160. *An Investigation of the "Ziegler" Catalysts obtained by treating Titanium Tetrachloride with Aluminium Alkyls.*

By M. L. Cooper and J. B. Rose.

An investigation of the catalytic materials obtained by treating titanium tetrachloride in petrol solution with aluminium alkyls is described. All products were isolated and analysed, attention being concentrated on the dark solids formed on mixing the reactants. Examination of these solids indicated that they were complexes of organo-aluminium compounds with the lower titanium chlorides. Reduction of $TiCl_4$ by AlR_3 is accompanied by the production of hydrocarbons, and a relationship was established between the volume of RH evolved and the degree to which the $TiCl_4$ was reduced. This was consistent with the liberation of free alkyl radicals, R·, which disproportionate when R is Et, Pr^n, or Bu^n, and abstract hydrogen from the solvent when R is Me. The structure of the complexes and the mechanism by which they catalyse the polymerisation of olefins are discussed.

Many references to the reaction between aluminium alkyls and titanium halides have appeared since Ziegler's discovery[1] that the brown or black solid product is an active catalyst for the polymerisation of ethylene at low pressures. It is generally agreed that these solids, which are insoluble in hydrocarbons,[2-4] are formed by reduction of titanium tetrachloride,[3,5,6] and the evolution of hydrocarbon gases, a necessary consequence of reduction by the alkyl, has been observed.[7] The evolution of ethane and ethylene, which can arise from the disproportionation of ethyl radicals, has been detected during the reaction between $AlEt_3$ and $TiCl_4$,[8] but no quantitative measurements were made. Other workers[9] have assumed that the alkyl radicals liberated during reduction react only by abstracting hydrogen from the solvent. It has been stated[7] that very little reduction beyond tervalent titanium occurs during the preparation of active catalysts from $AlBu^i_3$ and $TiCl_4$, but several patents[5,10] claim that the presence of bivalent titanium is essential for catalytic activity. Solids obtained from titanium tetrachloride and triethylaluminium contain Cl, Al, Ti, and ethyl groups, and it has been shown[8] that as the ratio $AlEt_3 : TiCl_4$ is increased the ratio Cl : Ti in the solids decreases, while the ratio Al : Ti increases. However, no complete analysis of these solids has been reported. In the present work

---

[1] Ziegler, *Angew. Chem.*, 1955, **67**, 541.
[2] Belgian Patent 546,846.
[3] Belgian Patent 545,087.
[4] Italian Patent 537,425.
[5] Italian Patent 549,915.
[6] Belgian Patent 540,459.
[7] Friedlander and Oita, *Ind. Eng. Chem.*, 1957, **49**, 1885.
[8] Longi, Mazzanti, Natta, and Pino, *Gazzetta*, 1957, **87**, 549.
[9] Anderson, Ashby, and Ludlum, *J. Amer. Chem. Soc.*, 1958, **80**, 1380.
[10] U.S.P. 2,721,189.

a quantitative study of the reaction has been attempted, in which all the products have been isolated and completely analysed.

EXPERIMENTAL

Materials.—Solvents were all sodium-dried analytical-reagent quality light petroleums, which were free from aromatic hydrocarbons. $AlMe_3$ (Found: Al, 37·5; C, 49·9; H, 12·5. Calc. for AlC_3H_9: Al, 37·5; C, 50·0; H, 12·5%), $AlPr^n_3$ (Found: Al, 17·5; C, 68·1; H, 13·4. Calc. for AlC_9H_{21}: Al, 17·3; C, 69·2; H, 13·6%), and $AlBu^n_3$ (Found: Al, 13·5; C, 69·2; H, 13·1. Calc. for $AlC_{12}H_{27}$: Al, 13·65; C, 72·7; H, 13·65%) were prepared by standard methods and diluted with light petroleum before use. $AlEt_3$ was obtained in methyl*cyclo*hexane solution and was not therefore analysed. The concentrations of aluminium alkyl in the solutions used were determined by analysing these solutions for aluminium.

