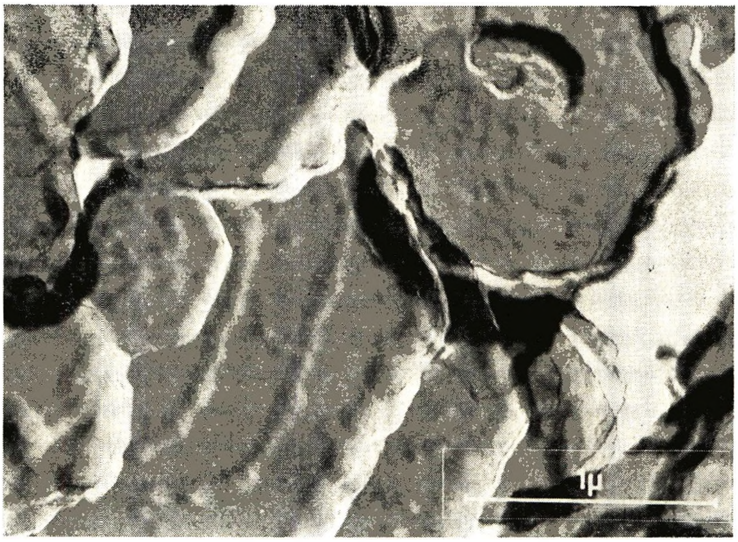


Fig. 9. $\alpha$-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of ethylene. 50,000×. Carbon replica.

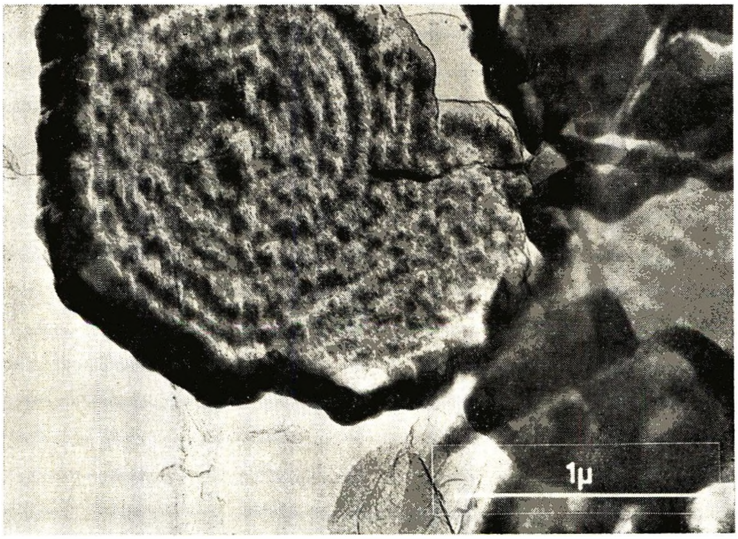


Fig. 10. $\alpha$-$TiCl_3$ crystals, after reaction with $AlMe_3$ and polymerization of ethylene. 50,000×. Carbon replica.

of Figure 7 that the concentration of centers on two adjacent sides of the polygonalized spiral is equal. This means that the structure around the active center is independent of the direction of the edge.

The same facts are observed when ethylene is polymerized (Figs. 8–10). Polymerization is, however, too fast in this case, and the polymer soon obscures the structural details of the catalyst surface. Proper handling of the carbon replicas is rendered difficult by the lack of a good solvent for

Fig. 11. Electron micrograph of mechanically ground α-$TiCl_3$. 11,000×. Carbon replica.

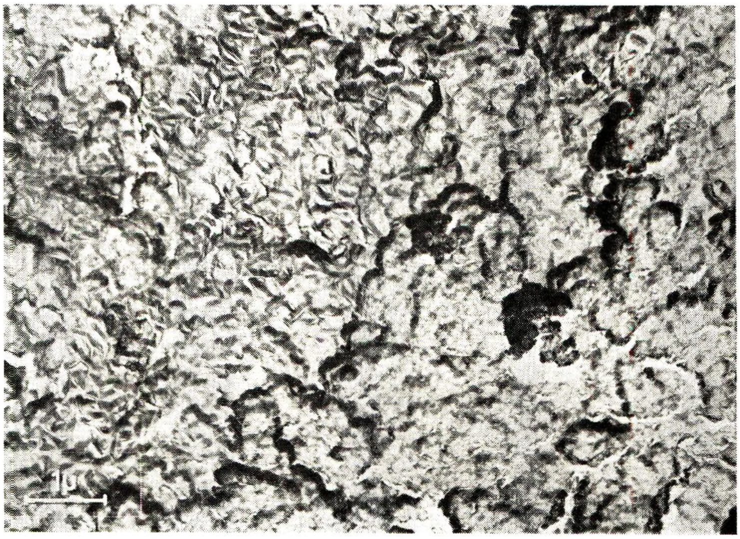


Fig. 12. Electron micrograph of a β-$TiCl_3$–$AlMe_3$ dry catalyst, after polymerization of propylene. 16,000×. Carbon replica.

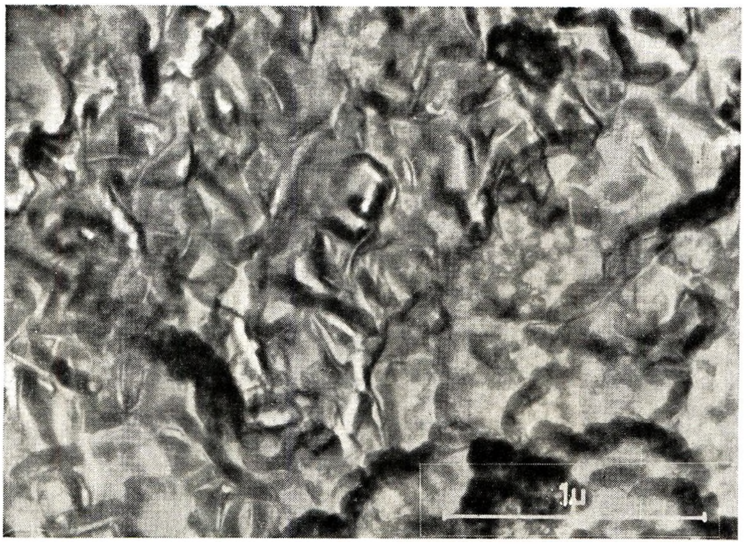


Fig. 13. Electron micrograph of a β-$TiCl_3$–$AlMe_3$ dry catalyst, after polymerization of propylene. 50,000×. Carbon replica.

polyethylene. One sees clearly the formation of polymer dots linked into a ribbon all along the growth spirals and the proliferation of polymer on the lateral faces.

Figure 11 is an electron micrograph of ground α-$TiCl_3$. The grinding was done under vacuum with the use of steel balls. The central big crystal has been cut diagonally and perpendicularly to the 001 face, increasing the lateral surface. In the middle of the same crystal a wedgelike fragment has been clipped off, laying bare several small lateral faces, and an enormous defect is thus created. The picture is a demonstration of how the number of active sites can be increased by grinding α-$TiCl_3$ prior to its use as a catalyst. Early in the study of stereospecific polymerization Natta and collaborators used grinding of α-$TiCl_3$ to this effect.[6]

The study of β-$TiCl_3$ by the same methods does not give detailed information. β-$TiCl_3$ appears as a material with no structure. Growth of polymer on β-$TiCl_3$–$AlMe_3$ catalysts merely shows that the number of active sites in this system is high. No organization of the polymer is seen in Figures 12 and 13, although the amount of propylene polymerized was kept as small as possible by using very short contact times.

## STRUCTURE OF THE LATERAL FACES OF α-$TiCl_3$

The results obtained by electron microscopy show that the lateral faces are the only crystallographic region where polymerization sites are found. The steps formed by the growth spirals, being parallel to the edges of the crystal, must crystallographically be assimilated to lateral faces. It is therefore of utmost importance to know the structure of the lateral faces.

At the opposite of the 001 basal plane, the lateral faces for reasons of stoichiometry present chlorine vacancies through which the surface titanium atoms become exposed and accessible from the outside. This situation has been very thoroughly discussed by Arlman.[7,8]

*A priori*, two ways are seen in which the lattice of $\alpha$-$TiCl_3$ can be cut in order to get hexagonal crystals. One gives lateral faces running parallel to the sides of the hexagones formed by the titanium atoms, and the other

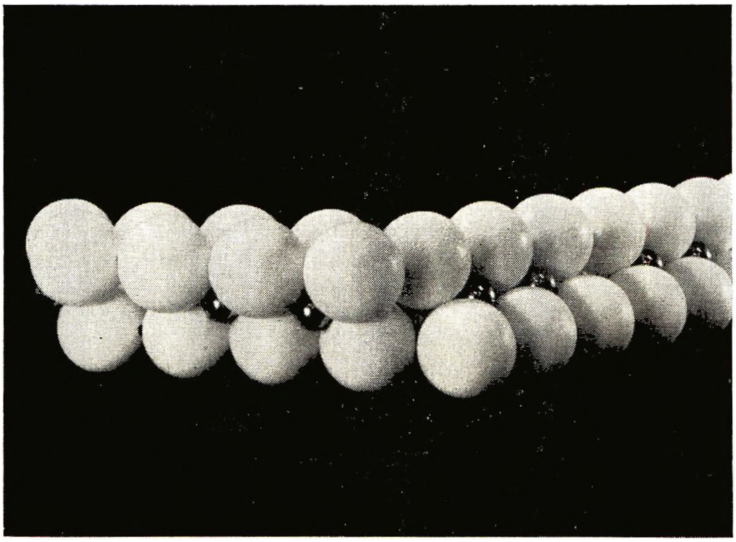


Fig. 14. Model of the lateral face of $\alpha$-$TiCl_3$ if this face is parallel to the sides of the titanium hexagon.

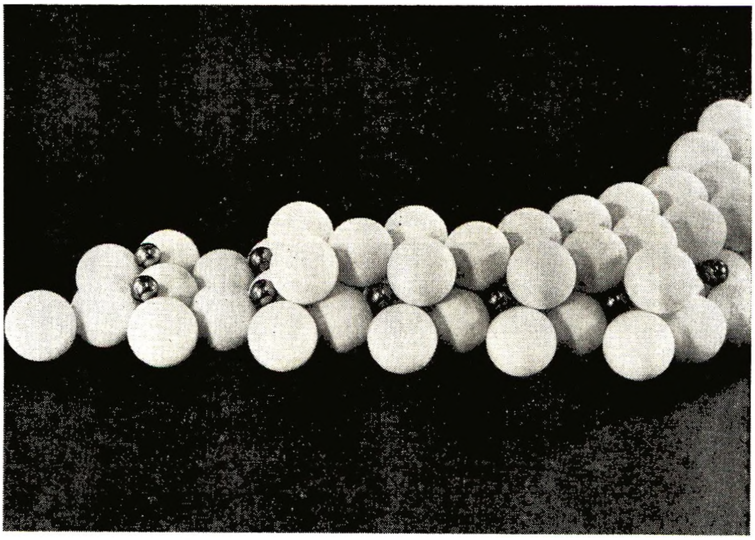


Fig. 15. Model of the lateral face of $\alpha$-$TiCl_3$ if this face is perpendicular to the sides of the titanium hexagon.

gives lateral faces perpendicular to these sides. The structure of the lateral faces obtained in the first case is shown in Figure 14. In this structure, which forms the basis of Arlman's discussion, pairs of octahedryl interstices are occupied by exposed titanium atoms with one site empty in between. In the second case, titanium atoms are found at a regular repeat distance while the chlorine atoms form a zigzag along the edge (Fig. 15). Which of the two is actually occurring can be determined by electron diffraction. When a crystal, fixed in space, is studied by electron microscopy and by electron diffraction one can measure the angle formed between an

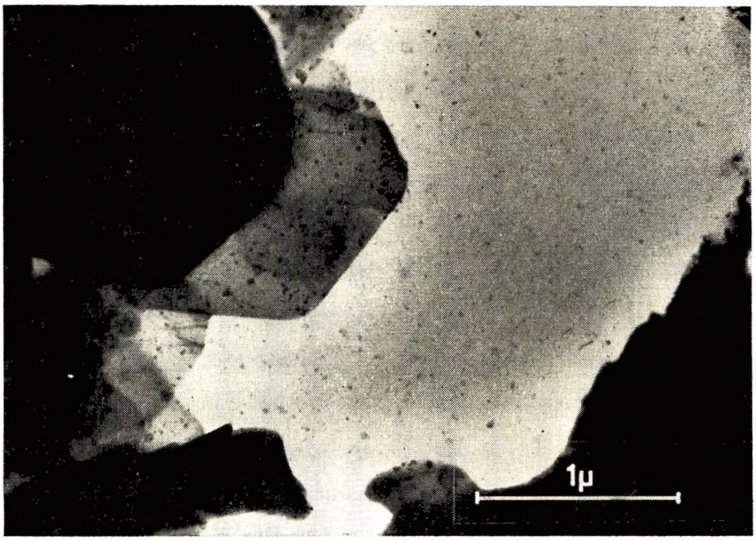


Fig. 16. Transmission electron micrograph of an $\alpha$-TiCl$_3$ sample.

Fig. 17. Electron diffraction pattern taken on the sample shown in Fig. 16. Aluminum added as reference.

edge located by microscopy and a crystallographic plane recognized by diffraction.

Experimentally this is done in the following way. Crystals of $TiCl_3$ suspended in heptane are deposited on a grid and introduced in a Siemens electron microscope. A crystal with well-developed hexagonal faces is located and the direction of its faces is determined (Fig. 16). The electron beam is then brought into focus close to a chosen crystal edge, and the diffraction pattern is photographed (Fig. 17). An angular correction has to be applied to the apparent rotation of the diffraction and transmission images. It is dependent on the apparatus and the enlarging factor. The results obtained with $\alpha$-$TiCl_3$ and also with $\gamma$-$TiCl_3$ are in keeping with the structure of Figure 14. The lateral faces are parallel to the sides of the hexagons formed by the titanium atoms in the lattice. Measurements done on several crystals of $\alpha$- and $\gamma$-$TiCl_3$ give angles of 3–5° between the direction of the edge and the direction of the hexagonal titanium array. This angle would be 30° if the structure shown in Figure 15 were the one actually occurring.

The structure of the lateral faces of $\alpha$-$TiCl_3$ is thus well established as far as the geometric disposition of the titanium atoms is concerned. However, the disposition of the chlorine atoms is open to discussion. Arlman[8] has elaborated the various possible chlorine arrangements which can all be derived from the regular arrangement shown in Figure 14 by shifting loosely bound chlorine atoms, i.e., chlorine atoms coordinated to only one titanium atom, into the vacancies of their titanium neighbor. If a stacking of several $TiCl_3$ layers is considered, one finds that in all of the possible arrangements every loosely bound chlorine atom is in close contact with another loosely bound chlorine atom. It is therefore questionable whether there are enough reasons to prefer one arrangement above all others. Whatever be the true situation, a certain mobility of the loosely bound chlorine atoms may be expected. The conclusions drawn by Arlman on the geometry around the exposed titanium atoms may therefore be retained as the best possible description of the potential active site in systems based on $\alpha$-$TiCl_3$.

## COMPARISON OF THE STEREOREGULATING POWER OF VARIOUS CATALYST COMBINATIONS

The stereospecificity of a given Ziegler-Natta catalyst may in principle be linked to two factors. One is the intrinsic stereoregulating power of the active center, which determines to what extent the monomer is incorporated in always the same geometric conformation into the growing chain. The other factor is the occurrence of steric inversions most probably due to exchange reactions involving the growing polymer chains and leading to their detachment from one active center and their attachment to another center. The existence of metal–bound polymer in solution has been clearly established[6,9–11] during polymerizations such as they are generally studiey, i.e., in a hydrocarbon medium containing free alkylating agent.

Polymerization of propylene from the gas phase on dry catalysts in the absence of free alkylating agent, a condition which was met in all our studies of dry catalysts, should in principle provide a method for the evaluation of the intrinsic stereospecificity of the polymerization centers involved.

