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REACTIONS OF ETHYLALUMINUM CHLORIDES WITH SODIUM SULFATE

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SUMMARY

Reactions of diethylaluminum chloride, ethylaluminum dichloride and ethylaluminum sesquichloride with sodium sulfate were carried out. Diethylaluminum chloride exchanges quantitatively chlorine for sulfate with sodium sulfate, and forms a n-heptane-soluble organometallic compound having the empirical formula $(C_2H_5)_4Al_2SO_4$ and a molecular weight of about 2300 in benzene. Two kinds of reaction are observed between ethylaluminum dichloride and sodium sulfate: formation of a complex which is insoluble in n-heptane and the dismutation reaction to diethylaluminum chloride. Reactions of ethylaluminum sesquichloride with sodium sulfate can be explained in forms of separate reactions of sodium sulfate with diethylaluminum chloride, and ethylaluminum dichloride.

INTRODUCTION

In a catalyst system for polymerization of propylene comprising titanium(III) chloride and ethylaluminum sesquichloride, an increase of the polymerization activity is observed when ethylaluminum sesquichloride is treated with sodium sulfate prior to use. It was suggested[1] that a reaction product of ethylaluminum sesquichloride with sodium sulfate is responsible for this higher activity. However, no study has yet been reported on the reaction between ethylaluminum chlorides and sodium sulfate.

RESULTS AND DISCUSSION

Reactions with diethylaluminum chloride

Reactions of diethylaluminum chloride with sodium sulfate in n-heptane were carried out. Analytical results for the liquid phase of the reaction product are shown in Table 1. The following conclusions can be drawn.

With increasing reaction time,

(1) the concentration of aluminum and ethyl groups remain unchanged, hence the C_2H_5/Al ratio remains 2;

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TABLE 1

REACTIONS OF DIETHYLALUMINUM CHLORIDE WITH SODIUM SULFATE IN n-HEPTANE
$(C_2H_5)_2AlCl/Na_2SO_4$ 1/2.

No.	Reaction conditions		Analysis of the liquid phase					
	Temp. (°C)	Time (h)	Al (wt %)	Na (wt %)	C_2H_5/Al	SO_4/Al	Cl/Al	Σ/Al^a
1	Blank		6.34		2.03		0.99	3.02
2	98	5	6.17	0.0	2.00	0.47	0.07	3.01
3	98	10	6.33	0.0	2.00	0.48	0.03	2.99
4	98	25	6.34	0.0	1.99	0.49	0.01	2.98

^{a} $\Sigma = C_2H_5 + Cl + 2\ SO_4$.

(2) the concentration of chlorine, hence the Cl/Al ratio, decreases rapidly;

(3) sulfate appears in the liquid phase and the SO_4/Al ratio increases to a final value of 0.5.

The infrared spectrum of the No. 4 sample in Table 1 was measured. A broad band at 1150–1200 cm^{-1} can be assigned to sulfate[2], and remaining bands are very similar to that of diethylaluminum chloride[3].

Evaporation of n-heptane from the No. 4 sample in Table 1 under reduced pressure in nitrogen atmosphere gave a white amorphous solid. This solid decomposes in air with evolution of white smoke, and reacts violently with water with evolution of ethane, in the same way as does diethylaluminum chloride. The decomposition residue contains sulfate and aluminum.

These results indicate the presence of a heptane-soluble alkylaluminum compound containing sulfate. It is thus reasonable to assume that the displacement reaction shown in eqn. (1) has occurred

$$2\,(C_2H_5)_2AlCl + Na_2SO_4 \rightarrow (C_2H_5)_4Al_2SO_4 + 2\ NaCl \qquad (1)$$

The reaction product $(C_2H_5)_4Al_2SO_4$ has already been reported to be synthesized by a reaction of diethylaluminum chloride with dimethyl sulfate[4]. The present equation (1) presents a new improved method.

