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TETRAETHYLALUMINOXANE REVISITED. SYNTHESIS AND PROPERTIES *

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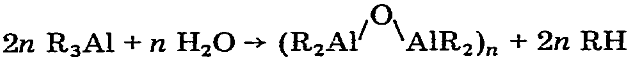
Summary

A new synthesis of tetraethylaluminoxane is carried out and two intermediate solid products isolated. They have been found to be oligoaluminoxanes, which dissolve in strong Lewis acids with formation of equilibrium complexes. A new model for aluminoxanes is proposed.

Introduction

Aluminoxanes have been extensively studied because of their catalytic properties. Aluminoxanes are usually obtained by the following reaction [1,2] (eq. 1)



$$2n\,R_3Al + n\,H_2O \rightarrow (R_2Al\overset{O}{\diagup\;\diagdown}AlR_2)_n + 2n\,RH \qquad (1)$$

(I)

In the case of R = Et it was assumed that the product I was trimeric [3a].

The present work was motivated by the observation that during purification of aluminoxane in vacuo at room temperature it was possible to distill off nearly one mol of R_3Al from I to yield a highly viscous oligomeric residue; the procedure was reversible even at elevated temperature, i.e. the residue dissolved in the removed R_3Al to re-form I.

A preliminary account has appeared [5].

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Results

Reaction of Et_3Al with H_2O at 1/1 molar ratio

The reaction between equimolar amounts of Et_3Al and H_2O was carried out in diethyl ether or toluene in the temperature range —70° C to room temperature. With diethyl ether as solvent the product mixture was a slightly opalescent homogeneous solution, but after several days a precipitate was observed. In the reaction in toluene, precipitation started before the reaction ended.

It is important to note that during the reaction less than 2 mol of ethane per 1 mol of H_2O were evolved [4]. The product II, isolated by distilling off the solvent under reduced pressure at room temperature, (eq. 2) was a white amorphous powder, insoluble in organic solvents. The amorphous structure of II was confirmed by X-ray examination. The Al content of II varied in the range 33.5—34.5% Al, suggesting a non-selective course of reaction and incomplete reaction of OH groups. Had all OH groups reacted, the product II would have had cyclic or very long chain structure, and the Al content would have been 37.5%.

$$n\ Et_3Al + n\ H_2O \xrightarrow[Et_2O\ \text{or}\ PhCH_3]{-70\ \text{to}\ 20^\circ C} \underset{\text{(II)}}{Et_2Al(OAlEt)_{n-1}OH} + (2n-1)\ EtH \qquad (2)$$

Thus the product II seems to be a mixture of oligomers, i.e. several fractions differing in the number of OAlEt units, formed by uncontrolled oligomerization in reaction 2. For simplicity however, equations are written only for one fraction with a fixed but unspecified value of *n*.

Use of slight excess of Et_3Al in the reaction leads to the same white amorphous powder, insoluble in organic solvents, 2 mol of EtH are evolved (eq. 3).

$$(n+1)\ Et_3Al + n\ H_2O \xrightarrow[Et_2O\ \text{or}\ PhCH_3]{-70\ \text{to}\ 20^\circ C} \underset{\text{(III)}}{Et_2Al(OAlEt)_{n-1}OAlEt_2} + 2n\ EtH \qquad (3)$$

Product II dissolves in organometallic compounds (Et_3Al, Me_3Al, $EtAlCl_2$, Et_2Zn, etc.) with evolution of small amounts of the relevant hydrocarbon. To solubilize II, at least an equimolar quantity of metalloorganic compound is required (eq. 4).

$$\underset{\text{(II)}}{Et_2Al(OAlEt)_{n-1}OH} + n\ R_3Al \xrightarrow[\text{no solvent}]{20^\circ C}$$

$$\underset{\text{(IV)}}{[Et_2Al(OAlEt)_{n-1}OAlR_2 \cdot (n-1)R_3Al]} + RH \qquad (4)$$

It is clear from reactions 2, 3 and 4, that a $1/n$-th part of the R_3Al taken is used in the reaction with OH groups of product II, and the remaining $(n-1)/n$-t part dissolves the product III to give IV.