An attempt was therefore made to measure the tacticity of samples of polypropylene obtained with various dry catalyst combinations. This meets with some difficulties. First of all, with the use of relatively little catalyst (about 1 g. of titanium chloride was used in our lab-scale experiments) only a small amount of polymer is obtained. Polyethylene can be obtained with a reasonable yield but not polypropylene. In both cases the rate of polymerization at less than atmospheric pressures of olefin, rather high at the start, slows down enormously as polymerization goes on. This is probably due to increasingly difficult diffusion of the monomer to the active center covered by the growing chain. Using excess alkylating agent in a hydrocarbon solvent one must regenerate poisoned centers and continuously form new ones during the polymerization, maintaining thus a high rate. Both effects are absent when a dry catalyst is used. For each of the runs giving rather little polymer, the only available practical method for tacticity measurement is the method of infrared absorbance ratios.[12] It is questionable whether, taken alone, this is a safe method for evaluating tacticity. Moreover, it is impossible to free the polymer satisfactorily from catalyst by conventional methods. The background line of the infrared spectrum of the polymer sample is therefore not as good as might be desired for intensity measurements. One has to restrict the method to the 10.03 $\mu$/10.27 $\mu$ ratio, since these bands are very close to each other and their intensity ratio is therefore less dependent on a badly defined background line. This absorbance ratio is considered rather well related to the isotacticity of the chains by several authors.[12–15] It seems, however, that the method based on the 8.5 $\mu$ band is to be preferred for polymers of low isotacticity.[16]

The 10.03 $\mu$/10.27 $\mu$ absorbance ratios measured for different samples of polypropylene and the catalyst combinations used are given in Table I.

TABLE I

| Sample | Catalyst | $I_{10.03\ \mu}/I_{10.27\ \mu}$ |
|---|---|---|
| 1 | $\alpha$-$TiCl_3$–$AlMe_3$ | 0.95 |
| 2 | $\alpha$-$TiCl_3$–$AlMe_3$ | 0.88 |
| 3 | $\alpha$-$TiCl_3$–$AlMe_3$–$C_6H_6$ | 0.82 |
| 4 | $\alpha$-$TiCl_3$–$AlMe_3$ | 0.80 |
| 5 | $\alpha$-$TiCl_3$–$ZnMe_2$ | 0.79 |
| 6 | $\alpha$-$TiCl_3$–$AlMe_2Cl$ | 0.73 |
| 7 | $\beta$-$TiCl_3$–$AlMe_3$ | 0.73 |
| 8 | $TiCl_2$–$AlMe_3$ | 0.68 |
| 9 | $\beta$-$TiCl_3$–$ZnMe_2$ | 0.59 |
| 10 | $TiCl_2$–$TiCl_3CH_3$ | 0.57 |
| 11 | $TiCl_2$–$TiCl_3CH_3$ | Not measurable |
| 12 | $\beta$-$TiCl_3$–$TiCl_3CH_3$ | Not measurable |

The $\alpha$-$TiCl_3$ used was prepared by the method given earlier,[17] the $\beta$-$TiCl_3$ was prepared by submitting a mixture of $TiCl_4$ and $H_2$ to a silent discharge, the $TiCl_2$ of samples 8 and 10 was obtained by disproportionation of $\alpha$-$TiCl_3$ at around 400°C., whereas the $TiCl_2$ sample 11 was obtained in the same way from violet Stauffer $TiCl_3$. All catalysts were dry catalysts except catalyst 3, which was a suspension in benzene with excess $AlMe_3$ present.

The results, in view of the above discussed difficulties, do not pretend to be accurate measurements of tacticity. They permit, however, a qualitative comparison of the intrinsic stereoregulating power of the various catalysts. The rank occupied by the $\alpha$-$TiCl_3$–$AlMe_2Cl$ catalyst is probably erroneous, in view of the well-established scale of stereospecificity $Al(C_2H_5)_2I > Al(C_2H_5)_2Br > Al(C_2H_5)_2Cl > Al(C_2H_5)_3$.[18] As absolutely certain stands out the low stereospecificity of all catalysts containing only titanium. In fact, the polypropylene samples obtained with this class of catalysts are all waxy. It is unfortunate that the $\alpha$-$TiCl_3$-$TiCl_3CH_3$ catalyst is not included in the table. The activity of this combination for propylene polymerization is practically nil. From earlier observations we know that it gives also rise to a waxy polymer.

All bimetallic systems based on $\alpha$-$TiCl_3$ give polymers of high tacticity. In the bimetallic systems based on $\beta$-$TiCl_3$ a difference was found between $AlMe_3$ and $ZnMe_2$: whereas the former gave a hard polymer, the latter gave a rubber. The comparison between $TiCl_2$–$AlMe_3$ and $TiCl_2$–$ZnMe_2$ could not be made because no polymer could be obtained with the last one.

The qualitative comparison of the rates of polymerization that could be made while running these polymerizations give the following orders:

$\alpha$-$TiCl_3$ catalysts:

$$AlMe_3 > AlMe_2Cl \gg ZnMe_2 > TiCl_3CH_3$$

$\beta$-$TiCl_3$ catalysts:

$$TiCl_3CH_3 > AlMe_3 > ZnMe_2$$

$TiCl_2$ catalysts:

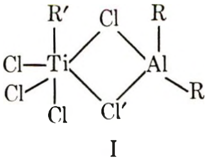
$$TiCl_3CH_3 > Al\ Me_3$$

## STEREOSPECIFICITY OF THE ACTIVE CENTER

It seems probable that the situation around the exposed titanium atoms in the lateral faces of $\alpha$-$TiCl_3$ is one of those described by Arlman. After alkylation such sites may become active. Arlman and Cossee[19–21] have given a detailed theory of stereospecific polymerization. The asymmetry of centers involving a titanium surface atom, an alkyl group, and a vacancy is the reason given for stereospecificity. The theory is in accord with the fact that the tacticity of polypropylene is linked to the titanium halide chosen, $\alpha$- and $\gamma$-forms being more stereospecific than $\beta$-$TiCl_3$. That centers of the Arlman-Cossee type are active in polymerization is supported by the fact that combinations such as $TiCl_3 + TiCl_3CH_3$ and $TiCl_2 + TiCl_3CH_3$, which contain only titanium as metal, are active catalysts. The interaction between $TiCl_3$ and $TiCl_3CH_3$ may be of two types: exchange, $TiCl_3 + TiCl_3CH_3 \rightarrow TiCl_2CH_3 + TiCl_4$, or epitactic adsorption of $TiCl_3CH_3$ on the faces of $TiCl_3$ having exposed titanium atoms. The interaction between $TiCl_2$ and $TiCl_3CH_3$ is presumably of the second kind.

In the $TiCl_3$–$AlR_3$ systems alkylation of the surface certainly occurs as a step in the overall reaction. The alkylation reaction does not need the presence of a chlorine vacancy. We have shown[1] that the fully coordinated 001 face undergoes chlorine–alkyl exchange in the first step of the catalyst-forming reaction. Alkylation of the exposed titanium atoms on the lateral faces leads to the centers described by Cossee and Arlman, containing four chlorine atoms, a chlorine vacancy, and an alkyl group octahedrically distributed around the titanium atom. Obviously the alkylating power of the metal alkyl plays a role in the number and localization of the titanium–alkyl bonds in the surface of $TiCl_3$.

A close study of the photographs reveals that on the well-formed α-$TiCl_3$ crystals (Fig. 5–7) the polymer grows in localized dots. Because of the long reaction time and the excess of monomer during polymerization it seems difficult to assume that only few active centers are able to initiate a polymer chain while many others remain unused. Complete coverage by polymer is found on defect-rich regions of α-$TiCl_3$ and on the surface of β-$TiCl_3$ catalysts. It is therefore safe to assume that all active centers do initiate polymerization. The dotwise formation of polymer indicates then that only few of the exposed titanium atoms in the lateral faces form effective active centers on reaction with aluminum alkyl. A reason has to be sought for the scarcity of the effective active centers. We believe that on a great number of exposed titanium atoms the addition of reaction products ($AlMe_2Cl$ or $AlMeCl_2$) deactivates the Cossee-Arlman centers by filling their chlorine vacancy. It is now well known that complex formation of active centers with amines profoundly changes the number and the nature of the centers.[18,22] Also, the strong inhibiting effect of $AlEtCl_2$ due to complex formation with the active center has been demonstrated.[11] This complex formation with the chloroalkyl aluminum compounds is seen as reversible, so that more specially in the presence of a solvent the active center might be deblocked by desorption. The nature of the alkylating agent would thus also by its complexing power intervene in the polymerization. The way in which the active site is blocked may be visualized in the case of chlorodimethylaluminum as shown in I,



I

where Cl′ represents the filled vacancy and R′ a chlorine atom or an alkyl group fixed by alkylation. This situation is in fact similar to the one described some years ago by Natta and his collaborators as epitactic adsorption.[23] It gives a surface compound similar to the one which we admit to be present all over the 001 face of the $\alpha$-$TiCl_3$–$AlMe_3$ catalyst.[3] Because polymerization necessitates a close approach of the monomer to the transition metal,[4,5,24] which is possible only if the blocking agent has left the vacancy, no catalytic activity is to be expected for the complex compound as such. It could be an active species if the titanium atom carries originally two vacancies. This particular situation which might very well exist in perturbed regions of the crystal will be proposed in this discussion as the stereospecific center of polymerization.

The blocking of the Arlman-Cossee center could also explain the differences between $TiCl_3$–$ZnMe_2$ and $TiCl_3$–$AlMe_3$ catalysts. A sizeable difference in polymerization activity, for ethylene as well as for propylene, exists between these two systems. This is difficult to explain if Arlman-Cossee centers were the general rule. Zinc alkyls are as powerful alkylating agents as aluminum alkyls, and alkylation of the surface must take place in both systems. A brief study of the dry $TiCl_3$–$ZnMe_2$ catalyst has led us to the conclusion that a great amount of zinc is retained in this catalyst. The infrared spectrum of the catalyst shows no Zn-C bonds, and this would indicate that zinc is retained as $ZnCl_2$ in the surface. Effective blocking of the vacancies by $ZnCl_2$ is our tentative explanation for the low activity of $TiCl_3$–$ZnMe_2$ dry catalysts.

The description of the active center as an Arlman-Cossee center, inactive when blocked and active when unblocked, although satisfactory in explaining catalytic activity, is not sufficient for explaining stereospecificity. In all likelihood Arlman-Cossee sites are present in the systems $TiCl_3$ + $TiCl_3CH_3$ and $TiCl_2$ + $TiCl_3CH_3$. Compared to bimetallic catalysts ($TiCl_3$ + $AlR_3$, $TiCl_3$ + $AlR_2Cl$, $TiCl_3$ + $ZnR_2$) they are poorly stereoregulating catalysts. Moreover, in the theory of Arlman and Cossee a special arrangement of the chlorine atoms in the surface of $\alpha$-$TiCl_3$ is required to confer stereospecificity to the active center. It is our opinion that with the other chlorine arrangements, which are energetically of equal probability, the Arlman-Cossee center does not present asymmetry and must yield atactic polymer.

It is also difficult to explain with the theory of Arlman and Cossee why $TiCl_2$–$AlMe_3$ catalysts are stereospecific. The chlorine atoms in the lateral faces of $TiCl_2$ are all linked either to three or to two exposed titanium atoms.[8] The replacement of a twofold coordinated chlorine atom by an alkyl group gives a surface alkyl group linked to two identical titanium atoms that are symmetrically placed with respect to the alkyl group and to the vacancies. A stereospecific placement of the entering monomer on such an active center appears impossible.

A model study of $\beta$-$TiCl_3$ catalysts also permits tests of the validity of the concepts of Arlman and Cossee as a general working hypothesis in explaining Ziegler-Natta catalysis. The crystallography of $\beta$-$TiCl_3$ has been established by Natta et al.[25] A brief description and a schematic representation were given in one of our earlier papers.[2] The titanium

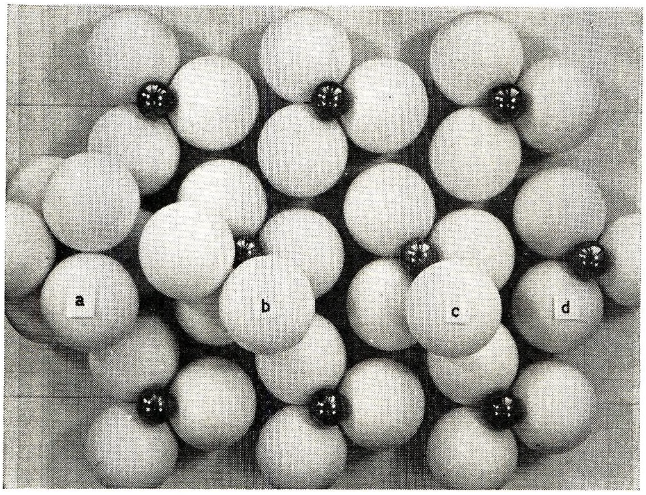
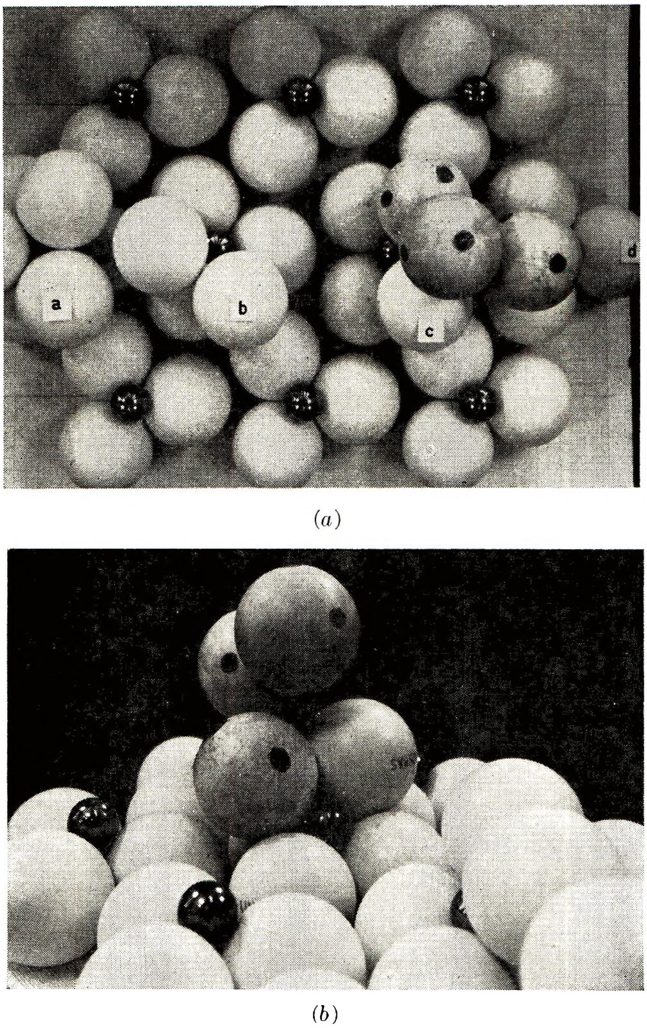


Fig. 18. Proposed model of the top face of $\beta$-$TiCl_3$ crystal: (*a*) no vacancy site; (*b*) one-vacancy site; (*c*) two-vacancy site; (*d*) three-vacancy site.

atoms in the lattice are octahedrically coordinated to six chlorine atoms. The external titanium atoms, at the top and at the bottom of the vertical stacks, are, however, incompletely coordinated if the stoichiometry is to be observed, and on the average are linked to $4^1/_2$ chlorine atoms. The four possible arrangements around these surface titanium atoms are represented in Figure 18. For statistical reasons the surface sites with one (b) and with two (c) vacancies should be favored. If an Arlman-Cossee center is formed on these sites by replacing a chlorine atom by an alkyl group no stereospecific center is obtained. In both cases a propylene molecule may be seen coordinated in the vacancy in two ways, having the methyl group at will either to the right or to the left. Very special configurations around the titanium atom will have to be imagined in order to explain stereospecificity in the case of $\beta$-$TiCl_3$–$AlR_3$ catalysts if Arlman-Cossee centers are considered. An explanation of the stereospecificity of these catalysts, admitted as being low but nevertheless existing, may also be offered in terms of complexation of aluminum alkyl derivatives on the Arlman-Cossee centers. The idea of the blocking of the center with one vacancy, which is well supported for the $\alpha$-$TiCl_3$ catalyst for reasons exposed above, may be applied also to the $\beta$-$TiCl_3$ catalyst. In the $\beta$-$TiCl_3$ surface, exposed titanium atoms with two vacancies must frequently occur. The complexation of an aluminum alkyl halide on these sites would give an active center. The chemical formula of this active center (see also model on Fig. 19) is in fact analogous to that of the soluble complexes synthesized by Natta and his collaborators. Whereas these complexes in solution present two potential vacancies on the titanium atom, the surface center as depicted has only one vacancy. We propose this center as the principle of stereospecific polymerization of Ziegler-Natta catalysts. Its formation is linked to the presence of surface titanium atoms with two vacancies in the surface of

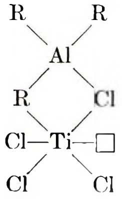


(*a*)

(*b*)

Fig. 19. Proposed model of a stereospecific active site: (*a*) top view; (*b*) lateral view.

