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SYNTHESIS AND PROPERTIES OF THE TRIMETHYLCHLOROALUMOXANE—DIETHYL ETHER COMPLEX

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Summary

An ether complex of trimethylchloroalumoxane was obtained from the reaction of lead monoxide with dimethylaluminium chloride. On the basis of NMR and IR spectra, thermoanalysis and molecular weight measurements, a structure of the complex has been proposed.

Introduction

Alumoxanes with the general formula $R_{4-n}X_nAl_2O$ (where R = CH_3, C_2H_5; $n = 0, 2$; X = Cl, C_2H_5O) were obtained by partial hydrolysis of organoaluminium compounds [1, 2] or by condensation of lithium dialkylaluminates with dialkylaluminium chlorides [3]. Tetramethylalumoxane, one of the products in the reaction of trimethylaluminium with lead monoxide, we have reported previously [4].

Due to the activity of alumoxanes as catalysts in the polymerization of some polar monomers there has been considerable interest in them in recent years [5-7]. For this reason we are carrying out investigations aiming to prepare and determine the properties and structure of methylalumoxanes.

Results and discussion

The trimethylchloroalumoxane—ethyl ether complex was obtained from the reaction of dimethylaluminium chloride with lead monoxide, after treating the post-reaction mixture with an excess of ethyl ether. The reaction may be represented by eqn. 1. The residue, after evaporation of the volatile components

$$4\ PbO + 8\ (CH_3)_2AlCl \rightarrow \text{post-reaction mixture} \xrightarrow{(C_2H_5)_2O}$$
$$(CH_3)_4Pb + 2\ PbCl_2 + Pb + 4\ (CH_3)_3ClAl_2O \cdot O(C_2H_5)_2 \qquad (1)$$

TABLE 1

IR SPECTRA OF ALUMOXANE WITH ETHYL ETHER AND DIMETHYLALUMINIUM CHLORIDE WITH ETHYL ETHER COMPLEXES

$(CH_3)_3ClAl_2O \cdot O(C_2H_5)_2$ (cm^{-1})	$(CH_3)_2AlCl \cdot O(C_2H_5)_2$ (cm^{-1})		Assignments [8]
1398s	1397s	CH_3—C	symmetrical deformation
1332m	1330m	CH_2	wagging
1292m	1288m	CH_2	twisting
1208s	1201s	CH_3	rocking
1155m	1155s	CH_3	rocking
1095m	1097s	CH_3	rocking
1027s	1030vs	C—O—C	antisymmetrical stretching
897s	898s	C—O—C	symmetrical stretching
840m	839m		
800vs			
770vs			
690vs	687vs	Al—C	antisymmetrical stretching
598s 582s	582s	Al—C	symmetrical stretching
534w	526w	Al—Cl	stretching
488w	489w		
495w			
411w	409m	Al—Cl	stretching

from the liquid phase, is a viscous, colourless liquid. This liquid mixes well with ethyl ether and aromatic solvents, however, its solubility in aliphatic solvents is limited. The composition of the obtained compound (in wt. %) is found: CH_3, 19.3; Al, 23.7; Cl, 15.9; $(C_2H_5)_2O$, 32.0. $(CH_3)_3ClAl_2O \cdot O(C_2H_5)_2$ calcd.: CH_3, 20.0; Al, 24.0; Cl, 15.8; $(C_2H_5)_2O$, 33.0.

The IR spectrum (Table 1) of the studied compound is characterized by the presence of strong absorption bands at 770 cm^{-1} and 800 cm^{-1}. These bands are attributed to the Al—O—Al stretching vibrations. The other absorption bands in the studied range of the alumoxane complex spectrum have their corresponding bands in the $(CH_3)_2AlCl \cdot O(C_2H_5)_2$ complex spectrum. Storr [2]