Reaction between Titanium Tetrachloride and Aluminium Alkyls at 20°.—(1) *Procedure.* Aluminium alkyls (0·0125—0·25 mole), dissolved in light petroleum (b. p. 100—120°), were added to stirred solutions of $TiCl_4$ (0·0125—0·05 mole), the total volume of solvent being 400 ml. When the alkyl was $AlEt_3$, $AlPr^n_3$, or $AlBu^n_3$ brown (low $[AlR_3]$ used) or black (high $[AlR_3]$ used) precipitates were formed immediately, but with $AlMe_3$ precipitation was so slow that the reaction could not conveniently be investigated at 20°. $AlEt_2Cl$ gave a precipitate with $TiCl_4$ less rapidly than $AlEt_3$, and $AlEtCl_2$ was still less reactive. After being stirred for 2 hr., the products were filtered, and the solid residues washed several times with light petroleum (b. p. 40—60°). All the above operations were carried out under nitrogen, air being rigorously excluded.

(2) *The solids.* Solvent was removed by drying, first under low vacuum (10^{-1} mm.), and then to constant weight under high vacuum (10^{-3} mm.). During the latter process, which took 48 hr., the solids lost *ca.* 10% of their weight, the material removed being trapped and then shown to be solvent by its infrared spectrum. When ethylene was passed through a suspension of the dried solid, obtained from $AlEt_3$ (0·02 mole) and $TiCl_4$ (0·025 mole), in light petroleum for 1·5 hr., 15 g. of solid polymer were obtained. The same weight of polymer was obtained when the experiment was repeated with use of a similar solid catalyst which had been washed and

TABLE 1. *Analysis of solids prepared at* 20°.

	Reactants			Composition of the solids				
				Atomic or group ratios of:				
Expt. No.	Moles $TiCl_4$ (moles)	Alkyl (moles)	Alkyl	Al : Ti	Cl : Ti	Alk : Ti	Alk : Al	Polymer: (C + H) as wt. %
1	0·025	0·02	$AlEt_3$	0·152	3·18	0·26	1·7	38
2	0·025	0·02	,,	0·159	3·26	0·20	1·3	41
40	0·025	0·025	,,	0·27	3·17	0·37	1·4	25
3	0·025	0·0375	,,	0·46	2·99	1·03	2·3	23
4	0·025	0·0375	,,	0·41	3·06	0·77	1·9	27
5	0·025	0·05	,,	0·58	2·78	1·19	2·0	20
6	0·025	0·05	,,	0·57	2·97	0·95	1·8	22
7	0·025	0·075	,,	0·41	1·88	1·41	3·4(?)	22
8	0·025	0·125	,,	0·42	1·82	1·31	3·1	21
9	0·025	0·25	,,	0·55	1·51	1·21	2·2	27
15	0·025	0·0075	$AlPr^n_3$	0·18	3·31	0·14	0·8	41
16	0·025	0·0125	,,	0·14	3·21	0·17	1·2	25
17	0·025	0·02	,,	0·12	3·13	0·16	1·3	7
10	0·05	0·05	,,	0·21	3·07	0·45	2·2	12
18	0·025	0·0375	,,	0·25	2·84	0·62	2·5	7
11	0·05	0·10	,,	0·49	2·42	1·27	2·6	8
12	0·05	0·15	,,	0·45	1·75	1·09	2·5	10
13	0·05	0·25	,,	0·37	1·35	0·96	2·6	18
14	0·025	0·25	,,	0·37	1·19	0·87	2·4	21
31	0·025	0·0125	$AlBu^n_3$	0·18	3·25	0·19	1·1	6
32	0·0125	0·0125	,,	0·15	2·98	0·25	1·7	11
33	0·0125	0·025	,,	0·34	2·49	0·81	2·4	2
34	0·0125	0·0375	,,	0·43	1·88	0·96	2·2	4
27	0·025	0·0375	$AlEt_2Cl$	0·14	3·20	0·34	2·4(?)	23
28	0·025	0·1125	,,	0·20	3·21	0·38	1·9	31
29	0·0125	0·0938	,,	0·29	3·14	0·26	0·9	53
30	0·0125	0·1875	,,	0·28	3·33	0·33	1·2	39

filtered off, but not dried. As the dried solids were very rapidly oxidised by air (many inflamed spontaneously) the weighed samples required for analysis, etc., were dispensed and then handled completely under nitrogen. The extent of oxidation by adventitious air was apparent from the difference between the total analysis and 100%; the figures quoted in the subsequent tables are based on analyses for which the sum C + H + Cl + Al + Ti% was generally $\geqslant$98%.