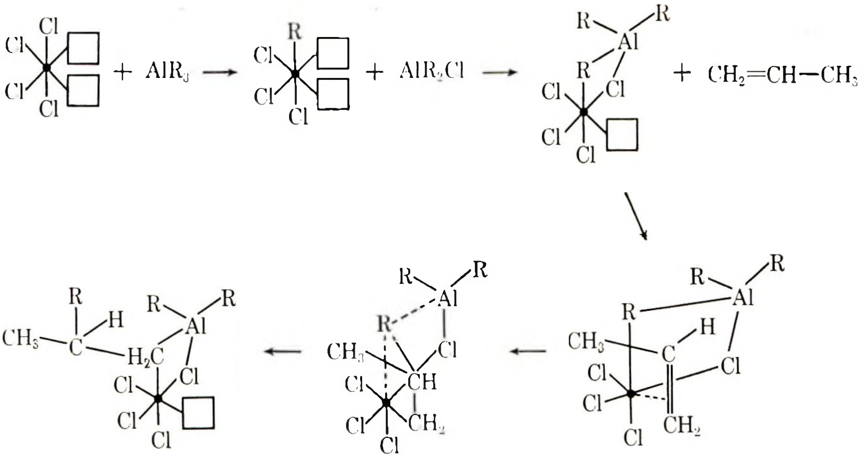
$TiCl_3$, whether $\alpha$ or $\beta$. It is not unsound to consider the presence of a sufficient number of two such vacancy sites in titanium trichlorides.



First, the observed stoichiometric ratios Cl/Ti are always somewhat less than 3 for $TiCl_3$ of various modifications. Secondly, crystals with well-developed faces like those of Figure 2 are exceptions and imperfect crystals are the rule in catalysts based on $TiCl_3$. An interesting feature of the proposed stereospecific center is that it cannot be further blocked by aluminum alkyl compounds. Indeed, even if the titanium atom can undergo coordination by virtue of its vacancy, steric hindrance between the substituents on the aluminum atom would prevent this coordination. In the next section a plausible mechanism of polymerization on the proposed stereospecific center is developed.

## MECHANISM OF STEREOSPECIFIC POLYMERIZATION OF PROPENE

The mechanism proposed is as follows:



where the filled circle (●) denotes Ti.

(*1*) The monomer, entering into the vacancy (Fig. 20) interacts with the titanium atom, forming a π-complex. The essentials of this reaction were extensively analyzed by Cossee.[20] In addition to the condition of maximal overlapping of the bonding orbitals the orientation of the propylene molecule is governed by polar interaction between the double bond $\underset{1}{\overset{\delta^-}{\mathrm{C}}}\mathrm{H_2}{=}\overset{\delta^+}{\mathrm{C}}\mathrm{H}{-}\mathrm{CH_3}$ and the $\overset{\delta^+}{\mathrm{Ti}}{-}\underset{\alpha}{\overset{\delta^-}{\mathrm{C}}}$ bond.[26] The stereospecific orientation of the methyl group is dictated by the requirement of minimal steric interaction with the external groups carried by the aluminum atom.

(*2*) Insertion of the π-complexed olefin in the Ti—C bond takes place as proposed by Cossee. In addition, a simultaneous rupture of the Al—C bond is postulated. The alkyl group $\underset{1}{\mathrm{C}}\mathrm{H_2}{-}\mathrm{CHR}{-}\mathrm{CH_3}$ is now linked only to titanium and carbon atom 1 occupies the original vacancy.

(*3*) An active center may be regenerated in two ways. (*a*) The aluminum atom with its two outer substituents rotates along the Cl—Al bond and anchors itself to the surface, with carbon atom 1 now forming the bridge. The new active center is then sterically different from the original one be-

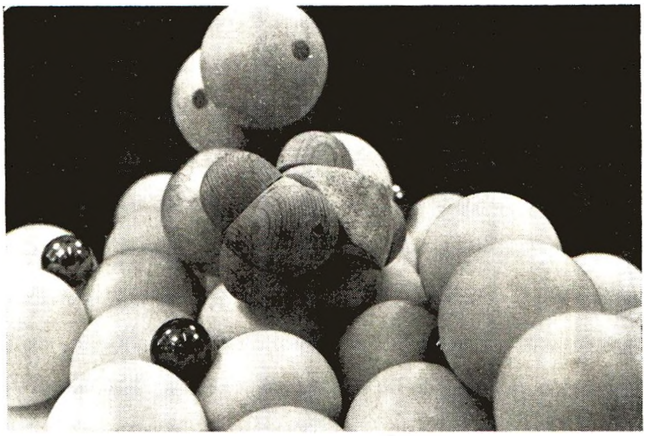


Fig. 20. Proposed model of a stereospecific active site, with a propylene molecule occupying the vacancy.

cause vacancy and bridging carbon atom have changed places. (*b*) Carbon atom 1 shifts to the position originally occupied by the $\alpha$-C atom of R. This rearrangement is to be preferred because a driving force for the back shifting of the chain is seen in the coordination of carbon atom $C_1$ to the aluminum atom. The active center is thus restored and this is the necessary condition for stereospecificity.

The same mechanism may apply to soluble bimetallic catalysts. The titanium atom in this case carries two potential vacancies symmetrically placed with regard to the plane of the bridge. Therefore the olefin can interact with the titanium atom on one side or on the other and no stereoregulation is to be expected.

In view of the complexity of the problem of Ziegler-Natta catalysis a summary of our essential conclusions on the nature and the structure of the active centers is in order.

(*1*) We do not believe that there is only one unique type of active center at work. Arlman-Cossee centers and bimetallic centers such as described by Natta and his collaborators and by Patat and Sinn may both be present in $TiCl_3 \cdot AlR_3$ catalysts.

(*2*) Blocking of the Arlman-Cossee centers by aluminum alkyl halides must be the general rule because of the strong tendency of coordination. An inactive bimetallic complex results. The blocking of the Arlman-Cossee center is believed to be reversible. The unblocked Arlman-Cossee center is nonstereospecific unless a special surface geometry orients the $\pi$-adsorbed olefin for steric reasons.

(*3*) If the titanium atom originally carried two vacancies, a stereospecific bimetallic active center is obtained.

(*4*) The presence of a Ti—C bond on an accessible titanium atom is the condition *sine qua non* for polymerization. The formation of active centers is for this reason restricted to the lateral faces and to perturbed regions of $\alpha$-$TiCl_3$ crystals, whereas the 00.1 face is totally inactive.

This mechanism does not claim great originality. In fact, it contains elements that are present in the mechanism proposed by Arlman and Cossee and in the mechanisms of catalysis on bimetallic compounds proposed by Patat and Sinn and also by Natta and his collaborators. Our only concern was to obtain the best possible fit between theory and experimental data.

The electron micrographs would not have been obtained without the valuable collaboration of Miss A. Fourdeux. Our thanks go to Mr. Terao who established by electron diffraction the structure of the lateral faces of α-$TiCl_3$. The authors are grateful to Mr. J. Gabant for his help in the difficult technique of sample preparation.

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## Résumé

Une étude par microscopie électronique de catalyseurs Ziegler-Natta et une comparaison qualitative de la stéréospécifité de ces catalyseurs sont présentées. Les catalyseurs observés ont été préparés en l'absence de tout autre produit qu'un chlorure de titane et un alkyl aluminium et la polymérisation a été réalisée sur le catalyseur ainsi formé sans autre addition que celle d'un monomère. L'observation par microscopie électronique de catalyseurs α $TiCl_3$-$AlMe_3$ permet de constater que les centres actifs, révélés par la présence du polymère, se situent sur les spirales de croissance, les faces latérales et les zones riches en défauts des cristaux de α $TiCl_3$. Ces emplacements étant considérés comme présentant de nombreux atomes de titane incomplètement coordonnés, le centre actif doit comporter une lacune sur le métal de transition. Comme, cependant, le nombre de centres actifs à ces emplacements est nettement inférieur au nombre des atomes de titane incomplètement coordonnés, on admet que le site $TiCl_3$ à une seule lacune initiale ne conduit normalement pas , lors de la réaction avec $AlMe_3$ , à un centre actif. On propose que cette réaction forme par complexation un composé bimétallique qui ne comporte plus de lacune sur le métal de transition. Il n'est toutefois pas exclu que la réaction de complexation soit réversible et que le site débloqué, du type proposé par Cossee, soit actif en ce cas. Toutefois, ces centres produiraient du polymère atactique. Une réaction similaire de complexation sur un site $TiCl_3$ à deux lacunes initiales conduit à un composé bimétallique ayant une lacune unique sur le métal de transition. Ce type de centre actif est repésenté par un modèle et un mécanisme de polymérisation est proposé. Ce type de site bimétallique conduirait à la formation de polymère isotactique.

## Zusammenfassung

Versuchsergebnisse über Ziegler-Natta-Katalysatoren, die auf elektronenmikroskopischen Beobachtungen beruhen, sowie ein qualitativer Vergleich der Stereospezifität der verschiedenen Katalysatorkombinationen werden mitgeteilt. Die Polymerisation des Olefins wird bei diesen Versuchen in der Gasphase an trockenen Katalysatoren in Abwesenheit von Lösungsmittel oder überschüssigem Aluminiumalkyl durchgeführt. Die kristallographische Struktur der Seitenflächen von α-$TiCl_3$ wird elektronenmikroskopisch und durch Elektronenbeugung bestimmt. Die elektronenmikroskopischen Aufnahmen von α-$TiCl_3$-$AlMe_3$-Katalysatoren zeigen, dass die aktiven Zentren, welche sich durch die punktweise Bildung des Polymeren zu erkennen geben, längs der Wachstumsspiralen an Seitenflächen und Oberflächendefekten liegen. Diese Oberflächenbereiche sind die einzigen, an welchen die Oberflächen-Titanatome unvollständig koordiniert sind. Das Vorhandensein von Chlorlücken und exponierten Titanatomen bildet daher eine wesentliche Voraussetz ung für aktive Zentren. Die Anzahl der aktiven Zentren ist aber klein im Vergleich zur Anzahl der unvollständig koordinierten Titanatome, und es wird daher angenommen, dass die normal auftretenden α-$TiCl_3$-Plätze mit einer Lücke bei der Reaktion von Aluminiumalkyl keine aktiven Zentren liefern. Es wird weiters angenommen, dass die Reaktion mit Aluminiumalkyl an solchen Plätzen schliesslich zu einem bimetallischen Komplex führt, welcher die ursprüngliche Lücke am titanatom ausfüllt. Es ist nicht ausgeschlossen, dass die Komplexbildung reversibel ist und dass der nichtblockierte alkylierte Platz, welcher den von Cossee vorgeschlagenen Typ besitzt, ein aktives Zentrum bildet. Dieses Zentrum würde aber ataktisches Polymeres liefern. Eine ähnliche Komplexbildung an einem $TiCl_3$-Platz mit ursprünglich zwei Lücken würde eine Lücke am Titanatom ungeändert lassen. Es wird angenommen, dass hier das Zentrum für die stereospezifische Polymerisation liegt. Ein Modell für dieses aktive Zentrum sowie ein Mechanismus für das Polymerwachstum an demselben werden vorgeschlagen.

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# Preparation and Polymerization of Some Vinyl Ester Amides of Pinic Acid

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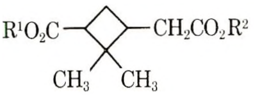
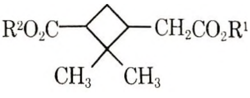
## Synopsis

The preparation of vinyl 2,2-dimethyl-3-morpholinocarbonylcyclobutaneacetate, vinyl 2,2-dimethyl-3-piperidinocarbonylcyclobutaneacetate, and vinyl 2,2-dimethyl-3-di-*n*-butylaminocarbonylcyclobutaneacetate has been achieved by selective amination followed by vinyl interchange. Homopolymers and vinyl chloride copolymers containing 25 and 30 wt.-% of the vinyl esteramides were prepared and evaluated as nonrigid plastics. The vinyl esteramides incorporated in vinyl chloride copolymers did impart some plasticization, but their effect was far below the effect of added plasticizer to a vinyl chloride polymer.

Poly(vinyl chloride) is plasticized by pinic acid diesters[1] but copolymers of vinyl chloride with various isomeric pinic acid esters (I, II),



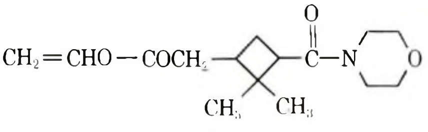
I



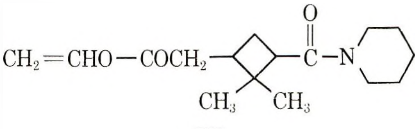
II

where R¹ is —CH=CH₂ and R² is —$C_2H_5$, —*n*-$C_4H_9$, or —$CH_2CH$—$(C_2H_5)(CH_2)_3CH_3$, did not exhibit internal plasticization by the vinyl ester incorporated in the polymer backbone.[2]

Since amides are often good plasticizers of polyvinyl chloride, the vinyl esteramides of pinic acid, where the amine moiety is morpholine (IIIa), piperidine (IIIb), or di-*n*-butylamine (IIIc) were prepared. The vinyl chloride



IIIa



IIIb

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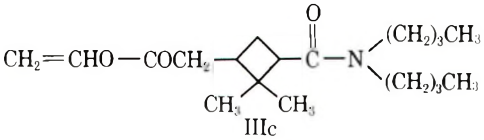

IIIc

copolymers containing approximately 15 and 30 wt.-% of the vinyl esteramide were prepared to examine the ability of these comonomers to act as internal plasticizers for the polymer.

The vinyl esters of 2,2-dimethyl-3-alkylaminocarbonylcyclobutaneacetic acid were prepared by reacting the amines (morpholine, piperidine, and di-*n*-butylamine) with ethyl 2,2-dimethyl-3-chlorocarbonylcyclobutaneacetate, hydrolyzing the ethyl ester to the free acid, and vinylating the resulting monoamides by vinyl interchange. The physical data on the various derivatives are tabulated in Tables I and II.

The conditions for preparing the morpholine reaction products are given in the experimental section. The piperidine and di-*n*-butylamine derivatives were prepared by the same processes.

It will be noted that the half amides of morpholine and piperidine were solids. The vinylation of these materials was hampered as a result of their poor solubility in vinyl acetate.

The vinyl esteramides were homopolymerized (see Table III) in a benzene solution at 60°C. The polymers were soft, tacky solids and readily adhered to glass surfaces.

The vinyl chloride copolymers containing approximately 25 and 30 wt.-% of the vinyl esteramide were prepared in an emulsion system at 60°C. with the use of ORR soap as the emulsifying agent and potassium persulfate as the initiator. The copolymer compositions and some physical data are listed in Table IV. During the reprecipitation procedure flexible films were obtained but were not examined. The copolymers were reprecipitated 15 times from tetrahydrofuran into water and three times into methanol before analysis. Each evaluation sample is a composite of 10–15 polymerization batches which were combined during the reprecipitation procedure.

## EXPERIMENTAL

### Ethyl 2,2-Dimethyl-3-chlorocarbonylcyclobutaneacetate

The acid chloride, b.p. 114°C. at 2 mm., of monoethyl pinate, was prepared by reacting thionyl chloride with the monoester obtained by esterification of pinic acid with one mole of ethanol.[3] The pinic acid was obtained from hypochlorite oxidation of *cis*-DL-pinonic acid. Gas chromatographic analyses of esters of the pinic acid gave two peaks which presumably resulted from the expected *cis* and *trans* isomers of the acid.

### Ethyl 2,2-Dimethyl-3-morpholinocarbonylcyclobutaneacetate

Morpholine, 378 g. (4.35 moles) dissolved in 1 liter of dry benzene was heated to reflux. The acid chloride above (400 g., 1.72 moles) was added dropwise at a rate sufficient to maintain a gentle boil. When cooled to

TABLE I

Amides of Pinic Acid (2,2-Dimethyl-3-carboxycyclobutaneacetic Acid)

| Amides | M.p., °C. | B.p., °C./mm. Hg | Yield, % | Refractive index $n_D^{20}$ | Neutral equivalent | | Formula | Calcd. | | | Found | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calcd. | Found | | C, % | H, % | N, % | C, % | H, % | N, % |
| Ethyl 2,2-dimethyl-3-aminocarbonylcyclobutaneacetates | | | | | | | | | | | | | |
| Morpholinocarbonyl- | — | 154/0.1 | 91 | 1.4903 | — | — | $C_{15}H_{25}O_4N$ | 63.56 | 8.90 | 4.94 | 62.87 | 8.98 | 5.11 |
| Piperidinocarbonyl- | — | 150/0.25 | 93 | 1.4901 | — | — | $C_{16}H_{27}O_3N$ | 68.29 | 9.67 | 4.98 | 68.54 | 9.65 | 4.75 |
| Di-*n*-butylaminocarbonyl- | — | 154/0.25 | 93 | 1.4681 | — | — | $C_{19}H_{35}O_3N$ | 70.09 | 10.84 | 4.35 | 70.38 | 10.91 | 4.24 |
| 2,2-Dimethyl-3-aminocarbonylcyclobutaneacetic acids | | | | | | | | | | | | | |
| Morpholinocarbonyl- | 158–160[a] | — | 96[b] | — | 255.3 | 234.5[b] | $C_{13}H_{21}O_4N$ | 61.15 | 8.29 | 5.49 | 61.45[c] | 8.37[c] | 5.50[c] |
| Piperidinocarbonyl- | 146–148[d] | 186–194/0.1[e] | 94[b] | — | 255.3 | 255.0[b] | $C_{14}H_{23}O_3N$ | 66.37 | 9.12 | 5.53 | 66.36[c] | 9.07[c] | 5.37[c] |
| Di-*n*-butylaminocarbonyl- | liq.[b] | 186/0.3[e] | 96[b] | — | 297.4 | 294.5[b] | $C_{17}H_{31}O_3N$ | — | — | — | — | — | — |

[a] Pure isomer, acetone.

