

A NOVEL CATALYST SYSTEM FOR THE LOW-PRESSURE POLYMERIZATION OF ETHENE

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OUR assumptions with respect to the growing entities in the Ziegler polymerization¹ have led us to attempt generation of these fragments by other means. The partial reduction of aluminium trichloride with alkali metal in the presence of ethene, followed by oxidation with $TiCl_4$, was found to be successful.

Results

- (1) $AlCl_3$ and K (1-2:1) suspended in heptane react in the presence of ethene with the formation of a black-grey solid reaction product; addition of $TiCl_4$ led to a rapid polymerization to polyethene (65°C, atmospheric pressure). The reactivity of the system increases to a maximum with increasing reaction time of $AlCl_3$ and K (1 hr). The reaction between $AlCl_3$ and K could also be carried out in a nitrogen atmosphere; however, polymerization took place only if the replacement of nitrogen by ethene was performed before the addition of $TiCl_4$.
- (2) The black-grey product, isolated by filtration, has the same

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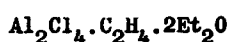
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¹ R. van Helden, A. F. Bickel, E. C. Kooyman, Tetrahedron Letters No. 12, 18 (1959).

reactivity in combination with TiCl_4 as the original system.

Decomposition of this material with water gives ethane (about 50% on K-intake) and hydrogen (about 30% on K-intake). The amount of ethane formed amounted to 93% based on ethene absorbed during the reaction of AlCl_3 and K. With D_2O more than 90% of the deuterio-ethanes produced had the composition $\text{C}_2\text{H}_4\text{D}_2$.

By extraction of the black-grey solid with ether a white compound A was obtained (yield 45% on Al-intake) which had the composition (Table 1):



(A) m.p. 74.6–75.2°C (vacuo)

TABLE 1

	Mol. wt. (ebullioscopic)	% Al	% Cl	% C_2H_6	% Et_2O
Calc. for A	372.1	14.5	38.1	7.54	39.9
Found	364; 370	14.7	38.2	7.42	35 ± 4*

* Mean value from 6 determinations

Decomposition with D_2O yielded more than 90% $\text{C}_2\text{H}_4\text{D}_2$. The ether-insoluble part, a black material, mainly consisted of Al and/or Al subhalides.

When the dietherate (A) was allowed to react with TiCl_4 in the presence of ethene no polymerization took place, but when 2 moles of AlCl_3 /mole of A were added, addition of TiCl_4 led to a rapid polymerization to polyethene.

Interaction of the black-grey solid or compound A + 2 AlCl_3 with TiCl_4 under nitrogen yields TiCl_3 and small amounts of ethene. Ethane was not formed.

Discussion

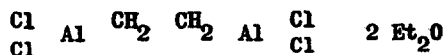
Since interaction of AlCl_3 and K under nitrogen and replacement by ethene shortly before addition of TiCl_4 gives the same results as when

carrying out the whole reaction under ethene, primary formation of Al-subhalides and/or Al would seem probable. Their presence is confirmed by the formation of hydrogen on decomposition with water.

The subhalides formed react with ethene to form compounds of the type

$$\text{AlCl}_2-\text{C}_2\text{H}_4-\text{AlCl}_2 \quad (\text{B})$$

The proposed structure of (A):



is supported by the formation of $\text{C}_2\text{H}_4\text{D}_2$ on decomposition with D_2O and by the known structure of the analogous boron compound $\text{Cl}_2\text{B}-\text{C}_2\text{H}_4-\text{BCl}_2$.²

When TiCl_4 is added before nitrogen has been replaced by ethene, the subhalides are oxidized to AlCl_3 and the formation of (B) is hence not possible: polymerization does not take place.

It seems reasonable to assume that on addition of TiCl_4 the initiating fragments (See ref. 1) are formed in the following way:

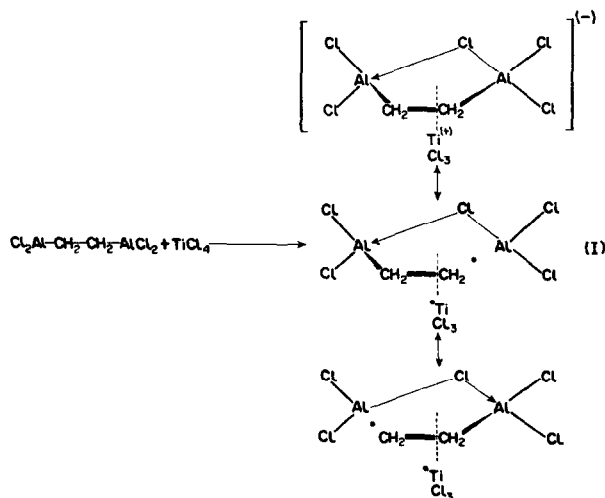
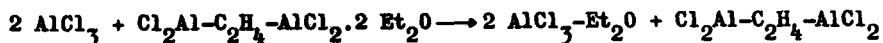


FIG. 1

A comparison of this reaction with that postulated in ref. 1 shows that a similar type of initiating species is formed in both cases. The formation of ethene is probably due to decomposition of I or by reaction with another equivalent of TiCl_4 in the same way as mentioned in ref. 1.

The activation of the system $\text{A} + \text{TiCl}_4$ by AlCl_3 is apparently due to the following reaction:



² W. H. Urry et al., J. Amer. Chem. Soc. **76**, 5299 (1954); E. B. Moore and W. N. Lipscomb, Acta Cryst. **9**, 668 (1956).