Weighed samples of the solids were examined as follows. (*a*) Microcombustion for carbon and hydrogen. (*b*) Hydrolysis with dilute sulphuric acid in a closed flask (to prevent the loss of halogen); the product was filtered to give a waxy residue, which was dried and weighed, and a solution which was analysed for Al, Ti, and Cl by standard methods. The nature of the waxy residue was established as follows. A mixture of dilute hydrochloric acid and methanol was added to the solid obtained by treating $TiCl_4$ (0·050 mole) with $AlEt_3$ (0·15 mole), and the wax obtained was filtered off, washed, and dried. The infrared spectrum of this solid showed that it was 98% polyethylene. A similar experiment carried out with the solid obtained from $TiCl_4$ and $AlPr^n_3$ gave polypropene as the principal solid product. (*c*) The gaseous hydrolysis products were examined by transferring a weighed sample to a flask fitted with a manometer, which was then evacuated. Dilute sulphuric acid (10 ml.) and a wetting agent were introduced and the pressure produced by gas evolution was measured. The volume of gas evolved at N.T.P. was calculated from the known volume of the flask and the pressure developed, and the composition of the gas measured by comparing its infrared spectrum with those of standard samples of the hydrocarbons known to be present. Hydrogen was determined by gas chromatography. (*d*) The solid obtained from $TiCl_4$ (0·05 mole) and $AlPr^n_3$ (0·15 mole) was heated in a sealed evacuated tube to 400° for 16 hr. A small quantity (*ca.* 0·1 ml.) of liquid was collected in a side tube cooled in liquid air. This vaporised when warmed to room temperature and an analysis of the gas remaining in the tube showed only a trace of methane.

TABLE 2. *Decomposition of solids obtained from* $AlPr^n_3$ *and* $TiCl_4$ *with dilute sulphuric acid.*

	Catalyst preparation				% of total carbon appearing as					Moles of H_2 evolved [2] per mole of Ti present
Expt.	Al : Ti reactant ratio	C in solid (%)	H in solid (%)	H per C_3	(*a*) C_3H_8	(*b*) C_3H_6	(*c*) $(C_3H_6)_n$	*a* + *b* + *c*	CH_4	
10	1·0	9·8	2·0	7	74·6	1·8	11·9	88·3	0·0	0·008
11	2·0	22·4	6·4	10	59·4 65·5	11·5 8·3	8·3	79·2 84·1	1·2 2·4	0·052 0·055
12	3·0	24·8	4·4	6	45·4 43·9	22·1 30·2	8·9	76·4 83·1	8·6 7·4	0·493 0·565
13	5·0	25·6	5·2	7	73·3 75·6	4·4 5·0	18·2	95·9 98·0	6·8 5·1	0·700 0·694
14	10·0	25·9	4·7	7	40·0	16·2	20·6	76·8	10·8	0·716

TABLE 3. *Analysis of filtrates from reactions between* $TiCl_4$ *and* $AlEt_3$ *at* 20°.

	Al : Ti ratio of	% of reactant appearing in filtrate			Colour of
Expt.	reactants	Al	Cl	Ti	filtrate
1	0·8	82	18	0·8	Light brown
2	0·8	82	20	1·2	
3	1·5	87	16	8·7	Brown
4	1·5	70	16	1·7	
5	2·0	70	34	3·2	Black
6	2·0	79	23	3·3	
7	3·0	85	53	3·3	
8	5·0	92	51	11	
9	10·0	95	49	26	

(3) *Numerical results.* The results of analyses carried out as described in sections 2(*a*) and 2(*b*) are given in Table 1. In calculating these data, the percentage of carbon and hydrogen present in the solids as alkyl groups was assumed to be the difference between the percentage of carbon and hydrogen found by microcombustion, and that of polymer isolated on hydrolysis; the alkyl ratios were therefore calculated from the percentage of carbon in the solids that did not appear as polymer on hydrolysis. This assumption is reasonable, for the H : C ratios in the solids were found to be close to those of the appropriate alkyl groups (see, *e.g.*, Table 2), and in the case of the solids obtained from $AlPr^n_3$ and $TiCl_4$ a high proportion of the volatile organic hydrolysis products [isolated as described in section 2(*c*)] were propane and propene (Table 2).