[b] Values on crude, undistilled acid.

[c] Crystalline material.

[d] Pure isomer, ethyl acetate.

[e] Distilled with disproportionation.

TABLE II
Vinyl Esters of Amides of Pinic Acid

| Vinyl 2,2-dimethyl-3-aminocarbonyl-cyclobutaneacetates | M.p., °C. | B.p., °C./mm. Hg | Yield, % | Refractive index $n_D^{20}$ | Hydrogenation equivalent |  | Formula | Calcd. |  |  | Found |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd. | Found |  | C, % | H, % | N, % | C, % | H, % | N, % |
| Morpholinocarbonyl- | 75[a] | 185/6.2 | 81 | 1.5018 | 281.3 | 280.92 | $C_{15}H_{23}O_4N$ | 64.03 | 8.24 | 4.98 | 63.93 | 8.20 | 4.85 |
| Piperidinocarbonyl- | liq. | 146–148/6.18 | 53 | 1.5007 | 279.4 | 280.5 | $C_{12}H_{25}O_3N$ | 68.78 | 9.02 | 5.01 | 68.90 | 9.10 | 5.06 |
| Di-*n*-butylamino-carbonyl- | liq. | 150–152/0.25 | 78 | 1.4765 | 323.4 | 322.2 | $C_{19}H_{33}O_3N$ | 70.53 | 10.29 | 4.33 | 70.70 | 10.18 | 4.51 |

[a] From ether–pentane, 2:1.

TABLE III
Solution Homopolymerization of the Vinyl Esteramides

| Vinyl ester | Wt. ester, g. | Wt. AIBN, g. | Benzene, ml. | Time, hr. | Temp., °C. | Calcd. |  |  | Found |  |  | $\eta_{inh}$[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | C, % | H, % | N, % | C, % | H, % | H, % |  |
| Vinyl 2,2-dimethyl-3-morpholinoamido-cyclobutaneacetate | 0.5 | 0.01 | 5 | 48 | 60 | 64.03 | 8.24 | 4.98 | 63.98 | 8.21 | 4.90 | 0.21 |
| Vinyl 2,2-dimethyl-3-piperidinoamido-cyclobutaneacetate | 0.5 | 0.01 | 5 | 44 | 60 | 68.78 | 9.02 | 5.01 | 68.91 | 9.05 | 5.00 | 0.19 |
| Vinyl 2,2-dimethyl-3-di-*n*-butylamido-cyclobutaneacetate | 0.5 | 0.01 | 5 | 46 | 60 | 70.53 | 10.29 | 4.33 | 70.50 | 10.20 | 4.50 | 0.23 |

[a] Inherent viscosity of a 0.5% tetrahydrofuran solution measured at 30°C.

## TABLE IV

Emulsion Copolymerization of Vinyl Chloride and Vinyl Esteramides at 60°C. for 72 hr.

| Vinyl ester (sample number)[a] | Monomer charge of each batch, wt.-% of vinyl ester[b] | Emulsifier and wt., g. | Water, ml. | Conversion, %[c] | Softening temperature, °C.[d] | N, %[e] | $\eta_{inh}$[f] | Amideester in copolymer wt.-%[g] |
|---|---|---|---|---|---|---|---|---|
| Vinyl 2,2-dimethyl-3-morpholinocarbonylcyclobutaneacetate | | | | | | | | |
| 67 | 25 | Triton X-301, 3.0 | 40 | 80 | 95 | 1.33 | 0.85 | 26.6 |
| 68 | 25 | ORR soap, 0.5 | 43 | 82 | 91 | 1.37 | 0.99 | 27.4 |
| 69 | 30 | Triton X-301, 3.0 | 40 | 78 | 90 | 1.11 | 0.79 | 22.2 |
| 89 | 30 | ORR soap, 0.5 | 43 | 76 | — | 1.25 | 0.96 | 19.0 |
| Vinyl 2,2-dimethyl-3-piperidinocarbonylcyclobutaneacetate | | | | | | | | |
| 103 | 25 | ORR soap, 0.5 | 43 | 82 | 90 | 1.29 | 1.15 | 23.5 |
| 104 | 30 | ORR soap, 0.6 | 45 | 79 | 90 | 1.14 | 1.30 | 22.9 |
| Vinyl 2,2-dimethyl-3-di-*n*-butylaminocarbonylcyclobutaneacetate | | | | | | | | |
| 88 | 25 | ORR soap, 0.5 | 43 | 75 | 80 | 1.18 | 1.28 | 26.4 |
| 95 | 25 | ORR soap, 0.5 | 43 | 84 | 95 | 1.09 | 1.34 | 23.7 |
| 94 | 30 | ORR soap, 0.5 | 43 | 78 | 94 | 1.35 | 1.34 | 30.1 |

[a] Each polymer sample is a composite of 10–15 individual polymerization batches.

[b] Each polymerization batch contained 10 g. of monomer in the ratio shown.

[c] Average conversion of all batches after two reprecipitations into water.

[d] Temperature at which the polymer begins to flow when heated between two cover glasses.

[e] Average of two determinations.

[f] Inherent viscosity of a 0.2% tetrahydrofuran solution measured at 30°C. in a No. 50 Cannon-Fenske viscometer.

[g] Calculated from the nitrogen content of the copolymer.

room temperature, morpholine hydrochloride, insoluble in benzene, was removed by filtration and washed with benzene. After the solvent was removed under reduced pressure, the product was distilled. The yield was 444 g. of a liquid.

### 2,2-Dimethyl-3-morpholinocarbonylcyclobutaneacetic Acid

The amide above (282.5 g., 1 mole) was dissolved in 300 ml. of 95% ethanol and saponified by the addition of 40 g. of sodium hydroxide dissolved in 100 ml. of water. The temperature rose to 50°C., and after 4 hr. the pH dropped to about 8. After 16 hr. the batch was diluted with 169 ml. of water, the alcohol removed by distillation by using a packed column, and the residue diluted further with 422 ml. of water. Extraction of the alkaline solution with chloroform gave 9.5 g. of starting material. Acidification, extraction with chloroform, and isolation by removal of solvent at 0.5 mm. 125°C. pot temperature gave 261 g. of waxy solid. Washing of 5 g. of the crude half amide with diethyl ether gave 3 g. of colorless solid, presumably the *cis* isomer, since it was present in the greater amount.

### Vinyl 2,2-Dimethyl-3-morpholinocarbonylcyclobutaneacetate

The crude half amide above was vinylated by the vinyl interchange procedure of Adelman.[4] The crude amide was melted and added in a molten state to the vinyl acetate. After addition of catalyst and allowing to stand awhile, crystallization of one of the half amides, presumably the *cis* isomer, occurred. After 72 hr., the solid, about one-third of the charge, was removed by filtration. The vinyl ester (filtrate) was isolated by the usual procedure. The recovered acid was reacted with more vinyl acetate and converted to vinyl ester. The results of vinylation are tabulated in Table II.

### Solution Homopolymerization of the Vinyl Esteramides

Each of the vinyl esteramides was homopolymerized in the following manner. A $^1/_2$-g. portion of the vinyl esteramide, 10 mg. of 2,2′-azobisisobutyronitrile and 5 ml. of AR grade benzene were placed in a tube connected by 24/40 standard taper joints to a stopcock.[5] A stream of nitrogen was bubbled through the solution for 10 min. before the top section of the tube was placed in position. The tube was cooled in a Dry Ice–acetone bath and then evacuated to 1 mm. of pressure and the stopcock was closed. After warming to room temperature, the tube was placed in a Fisher Isotemp oven at 60°C. for 48 hr. The viscous polymer solution was poured into 50 ml. of methanol, and a gummy polymer separated on the beaker walls. After three reprecipitations into methanol from benzene the residual solvents were recovered under reduced pressure. The polymer remained very soft and tacky. Inherent viscosities were determined on 0.5% solutions in tetrahydrofuran in a No. 50 Cannon-Fenske viscometer. The polymers are described in Table III.

## Emulsion Copolymerization of Vinyl Chloride with the Vinyl Esteramides

The vinyl chloride copolymers containing 25 and 30 wt.-% of vinyl 2,2-dimethyl-3-morpholinocarbonylcyclobutaneacetate, vinyl 2,2-dimethyl-3-piperidinocarbonylcyclobutaneacetate, and vinyl 2,2-dimethyl-3-di-*n*-butyl-aminocarbonylcyclobutaneacetate were prepared in the following manner.

Each evaluation sample was obtained by combining 10–15 individual polymerization batches during the reprecipitation procedure. Each individual polymerization batch contained a starting charge of 10 g. of monomers (2.5 g. and 7.5 g. or 3.0 g. and 7.0 g. of the vinyl esteramide and vinyl chloride, respectively). To a 110 ml. polymerization tube (Ace Glass T1506) was added the appropriate amount of vinyl esteramide, 0.6 g. of ORR soap, 4.0 ml. of a 2.5% potassium persulfate solution and 43 ml. of deoxygenated water. The vinyl 2,2-dimethyl-3-morpholinocarbonylcyclobutaneacetate copolymers were prepared by using Triton X-301 (Rohm and Haas), a 20% solution of an alkylaryl sulfonate and 40 ml. of water). The tube was cooled in a Dry Ice–acetone bath and a slight excess of condensed vinyl chloride was added. The tube was capped with a crown-type bottle top after the excess vinyl chloride evaporated.

The polymerization tubes were placed in a constant-temperature tumbler bath for 72 hr. at 60°C. The copolymer emulsions were coagulated by pouring into 400 ml. of a saturated salt solution. The copolymer batch was filtered and washed two times with water and two times with methanol. The copolymer was dissolved in tetrahydrofuran (10% solution) and reprecipitated a total of 15 times into water and two times into methanol.

A 1-gal. Waring Blendor was used for the reprecipitation into water. The rate of agitation was about 7000 rpm. The methanol was stirred with a spatula during the reprecipitations. The copolymers precipitated in fibrous strands during reprecipitation into water and methanol under the conditions described.

The copolymers were dried in air for 72 hr. and in a vacuum oven at room temperature for 24 hr. before analysis. The inherent viscosities were determined on 0.2% solutions in tetrahydrofuran in a No. 50 Cannon-Fenske viscometer. The softening points were determined on a Kofler hot stage and are the temperature at which the copolymers began to flow. The elemental analyses were determined by Micro-Tech Laboratories, Skokie, Illinois. The copolymer data are listed in Table IV.

## Evaluation

These copolymers were found to be thermally sensitive, and preliminary attempts to process them by conventional melting and molding procedures at 280–300°F. resulted in severe degradation. Because of this development and the limited quantity of material available, thermal processing was abandoned in favor of a film casting method.

The evaluations were obtained on specimens die-cut from 37–54 mil thick sheets prepared by casting on a confined mercury surface, a tetra-

TABLE V
Physical Characteristics of Some Vinyl Esteramide–Vinyl Chloride Copolymers

| Sample no. | Vinyl esteramide comonomer in polymer | Ester amide (on $N_2$ basis), %[a] | Relative modulus of elasticity, psi | Yield point, psi | Tensile strength, psi | Elongation, % | $T_f$, °C. | $T_4$, °C. |
|---|---|---|---|---|---|---|---|---|
| | Vinyl 2,2-dimethyl-3-morpholinocarbonylcyclobutaneacetate | | | | | | | |
| 67 | | 26.6 | 57,400 | 2000 | 1330 | 90 | 10 | 22 |
| 68 | | 27.4 | 34,200 | 1290 | 1230 | 120 | 17 | 24 |
| 69 | | 22.2 | 62,300 | 2470 | 1630 | 15 | −5 | 7 |
| | Vinyl 2,2-dimethyl-3-piperidinocarbonylcyclobutaneacetate | | | | | | | |
| 103 | | 25.5 | 49,500 | 1800 | 1180 | 60 | 10 | 22 |
| 104 | | 22.9 | 41,300 | 1604 | 1060 | 80 | 7 | 16 |
| | Vinyl 2,2-dimethyl-3-di-*n*-butylaminocarbonylcyclobutaneacetate | | | | | | | |
| 88 | | 26.4 | 30,700 | 1330 | 1200 | 100 | 11 | 21 |
| 95 | | 23.7 | 88,400 | 4030 | 3500 | 10 | 14 | 26 |
| 94 | | 30.1 | 32,900 | 1830 | 1160 | 90 | 14 | 22 |
| | Vinyl chloride–vinyl acetate copolymer | None | — | 7700 | 6830 | 128 | 75 | |
| | Vinyl chloride–vinyl acetate copolymer with 35% di-2-ethylhexyl phthalate | None | 1,600[b] | — | 3050 | 350 | −24 | −3 |

[a] Vinyl esteramide incorporated.
[b] At 100% elongation.

hydrofuran solution containing 15 g. of the respective copolymers, 0.075 g. of stearic acid, and 0.15 g. of Advastab T-360 stabilizer (polymeric tin mercaptide, Advance Division, Carlisle Chemical Works). After setting for 48 hr. at room temperature to allow the bulk of the solvent to evaporate, the sheets were stripped from the mercury surface and aged for 24 hr. at room temperature. They were then heated in a forced draft oven for 12 hr. at 65°C. followed by another aging at room temperature for 30 days to desolventize the film.

Even after these treatments, traces of solvent remained, as evidenced by the strong aroma of tetrahydrofuran which emanated from the stressed film in tension tests. The pattern of the results, however, appears to rule out any significant solvent contribution in these tests.

Tensile strength, modulus of elasticity, yield point, and elongation measurements were made in conformance with ASTM D-638 for rigid and semirigid compositions, except for the use of a 1-in. gauge length rather than the 2-in. called for in the test. Torsional stiffness measurements were made in conformance to ASTM 1043-61T.

The results of these tests are presented in Table V. Examination of these data and comparison with those for other vinyl copolymers previously investigated in this laboratory[2,6,7,8] shows without question that of these copolymers those incorporating a vinyl esteramide comonomer exhibit the greatest degree of internal plasticization. The extent of this plasticization is, however, still far short of what is desired. For all practical purposes, the currently studied copolymers are essentially rigid to semirigid compositions and display neither the flexibility nor low-temperature characteristics usually associated with externally plasticized vinyl chloride copolymer compositions. Furthermore, they exhibit tensile strengths which are, with but one exception, far below that exhibited by a more effectively externally plasticized poly (vinyl chloride) composition. This behavior is in accord with a conclusion deduced by Doolittle[9] from the mechanistic theory of plasticization which states that an internally plasticized polymer having adequate low-temperature performance can be expected to exhibit a poor tensile strength considerably below that of an externally plasticized composition of comparable low-temperature performance.

The correlations between the degree of comonomer incorporation and response in the overall physical characteristics of each respective copolymer group is frequently anomalous and in general poor. It is not unreasonable, therefore, to infer that these poor relationships or apparent inconsistencies might well be reflections of variably masking effects caused by other polymeric parameters either molecular weight distributional differences or nonhomogeneous comonomer distributional patterns within the copolymers, or possible combinations of both. For example theoretically these polymeric compositions could be, (*1*) true copolymers of statistically distributed comonomeric units, or (*2*) true copolymers with badly distorted nonstatistical comonomer distribution, or (*3*) just physical mixtures of homopolymers as well as mixtures of some or all of these in varying degrees.

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## Résumé

La préparation d'acétate de vinyl-2,2-diméthyl-3-morpholinocarbonylcyclobutane, d'acétate de vinyl-2,2-diméthyl-3-piperidinocarbonylcyclobutane et de l'acétate de vinyl-2,2-diméthyl-3-di-n-butylaminocarbonylcyclobutane a été réalisée par amination sélective suivie d'interéchange vinylique. Les homopolymères et les copolymères de chlorure de vinyle contenant 25 à 30% des esteramides vinyliques ont été préparés; on en a évalué la propriété comme plastique rigide. Les esteramides vinyliques incorporés dans le chlorure de vinyle confèrent à celui-ci une certaine plastification, mais leur effet est de loin inférieur à l'effet d'une plastifiant additionné à un chloure de polyvinyle ordinaire.

