

STUDIES ON LOW-PRESSURE POLYMERIZATION OF ETHENE  
THE INTERACTION OF  $\text{AlEt}_2\text{Cl}$  AND  $\text{TiCl}_4$ . POLYMERIZATION OF  
ETHENE AT LOW TEMPERATURE; FORMATION OF BIFUNCTIONAL PRODUCTS

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POLYMERIZATION mechanisms are usually divided into three categories, according to the nature of the growing entities, viz. cationic, anionic and free radical. For various reasons, none of these seemed to hold in the case of Ziegler polymerizations. The presence of a new type of intermediate fragments therefore seemed likely.

The starting point of the present investigation was the interaction of the catalyst components mostly employed in the Ziegler polymerisation of ethene, viz. diethylaluminium chloride and titanium tetrachloride.

Results

- (1) Diethylaluminium chloride is usually represented by the formula  $\text{AlEt}_2\text{Cl}$ . Ebullioscopic determination of the molecular weight (in benzene) indicated that this compound is actually a dimer  $(\text{AlEt}_2\text{Cl})_2$ .
- (2) Interaction of  $(\text{AlEt}_2\text{Cl})_2$  and  $\text{TiCl}_4$  in benzene solution at  $25^\circ\text{C}$  under nitrogen yielded a brown precipitate and gaseous products. At Al/Ti ratios of 0.5-3.3 mainly ethane was isolated (50-58% on  $\text{Ti}^{3+}$

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formed) and only small amounts of hydrogen, butane and butene (total 1-3% on  $Ti^{3+}$ ). At high Al/Ti ratios ethene was also formed (1-2% on  $Ti^{3+}$ ).

The brown precipitate consists mainly of  $TiCl_3$ ; in addition small amounts of polyethene (2-6 wt.%, 10-30% on  $Ti^{3+}$  calculated as  $C_2H_4$ ), Al (2-4 wt.%) and  $Ti^{4+}$  (3-6 wt.%) are present even after thorough extraction with boiling benzene. Only very small amounts of ethyl-aluminium compounds were found in the washed precipitate (0.1 wt.%  $C_2H_5$ ). The filtrate contained most of the Al (>90% on intake) partly as unconverted AlEt compounds, partly in the form of organic Al compounds of higher molecular weight. The presence of the latter compounds was proved by oxygenation of the filtrate and subsequent hydrolysis of the solid Al-alkoxy compounds. Primary aliphatic alcohols were obtained with an average mol. wt. of 400. The amounts isolated in various experiments corresponded to 10-30%  $C_2H_4$  on  $Ti^{3+}$ . The intake of ethyl equivalents could be nearly completely accounted for on the basis of ethane, ethene polymer of high mol. wt. and organic Al compounds. Analogous experiments with  $(AlEt_2Cl)_2$  alone in the presence of ethene showed that in this case higher Al compounds are not formed. When the reaction is brought to completion all Ti is present in the precipitate (>95%). Both the filtrate and the washed precipitate are inactive with respect to ethene polymerization.

(3) Li-ethyl and  $TiCl_4$  (Li/Ti = 1) gave, besides LiCl and  $TiCl_3$  (52% on Ti intake), ethane (43.8% on Ti-intake), ethene (1.6%) and butane (0.5%). From the precipitate polyethene was isolated (the amount corresponded to 10%  $C_2H_4$ ).

$(\text{AlEtCl}_2)_2$  and  $\text{TiCl}_4$  (Al/Ti = 1) also gave  $\text{TiCl}_3$  and ethane (39% on  $\text{Ti}^{3+}$ ).

(4) Polymerization of ethene at  $-10^\circ\text{C}$  with  $(\text{AlEt}_2\text{Cl})_2$  and  $\text{TiCl}_4$  as catalysts mainly gave soluble low mol. wt. polymers (80% on ethene converted, average mol. wt. 400). Filtration of the reaction mixture under nitrogen and treatment of the filtrate with oxygen and subsequent hydrolysis yielded a fraction consisting only of alcohols (A, 70% on Ti intake) and a fraction consisting only of olefins (B, 470% on Ti intake). Distillation of A gave two alcohol fractions which contained about one double bond per two molecules (ozonometric and infra-red analysis, Table 1). The alcohols were exclusively primary alcohols.