(4) *Filtrates.* Filtrates from reactions between $TiCl_4$ and $AlEt_3$ were treated with dilute sulphuric acid, and the aqueous extract analysed for Al, Cl, and Ti by standard methods (see Table 3). The black filtrates did not give precipitates on standing, but when they were centrifuged in closed tubes at 11,000 r.p., a black solid separated out, leaving the liquid clear and almost colourless. Thus it appears that the soluble products are not deeply coloured, the intense colour and the titanium content of some filtrates being due to finely divided solids that had passed through the filter. Ethylene was passed through several of the filtrates for 0·5 hr., but no absorption occurred and no polymer separated on addition of methanol. Filtrates from reactions between $TiCl_4$ and AlR_3, where R = Et or Pr-, were treated with a few c.c. of methanol, filtered, evaporated to dryness, and the solids retained. Examination of their infrared absorption spectra showed them to be polyethylene when R = Et and polypropene when R = Pr^n.

TABLE 4. *Alkyls present in the filtrates from reactions between* AlR_3 *and* $TiCl_4$ *at* 20°.

Expt.	Alkyl	Al : Ti reactant ratio	Compn. of filtrate: ratios Cl : Al	Alk : Al	Expt.	Alkyl	Al : Ti reactant ratio	Compn. of filtrate: ratios Cl : Al	Alk : Al
1	$AlEt_3$	0·8	1·25	1·75	11	$AlPr^n_3$	2·0	1·05	1·95
17	$AlPr^n_3$	0·8	1·30	1·70	33	$AlBu^n_3$	2·0	0·90	2·10
40	$AlEt_3$	1·0	0·93	2·07	7	$AlEt_3$	3·0	0·83	2·17
10	$AlPr^n_3$	1·0	1·18	1·82	12	$AlPr^n_3$	3·0	0·88	2·12
32	$AlBu^n_3$	1·0	1·20	1·80	34	$AlBu^n_3$	3·0	0·80	2·20
3	$AlEt_3$	1·5	0·61	2·39	8	$AlEt_3$	5·0	0·46	2·54
18	$AlPr^n_3$	1·5	0·90	2·10	13	$AlPr^n_3$	5·0	0·57	2·43
6	$AlEt_3$	2·0	0·58	2·42	9	$AlEt_3$	10·0	0·21	2·79
					14	$AlPr^n_3$	10·0	0·27	2·71

The ratios of Cl : Al in the filtrates, and the Alk : Al ratios calculated from them, are recorded in Table 4; the values obtained when the alkyl was $AlEt_3$ were determined as described above, and those for the other alkyls by calculation from the compositions of the corresponding solids, it being assumed that the filtrates did not contain significant amounts of $TiCl_4$. In the last four experiments it is also assumed that the composition of the solid passing through the filter is not much different from that which the filter retains.

TABLE 5. *Analysis of solids prepared at* ca. 100°.

Expt. No.	Reactants $TiCl_4$ (moles)	Alkyl (moles)	Alkyl	Composition of the solids: Atomic or group ratios of Al : Ti	Cl : Ti	Alk : Ti	Alk : Al	Polymer: (C + H) as wt. %
41	0·025	0·025	$AlMe_3$	0·077	2·70	0·20	2·6	36
42	0·025	0·0375	,,	0·22	2·81	0·57	2·6	8
43	0·025	0·050	,,	0·33	2·41	0·93	2·8	11
44	0·025	0·075	,,	0·56	1·54	1·83	3·3	*
36	0·05	0·04	$AlEt_3$	0·19	3·28	0·15	0·8	22
37	0·05	0·075	,,	0·20	2·77	0·42	2·1	36
38	0·025	0·05	,,	0·40	2·36	0·62	1·6	18
39	0·05	0·15	,,	0·56	1·69	1·02	1·8	16
19	0·025	0·0075	$AlPr^n_3$	0·14	3·22	0·15	1·1	22
20	0·025	0·0125	,,	0·16	3·32	0·07	0·4	36
21	0·05	0·04	,,	0·15	3·06	0·18	1·2	6
22	0·05	0·075	,,	0·33	2·84	0·45	1·3	5
23	0·05	0·10	,,	0·29	2·51	0·49	1·7	3
24	0·025	0·075	,,	0·39	1·82	0·76	2·0	4
25	0·025	0·125	,,	0·36	0·82	0·55	1·0	13
26	0·025	0·25	,,	1·51	0·14	0·82	0·5	6

* Not measured.