## Zusammenfassung

Die Darstellung von Vinyl-2,2-dimethyl-3-morpholinocarbonylcyclobutanacetat, Vinyl-2,2-dimethyl-3-piperidincarbonylcyclobutanacetat und Vinyl-2,2-dimethyl-3-di-n-butylaminocarbonylcyclobutanacetat wurde durch selektive Aminierung mit darauffolgendem Vinylaustausch erreicht. Homopolymere und Vinylchloridcopolymere mit 25 und 30 Gewichts% an Vinylesteramid wurden dargestellt und auf ihre Verwendbarkeit als nichtstarre Plastomere überprüft. Die in Vinylchloridcopolymere eingebauten Vinylesteramide besassen eine gewisse Weichmacherwirkung, ihr Einfluss lag aber weit unterhalb des Einflusses eines dem Vinylchloridpolymeren zugesetzten Weichmachers.

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# Polymers from Vinyl Esters of Perhydrogenated Rosin

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## Synopsis

Vinyl esters of tetrahydro acids from perhydrogenated rosin have been homopolymerized; copolymerized with vinyl chloride, vinyl acetate, butadiene; and terpolymerized with styrene and acrylonitrile. Materials containing such vinyl esters of tetrahydro acids can be readily crosslinked with peroxide.

## INTRODUCTION

Commercial rosin, depending upon its source, is sold as gum, wood, and tall oil rosins. The two latter types account for the bulk of the material sold in this country. One of the most important uses for rosin of this sort in the field of polymers has been through modification by hydrogenation and disproportionation reactions by use of hydrogenation catalysts to make them useful emulsifiers in GRS rubber manufacturing processes. This treatment removed the conjugated diene system of the resin acids present but was not sufficiently vigorous to remove isolated double bonds. Although these materials were useful as emulsifier in free-radical polymerizations for GRS rubber, their vinyl esters have not found use commercially, presumably because polymers from esters were unattractive.

A perhydrogenated rosin prepared by the complete hydrogenation of wood rosin is available on a limited scale from Hercules Powder Company. The vinyl ester of this material was made by the vinyl interchange reaction with vinyl acetate in the presence of a mercuric sulfate catalyst.[1] This paper is a report of work undertaken to prepare polymers having useful properties from a completely hydrogenated rosin.

## RESULTS AND DISCUSSION

### Monomer

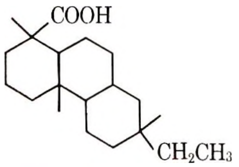
Samples of the monomer were provided by the Naval Stores Division of the Southern Utilization Research and Development Division of the Agricultural Research Service. The mass spectrographic analysis of the methyl

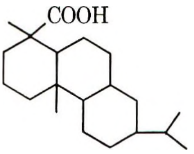
TABLE I
Mass Spectrographic Analysis

| | Composition | | | |
|---|---|---|---|---|
| Product | Diene acids, % | Dihydro acids, % | Tetrahydro acids, % | Dehydro acids, % |
| Perhydrogenated rosin | Nil | 1-2 | 89 | 1 |

esters of various acids in the perhydrogenated rosin, from which our monomer originated, is given in Table I.*

The balance of the perhydrogenated rosin consisted of neutral fractions. The tetrahydro acids consisted of two components: tetrahydropimaric acid (28.1%) and tetrahydroabietic acid (71.9%).


Tetrahydropimaric acid


Tetrahydroabietic acid

The mass spectra were quantitatively interpreted by using a 14-component matrix for the calculation.

The vinyl ester (VTA) was supplied as a water-clear, unstabilized viscous oil of the following physical constants: b.p. 160°C./0.2 mm., $n_D^{29}$ 1.5080. Thin-layer chromatography of the vinyl ester on silica gel showed only one spot, and infrared data showed no absorption bands for hydroxyl, free carboxyl, epoxide or unsaturation other than the vinyl ester. The material when treated with potassium iodide and a starch solution gave no noticeable coloration indicating no hydroperoxide presence. The monomer has a good shelf life under nitrogen at room temperature. In air at elevated temperatures it tends to form hydroperoxides. Distillation under reduced pressure should be done in the presence of an inhibitor to prevent the monomer from polymerizing.

## Homopolymerization

VTA has been homopolymerized in three systems: bulk, solution, and emulsion. The experimental data are given in Table II. The polymers from the three systems were obtained as white powders which could be molded (at about 160°C.) into water-clear but brittle films. The low inherent viscosities are due, no doubt, to the chain-transfer activity of the five tertiary hydrogens. All the homopolymers were soluble in benzene and tetrahydrofuran. Of the two initiators, AIBN and DEABIB, the

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* We are indebted to Herman I. Enos, Jr., Hercules Powder Co., Wilmington, Delaware, for these values.

TABLE II
VTA Homopolymers[a]

| System | Catalyst[b] | Conversion, % | $\eta_{inh}$[c] |
|---|---|---|---|
| Bulk | AIBN | 83 | 0.10 |
| 25% Solution, benzene | AIBN | 70 | 0.06 |
| Emulsion[d] | AIBN | 76 | 0.16 |
| Emulsion | DEABIB | 78 | 0.13 |

[a] All of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end for 48 hr. and with the use of about 5% catalyst.

[b] AIBN = azobisisobutyronitrile; DEABIB = diethyl azobisisobutyrate.

[c] Determined on solutions of 0.400–0.455 g./100 ml. tetrahydrofuran.

[d] Siponate DS-10 (alkyl-substituted benzene sodium sulfonate) used as emulsifier.

latter is much more soluble in the vinyl ester; however, no differences were noted in the emulsion polymerization results.

Because of the tertiary hydrogens (potential curing sites), curing of the bulk homopolymer was investigated. The curing composition was prepared in a tetrahydrofuran solution with 10% of dicumyl peroxide (Di-Cup, Hercules Powder Co., 96–99% pure), and the cure itself was done on a cast, dried film at 160°C. for 30 min. A completely insolubilized material was produced. Considering that only 10% of dicumyl peroxide was used, a high crosslinking efficiency is indicated.

## Copolymerization

**Vinyl Chloride/VTA Copolymers.** A set of emulsion vinyl chloride/VTA copolymers was prepared. The experimental data are given in Table III. All of the copolymers were isolated as white powders which could be molded

TABLE III
Emulsion Vinyl Chloride/VTA Copolymers[a]

| Charged composition | | Amt. catalyst ($K_2S_2O_8$), parts/100 parts monomer | Polymerization time, hr. | Conversion, % | Ester, %[b] | $\eta_{inh}$[c] |
|---|---|---|---|---|---|---|
| VCl, wt.-% | VTA, wt.-% | | | | | |
| 92 | 8 | 2 | 33 | 86 | 5.0 | 0.70 |
| 90 | 10 | 3 | 48 | 83 | 8.0 | 0.68 |
| 85 | 15 | 2 | 33 | 89 | 10.0 | 0.57 |
| 80 | 20 | 3 | 48 | 79 | 16.0 | 0.61 |
| 70 | 30 | 3 | 48 | 75 | 25.0 | 0.57 |
| 60 | 40 | 3 | 48 | 67 | 32.0 | 0.52 |

[a] Siponate DS-10 used as emulsifier; all of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end.

[b] By weight, based on analysis for C, H, Cl in the copolymer (see Experimental section).

[c] Determined on solutions of 0.151–0.410 g./100 ml. tetrahydrofuran.

TABLE IV
Vinyl Chloride/VTA Films

| Composition | | |
|---|---|---|
| Vinyl chloride, % | VTA, % | Properties of films |
| 95 | 5 | Tough, brown |
| 92 | 8 | Tough, brown |
| 90 | 10 | Somewhat brittle, brown |
| 84 | 16 | Brittle, brown |
| 75 | 25 | Brittle, dark tan |
| 68 | 32 | Very brittle, tan |

(at about 180°C.) into transparent films. The properties of the films are given in Table IV.

All of the copolymers were soluble in tetrahydrofuran. In view of the easy curing properties of VTA it was of interest to attempt to make one of the tough copolymers insoluble. The curing composition was prepared in a tetrahydrofuran solution using the 92/8 copolymer and 20% dicumyl peroxide. The cure itself was done on a cast, dried film at 160°C. for 30 min. A completely insoluble, tough, film was obtained. A poly(vinyl chloride) film, run as a control, was still soluble after the curing period.

It is reported[2] that vinyl esters are less reactive than vinyl chloride and the difference in the $r_1r_2$ values is quite considerable. Furthermore, the nature of the aliphatic acid moiety of a vinyl ester apparently has little influence on the reactivity ratios with other vinyl monomers.[3] Thus, to get information on the homogeneity of vinyl chloride/VTA copolymers fractionation of the 75/25 copolymer was conducted (see Experimental section). The analytical and inherent viscosity data are given in Table V. Apparently about two-thirds of the 25% VTA found in the copolymer was essentially a homopolymer. Such a distribution is not surprising in view of the $r_1r_2$ values in general and the bulky hydrocarbon structure of VTA in particular. The recovery in the fractionation was only 90% mainly because of extremely stable emulsion formations. The precipitation of second and third fractions could be affected only with hydrochloric acid solutions as the addition of methanol or water caused no precipitation. Such a behavior is indicative of polymer solvation.

TABLE V
Analytical and Inherent Viscosity Data on a Fractionated Vinyl Chloride/VTA Copolymer

| Sample | Wt., g. | Cl, % | $\eta_{inh}$ |
|---|---|---|---|
| Entire sample | 3.00 | 42.33[a] | 0.57 |
| Fraction 1 | 0.55 | 8.30 | 0.19 |
| Fraction 2 | 1.14 | 48.89 | 0.70 |
| Fraction 3 | 1.00 | 50.20 | 0.68 |

[a] Chlorine content of poly(vinyl chloride) is 56.74%.

TABLE VI
Emulsion Vinyl Acetate/VTA Copolymers[a]

| Charged composition | | | | | |
|---|---|---|---|---|---|
| VAc, wt.-% | VTA, wt.-% | Polymerization time, hr. | Conversion, % | VTA, %[b] | $\eta_{inh}$[c] |
| 80 | 20 | 4 | 98 | 25 | 2.23 |
| 70 | 30 | 3 | ~100 | 30 | 1.90 |
| 60 | 40 | 3 | ~100 | 42 | 1.41 |
| 50 | 50 | 3 | ~100 | 53 | 1.15 |
| 40 | 60 | 3 | 94 | 64 | 0.90 |

[a] Siponate DS-10 used as emulsifier; all of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end and with about 2% of $K_2S_2O_8$ as a catalyst.

[b] By weight, based on analysis for C and H in the copolymer (see Experimental section).

[c] Determined on solutions of 0.11–0.225 g./100 ml. tetrahydrofuran.

**Vinyl Acetate/VTA Copolymers.** Five different emulsion vinyl acetate copolymers have been prepared. The experimental data are given in Table VI.

The emulsion polymerization of vinyl acetate is characterized by great susceptibility of the vinyl acetate radical to effects (chain transfer or retarding) of other substances in the system.[4] The data recorded in Table VI were obtained on one batch of VTA; however, trace variations in the composition of other batches of VTA caused differences in the results. Extended polymerization time and/or work-up or drying at elevated temperatures insolubilizes the copolymers. While in other systems VTA slowed down the polymerization rate and acted as an efficient chain transfer agent, none of these effects were observed with vinyl acetate. Such a behavior again demonstrates the similarity in reactivity of the vinyl ester double bonds regardless of the type of the acid involved.

High molecular weight copolymers were obtained. An indication of the efficient copolymerization can be gained from the 36/64 vinyl acetate/VTA copolymer which had a high $\eta_{inh}$ (0.90) as compared to VTA (0.16). All of

TABLE VII
Vinyl Acetate/VTA Films

| Composition | | |
|---|---|---|
| Vinyl acetate, % | VTA, % | Properties of films |
| 75 | 25 | Transparent, tough, somewhat rigid |
| 70 | 30 | Transparent, soft, extremely tough |
| 58 | 42 | Transparent, soft, tough |
| 47 | 53 | Transparent, soft, tough |
| 36 | 64 | Transparent, very soft, weak |

the copolymers were obtained as light tan colored soft masses soluble in tetrahydrofuran and chloroform. The properties of the materials molded (at about 150°C.) into films are given in Table VII. All of the copolymers exhibited elastic properties resembling somewhat those of a sluggish rubber.

**Butadiene/VTA Copolymers.** A series of seven different butadiene/VTA copolymers has been made. The experimental data are given in Table VIII.

TABLE VIII
Emulsion Butadiene/VTA Copolymers[a]

| Charged composition | | | | Conversion, % | | | |
|---|---|---|---|---|---|---|---|
| Molar | | Wt.-% | | | | | |
| VTA | BD | VTA | BD | Unbuffered | Buffered[b] | Butadiene, %[c] | $\eta_{inh}$[d] |
| 2 | 1 | 92 | 8 | 9 | — | ~1 | 0.17 |
| 1 | 1 | 86 | 14 | 8 | — | ~2 | 0.23 |
| 1 | 2 | 76 | 24 | 7 | — | 12.0 | 0.28 |
| 1 | 4 | 61 | 39 | 8 | 31 | 43 | 0.52 |
| 1 | 6 | 51 | 49 | 10 | — | — | Insoluble[e] |
| 1 | 12 | 34 | 66 | 8 | 97 | 70 | Insoluble[c] |
| 1 | 24 | 21 | 79 | — | 93 | 96 | Insoluble[e] |

[a] Siponate DS-10 used as emulsifier; all of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end for 48 hr. and with about 2% of $K_2S_2O_8$ as catalyst.

[b] pH 7.00.

[c] By weight, based on analysis for C and H in the polymer.

[d] Determined on solutions of 0.391–0.449 g./100 ml. of tetrahydrofuran.

[e] Insoluble in hot tetrahydrofuran or benzene or both.

Although an unfavorable $r_1r_2$ relationship for the monomers in question is reported,[2] it was of interest to see what copolymers could be obtained. In the polymerization no chain transfer agent was used as the chain transfer activity of VTA was assumed to be sufficient. It was noted in the work that increasing the pH not only increased the conversion but also the butadiene content in the copolymer. The infrared absorption spectra showed clearly that compositions containing both components were obtained. For example, the characteristic carbonyl absorption at 1725 cm.$^{-1}$ for VTA and the characteristic unsaturation absorptions at 915, 998, 1650, 1675, and 1835 cm.$^{-1}$ for polybutadiene were all observed changing in their intensity in correspondence with the analytical data for the copolymers. Unfortunately, because of their insolubility fractionation could not be done. Thus, the extent of copolymer formation is not ascertained. The copolymers containing more than 43%, by weight, of butadiene were completely insoluble in hot tetrahydrofuran or benzene or both. This may be mainly due to the long polymerization time causing the butadiene segments to crosslink. The polymers were obtained as white rubbery crumbs and could be molded into translucent, weak films. The 30/70 and 4/96 VTA/butadiene copolymers gave stronger and somewhat tougher films.

On the basis of the infrared spectra of the copolymers and the literature data,[5–7] the polybutadiene segments and/or homopolymer appear to contain a high 1,2-adduct structure. Thus, for example, the terminal unconjugated carbon–carbon double bond absorption in hydrocarbons occurs at a lower frequency (1645–1650 cm.$^{-1}$) than the absorption for internal carbon–carbon double bonds (above 1650 cm.$^{-1}$).[5] The characteristic absorption bands for 1,2-structure on polyhydrocarbon chains are reported[7] at 3100, 1850, 1650, 1420, 995, and 915 cm.$^{-1}$ and were observed in our spectra. However, a preponderance of 1,2-structure under the experimental conditions used was an unlikely possibility, in view of all the existing butadiene copolymer literature. Consequently, five different copolymers were titrated with perbenzoic acid[8–10] which under proper conditions is specific for internal unsaturation. The titration data are given in Table IX. The data would indicate that a higher than normally expected 1,2-butadiene incorporation had occurred for the higher butadiene content copolymers. However, the higher 1,2-structure was also indicated for copolymers which were probably more tightly crosslinked and, thus, not all internal double bonds were available for oxidation.

TABLE IX

Amount of Internal Unsaturation in Butadiene/VTA Copolymers

| Charged composition | | | | |
|---|---|---|---|---|
| VTA, wt.-% | Butadiene, wt.-% | Butadiene found, %[a] | Internal unsaturation, % | Ratio 1,4/1,2 |
| 100 | — | — | 2.5 | — |
| 86 | 14 | ~2 | 76 | 76/24 |
| 76 | 24 | 12 | 76 | 76/24 |
| 61 | 39 | 43 | 70 | 70/30 |
| 34 | 66 | 70 | 66 | 66/34 |
| 21 | 79 | 96 | 56 | 56/44 |

[a] By weight, based on analysis for C and H in the polymers.

