The Preparation of Hydride-free Triethylaluminum and Its Reaction with Titanium Tetrachloride

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In order to clarify the mechanism of the Ziegler catalysis for the polymerization of α-olefins, many investigations concerning the reaction between the catalyst components, namely, triethylaluminum and titanium tetrachloride, have been reported. All authors have observed the rapid reduction of titanium tetrachloride to the lower valency states.

Roha et al.(1) proposed that the reduction of titanium tetrachloride during the reaction with triethylaluminum was due to the effect of the diethylaluminum hydride present in the triethylaluminum. They stated that the diethylaluminum hydride present as an impurity in triethylaluminum has a strong reducing power and that the triethylaluminum, which had been treated with ethylene at a high pressure in an attempt to decrease the hydride content, did not show any appreciable reduction of titanium tetrachloride, although a clear orange solution was obtained.

In order to study the true behavior of triethylaluminum, hydride-free triethylaluminum was prepared and the reactivity of trialkylaluminum with titanium tetrachloride was investigated.

Experimental

Material.—*Crude Triethylaluminum.*—A commercial reagent (Texas Alkyls Corp.) was used.

Diethylzinc.—A commercial reagent (Sankyo Yuki Co.) was distilled at 50°C/64 mmHg.

Titanium Tetrachloride.—A commercial reagent (Kishida Chem. Co.) was distilled at 136—137°C.

n-Hexane.—Commercial-grade *n*-hexane (Phillips Petroleum Co.) was refluxed on sodium wire, distilled, and stored over a molecular sieve.

Ethylene.—Commercial high-purity ethylene (Nihon Sekiyu Co.) was used after having been dried with a molecular sieve.

Analysis.—Elemental analysis was done according to the standard methods as follows: aluminum, gravimetric oxine method; zinc, titration method using ethylenediamine tetraacetic acid; carbon and hydrogen, microcombustion method. The determination of the alkyl group or hydrogen bound to aluminum or zinc was accomplished by the hydrolysis and the volumetric measurement of the alkane and hydrogen evolved. The above gaseous hydrolysis products were analyzed by gas chromatography at room temperature using a column 5 m. long × 4.5 mm. diameter packed with alumina containing 25% acetonylacetone (for hydrogen) and with "C-22" (Shimadzu Seisakusyo) containing 25% liquid paraffin (for hydrocarbons). Furthermore, the trace of diethylaluminum hydride in triethylaluminum was analyzed qualitatively by means of the infrared spectrum and the isoquinoline test. Diethylaluminum hydride shows a deep infrared absorption at about 5.7 μ(2) and forms a deep red complex with isoquinoline.(3) For the measurement of the infrared spectrum, a Perkin-Elmer model 137 was used.

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1) M. Roha, U. C. Kreider, M. R. Frederic and W. L. Beears, *J. Poly. Sci.*, **38**, 51 (1959).

2) G. Schomberg and E. C. Hoffman, *Z. Elektrochem.*, **61**, 1110 (1957).

3) F. Bonitz, *Chem. Ber.*, **88**, 742 (1955).

The Preparation of Hydride-free Triethylaluminum.—Crude triethylaluminum (45 cc.) and 100 cc. of *n*-hexane were introduced, under a nitrogen atmosphere, into a 200 cc. flask equipped with a dropping funnel, a stirring bar, and a gas outlet connected to a nitrogen surge tube. The flask was set in a bath kept at −30°C using dry ice - *n*-hexane. Diethylzinc (5 cc.) dissolved in 100 cc. of *n*-hexane was dropped into the stirred solution of crude triethylaluminum. A white precipitate was thus formed. After the dropping was completed, the temperature of the flask was gradually raised to room temperature. The white precipitate then turned dark gradually. At about 20°C the precipitate instantaneously turned black. The supernatant colorless liquid was distilled under reduced pressure. A main fraction (a colorless liquid), distilled at 64—66°C/6 mmHg, was analyzed as follows: Found: Al, 23.56; C, 63.27; H, 13.21; Zn, 0.00; Calcd. for $Al(C_2H_5)_3$: Al, 23.63; C, 63.12; H, 13.24%. The results of the determination of the hydride by means of the infrared spectrum, the isoquinoline test and hydrolysis are shown in Table I.