Reaction between Titanium Tetrachloride and Aluminium Alkyls at ca. 100°.—It was suspected that gaseous hydrocarbons were produced during the reaction at 20°, but that they dissolved in the solvent. Solutions of titanium tetrachloride in boiling light petroleum (b. p. 100—120°) were therefore treated under reflux with aluminium alkyl solutions, and the gases which boiled off through the condenser were collected. The volume of gas evolved at N.T.P. was determined, and the composition of the gas measured by infrared spectroscopy. Isolation and analysis of the solid products were carried out as previously described. When the alkyl was $AlMe_3$ the gases evolved were methane (80—90%) and ethylene (10—20%), while with $AlEt_3$, ethane (94 ± 2%) and ethylene (6 ± 2%) were obtained. $AlPr^n_3$ gave propane and propene, the proportion of the latter rising from 10 to 35% as the Alkyl : $TiCl_4$ ratio was increased from 0·5 to 5·0 : 1. When ethylene was passed through the total reaction products rapid absorption occurred and solid polymers were obtained.

DISCUSSION

It appears that the Ziegler catalyst's activity is associated with its insoluble solid component, the composition of which depends upon its preparation. The average valency of titanium in the solids (Table 6), calculated from the analytical data on the assumption that the Al, Cl, and alkyl radicals all exert their normal covalencies, ranges from 3 to <1, the extent to which $TiCl_4$ is reduced depending largely on the amount of $AlAlk_3$ used. Bivalent titanium reacts with acids to give hydrogen,[11] so that the formation of hydrogen on hydrolysis of the solids (see Table 2) confirms the presence of titanium in a valency state lower than 3. With the exception of $AlMe_3$, all the trialkyls investigated appear to have roughly the same power to reduce $TiCl_4$, but the dialkyl chloride, $AlEt_2Cl$, was less reactive and did not reduce the valency of titanium much below 3. The ratio Alk : Al in the filtrate from reactions between $TiCl_4$ and $AlAlk_3$ investigated at 20° (Table 4) ranged from 1·7 to 2·8, so that the dialkyl chlorides can play only a small part in the reduction.

Results from the reactions at 100° show that there is usually close agreement between the valency of titanium in the solid calculated from the analytical results (col. A, Table 7) and that deduced from the volume of alkane (col. B) on the assumption that $\frac{1}{2}$ mole of alkane is produced for every unit reduction of a titanium g.-atom. Thus the alkyl groups, R, liberated on reduction disproportionate as follows: $2R \longrightarrow R(-H) + R(+H)$, when R is Et, Pr^n, or Bu^n. However, the relative proportions in which alkene and alkane were evolved were always less than 1 : 1 because much of the alkene polymerised, the polymer appearing in both the solids and the filtrates. Ethylene is polymerised by Ziegler catalysts more readily than propene, so that the alkene to alkane ratio obtained when $TiCl_4$ was treated with $AlPr^n_3$ was, as expected, greater than when $AlEt_3$ was used. The above correlation, between the valency of titanium in the solid and the volume of alkane evolved, was not obtained with $AlMe_3$, considerably more methane being produced than would be expected if quantitative disproportionation of the liberated methyl groups had occurred. Thus it appears that the alkyl groups are liberated as free radicals, for it is known [12] that the Et, Pr^n, and Bu^n free radicals disproportionate in solution, while free methyl radicals react principally by abstracting hydrogen from the solvent.

TABLE 6. *Valency of titanium in the solids obtained at* 20°.

Expt. No.	Alkyl	Al : Ti ratio	Average Ti valency in solid	Expt. No.	Alkyl	Al : Ti ratio	Average Ti valency in solid
15	$AlPr^n_3$	0·3	2·91	7	$AlEt_3$	3·0	2·04
16	$AlPr^n_3$	0·5	2·96	12	$AlPr^n_3$	3·0	1·49
17	$AlPr^n_3$	0·8	2·93	34	$AlBu^n_3$	3·0	1·55
40	$AlEt_3$	1·0	2·83	28	$AlEt_2Cl$	*3·0	2·99
10	$AlPr^n_3$	1·0	2·89	8	$AlEt_3$	5·0	1·87
32	$AlBu^n_3$	1·0	2·78	13	$AlPr^n_3$	5·0	1·20
27	$AlEt_2Cl$	*1·0	3·12	29	$AlEt_2Cl$	*5·0	2·53
6	$AlEt_3$	2·0	2·31	9	$AlEt_3$	10·0	1·07
11	$AlPr^n_3$	2·0	2·22	14	$AlPr^n_3$	10·0	0·95
33	$AlBu^n_3$	2·0	2·28	30	$AlEt_2Cl$	*10·0	2·82

* The Al : Ti ratio quoted is two-thirds of that used, so that the ratios quoted for $AlEt_2Cl$ are comparable with those quoted for AlR_3.