**Styrene/Acrylonitrile/VTA Terpolymers.** Another combination of monomers which according to their reactivity ratios leaves the copolymerization efficiency an open question is the styrene/acrylonitrile/VTA composition. Four emulsion terpolymers of varying composition were prepared. The experimental data are given in Table X.

First of all, the work indicated that VTA can be incorporated into the styrene/acrylonitrile compositions up to 29 wt.-%. All of the terpolymers were obtained as very light tan powders which could be molded (at about 180°C.) into clear but brittle films. All of the terpolymers were only slightly soluble in tetrahydrofuran; however, they were completely soluble in *N*-methylpyrrolidone.

TABLE X
Styrene/Acrylonitrile/VTA Emulsion Terpolymers[a]

| Charged composition | | | | | | |
|---|---|---|---|---|---|---|
| VTA, wt.-% | Styrene, wt.-% | AN, wt.-% | Conversion, % | VTA, %[b] | AN, %[b] | $\eta_{inh}$[c] |
| 10.8 | 61.2 | 28 | 90 | 8 | 30 | 5.44 |
| 21.6 | 50.4 | 28 | 88 | 11 | 33 | 4.96 |
| 35 | 35 | 30 | 84 | 23 | 40 | — |
| 32.4 | 39.6 | 28 | 76 | 29 | 31 | 3.82 |

[a] Siponate DS-10 used as emulsifier; all of the polymerizations were conducted at 60 ± 2°C. by tumbling the tubes end-over-end for 24 hr. and with about 2% $K_2S_2O_8$ as a catalyst.

[b] By weight, based on analysis for C, H, and N in the polymers.

[c] Determined on solutions containing 0.106–0.374 g./100 ml. *N*-methylpyrrolidone.

If any of the above terpolymers is combined with a butadiene/acrylonitrile rubber in the latex state and coprecipitated, a composition is obtained that gives a flexible and very tough film.

Polymers of the following weight compositions were prepared for physical property evaluations as thermoplastics and as cotton treating agents: (*1*) vinyl tetrahydroabietate homopolymer; (*2*) 95/5, vinyl chloride/VTA; (*3*) 93/7, vinyl chloride/VTA; (*4*) 90/10, vinyl chloride/VTA; (*5*) 72/28, vinyl acetate/VTA; (*6*) 58/42, vinyl acetate/VTA; (*7*) 31/39/30, VTA/styrene/acrylonitrile; (*8*) 8/62/30–78/22, VTA/styrene/acrylonitrile combined with butadiene/acrylonitrile; (*9*) 13/55/32–78/22, VTA/styrene/acrylonitrile combined with butadiene/acrylonitrile; (*10*) 21/46/33–78/22, VTA/styrene/acrylonitrile combined with butadiene/acrylonitrile.

Each of the polymers was prepared according to the procedures given in the experimental part.

## EXPERIMENTAL

### Homopolymerization

**Bulk.** VTA (8.0 g.) and AIBN (0.4 g.) were charged under nitrogen in a pressure tube (1 × 7 in.) and polymerized at 60±2°C. by tumbling end-over-end for 48 hr. A white solid plug had formed. The material was dissolved in 50 ml. of tetrahydrofuran (THF), and precipitated in 250 ml. of methanol. The suspension was allowed to stand for 2 days before filtering; the yield was 6.6 g. (83%) of vacuum-oven dried (50°C./21 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomer.

**Solution.** VTA (4.0 g.), AIBN (0.2 g.), and dry, thiophene-free benzene (12 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.) and polymerized at 60 ± 2°C. by tumbling end-over-end for 48 hr. The charge had formed a hazy viscous solution. The solution was poured into 200 ml. of methanol and the isolated material was dissolved in 50 ml. of

THF and reprecipitated in methanol (250 ml.). The suspension was allowed to stand for 2 days before filtering. The yield was 2.8 g. (70%) of vacuum oven-dried (50°C./21 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomer.

**Emulsion.** VTA (4.0 g.), DEABIB (0.2 g.), Siponate DS-10 (0.04 g.), and air-free, distilled water (12 ml.) were charged under nitrogen in a pressure tube (1 × 7 in.), emulsified at room temperature and polymerized at 60 ± 2°C. by tumbling end-over-end for 48 hr. Emulsion, containing some solid material, was formed. The mixture was poured into 200 ml. of methanol and the isolated material was dissolved in 50 ml. of THF and reprecipitated in 250 ml. of methanol. The mixture was allowed to stand for 2 days before filtering. The yield was 3.1 g. (78%) of vacuum oven-dried (50°C./21 hr.) material. The infrared spectrum showed no characteristic absorption bands for the monomer.

ANAL. Calcd. for $C_{22}H_{36}O_2$: C, 79.46%; H, 10.91%. Found, monomer: C, 79.68%; H, 10.94%. Found, emulsion homopolymer: C, 79.76%; H, 10.86%.

## Copolymerization

**Vinyl Chloride/VTA Copolymers.** VTA (1.0 g.), potassium persulfate (0.3 g.), Siponate DS-10 (0.3 g.), and air-free, distilled water (30 ml.) were charged under nitrogen into a pressure tube (1.5 × 7 in.). The tube was then cooled to about −15°C. and vinyl chloride (9.0 g.) was added. An excess of vinyl chloride was used to purge the tube of air before capping. The contents were emulsified at room temperature and then polymerized at 60 ± 2°C. by tumbling end-over-end for 48 hrs. A thick and somewhat lumpy latex was produced. It was poured into 300 ml. of methanol, the isolated material dissolved in 150 ml. of THF, filtered, and reprecipitated in 400 ml. of methanol. The yield was 8.3 g. (83%) of vacuum oven-dried (50°C./24 hr.) white powder. The infrared spectrum showed no characteristic absorption bands for the monomers. The procedure for the other compositions was similar to the one described.

ANAL. Calcd. for 95% $C_{22}H_{36}O_2$/5% $C_2H_3Cl$: C, 40.48%; H, 5.13%; Cl, 53.90%. Found: C, 40.74%; H, 5.16%; Cl, 54.12%.

Calcd. for 92% $C_{22}H_{36}O_2$/8% $C_2H_3Cl$: C, 41.73%; H, 5.32%; Cl, 52.20%. Found: C, 41.58%; H, 5.32%, Cl, 52.13%.

Calcd. for 90% $C_{22}H_{36}O_2$/10% $C_2H_3Cl$: C, 42.56%; H, 5.43%; Cl, 51.20%. Found: C, 42.45%; H, 5.54%; Cl, 51.20%.

Calcd. for 84% $C_{22}H_{36}O_2$/16% $C_2H_3Cl$: C, 45.04%; H, 5.80%; Cl, 47.66%. Found: C, 45.01%; H, 5.83%; Cl, 47.93%.

Calcd. for 75% $C_{22}H_{36}O_2$/25% $C_2H_3Cl$: C, 48.76%; H, 6.35%; Cl, 42.56%. Found: C, 48.74%; H, 6.42%; Cl, 42.33%.

Calcd. for 69% $C_{22}H_{36}O_2$/32% $C_2H_3Cl$: C, 51.66%; H, 6.78%, Cl, 38.58%. Found: C, 51.70%; H, 6.84%; Cl, 38.34%.

**Vinyl Acetate/VTA Copolymers.** Vinyl acetate (3.0 g.), VTA (2.0 g.), $K_2S_2O_8$ (0.1 g.), Siponate DS-10 (0.15 g.), and air-free distilled water (20 ml.) were charged under nitrogen in a pressure tube (1.5 × 7 in.). The contents were emulsified at room temperature and polymerized at 60 ± 2°C. by tumbling end-over-end for 3 hr. Very good latex was obtained. It was then poured into boiling, acidic (pH 1) water (350 ml.) in a Waring Blendor. The fluffy precipitated material was filtered and then dissolved in chloroform (200 ml.) and combined with 50/50 MeOH/$H_2O$ mixture and placed in a Rotovac at about 40°C. The stripping was continued until the liquid phase became clear. At this point the liquid was decanted and the syrupy material was dried in a vacuum oven (33°C./48 hr.). The yield was 5 g. (100%) of the dried material. The infrared spectrum showed no characteristic absorption bands for the monomers. The dried material had formed a small amount of gel when dissolved in chloroform. The material formed a tough, transparent film. The procedure for the other compositions was similar to the one described.

ANAL. Calcd. for 75% $C_4H_6O_2$/25% $C_{22}H_{36}O_2$: C, 61.68%; H, 8.04%. Found: C, 61.75%; H, 8.03%.
Calcd. for 70% $C_4H_6O_2$/30% $C_{22}H_{36}O_2$: C, 62.86%; H, 8.23%. Found: C, 62.84%; H, 8.26%.
Calcd. for 58% $C_4H_6O_2$/42% $C_{22}H_{36}O_2$: C, 65.71%; H, 8.69%. Found: C, 65.71%, H, 8.77%.
Calcd. for 47% $C_4H_6O_2$/53% $C_{22}H_{36}O_2$: C, 68.32%; H, 9.11%. Found: C, 68.40%; H, 9.14%.
Calcd. for 36% $C_4H_6O_2$/64% $C_{22}H_{36}O_2$: C, 70.92%; H, 9.56%. Found: C, 70.95%; H, 9.72%.

**Butadiene/VTA Copolymers.** Potassium persulfate (0.182 g.), Siponate DS-10 (0.182 g.), VTA (3.1 g.), air-free distilled water (14 ml.), and air-free Beckman pH 7.00 buffer solution (14 ml.) were charged under nitrogen in a pressure tube (1.5 × 7 in.). The tube was cooled to about −10°C. and butadiene (6.0 g., high purity) was added. An excess of butadiene was used to purge the tube before capping. The charge was emulsified at room temperature and polymerized at 60 ± 2°C. by tumbling end-over-end for 48 hr. A blue latex was formed. The latex was poured into 350 ml. of methanol, allowed to stand for 2 days, then made strongly acidic (pH about 1) with 10% HCl and placed in a Dry Ice–acetone bath. The isolated material was washed with methanol and then suspended in a mixture of benzene/THF (125 ml./25 ml.). The suspension was warmed to boiling and then precipitated out in 400 ml. of methanol in a Waring Blendor. The yield was 8.8 g. (97%) of vacuum oven-dried (45–50°C./24 hr.) material. The infrared spectra agreed with the expected compositions and showed no characteristic absorptions for the monomers. The procedure for the other compositions was similar to the one described.

ANAL. Calcd. for 99% $C_{22}H_{36}O_2$/1% $C_4H_6$: C, 79.55%; H, 10.91%. Found: C, 79.55%; H, 10.65%.
Calcd for 98% $C_{22}H_{36}O_2$/2% $C_4H_6$: C, 79.64%; H, 10.91%. Found: C, 79.57%; H, 10.56%.
Calcd. for 88% $C_{22}H_{36}O_2$/12% $C_4H_6$: C, 80.58%; H, 10.95%. Found: C, 80.88%; H, 10.90%.

Calcd. for 57% $C_{22}H_{36}O_2$/43% $C_4H_6$: C, 83.44%; H, 11.06%. Found: C, 83.70%; H, 10.79%. Residue: 1.25%.

Calcd. for 30% $C_{22}H_{36}O_2$/70% $C_4H_6$: C, 85.94%; H, 11.16%. Found: C, 86.06%; H, 10.81%. Residue: 2.85%.

Calcd. for 4% $C_{22}H_{36}O_2$/96% $C_4H_6$: C, 88.35%; H, 11.26%. Found: C, 88.31%; H, 11.02%. Residue: 0.81%.

**Styrene/Acrylonitrile/VTA Terpolymers.** Potassium persulfate (0.50 g.), Siponate DS-10 (0.50 g.), VTA (2.70 g.), styrene (15.3 g., freshly distilled), acrylonitrile (7.00 g., freshly distilled), and air-free, distilled water (150 ml.) were charged under nitrogen in a pressure tube (2 × 9 in.), emulsified at room temperature, and polymerized at 60 ± 2°C. by tumbling end-over-end for 24 hr. A very thick, semicongealed latex was produced. The latex was diluted with distilled water and total solids analysis run to obtain the conversion (90%).

The resin was isolated by pouring the latex in liter of methanol containing 1 ml. of concentrated HCl. The isolated material was suspended in boiling tetrahydrofuran (500 ml.) and reprecipitated in 2 liters of methanol. The yield was 22.5 g. (90%) of vacuum oven-dried (48°C./20 hr.) light tan powder. The infrared spectrum showed no absorption bands characteristic for the monomers. The powder could be molded (at about 180°C.) into clear, brittle films. The procedure for the other composition was similar to the one described above.

ANAL. Calcd. for 8% $C_{22}H_{36}O_2$/62% $C_8H_8$/30% $C_3H_3N$: C, 83.93%; H, 7.38%; N, 7.92%. Found: C, 84.13%; H, 7.28%; N, 8.07%.

Calcd. for 11% $C_{22}H_{36}O_2$/56% $C_8H_8$/33% $C_3H_3N$: C, 82.82%; H, 7.40%; N, 8.72%. Found: C, 83.17%; H, 7.15%; N, 8.92%.

Calcd. for 23% $C_{22}H_{36}O_2$/37% $C_8H_8$/40% $C_3H_3N$: C, 79.56%; H, 7.63; N, 10.56%. Found: C, 79.35%; H, 6.98%; N, 10.36%.

Calcd. for 29% $C_{22}H_{36}O_2$/40% $C_8H_8$/31% $C_3H_3N$: C, 80.98%; H, 8.00%; N, 8.18%. Found: C, 80.62%; H, 7.41%; N, 8.04%.

**Fractionation of 75/25 Vinyl Chloride/VTA Copolymer.** A 3.0 g. sample of the copolymer was dissolved in 300 ml. of THF. The first fraction (0.55 g.) was obtained by adding 400 ml. of methanol. An attempt to obtain the next fraction was made by adding 100 ml. of methanol followed by 400 ml. of water. Only a hazy blue-colored "solution" was formed. Next, the total volume (1.2 liters) was concentrated to 400 ml. This produced only a viscous blue-colored emulsion. Another 100 ml. of water were added without any precipitate formation. The next fraction (1.14 g.) was then obtained by adding 5 ml. of 1% HCl solution. The mixture was allowed to stand for 4 hr. before centrifuging and filtering. To obtain the third fraction (1.00 g.), 10 ml. of 10% HCl was necessary, as additions of 5 ml. of 1% HCl produced no precipitate. The mixture was allowed to stand for a day before centrifuging and filtration. All of the fractions were washed with methanol and dried in a vacuum oven at 55°C./24 hr. As a result of the difficulties experienced in the fractionation, the total recovery was only 90%.

**Determination of Internal Unsaturation in Butadiene/VTA Copolymers.** Preparation of indicator solution, perbenzoic acid, and sodium thiosulfate solution as well as its standardization were all identical to that in an earlier communication.[10] The procedure for the oxidation of polymer samples was also essentially similar to the one described in the same reference. For the calculation for the internal unsaturation the following relationship was used:

$$\%\ \text{Unsaturation} = \frac{(\text{ml}_{\text{blank}} - \text{ml}_{\text{sample}})(N_{\text{Na}_2\text{S}_2\text{O}_3})(\text{Mol. wt.}) \times 100 \times 4}{2000 \times (\text{Wt. of sample, g./100 ml.})}$$

For the molecular weight the repeating unit was calculated from the analytical data and was used as such.

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## Résumé

Les esters vinyliques des acides tétrahydrogénés de la colophane perhydrogénée ont été homopolymérisés, copolymérisés avec le chlorure de vinyle, l'acétate de vinyle, le butadiène, et terpolymérisés avec le styrène et l'acrylonitrile. Les matériaux contenant de tels esters vinyliques des acides tétrahydrogénés peuvent être facilement pontés au moyen de peroxyde.

## Zusammenfassung

Vinylester der Tetrahydrosäuren aus perhydriertem Kolophonium wurden homopolymerisiert, mit Vinylchlorid, Vinylacetat und Butadien kopolymerisiert sowie mit Styrol und Acrylnitril gemeinsam terpolymerisiert. Stoffe, die solche Vinylester von Tetrahydrosäuren enthalten, können leicht mit Peroxyden vernetzt werden.

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# $AlEt_3$–Metal Soap Catalysts for the Polymerization of Epoxides

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## Synopsis

Epoxides, propylene oxide in particular, were polymerized by a catalyst system consisting of $AlEt_3$–metal soap, to high molecular weight polyethers in high conversion. Carboxylic acid salts of Ti, V, Cr, Zr, Mo, Co, and Ni, transition metals of groups IV–VIII in the Periodic Table, were most preferable. Metal salts of stearic, octanoic, lauric and naphthenic acid were examined as catalyst components and proved to be very active for the polymerization of epoxides when used with an organoaluminum compound such as $AlEt_3$ or $AlEt_2Cl$. Copolymerization of propylene oxide and allyl glycidyl ether was successfully carried out with an $AlEt_3$–Zr octoate catalyst.