Reactions with ethylaluminum dichloride

When ethylaluminum dichloride was a reactant, the situation was very different. The following conclusion can be drawn from the analytical results of the liquid phase shown in Table 2. With increasing reaction severity,

(1) the concentration of aluminum decreases extremely;

(2) the C_2H_5/Al ratio increases;

(3) the Cl/Al ratio decreases;

(4) sulfate appears in the liquid phase.

Loss of aluminum from the liquid phase indicates the formation of a heptane-insoluble compound by the reaction of ethylaluminum dichloride with sulfate. It is well known that ethylaluminum dichloride reacts with sodium chloride to form heptane-insoluble ionic complex $NaC_2H_5AlCl_3$[5]. Loss of aluminum in the present case may be explained by a similar formation of a complex between sodium sulfate and ethylaluminum dichloride. It is also well known that ethylaluminum dichloride

TABLE 2

REACTIONS OF ETHYLALUMINUM DICHLORIDE WITH SODIUM SULFATE IN n-HEPTANE

No.	Reaction conditions			Analysis of the liquid phase					
	Temp. (°C)	Time (h)	$Na_2SO_4/C_2H_5AlCl_2$	Al (wt %)	Na (wt %)	C_2H_5/Al	SO_4/Al	Cl/Al	Σ/Al[a]
5	Blank			6.53		0.99		2.03	3.02
6	25	1	0.6	2.52	0.0	1.34	0.07	1.51	3.08
7	25	24	0.6	1.51	0.0	1.58	0.18	1.09	3.13
8	25	1	1.2	0.70	0.0	1.96	0.29	0.48	3.02
9	100	24	1.0	0.65	0.0	1.85	0.45	0.24	2.99

[a] $\Sigma = C_2H_5 + Cl + 2\,SO_4$.

can be dismutated to diethylaluminum in the presence of sodium chloride[6]. The increase in the C_2H_5/Al ratio indicates that the dismutation reaction also proceeds, even at room temperature, in the presence of sodium sulfate.

The extent of the dismutation reaction is only small, however, judging from the data in Table 2. Diethylaluminum chloride formed by the dismutation reaction can react with sodium sulfate and form a product containing sulfate as shown in equation (1).

Reactions with ethylaluminum sesquichloride

Reactions between ethylaluminum sesquichloride and sodium sulfate were

TABLE 3

REACTIONS OF ETHYLALUMINUM SESQUICHLORIDE WITH SODIUM SULFATE IN n-HEPTANE
$(C_2H_5)_3Al_2Cl_3/Na_2SO_4$ 5/3.

No.	Reaction conditions		Analysis of the liquid phase (Moles in 100 g of solvent)								
	Temp. (°C)	Time (h)	Al	C_2H_5	Cl	SO_4	Na	C_2H_5/Al	Cl/Al	SO_4/Al	Σ/Al[a]
10	Blank		0.39	0.58	0.58			1.5	1.5		3.0
11	25	1	0.27	0.49	0.31			1.8	1.2		3.0
12	60	24	0.25	0.47	0.22	0.029		1.9	0.9	0.10	3.0
13	100	24	0.22	0.43	0.10	0.067		1.9	0.4	0.30	2.9

[a] $\Sigma = C_2H_5 + Cl + 2\,SO_4$.

carried out, and the analytical results for the liquid phase are shown in Table 3. With increasing reaction severity,

(1) the aluminum concentration decreases gradually;
(2) the C_2H_5/Al ratio increases and reaches 2;
(3) the Cl/Al ratio decreases;
(4) SO_4 appears in the liquid phase.

Since ethylaluminum sesquichloride is an equimolar mixture of diethylaluminum chloride and ethylaluminum dichloride[7], the above findings can be explained in terms of the reactions of these alkylaluminum chlorides with sodium sulfate: *i.e.*, reaction (1), followed by the reactions shown in eqns. (2) and (3).

$$2\,C_2H_5AlCl_2 \rightarrow (C_2H_5)_2AlCl + AlCl_3 \quad (2)$$

$$C_2H_5AlCl_2 + Na_2SO_4 \rightarrow \text{Complex} \quad (3)$$

Moles of $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$, and $(C_2H_5)_4Al_2SO_4$ in the liquid phase were calculated using the analytical data of Cl, C_2H_5, and Al in Table 3, and the results are summarized in Table 4. Moles of $(C_2H_5)_4Al_2SO_4$ calculated was compared

TABLE 4

CONCENTRATION OF DIETHYLALUMINUM CHLORIDE, ETHYLALUMINUM DICHLORIDE AND BIS(DIETHYLALUMINUM) SULFATE

Calculated from the Al, C_2H_5, and Cl concentration in Table 3.