The valency of titanium calculated for the solids obtained in Expts. 25 and 26 (Table 7)

---

[11] Sidgwick, “The Chemical Elements and their Compounds,” O.U.P., Oxford, 1950, p. 651.

[12] Kharasch and Reinmuth, “Grignard reactions of non-metallic substances,” Constable and Co. Ltd., London, 1954, p. 124.

TABLE 7. *Reduction of titanium tetrachloride by aluminium alkyls at* 100°.

			Valency of Ti in solid					Valency of Ti in sold	
Expt.	Alkyl	Al : Ti ratio	A	B	Expt.	Alkyl	Al : Ti ratio	A	B
20	$AlPr^n_3$	0·5	2·91	3·13	38	$AlEt_3$	2·0	1·78	1·80
36	$AlEt_3$	0·8	2·86	2·98	23	$AlPr^n_3$	2·0	2·13	2·36
21	$AlPr^n_3$	0·8	2·79	3·06	44	$AlMe_3$	3·0	1·69	−0·67
41	$AlMe_3$	1·0	2·67	2·48	39	$AlEt_3$	3·0	1·03	0·77
42	$AlMe_3$	1·5	2·72	1·97	24	$AlPr^n_3$	3·0	1·41	1·42
37	$AlEt_3$	1·5	2·69	2·48	25	$AlPr^n_3$	5·1	0·29	−1·36
22	$AlPr^n_3$	1·5	2·30	2·34	26	$AlPr^n_3$	10·0	−3·57	−6·4
43	$AlMe_3$	2·0	2·35	1·04					

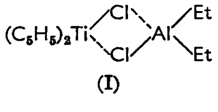
is not reasonable, and indicates that these solids contain metallic (and not tervalent) aluminium. The metal could be formed by reactions such as

$$Al(CH_2{\cdot}CH_2{\cdot}CH_3)_3 \longrightarrow AlH(CH_2{\cdot}CH_2{\cdot}CH_3)_2 + CH_2{:}CH{\cdot}CH_3$$
$$AlH(CH_2{\cdot}CH_2{\cdot}CH_3)_2 \longrightarrow Al + 1\tfrac{1}{2}H_2 + 2CH_2{:}CH{\cdot}CH_3$$

which are known [13a,14] to occur during the pyrolysis of aluminium alkyls, and it is significant that anomalous values were not obtained for the valency of titanium in similar experiments performed at 20° (Expts. 13 and 14 in Table 6).

It has been suggested [7,8] that the reduction of $TiCl_4$ by $AlAlk_3$ proceeds *via* alkyltitanium halides, *e.g.*, $TiCl_3Alk$, $TiCl_2Alk_2$, which decompose to give lower titanium halides and alkyl radicals. These intermediates would certainly be unstable, for all attempts made to isolate titanium alkyls [15] failed. However, aluminium alkyls readily form co-ordination compounds, *e.g.*, $Me_3\overset{-}{Al}{\cdot}\overset{+}{N}Me_3$ and $K^+Al\overset{-}{E}t_3F$,[13b] with electron donors, so that the first step in their reaction with $TiCl_4$ may well be the formation of complexes such as $Cl_3Ti\overset{+}{Cl}{\cdot}\overset{-}{Al}Alk_3$ or $Cl_2Ti(\overset{+}{Cl}\overset{-}{Al}Alk_3)_2$. These could then decompose directly by homolytic fission of the appropriate Ti–Cl and Al–Alk bonds. Monomeric alkyls are required for the formation of these complexes, so that, in agreement with our experiments, those alkyls which form particularly stable dimers, *e.g.*, $AlMe_3$,[13c] $AlAlk_2Cl$,[13d] would not be expected to react as readily as the higher trialkyls whose dimers are more readily dissociated.