TABLE I. THE ANALYSIS OF TRIETHYLALUMINUM

$AlEt_3$			Crude	Purified
Infrared spectrum (5.7 μ)			+	−
Isoquinoline test			+	−
Hydrolysis	Gas evolved	mol./mol. $AlEt_3$	2.98	2.98
	Ethane	vol. %	93.16	98.44
	Ethylene	vol. %	0.33	0.00
	n-Butane	vol. %	3.14	1.56
	Hydrogen	vol. %	3.37	0.00

The Reaction of Crude Triethylaluminum with Diethylzinc.—Crude triethylaluminum (9.2 g., 0.081 mol.) was introduced under a nitrogen atmosphere into a 50 cc. test tube equipped with a magnetic stirrer, a gas outlet connected to a gas burette, and a dropping funnel. The test tube was then set in an oil bath kept at 60°C. To the stirred crude triethylaluminum, 10.0 g. (0.088 mol.) of diethylzinc was added from the dropping funnel over a 10 min. period, after which stirring was continued for a further 20 min. The reaction thus proceeded, separating a black metallic powder, and 6.2 mmol. of gas was evolved during the reaction. The composition of the gaseous products, as determined by gas chromatographic analysis, is shown in Table II.

TABLE II. THE COMPOSITION OF THE GASEOUS PRODUCTS EVOLVED DURING THE REACTION BETWEEN CRUDE $AlEt_3$ AND $ZnEt_2$

Component	Vol. %
Hydrogen	70.0
Ethane	29.1
n-Butane	trace

When the black precipitate was filtered, washed with dried *n*-hexane, and dried, 0.46 g. of a matallic solid was obtained. It was 97.37% zinc and 0.24% aluminum, and so it seems to be almost pure zinc metal. (Zn, 6.85 m atom).

To the filtrate a few drops of diethylzinc were then added. No further change was observed. On the other hand, when a few drops of crude triethylaluminum were added to the filtrate, a black precipitate separated again.

The Treatment of Crude Triethylaluminum with Ethylene.—A solution of 10 g. (0.088 mol.) of triethylaluminum in 50 cc. of dry *n*-hexane was treated with ethylene at 40—60 kg./cm² at 90°C for 18.5 hr. in an autoclave. Ethylene (0.56 mol.) was absorbed smoothly. *n*-Hexane was then stripped from the resultant to obtain 25.7 g. of a colorless liquid. The average chain length (carbon number) was calculated as 6.3 on the assumption that all the ethylene absorbed was consumed in the "Aufbau Reaktion." The reaction product was hydrolyzed as usual. The composition of the evolved gas was analyzed by gas chromatography. Table III shows the composition of the evolved gas.

TABLE III. THE COMPOSITION OF THE GAS EVOLVED UPON HYDROLYSIS

Component	Composition vol. %
Ethane	11.3
n-Butane	86.7
Hydrogen	2.0
(Total gas	1.73 mmol./g.-Product)

TABLE IV. THE DISTRIBUTION OF THE GROUPS BOUND TO ALUMINUM

Group	Composition mol. %
Ethyl	1.9
n-Butyl	14.6
Hydride	0.3
Longer alkyls	83.2*

* Calculated as 100 minus the sum of the percentages of the above groups.

TABLE V. THE REACTION OF TRIALKYLALUMINUM WITH TITANIUM TETRACHLORIDE

Run No.	AlR_3	Ethylene* treatment	Reaction
1	Crude $AlEt_3$	−	A dark brown precipitate was formed instantaneously
2	Crude $AlEt_3$	+	A dark brown precipitata was formed instantaneously
3	Pure $AlEt_3$	−	A dark brown precipitata was formed instantaneously
4	Pure $AlEt_3$	+	A dark brown precipitate was formed instantaneously
5	$AlEt_3$ treated with ethylene at a high pressure	−	Clear yellow solution (slightly orange-colored)
6	$AlEt_3$ treated with ethylene at a high pressure	+	Clear yellow solution

* Ethylene was passed into the AlR_3 benzene solution at atmospheric pressure and at room temperature for 30 min.

The distribution of the groups bound to aluminum is shown in Table IV.

The Reaction of Various Trialkylaluminum Species with Titanium Tetrachloride.—To trialkylaluminum (0.274 g.) dissolved in 200 cc. of dry benzene in a 300 cc. conical flask, titanium tetrachloride (3 cc.) in benzene (1 mmol./cc.) was added drop by drop at room temperature.

The same procedure was then repeated using a benzene solution of trialkylaluminums which had been treated with ethylene bubbled in at atmospheric pressure and at room temperature for 30 min.

The results of the reactions are shown in Table V.