No.	$(C_2H_5)_2AlCl$[a]	$C_2H_5AlCl_2$[a]	$(C_2H_5)_4Al_2SO_4$[a]
12	0.16	0.03	0.03
13	0.08	0.01	0.065

[a] Moles in 100 g of solvent.

with experimental value of SO_4 in Table 3. Fair agreement between these figures indicates that the above assumption is correct.

The extent of the above three reactions was estimated using the data in Table 3 and 4. Under the reaction conditions of experiment No. 12 in Table 3, 72% of the ethylaluminum dichloride reacts according to the equation (3), 13% is dismutated by the equation (2) and 15% remains unreacted, while 27% of diethylaluminum chloride reacts according to the equation (1) and 73% remains unreacted. At the severer reaction conditions of experiment No. 13 in Table 3, 87% of ethylaluminum dichloride reacts according to equation (3), 8% is dismutated and 5% remains unreacted, while 62% of diethylaluminum chloride reacts according to the equation (1) and 38% remains unreacted.

Cryoscopic measurements

Cryoscopic measurements of the reaction product of diethylaluminum chloride with sodium sulfate in benzene were carried out and the results are reported

TABLE 5

CRYOSCOPIC MEASUREMENT OF THE REACTION PRODUCT OF DIETHYLALUMINUM CHLORIDE WITH SODIUM SULFATE IN BENZENE[a]

No.	Solute (g)	Benzene (g)	ΔT found (°C)	Mol. wt. found
14	0.9982	13.2977	0.172	2234
15	3.7406	19.2668	0.428	2323

[a] Analysis of the reaction product: C_2H_5/Al 2.06, SO_4/Al 0.50, Cl/Al 0.003.

in Table 5. Two measurements at different concentrations gave about the same indicated molecular weight. This surprisingly high molecular weight, which is about eight or nine times that corresponding to $(C_2H_5)_4Al_2SO_4$, suggests to us the association of this compound through interaction of the oxygen atom of sulfate with electron deficient aluminum.

EXPERIMENTAL

Materials

Commercial benzene and n-heptane were shaken with sulfuric acid, washed with water and dried by refluxing over sodium. They were carefully distilled at atmospheric pressure.

Sodium sulfate (G.R.) was pulverized, and the powder of 300 Tayler mesh pass was calcined at 400° for 4 h. It was stored over anhydrous calcium chloride.

Ethylaluminum chlorides were obtained from Ethyl Corp., and were distilled at reduced pressure in a nitrogen atmosphere.

Reactions

Sodium sulfate was first added into a previously dried flask equipped with a stirrer. The flask was purged with nitrogen, and then ethylaluminum chlorides diluted in heptane or benzene were introduced. The reaction mixture was kept at the temperature indicated in the Tables. After a predetermined time, the liquid phase was removed by hypodermic syringe and submitted to analysis.

Analyses

Ethyl groups were determined by measuring the ethane evolved by the reaction between a sample and water. Chlorine was determined by conventional Mohr titration, after a sample had been decomposed with nitric acid. Sulfate was determined as barium sulfate. Aluminum was determined by EDTA method using standard iron solution and salicylic acid as an indicator. The molecular weight of the reaction product was determined by cryoscopic measurement carried out under nitrogen atmosphere in anhydrous benzene, with the use of a Beckmann thermometer in a closed vessel equipped with a stirrer.

IR spectra were run immediately after loading a sample into a KRS-5 cell (0.1 mm thickness of solution) under nitrogen atmosphere using a Nihon Bunko Model DS-402 G.

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