TABLE 1. Composition of alcohols

B.p. fraction $^\circ\text{C}/\text{mm Hg.}$	% on A	% oxygen	average mol. wt.	oxygen atoms/mole	Double bonds/mole
80-140/0.1	31	6.5	271	1.10	0.40
140-200/0.1	27	4.9	337	1.03	0.67

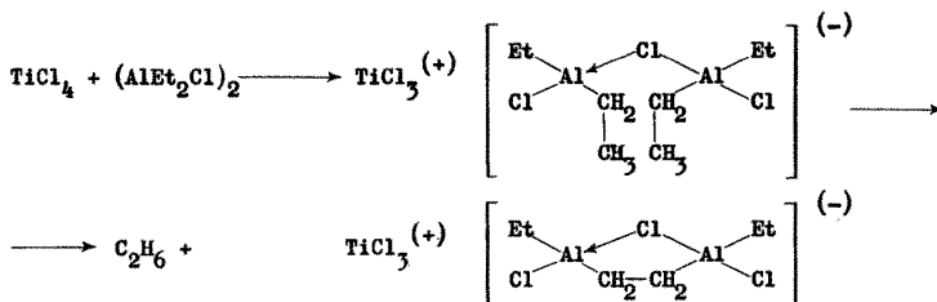
B was found to consist of a mixture of alkyl- and dialkyl-ethenes. On a molar basis the total amount of products was 5 times greater than the amount of  $\text{TiCl}_4$  used. It was verified that with  $(\text{AlEt}_2\text{Cl})_2$  alone under the same conditions low mol. wt. polymers are not formed.

### Discussion

#### A. Formation of ethane

The formation of ethane may have been due either to an intermolecular or an intramolecular process. Since little butane was formed free ethyl radicals cannot have been operative. This suggests ethane formation to be an intramolecular process, occurring simultaneously with ethyl

formation by abstraction of a hydrogen atom from another ethyl group in the Al-fragment:



I

Such a hydrogen abstraction process may be facilitated by the resonance stabilization of I, which may occur in the following way:

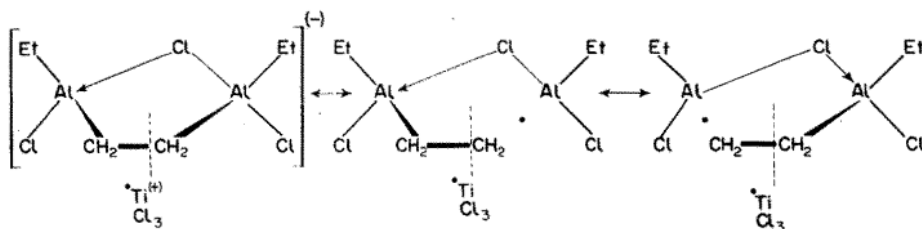


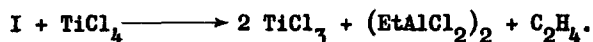
FIG. 1

It is seen that the essential hypothesis involved is the formation of an >Al-CH<sub>2</sub>-CH<sub>2</sub> fragment which is stabilized by interaction with trivalent Al- and/or trivalent Ti-compounds.

We consider the stabilized fragment to be the initiating species for the polymerization of ethene (see B).

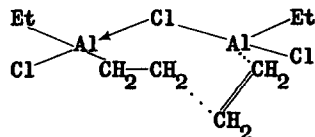
Similar structures may be written for the products formed by interaction of  $\text{TiCl}_4$  and  $(\text{AlEtCl}_2)_2$  or Li-Et.

The formation of polyethene and in some cases ethene upon interaction of  $\text{TiCl}_4$  and  $(\text{AlEt}_2\text{Cl})_2$  may take place by decomposition of I with formation of unstable Al compounds or by reaction of I with another equivalent of  $\text{TiCl}_4$ :



#### B. Chain growth, termination and transfer in ethene polymerization

We assume chain growth to take place by a four-centre reaction between  $\text{C}_2\text{H}_4$  and the long, weak  $\text{Al}\cdot\text{CH}_2$  or  $\text{Ti}\cdot\text{CH}_2$  bond of I, forming fragments of a similar resonance-stabilized structure as the initiating fragment:



Since a four-centre addition should be highly sensitive to steric influences - cf. Diels-Alder additions - this assumption might explain the high degree of stereo-specificity observed in polymerizations of this type.

In the absence of ethene the stabilized  $>\text{Al}(\text{CH}_2)_n$  fragment disappears by disproportionation, producing Al-compounds which contain saturated as well as unsaturated alkyl groups:

$>\text{Al}-(\text{CH}_2)_n-\text{CH}_2-\text{CH}_3$  and  $>\text{Al}-(\text{CH}_2)_n-\text{CH}=\text{CH}_2$ . Upon addition of oxygen and subsequent hydrolysis these products give saturated and unsaturated alcohols.

The formation of several molecules of alkenes per molecule of  $\text{TiCl}_4$  indicates that a transfer mechanism occurs. It may take place by interaction of ethene with the growing fragment, regenerating a primary initiating fragment I and a molecule of alkene.