The catalytic solids always contain Ti, Al, and alkyl groups, but there is, as yet, no direct evidence indicating to which metal atom the alkyl groups are attached. Thus there are two main theories concerning these catalysts: (*a*) They contain titanium alkyls, *e.g.*, $TiCl_3Alk$, and olefin polymerisation occurs at the reactive Ti–Alk bonds.[16,9] (*b*) They are mixtures or complexes of the lower titanium halides with aluminium alkyls (or chloroalkyls) and polymerisation occurs by addition of olefin molecules to the Al–Alk bonds.[16] End-group analysis of polymers produced with selected catalysts [16] has provided some support for the second alternative. Our results show that the solids cannot contain significant quantities of $AlCl_3$, for the dialkyl chlorides play little part in the reduction of $TiCl_4$ and the alkyl dichlorides react even less readily. They also indicate the absence of highly unstable bonds, for the activity of the solids was not reduced by high-vacuum drying. Further, although the ratio Alk : Ti, in the solids varied by a factor of 10, the Alk : Al ratio was usually between 1 and 3 (see Table 1). These data are consistent with the second theory, while the failure to obtain aluminium alkyls from the solids either by vacuum drying or by pyrolysis shows that the alkyls are chemically bound, rather than absorbed physically, to the titanium halides. Natta and his co-workers [17] have recently prepared a blue complex, to which the bridge structure, (I)



(I)

---

[13] Coates, " Organo-metallic Compounds," Methuen and Co. Ltd., London, 1956, (*a*) p. 72; (*b*) p. 79; (*c*) p. 75; (*d*) p. 82.

[14] Lecture given by Schultz, of the Hercules Powder Corporation, at Massachusetts, U.S.A., July, 1956.

[15] *E.g.*, Gilman and Jones, *J. Org. Chem.*, 1954, **10**, 505.

[16] Giannini, Mantica, Mazzanti, Natta, Peraldo, and Pino, *Chimica e Industria*, 1957, **39**, 19.

[17] *Idem*, *J. Amer. Chem. Soc.*, 1957, **79**, 2975.

has been attributed, by treating di(*cyclo*pentadienyl)titanium dichloride with $AlEt_3$. However, this complex appears to be very different from the insoluble infusible solids under investigation, for it is soluble in hydrocarbons, melts at 126—130°, and is far less active as a polymerisation catalyst.[17] Further, only the expected gaseous hydrocarbon, ethane, was evolved when the complex (I) was treated with water,[17] whereas the solids obtained by treating $TiCl_4$ with $AlPr^n_3$ gave propane, propene, methane, and hydrogen on hydrolysis. Thus it appears that Natta's complex is not a good analogy for the Ziegler catalyst.

Solids obtained from $TiCl_4$ and $AlEt_3$ give *X*-ray diffraction patterns resembling that of $TiCl_3$ and it has been suggested that they contain layers of titanium atoms similar to those in $TiCl_3$ (or $TiCl_2$ which also has a layer lattice structure [18]), although the arrangement of the layers relative to one another may be different.[19] Thus it is possible that the solids have layer structures similar in nature to those of the lower titanium halides, in which the chlorine layers are modified by partial replacement of chlorine ions with anions such as $\mathrm{Al\bar{C}lEt_3}$, $\mathrm{Al\bar{C}l_2Et_2}$, or $\mathrm{Al\bar{C}l_3Et}$, these anions being formed by the co-ordination of $AlEt_3$, $AlEt_2Cl$, or $AlEtCl_2$ with chlorine ions already present in the lattice. This type of structure is consistent with both the physical properties and the chemical composition of the solids. The formation of propene and methane as well as propane during the hydrolysis of solids obtained from $AlPr^n_3$ and $TiCl_4$ appears to be connected with the presence of titanium in a valency state below 3 (compare Tables 2 and 6). Solids in which the average valency of titanium was well below 3 also gave considerable quantities of hydrogen on hydrolysis (Table 2), and it is possible that the hydrogen atoms first produced, which normally combine to give hydrogen molecules, also react with the anions:

$$\begin{aligned}
\mathrm{Ti^{2+} + H_2O} &\longrightarrow \mathrm{Ti^{3+} + OH^- + H} \\
\mathrm{2H\cdot} &\longrightarrow \mathrm{H_2} \\
\mathrm{H\cdot + \bar{A}l(C_3H_7)_3Cl} &\longrightarrow \mathrm{H\bar{A}l(C_3H_7)_2Cl + C_3H_7\cdot}
\end{aligned}$$