## INTRODUCTION

In recent years, poly(alkylene oxides) have been studied extensively and have found new applications. Various copolymers, including an elastomeric copolymer of propylene oxide and an unsaturated epoxide have been reported.[1] We report here a study of a new catalyst system composed of $AlEt_3$ and carboxylic acid salts of transition metals for the polymerization of epoxides, in particular, propylene oxide.

## EXPERIMENTAL

### Materials

Benzene and *n*-hexane were distilled over sodium wire and stored with calcium hydride ($CaH_2$). Ethyl Corporation $AlEt_3$ and $AlEt_2Cl$ were used as received in benzene or *n*-hexane solution. Metal soaps were synthesized from inorganic metal salts and the corresponding sodium salts of organic acids by double decomposition.

### Polymerization

All manipulations were performed under prepurified nitrogen which passed through phosphorus pentoxide before use. The polymerizations were conducted in glass tubes sealed with a glass stopper. The order of addition of reagents was metal soap, benzene or *n*-hexane, then $AlEt_3$ solution. The reaction mixture was stirred for several minutes and the complex catalyst prepared *in situ*. Monomer was added last, the tube was sealed with a glass stopper, and polymerization was carried out at room temperature.

At the end of the reaction time the tube was opened, methanol containing a small amount of 3,5-di-*tert*-butyl-4-hydroxytoluene was added to stop the reaction, and the reaction product was dissolved in benzene. The benzene solution of the polymer was washed with 1*N* HCl, water, dilute aqueous $Na_2CO_3$, and distilled water until it was neutralized. The polymer was finally dried *in vacuo* to constant weight by freeze drying, or recovered from the benzene solution by steam distillation. The intrinsic viscosity was measured in benzene at 30°C.

### Copolymerization

The copolymerization of propylene oxide and allyl glycidyl ether was carried out at 50°C. for 20 hr. in a beverage bottle sealed with a crown cap. The other procedures and the order of addition of reagents were the same as in the homopolymerization of propylene oxide. Reactants and materials used for the polymerization were as follows: propylene oxide, 70 ml.; allyl glycidyl ether, 5 ml.; Zr octoate, 10.36 mmole; $AlEt_3$, 10.36 mmole; benzene, 700 ml.; and *n*-hexane, 100 ml. The copolymer was obtained in 92% yield and had an intrinsic viscosity of 7.9 in benzene at 35°C. The vulcanization and the properties are shown in Table V.

## RESULTS AND DISCUSSION

The results listed in Table I show that various catalyst systems consisting of $AlEt_3$ and a number of transition metal salts of carboxylic acids are quite effective in the polymerization of propylene oxide; however, some differences were observed between the results obtained from the metals of group IV–VI and from the metals of group VIII, ignoring the effect of the organic acid moiety. The metal salts of groups IV–VI give rise to some low molecular weight polymer, although in high conversion, whereas the metal salts of group VIII tend to give high molecular weight polymer but in poor conversion. The catalyst system of $AlEt_3$–Zr octoate, among the former, is the most effective in giving a high molecular weight polymer in high conversion, generally in quantitative yield. The results are given in Tables II and III. The optimum molar ratio of $AlEt_3$–Zr octoate seems to be 1, to judge from the polymer yield and the intrinsic viscosity. Table II shows that the minimum quantity of Zr octoate is about 0.148, which corresponds to 0.5 mole-% based on the monomer. It is apparent from Table III that the polymerization reaction is completed within 20 hr. at room temperature (20–25°C.); however, the reaction was completed within several hours at 50°C.

Although the cocatalytic effect is apparent from the experiment of run 154 in Table II, various catalyst systems consisting of Al compounds–Zr compounds were examined for further confirmation of the catalytic activity of $AlEt_3$–Zr octoate. The results are summarized in Table IV.

The catalyst systems examined in runs 156, 181, and 183 were inactive for the polymerization of propylene oxide, and the resulting products consisted of catalyst residues containing a small amount of polymers. The polymers obtained from runs 157, 179, and 180 were found to contain polyether and a considerable quantity of catalyst residues by infrared spectral

TABLE I

Polymerization of Propylene Oxide by Various Catalyst Systems[a]

| Run no. | Metal salt of organic acids | AlEt$_3$, mmole | Solvent | Vol. solvent, ml. | Polymer yield | | Intrinsic viscosity |
|---|---|---|---|---|---|---|---|
| | | | | | g. | % | |
| 113 | Co naphthenate | 3.0 | Benzene | 50 | 1.40 | 33.0 | 1.07 |
| 117 | Co octoate | 3.0 | Benzene | 50 | 0.23 | 5.4 | 2.51 |
| 118 | Co octoate | —[b] | Benzene | 50 | 0.24 | 5.7 | — |
| 119 | Co naphthenate | 3.0 | Hexane | 50 | 1.83 | 43.2 | 3.10 |
| 120 | Co naphthenate | 3.0 | Hexane | 50 | 1.27 | 30.0 | 3.52 |
| 123 | Ti naphthenate | 1.18 | Hexane | 20 | 0.90 | 47.0 | 1.36 |
| 124 | V naphthenate | 1.18 | Hexane | 20 | 1.25 | 83.0 | — |
| 125 | Cr naphthenate | 0.89 | Hexane | 20 | 1.36 | 80.0 | 1.98 |
| 145 | Ni naphthenate | 0.89 | Hexane | 20 | 0.62 | 36.6 | 2.44 |
| 136 | Mo naphthenate | 1.18 | Hexane | 20 | 1.70 | 100 | — |
| 137 | Co stearate | 0.89 | Hexane | 20 | 0.75 | 44.2 | 2.89 |
| 144 | Zr octoate | 1.18 | Hexane | 20 | 1.70 | 100 | 4.02 |

[a] In runs 113–120, 1.0 mmole metal salt, 50 ml. solvent, and 5 ml. propylene oxide were used. In other runs, 0.296 mmoles of metal salt, 20 ml. of solvent, and 2 ml. of propylene oxide were used. In all cases polymerization was continued for 72 hr. at room temperature.

[b] AlEt$_2$Cl, 3.0 mmole.

TABLE II

Polymerization of Propylene Oxide by AlEt$_3$–Zr Octoate[a]

| Run no. | Zr octoate, mmole | Al/Zr molar ratio | Polymer yield | | Intrinsic viscosity | Remarks |
|---|---|---|---|---|---|---|
| | | | g. | % | | |
| 149 | 0.296 | 6 | 1.36 | 80.0 | 0.98 | |
| 148 | 0.296 | 3 | 1.58 | 93.0 | 2.16 | |
| 147 | 0.296 | 2 | 1.65 | 97.3 | 2.94 | |
| 150 | 0.296 | 1 | 1.67 | 98.3 | 6.02 | |
| 152 | 0.148 | 2 | 1.34 | 78.9 | 6.28 | |
| 153 | 0.074 | 1 | 0.09 | 5.3 | — | Cat. residue + polymer |
| 155 | 0.148 | 0.5 | 0.06 | 4.0 | — | Cat. residue + polymer |
| 154 | 0 | —[b] | 0.07 | 4.1 | — | Polymer |
| 182 | 0.296 | 0.75 | 0.50 | 29.4 | 4.07 | |

[a] In each run, 2 ml. of propylene oxide and 20 ml. of hexane were used. Polymerization was carried out at room temperature for 20 hr.

[b] [Al] = 0.296 mmole.

TABLE III
Polymer Yield at Various Reaction Times in Polymerization of Propylene Oxide by $AlEt_3$–Zr Octoate[a]

| Run no. | Reaction time, hr. | Polymer yield | | Intrinsic viscosity |
|---|---|---|---|---|
| | | g. | % | |
| 162 | 20 | 1.69 | 99.4 | 6.50 |
| 178 | 7 | 1.00 | 58.8 | 6.08 |
| 177 | 3 | 0.84 | 49.4 | 5.56 |
| 176 | 1 | 0.37 | 21.8 | 4.57 |

[a] In each run, 2 ml. of propylene oxide was polymerized in 20 ml. of benzene at room temperature.

TABLE IV
Polymerization of Propylene Oxide by Al Compounds–Zr Compounds[a]

| Run no. | Zr compound[b] | Al compound[b] | Solvent | Polymer yield | | Intrinsic viscosity |
|---|---|---|---|---|---|---|
| | | | | g. | % | |
| 156 | Zr octoate | $Al(acac)_3$[c] | Hexane | 0.12 | [d] | — |
| 157 | Zr octoate | $Al(O\text{-}i\text{-}C_3H_7)_3$ | Hexane | 0.20 | [d] | — |
| 160 | Zr octoate | $AlEt_2Cl$ | Benzene | 0.19 | 11.0 | 1.77 |
| 162 | Zr octoate | $AlEt_3$ | Benzene | 1.69 | 98.5 | 6.50 |
| 179 | 0 | $Al(acac)_3$<br>$AlEt_3$[c] | Hexane | 0.04 | 2.4 | 1.32 |
| 180 | 0 | Al octoate<br>$AlEt_3$ | Hexane | 0.45 | 26.5 | 3.58 |
| 181 | 0 | Al octoate | Hexane | 0.09 | 5.3 | — |
| 183 | Zr octoate | Al octoate | Hexane | 0.13 | 7.6 | 0.85 |

[a] In each run, 2 ml. of propylene oxide was polymerized in 20 ml. of solvent at room temperature for 20 hr.

[b] 0.296 mmole used unless otherwise noted.

[c] Al triacetylacetonate.

[d] Catalyst residue contained a trace of polymer as confirmed by infrared spectra.

[e] 0.890 mmole.

TABLE V
Vulcanization and Properties of POR[a]

| Vulcanization[b] | 300% Modulus, kg./cm.² | Tensile strength, kg./cm.² | Elongation, % |
|---|---|---|---|
| 150°C., 30 min. | 35 | 160 | 1150 |
| 150°C., 60 min. | 45 | 150 | 760 |

[a] POR contains 6% of allyl glycidyl ether by weight (confirmed by iodine value).

[b] Vulcanization recipe: POR, 100 parts; ISAF, 45.0 phr; ZnO, 3.0 phr; stearic acid, 1.0 phr; sulfur, 0.8 phr; tetramethylthiuram disulfide, 0.6 phr; 3,5-di-*tert*-butyl-4-hydroxytoluene (Ionol), 0.18 phr.

analysis. The results suggest that only the catalyst system $AlEt_3$–Zr octoate is effective in the polymerization of propylene oxide.

The elastomeric copolymer of propylene oxide and allyl glycidyl ether (POR) was vulcanized according to the techniques applied for general purpose rubbers. A typical vulcanization system and vulcanizate properties are shown in Table V. High elongation is presumed to be a characteristic of propylene oxide rubber because of the free rotation around the oxygen–carbon bond.

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## Résumé

Les époxydes, et l'oxyde de propylène en particulier, ont été polymérisés par un système catalytique consistant en $AlEt_3$ et un savon metallique; ces produits ont ainsi été transformés en polyéthers de poids moléculaires élevés et à un degré de conversion élevés également. Les sels d'acides carboxyliques de Ti, V, Cr, Zr, Mo, Co, Ni, métaux de transition des groupes IV–VIII dans le système périodique ont été trouvé les meilleurs. Les sels métalliques des acides stèariques, octanoiques, lauriques et naphthéniques ont été examinés comme composants catalyseurs et se sont révélés les plus actifs pour la polymérisation d'époxydes lorsqu'ils ont été utilisés concomitament à un dérivé organoaluminique tel que $AlEt_3$ ou $AlEt_2Cl$. La copolymérisation de l'oxyde de propylène et de l'éther allyl glycidylique a été effectuée avec succès au moyen d'un catalyseur à base de $AlEt_3$–Zr octoate.

## Zusammenfassung

Epoxyde, besonders Propylenoxyd, wurden mit einem Katalysatorsystem aus $AlEt_3$ und Metallseife mit hoher Ausbeute zu hochmolekularen Polyäthern polymerisiert. Ti-, V-, Cr-, Mo-, Co- und Ni-Salze von Carbonsäuren, also Übergangsmetalle der Gruppen IV bis VIII des periodischen Systems waren am besten geeignet. Metallsalze von Stearin-, Oktan-, Laurin- und Naphtensäure wurden als Katalysatorkomponenten untersucht und erwiesen sich bei Verwendung mit einer Organoaluminiumverbindung wie $AlEt_3$ oder $AlEt_2Cl$ als sehr aktiv bei der Epoxydpolymerisation. Die Copolymerisation von Propylenoxyd und Allylglycidyläther wurde mit einem $AlEt_3$–Zr-Oktoat katalysator erfolgreich durchgeführt.

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# NOTES

## *Ultraviolet Spectrum of a Glass Resin*

The use of organic vehicles for coatings on thermal control surfaces of space systems has increased the requirement for radiation stability of these materials in a vacuum environment.

The apparent radiation stability of unpigmented silicone resins as compared to pigmented resins when exposed to ultraviolet radiation in a vacuum indicates the instability of the latter arises from photolysis of the pigment rather than of the vehicle. In an attempt to understand more fully the mechanism giving rise to the aforementioned response, the photolysis of the glass resin is being studied independent of the photolysis of the pigment. The transmission spectrum of a thin silicone resin film for vacuum ultraviolet wavelengths was obtained and is presented herein.

Since the methyl group does not strongly absorb radiation of wavelengths longer than 1500 A.,[1] the ultraviolet transmission spectrum of a methylsilicone resin should be similar to that of fused silica for wavelengths greater than 1500 A.

The material is Owens Illinois Type 650 glass resin and was precured according to the manufacturer's directions. Several films of $\sim 2 \times 10^{-3}$ cm. thickness were prepared by dissolving the B-stage material in acetone until viscosity was adequate for application of a coating by spraying. A small volume ($\sim 10^{-2}$ ml.) of the solution was then dropped upon distilled water. (Spraying techniques did not form acceptable films.) The film so formed was lifted onto a special support for transmission experiments while still pliable. The films were then cured by different techniques such as air drying, vacuum oven or infrared heating.

Spectra in the range 2–15 $\mu$ were obtained with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer. An example of such a spectrum is shown in Figure 1. The spectrum is similar to that described elsewhere,[2] except that the existence of hydroxyl band at 3 $\mu$ is more pronounced. Additional curing did not result in the elimination of this band for any particular sample.

The transmission spectrum for the range 1150–2300 A. was obtained with the use of a Jarrel-Ash scanning vacuum grating monochromator having a Seya-Namioka mounting. A microwave-excited hydrogen discharge in a Broida cavity was used as the radiation source. The lamp had a LiF window and was operated at a pressure of 2 torr. The resolution of the monochromator was approximately 11 A. The transmission spectrum

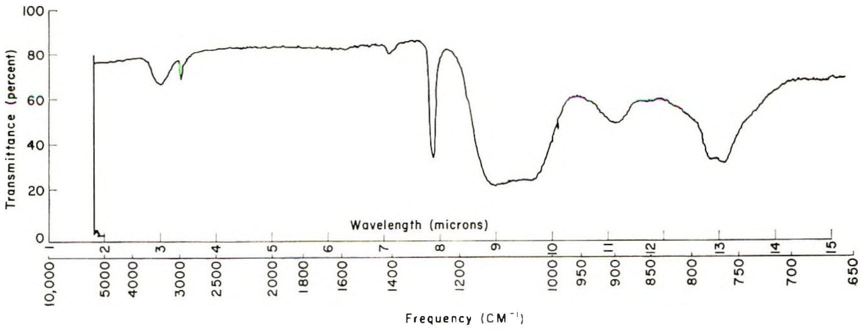

Fig. 1. Infrared transmission spectrum.

so obtained is shown in Figure 2. (Structure evident for wavelengths below 1600 A. is not shown.) It is seen that the absorption edge is at approximately 1700 A.

The data are compared to those obtained for a 1-mm. thick fused quartz plate and also to the manufacturer's data which were presented for a $^1/_8$-in. thick sample. The transmission spectrum of silicone shows a more abrupt cutoff than the fused silica sample, although the fused silica does transmit shorter wavelengths.