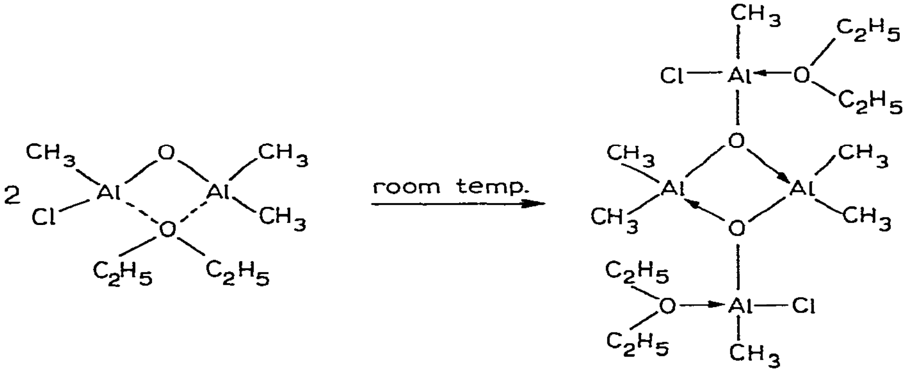
TABLE 2

INCREASE OF MOLECULAR WEIGHT OF TRIMETHYLCHLOROALUMOXANE—ETHYL ETHER COMPLEX OVER PERIOD OF TIME

Time (d)	Mol. wt.	Degree of association, *n*
	224.5 (monomer)	1
1	237.0	1.05
4	277.1	1.23
14	294.8	1.31
35	310.9	1.38
60	323.6	1.47

and Tani [3] also observed in the IR spectra of compounds containing Al—O—Al bonds strong absorption in the 720-800 cm^{-1} range.

As is confirmed by the molecular weight determinations over a period of time (Table 2), the trimethylchloroalumoxane—ethyl ether complex immediately after synthesis, occurs as a monomer (n = 1.05). The increase of its molecular weight shows that it exhibits a tendency to associate. Sixty days after the synthesis, the degree of association was n = 1.47. Eqn. 2 represents the formation of a dimeric structure.

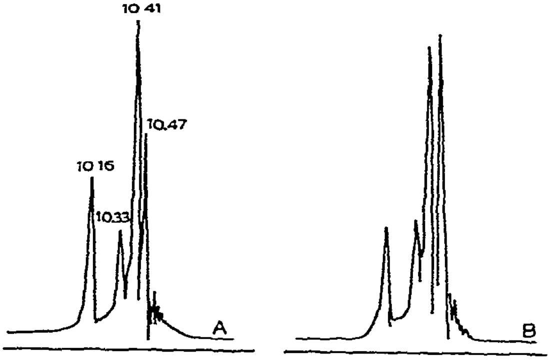


(2)

(I) (II)

In the PMR spectra of the trimethylchloroalumoxane—ethyl ether complex four signals are present corresponding to protons of methyl groups bonded with aluminium (τ_1 = 10.16, τ_2 = 10.33, τ_3 = 10.41 and τ_4 = 10.47 ppm) and also doubled multiplets of the ether's ethyl groups. With the increase of the complex's degree of association an increase in intensity of τ_2 and τ_4 signals and a decrease in intensity of τ_1 and τ_3 signals is observed (Fig. 1). The ratio of the signals' intensity in both these pairs is 1/2. Signals τ_1 and τ_3 were attributed to the complex's monomeric structure and signals τ_2 and τ_4 to the dimeric structure. The "internal chemical shift" of signals corresponding to the monomeric structure ($\tau_3 - \tau_1$) is 25 Hz and to the dimeric one ($\tau_4 - \tau_2$) is 14 Hz. This indirectly means that the difference in acidity of the aluminium atoms decreases in the dimeric structure. Also the average electron density on the carbon atom of methyl groups is higher for the dimeric form. The signals of methyl groups corresponding to this structure (τ 10.33 and 10.47 ppm) lie in a higher field than signals corresponding to the monomeric structure (τ 10.16 and 10.41 ppm).

Thermal analysis and pyrolysis of the trimethylchloroalumoxane—ethyl ether complex were carried out (Fig. 2). In the 80 to 220°C range of temperature a homogeneous decrease of mass occurs (curve TG). This decrease of 32.0% exactly represents the contents of ethyl ether in the complex. The cleavage of coordination bonds in the complex followed by evaporation of the free ethyl ether are endothermic processes, this is reflected by the character of curve DTA in the 80-220°C range of temperature. The next clearly observable thermal effect occurs after the ethyl ether draws away and this is an exothermic one. It could probably have appeared at a lower temperature but the former endothermic effect partially added to it. The exothermic effect is followed by a further, but less intensive, mass decrement.