Propene and methane could both be formed in such a system; the former by disproportionation of propyl radicals, and the latter *via* the series of reactions postulated by Steacie [20] to explain the formation of methane in gaseous systems containing hydrogen atoms and propyl radicals at temperatures below 100°:

$$\begin{aligned}
\mathrm{2C_3H_7\cdot} &\longrightarrow \mathrm{C_3H_6 + C_3H_8} \\
\mathrm{C_3H_7\cdot + H\cdot} &\longrightarrow \mathrm{C_2H_5\cdot + CH_3\cdot} \\
\mathrm{C_2H_5\cdot + H\cdot} &\longrightarrow \mathrm{2CH_3\cdot} \\
\mathrm{CH_3\cdot + H\cdot} &\longrightarrow \mathrm{CH_4}
\end{aligned}$$

Propane would also be formed by direct hydrolysis of the complex anions.

Initiation of olefin polymerisations, catalysed by the lattice structure suggested above, is more likely to occur at the titanium atoms than at the complex anions, for complexes formed from aluminium alkyls and electron donors react less readily with ethylene than do the alkyls themselves [21] and the catalytic activity of the solid is much greater than that of aluminium alkyls. Further, titanium dichloride is, by itself, a catalyst for ethylene polymerisations,[22] and in this case titanium atoms appear to be the only sites available for initiation. It is therefore suggested that ethylene molecules become

---

[18] Wells, " Structural Inorganic Chemistry," Clarendon Press, Oxford, 1950, p. 278.

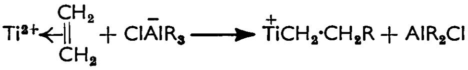
[19] Howells, personal communication.

[20] " Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, 1954, p. 468.

[21] Ziegler, " Perspectives in Organic Chemistry " (Ed. by Todd), Interscience Publishers Ltd., London, 1956, p. 191.

[22] B.P. 778,639.

attached to titanium atoms and that the absorbed olefin then reacts with the complex anions in the lattice:



$$\mathrm{Ti^{2+}\!\leftarrow\!\overset{CH_2}{\underset{CH_2}{\|}} + Cl\bar{A}lR_3 \longrightarrow \overset{+}{T}iCH_2{\cdot}CH_2R + AlR_2Cl}$$

Polymerisation at each centre then proceeds by interposition and chain-transfer reactions similar to those occurring during the interaction between ethylene and aluminium alkyls discovered by Ziegler.[23] This mechanism would give the end groups, R and $C{:}CH_2$, found experimentally by Natta and his co-workers.[16]

$$\mathrm{\overset{+}{T}i{\cdot}CH_2{\cdot}CH_2R + \mathit{n}C_2H_4 \longrightarrow \overset{+}{T}i{\cdot}CH_2{\cdot}CH_2{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}R}$$

$$\mathrm{\overset{+}{T}i{\cdot}CH_2CH_2{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}R + C_2H_4 \longrightarrow \overset{+}{T}i{\cdot}CH_2{\cdot}CH_3 + CH_2{:}CH{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}R}$$

A second mechanism, which gives the same end groups, may be postulated in which bivalent titanium reduces ethylene with the liberation of a hydride ion:

$$\mathrm{Ti^{2+} + CH_2{:}CH_2 \longrightarrow Ti^{3+}{\cdot}CH{:}CH_2 + H^-}$$

The hydride ion passes into the lattice while chain propagation proceeds by interposition, and termination by reaction of the active centre with a complex anion from the lattice.

$$\mathrm{Ti^{3+}{\cdot}CH{:}CH_2 + \mathit{n}C_2H_4 \longrightarrow Ti^{3+}{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}CH{:}CH_2}$$

$$\mathrm{\bar{A}lR_3Cl + Ti^{3+}{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}CH{:}CH_2 \longrightarrow Ti^{2+} + R{\cdot}[CH_2{\cdot}CH_2]_{\mathit{n}}{\cdot}CH{:}CH_2 + AlR_2Cl}$$

The authors thank their colleagues, particularly Drs. J. W. C. Crawford and P. A. Small, at the Research Department of this Division, for discussions, and Mr. M. E. A. Cudby for technical assistance. Infrared absorption spectra were measured by Messrs. R. G. J. Miller and H. A. Willis, and analyses performed by the Division Analytical Department.

Imperial Chemical Industries Limited, Plastics Division,
Welwyn Garden City, Herts.

[*Received, July* 30*th*, 1958.]

---

[23] Ziegler, *Angew. Chem.*, 1952, **64**, 323.