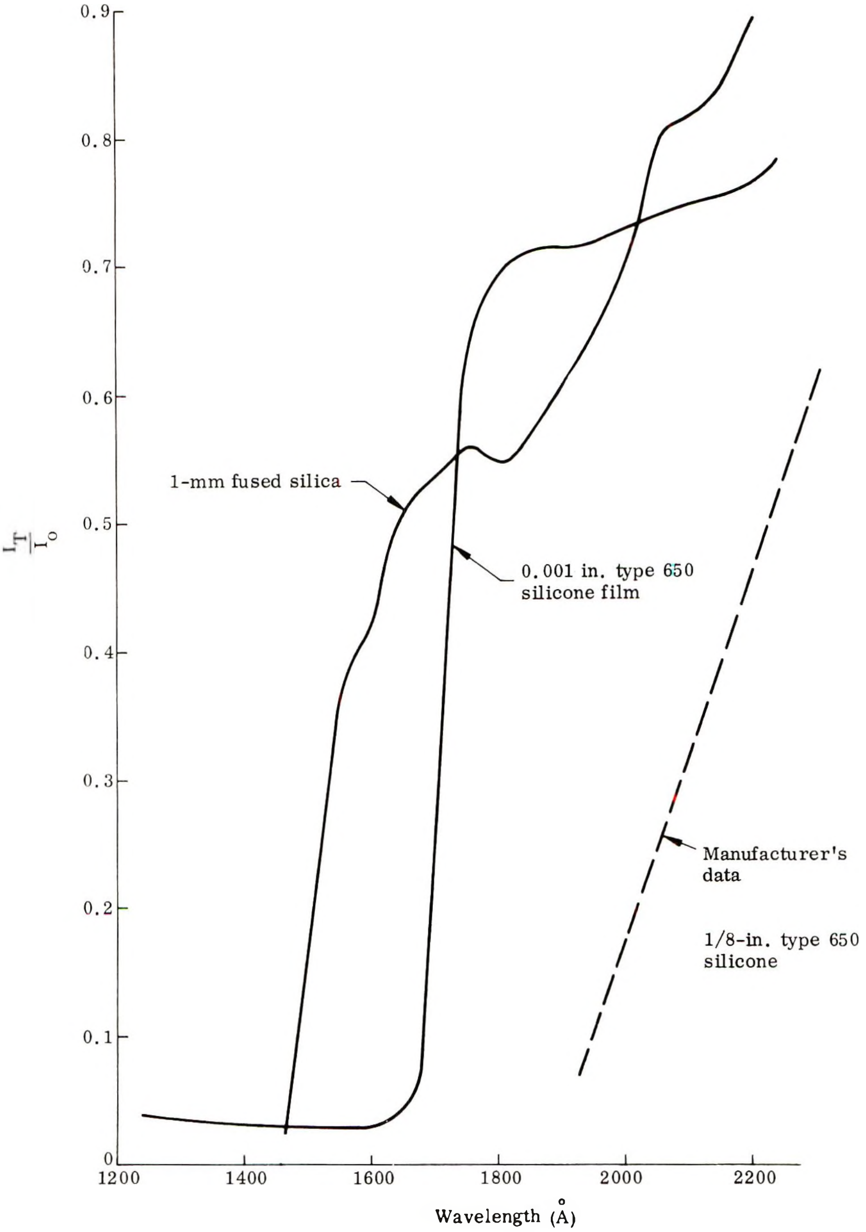

Fig. 2. Ultraviolet transmission spectrum.

Since reflection or scattering was not measured simultaneously, the absolute energy absorption coefficient cannot be presented. It is evident, however, that in order to study the effect of radiant energy deposition in this silicone resin, the use of wavelengths shorter than 1700 A. would be most appropriate.

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## *Copolymerization of Methyl Methacrylate and Diethyl Fumarate and the Homopolymerization of Diethyl Fumarate*

In the course of our studies on the crosslinking reactions of the unsaturated polyester, poly(ethylene fumarate), (PEF), with styrene[1-3] and methyl methacrylate (MMA),[2] we have investigated the copolymerization of MMA with diethyl fumarate (DEF). There is no record in the literature of the reactivity ratios for this monomer pair, and we report our findings here.

Copolymerization of MMA and DEF were carried out in dioxane solution at 60°C. but the reactivity ratios should be independent of the reaction medium.[4] The transfer constants to dioxane are small for the radicals involved.[5] Table I records the results for two typical runs. It is clear that the copolymer is rich in MMA even for a monomer feed which has DEF in excess. The reactivity ratios were calculated by using the integral equation of Mayo and Lewis, and from the $r_1$ versus $r_2$ plot are found to be $r_1 = 2.10 \pm 0.4$ and $r_2 = 0.05 \pm 0.1$. Table II summarizes the $r_1$, $r_2$ values for some analogous monomer systems. The values reported for the MMA–DEF system appear to be of the correct order of magnitude, and, as might be expected, are similar to the values for fumaronitrile and maleic anhydride corrected to 60°C.

TABLE I

MMA–DEF Copolymerization ($M_1$ = Diethyl Fumarate, $M_2$ = Methyl Methacrylate)

| $[M_1]_0$, moles | $[M_2]_0$, moles | Copolymer C, % | Copolymer H, % | Copolymer O, % | Mole fraction MMA in copolymer |
|---|---|---|---|---|---|
| 0.0406 | 0.1875 | 58.9 | 7.9 | 33.2 | 0.8951 |
| 0.1520 | 0.0749 | 58.6 | 7.5 | 33.9 | 0.7160 |

TABLE II

*r* Values for Some MMA Copolymerizations

| Copolymer system $M_1$ | Copolymer system $M_2$ | $r_1$ | $r_2$ | *T*, °C. | Reference |
|---|---|---|---|---|---|
| MMA | DEF | 2.10 ± 0.4 | 0.05 ± 0.1 | 60 | This work |
| MMA | Maleic anhydride | 3.5 | 0.03 | 60 | 6 |
| MMA | Maleic anhydride | 6.7 ± 0.2 | 0.02 | 75 | 7 |
| MMA | Diethyl maleate | 20.0 | 0 | 60 | 9 |
| MMA | Fumaronitrile | 3.5 ± 0.5 | 0.01 ± 0.01 | 79 | 8 |

Recent work has shown that a number of 1,2-disubstituted ethylene monomers can be polymerized by a free-radical mechanism, e.g. maleic anhydride,[10] itaconic anhydride,[11] and indene.[12] Since our crosslinking studies have been directly concerned with the reactivity of the fumarate double bond, we have investigated the copolymerization of PEF with DEF and also the homopolymerization of DEF. It has been reported in the patent literature[13,14] that diesters of maleic and fumaric acid polymerize with difficulty by free-radical methods to yield soft, tacky thermoplastic resins. PEF ($\bar{M}_n$ = 1,700) and DEF were copolymerized in bulk at 100°C. under high vacuum with benzoyl peroxide as initiator. After several hours, insoluble microgels appeared in the solution. This gel material was collected, worked up in methanol, and dried under vacuum. The polymer analysis in Table III and the infrared spectrum indicate the formation of a copoly-

TABLE III

Analysis of PEF–DEF Copolymer and DEF Homopolymer

| Sample | C, % | H, % | O, % | OEt, % |
|---|---|---|---|---|
| PEF–DEF copolymer | 53.7 | 5.8 | 40.5 | 32.9 |
| DEF | 55.8 | 6.9 | 37.3 | 52.3 |
| PEF | 49.0 | 4.4 | 46.6 | 0 |
| Poly(DEF) | 55.4 | 6.7 | 37.8 | 42.1[a] |

[a] The low analysis is probably due to steric effects preventing all the ethoxy groups from reacting.

mer. In view of the difficulty in freeing the polymer from all traces of unreacted monomers the copolymer composition cannot be accurately determined. However, the formation of a copolymer gel in this system was indicative of a reaction between the DEF monomer and the polyester double bond. We therefore studied the bulk polymerization of DEF at 100°C. using benzoyl peroxide as initiator, again under high vacuum conditions. After 48 hr. an appreciable increase in the viscosity of the reaction medium was observed. The polymer was precipitated from petroleum ether (b.p. 100–120°C.) and dried under vacuum. The product was a solid white powder, soluble in dioxane and methanol; $[\eta] = 0.083$ dl./g. (25°C.), $\bar{M}_n = 18{,}000 \pm 2{,}000$ (osmometry, 25°C.), $\bar{M}_n = 16{,}500 \pm 4{,}000$ (ebulliometry). Chemical analysis results are given in Table III. The infrared spectrum was identical to that of the monomer except for the absence of the double bond bands at 977 and 1640 cm.$^{-1}$.

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## *Vinyl Esters of Rosin*

Rosin was first vinylated by Reppe.[1] The ester gave, by free-radical initiation, low molecular weight polymers which were resins of little value. This might be expected as a result of the presence of the conjugated diene system in the resin acids present in conventional rosin. Ropp[2] describes some copolymers of vinyl acetate and vinyl stearate with vinyl esters of hydrogenated and dehydrogenated rosins. These apparently gave more satisfactory polymers than obtainable from rosin. Montgomery et al.[3] described the preparation of a perhydrogenated rosin which is for all practical purposes completely hydrogenated. Rosins having a high degree of unsaturation are available commercially and are prepared by direct catalytic hydrogenation of rosin or by disproportionation resulting from heating rosin to 150°C. with hydrogenation catalysts.

A comparison of the compositions of the three types of rosin are given in Table I.

TABLE I
Composition of Hydrogenated and Disproportionated Rosins[a]

| | Resin acid compositions, % | | | |
|---|---|---|---|---|
| | Two double bonds[b] | Single double bonds | No double bonds | Dehydrogenated |
| Perhydrogenated | Nil | 1–2 | 88 | 1 |
| Disproportionated | 3 | 26 | 5–7 | 57 |
| Hydrogenated | 1–3 | 69 | 2–6 | 11 |

[a] Data obtained from supplier, Hercules Powder Company, Wilmington, Delaware.
[b] Nonconjugated.

Vinyl esters were made from the three types of rosin and a comparison of their behavior toward polymerization under similar conditions was made (Table II).[4] The perhydrogenated rosin gave better conversions to polymers than did the hydrogenated and disproportionated materials.

TABLE II
Vinyl Esters of the Three Rosins and Monomer Conversions

| Type | Rosin neutral equivalent[a] | Yield, % | Boiling point, °C./mm. Hg | Hydrogenation equivalent | Refractive index $n_D^{20}$ | Conversions, % polymer[b] |
|---|---|---|---|---|---|---|
| Prehydrogenated | 346.8 | 79.2 | 168–172/0.5 | 342.4 | 1.5088 | 83 |
| Hydrogenated | 342 | 79.0 | 172–180/0.8 | 337.8 | 1.5196 | 11 |
| Disproportionated | 360 | 76.0 | 170–186/0.4 | 354.2 | 1.5289 | 20 |

[a] Contains nonacidic materials. Pure resin acid value is 302.
[b] Data of Liepins and Marvel.[4]

The method used for vinylation was that of Adelman[5] and others[6] and involved ester interchange with vinyl acetate with a mercuric catalyst.

### Experimental

A typical vinylation consisted of dissolving the rosin (370 g., 1.06 mole), in 1760 ml. (19 mole) vinyl acetate and adding at room temperature 0.32 g. copper resinate, 6.40 g. mercuric acetate and 1.60 g. concentrated sulfuric acid. When about 1 mole-equivalent of acetic acid had been liberated the reaction was considered complete and the batch was worked up by distilling excess vinyl acetate *in vacuo*. The residue was washed with dilute aqueous mineral acid, dilute alkali then distilled *in vacuo* bulb-to-bulb and fractionated. Yield and other data are tabulated in Table II.

Mention of commercial products by name is for purposes of identification only and does not constitute their endorsement by the Department over others which might be applicable.

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## *ESR Study on the Solid-State Polymerization of N-Vinylcarbazole Initiated by Electron Acceptors*

It has recently been reported by several workers that *N*-vinylcarbazole (*N*-VCZ) is easily polymerized by electron acceptors.[1-4] These authors considered that this polymerization may be initiated by cation radicals derived from charge transfer complexes between *N*-VCZ and acceptor and some of these authors considered this polymerization proceeded by cationic propagation. However, the exact nature of the mechanism has not yet been elucidated.

In view of the fact that charge-transfer complexes may play an important role in initiating the polymerization of *N*-VCZ with gaseous catalyst, such as halogen or sulfur dioxide as acceptor, the present authors attempted to elucidate the mechanism of initiation by ESR spectroscopy. ESR studies have recently been reported for a number of molecular complexes of polycyclic compounds with a variety of electron acceptors.[5-8] *N*-VCZ was recrystallized from *n*-hexane. Commercially highly purified $Cl_2$ and $SO_2$ (>99%) gases were used. Conversions were determined gravimetrically after washing. The reaction mixture was washed with methanol to eliminate unreacted monomer. The complexes were prepared by adding small amounts of electron acceptors to solid vinyl carbazole. ($SO_2$ complex was heated at 50°C. for 5 hr. after adding $SO_2$ gas to the *N*-VCZ.) ESR spectra were recorded with a Varian 4500 spectrometer with 100 Kc field modulation at 77°K. about 10 min. later after making the complexes at room temperature. Results are summarized in Tables I and II. ESR spectra obtained for almost all complexes were singlet spectra and no hyperfine splitting could be resolved for the solid. The *g*-values were close to that of DPPH. Polymer was obtained from the samples showing ESR signal. The more the electron acceptors were added, the stronger was the intensity of the ESR signal and the greater the polymer yield. The radical concentration was almost constant for over 13 hr. in *N*-VCZ–$Cl_2$ system at

TABLE I
Polymerization of *N*-Vinyl Carbazole in the Presence of Chlorine or Sulfur Dioxide

| Acceptor | Concentration, mole-% | Temp., °C. | Time, hr. | Conversion, % |
|---|---|---|---|---|
| $Cl_2$ | 6.8 | 20 | 0.2 | 58 |
| $Cl_2$ | 6.8 | 20 | 18 | 66 |
| $SO_2$ | 2.3 | 50 | 24 | 88 |
| $SO_2$ | 2.3 | 30 | 24 | 42 |

TABLE II
ESR Spectra of Charge Transfer Complexes in Solid State

| Donor | Acceptor | Color of complex | ESR spectra | $\Delta H_{msl}$, gauss |
|---|---|---|---|---|
| *N*-VCZ | $Cl_2$ | Dark green | Singlet | 7.6 |
| " | $Br_2$ | Black | " | 9.5 |
| " | $I_2$ | Brown | " | 11.4 |
| " | $BF_3$ | Dark blue | " | 7.6 |
| " | $SnCl_4$ | White-green | " | 10.0 |
| " | $SO_2$ | Yellow | Asymmetric doublet | — |
| Carbazole | $Cl_2$ | Yellow | Singlet | 12.4 |
| " | $SO_2$ | Yellow | Not clear | — |
| Poly-*N*-VCZ | $Cl_2$ | Gray | Singlet | 9.4 |

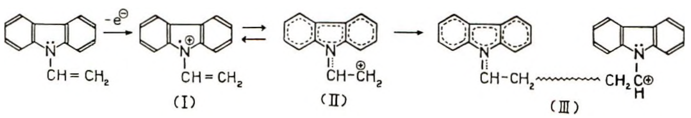

Fig. 1. Presented mechanism of polymerization of *N*-vinylcarbazole initiated by electron acceptors.

20°C. in which polymerization proceeded. The paramagnetic species at an earlier stage might be assigned to the cation radical formed by the electron transfer reaction between *N*-VCZ and electron acceptor [(I) and (II) in Fig. 1]. Polymerization is initiated from this cation-radical. One of the possible mechanisms of polymerization of *N*-vinylcarbazole by cationic propagation was shown in Figure 1. When the polymerization proceeds, radical delocalized over the carbazole ring [(III) in Fig. 1] remains according to this mechanism, and this radical would show the singlet spectrum responsible for the ESR signal at a later stage. This would result in the constancy of radical concentration during polymerization. On the other hand, the colors of the complexes with carbazole and poly-*N*-vinylcarbazole were lighter than those with *N*-VCZ. This may be due to the shorter conjugated system in carbazole and poly-*N*-VCZ than in *N*-VCZ. However, only the *N*-VCZ–$SO_2$ system showed an asymmetric doublet spectrum. This is supposed to be caused by the unpaired electron localized on $SO_2$.

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# ERRATUM

## The Thermal Expansion of Cellulose, Hemicellulose, and Lignin

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On page 27, line 11: $6.0 \times 10^{-4}$ should read $6.0 \times 10^{-5}$.

On page 43, equation (6): $\dfrac{1}{w_u} \dfrac{d[w_u(\bar{v}_w - \bar{v}_u)]}{dT}$ should read $\dfrac{(\bar{v}_w - \bar{v}_u)}{w_u} \dfrac{dw_u}{dT}$.

On page 46, line 6: $[d(\bar{v}_s)d/dT]$ should read $[d(\bar{v}_s)_d/dT]$.

On page 48, line 35: 5,1 bis $5{,}0.10^{-5}$ should read 5,1 bis $6{,}0.10^{-5}$.