Discussion

The Preparation of Hydride-free Triethylaluminum.—Triethylaluminum free from hydride can be prepared by treating triethylaluminum containing the hydride with diethylzinc. It is postulated that the reaction proceeds according to the following equations:

$$Et_2AlH + Et_2Zn \longrightarrow Et_3Al + EtZnH \qquad (1)$$

$$Et_2AlH + EtZnH \longrightarrow Et_3Al + ZnH_2 \qquad (2)$$

$$2EtZnH \longrightarrow Et_2Zn + ZnH_2 \qquad (3)$$

$$EtZnH \longrightarrow Zn + EtH \qquad (4)$$

$$ZnH_2 \longrightarrow Zn + H_2 \qquad (5)$$

Equations 4 and 5 are supported by the fact that the reaction gives metallic zinc and a nearly equimolar quantity of a gas consisting mainly of hydrogen and ethane.

The gas evolved during the reaction contained 70 mol. % of hydrogen. However, it is uncertain that the second-step alkylation shown in Eq. 2 can proceed. The disproportionation of ethylzinc hydride as shown in Eq. 3 should also be considered.

Assuming that the reactions of 1—5 proceeded quantitatively, the hydride-group content in the groups bound to the aluminum of crude triethylaluminum was calculated to be 4.3%. This value nearly coincided with the analytical value of 3.4% (Table I).

The Reaction of Ziegler-catalyst Components.—In order to clarify the mechanism of Ziegler catalysis, many investigations concerning the reaction of the catalyst components, e. g., triethylaluminum and titanium tetrachloride, have been reported. All the authors agree that titanium tetrachloride is alkylated by triethylaluminum and that then the alkyl-titanium bond is decomposed to yield titanium species of lower valency states. Although some catalysts which are comprised only quadrivalent titanium species have been proposed,²⁾ the reduction of titanium in the case of a Ziegler catalyst consisting of triethylaluminum and titanium tetrachloride is noticeable as a reaction important to an analysis of the catalytic mechanism. However, the mechanism of the reduction of titanium tetrachloride has not yet been clarified in detail.

Roha et al.¹⁾ found that the triethylaluminum treated with ethylene at a high pressure and temperature does not reduce titanium tetrachloride; they therefore proposed that the reduction of titanium tetrachloride is due to the effect of the diethylaluminum hydride present as an impurity in triethylaluminum, which hydride has a stronger reducing ability.

Sinn et al.⁴⁾ proposed that the presence of a small quantity of water is necessary for Ziegler catalysis.

In fact, it is important to notice the effects of the components present in small quantities in the catalyst system.

In order to study the role of the impurities present in trialkylaluminum, we studied the reactions between titanium tetrachloride and various trialkylaluminums, namely, commercial crude triethylaluminum which contained a small quantity of the hydride (diethylaluminum hydride), purified triethylaluminum free from hydride, and trialkylaluminum which had been obtained by the treatment of commercial triethylaluminum with ethylene at a high pressure and temperature.

The experimental results showed that even when the purified triethylaluminum was used, the instantaneous reduction of titanium tetrachloride occured, just as in the case of crude triethylaluminum containing diethylaluminum hydride.

On the other hand, trialkylaluminum with longer alkyl chains, which had been obtained by treating crude triethylaluminum with ethylene at a high pressure and temperature, could not reduce titanium tetrachloride to the lower valency states; rather, a clear yellowish-orange solution was obtained.

The fact that the triethylaluminum treated with ethylene at a high pressure and temperature, even though with a detectable amount of an aluminum-hydrogen bond, did not reduce titanium tetrachloride might be explained in terms of the steric hindrance of its long alkyl groups.

We might also conclude that the reduction of titanium tetrachloride with triethylaluminum is not caused only by the hydride present in it as an impurity.

Summary

Hydride-free triethylaluminum has been prepared by destroying diethylaluminum hydride by reaction with diethylzinc.

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4) Hj. Sinn, H. Winter and W. v. Tirpitz, *Makromol. Chem.*, **48**, 59 (1961).

The reaction of hydride-free triethylaluminum and titanium tetrachloride in benzene shows the instantaneous reduction of titanium tetrachloride. It has been concluded that the reduction of titanium tetrachloride is not caused only by the presence of diethylaluminum hydride as an impurity in triethylaluminum, as has been proposed by Roha. Triethylaluminum treated with ethylene at a high pressure does not reduce titanium tetrachloride under ordinary conditions, even though it contains appreciable amounts of the hydride.

On the basis of the above facts, the reaction of Ziegler-catalyst component has been discussed.

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