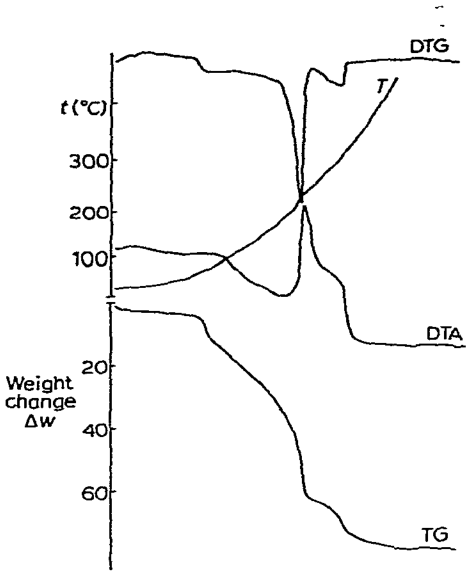
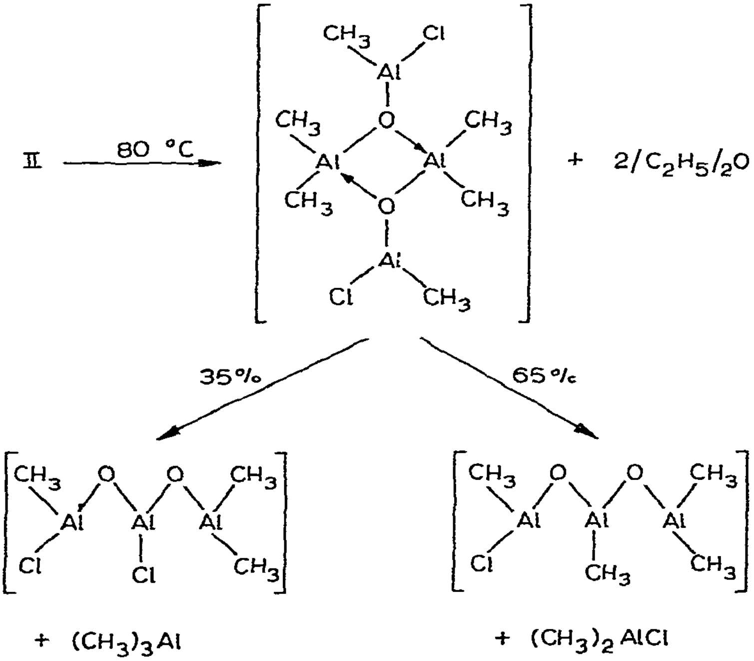


Fig. 1. PMR spectra (τ, ppm) of Al—CH_3 groups, depending on the degree of association *n*. (A *n* = 1.23; B *n* = 1.47).

Fig. 2. Thermogram of the $(CH_3)_3ClAl_2O \cdot O(C_2H_5)_2$ sample.

SCHEME 1



Pyrolysis carried out in a macroscopic scale in the 20-360°C temperature range allowed the isolation of the volatile decomposition products. Composition analysis and the PMR spectrum of the distillate obtained after pyrolysis of the trimethylchloroalumoxane—ethyl ether complex show that it is a mixture of trimethylaluminium— and dimethylaluminium chloride—ether complexes (35 and 65% respectively).

Pyrolysis products and the exothermic effect observed in thermal analysis shows that at a higher temperature (200°C) the alumoxane disengaged from the complex undergoes polycondensation with the isolation of trimethylaluminium and dimethylaluminium chloride. The reaction scheme 1 is proposed.

Experimental

Oxygen and moisture were excluded in all the reactions by known methods. IR spectra were recorded on a Zeiss UR-10 spectrometer from a liquid film closed in a polyethylene bag between KBr plates. PMR spectra were recorded on a Jeol-JNM-100MH apparatus from 7% benzene solutions which was also used in cryoscopic determinations. TMS was used as external standard. Thermal analyses were carried out with a Derivatograph apparatus of the F. Paulik, J. Paulik and L. Erdey system. Molecular weights were determined by the cryoscopic method in benzene solutions.

Preparation of the trimethylchloroalumoxane—ethyl ether complex

Synthesis was carried out in a glass reactor equipped with a stirrer, thermometer, dropper, and a Shott's type head joined with a receiver. 48.2 g of lead monoxide and 32 ml of n-hexane were placed in the reactor, and a suspension was formed, then 20.0 g of dimethylaluminium chloride was dropped in over 4 h at 20-25°C. After the addition of the dimethylaluminium chloride was complete, the stirring was prolonged for an hour, then 70 ml of ethyl ether was added over 1 h at 20-25°C. After dropping in the ethyl ether, the reactor's contents were allowed to separate. The colourless organic layer was filtered off and the precipitate left in the reactor was extracted twice with small portions of ethyl ether. The extracts were filtered off and the solvents evaporated from the combined filtrates under reduced pressure. The remaining volatile components were removed at 25°C under a pressure of 1×10^{-4} Torr. 9.1 g of the $(CH_3)_3ClAl_2O \cdot O(C_2H_5)_2$ was obtained.

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