Alternative synthesis of tetraethylaluminoxane

The addition of the second mol of Et_3Al to the product II yields an oily, colourless, slightly opalescent liquid soluble in organic solvents (eq. 5).

$$\underset{(II)}{Et_2Al(OAlEt)_{n-1}OH} + n\ Et_3Al \xrightarrow[\text{no solvent}]{20^\circ C} EtH + \underset{(V)}{[Et_2Al(OAlEt)_{n-1}OAlEt_2 \cdot (n-1)\,Et_3Al]} \qquad (5)$$

It should be noted that reactions 2 and 5 are stoichiometrically equivalent to reaction 1.

The identification of V was based on ^1H NMR and IR spectra, elemental analysis, and behaviour in vacuo at room and elevated temperature.

The product V was found to be exactly equivalent to the tetraethylaluminoxane obtained in reaction 1, i.e. to the tetraethylaluminoxane I [3]. It was also found that in vacuo at elevated temperature product I yielded III, and that the process was reversible:

$$I \rightleftharpoons n\ Et_3Al + III$$

Complexation of oligoaluminoxanes by strong Lewis acids

Reaction of II with equimolar quantity of Me_3Al yields an oily, opalescent, colourless liquid, soluble in organic solvents (eq. 6).

$$\underset{(II)}{Et_2Al(OAlEt)_{n-1}OH} + n\ Me_3Al \xrightarrow[\text{no solvent}]{20^\circ C} MeH + \underset{(VI)}{[Et_2Al(OAlEt)_{n-1}OAlMe_2 \cdot (n-1)\,Me_3Al]} \qquad (6)$$

The dissolution is exothermic, and small amounts of methane are evolved. Signals from Me_3Al protons were found in ^1H NMR spectrum of the product VI, as well as two markedly broadened signals from the ethyl groups in the oligomeric portion. Distillation gave only Me_3Al, and so there had been no exchange of Et and Me groups. The products II and III dissolved in $BF_3 \cdot OMe_2$; the temperature increased significantly on dissolution, and rapid evolution of gaseous dimethyl ether was observed, and at the same time BF_3 complexed with the

TABLE 1

IDENTIFICATION OF PRODUCT V

High vacuum conditions	$V \rightleftharpoons (n-1)\,R_3Al$ + oligomers III	
% Al	calcd. 29.03	found 28.9
^1H NMR [a] (ppm)	(CH_3)(t) 8.69, (CH_2)(q) 9.47, δ(Et) 0.78	
	Complex of V with *n* PhCN	
^1H NMR [a] (ppm)	(CH_3)(t) 8.27, (CH_2)(q) 9.41, δ(Et) 1.14	

[a] Solvent: $PhCH_3$ as internal standard at τ 7.66, +20°C.

oligomer:

$$\underset{\text{(III)}}{Et_2Al(OAlEt)_{n-1}OAlEt_2} + (n-1)BF_3\cdot OMe_2 \xrightarrow[\text{no solvent}]{20^\circ C}$$
$$Me_2O^{\uparrow} + \underset{\text{(VII)}}{[Et_2Al(OAlEt)_{n-1}OAlEt_2\cdot(n-1)BF_3]} \quad (7)$$

The complex VII was unstable at room temperature, and decomposes with slow evolution of BF_3. After several hours product III was recovered (eq. 8).

$$[Et_2Al(OAlEt)_{n-1}OAlEt_2\cdot(n-1)BF_3] \xrightarrow[\text{temp.}]{\text{room}}$$
$$(n-1)BF_3^{\uparrow} + \underset{\text{(III)}}{Et_2Al(OAlEt)_{n-1}OAlEt_2} \quad (8)$$

Discussion

From the results it seems that aluminoxanes can be considered as a special case of equilibrium complexes of the strong Lewis acid R_3Al with an oligomeric species (eq. 9).

$$R_2Al(OAlR)_{n-1}OAlR_2\cdot\ (n-1)R_3Al$$
$$\rightleftharpoons \underset{\text{(IX)}}{R_2Al(OAlR)_{n-1}OAlR_2} + \frac{n-1}{2}(R_3Al)_2 \quad (9)$$

There is a dynamic equilibrium IX with tetraethylaluminoxane, (R = Et), because of the comparable Lewis acidities of Et_3Al and acidic sites in the oligomer, with the result that there is a competition between (i) an equilibrium complex of oligomers and Et_3Al and (ii) two oligomeric chain clusters.

It is now clear that when reaction of equimolar amounts of Et_3Al and H_2O, eq. 2 is carried out in a polar solvent (Et_2O, DME), precipitation of the oligomer II is inhibited because of the competition between the polar solvent and oligomeric clusters, while in nonpolar solvents (toluene) the precipitation occurs readily.

One of many possible structures of tetraethylaluminoxane is shown in Fig. 1. In Fig. 1 the numbers of Al atoms in a single chain, O atoms in a single chain, and Al atoms in free (or complexed) Et_3Al, are equal respectively, to $x_i + 1, x_i, x_i - 1$. The Al/O ratio is thus $(x_i + 1 + x_i - 1)/x_i = 2/1$, where i (which is m or n) represents the number of OAlEt units in Fig. 1. The notation used follows from the stoichiometry of reactions 2 and 4.

The properties of tetraethylaluminoxane and its complexes with electron donors can be better explained in terms of the proposed structure by assuming that tetraethylaluminoxane is normally trimeric but monomeric in complexes with electron donors [3]. All available experimental data for tetraethylaluminoxane seem to refer to Et_3Al which is quasi-free or complexed with electron donors in the presence of oligomeric carrier.

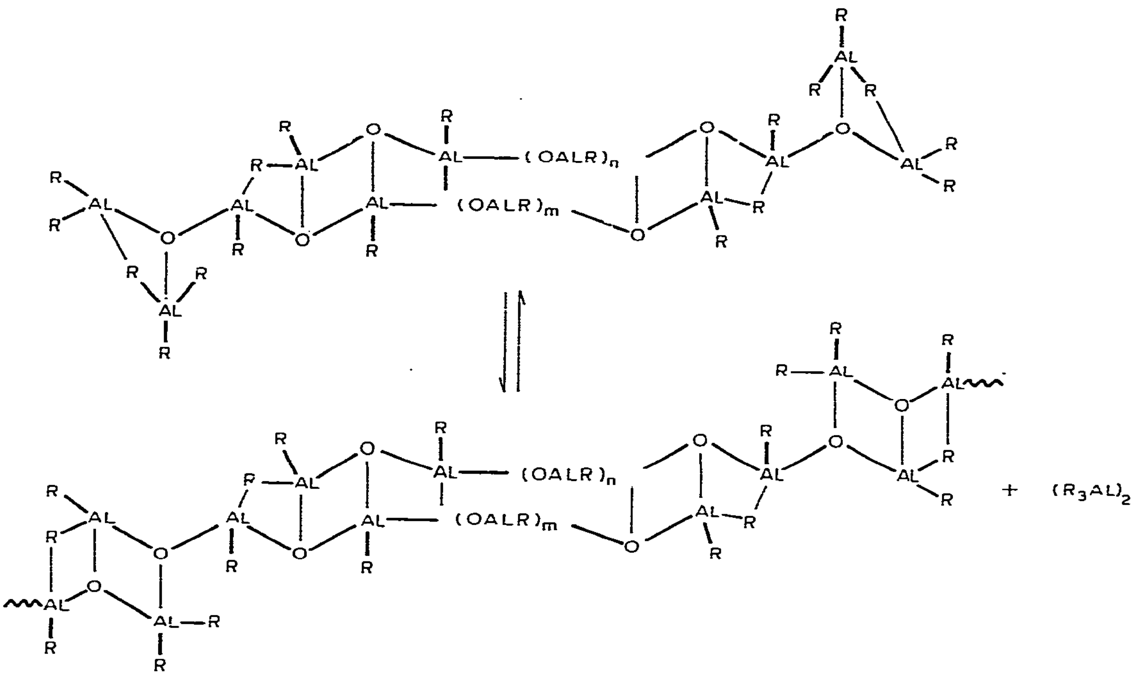

Fig. 1. Dynamic equilibrium in aluminoxane.

It should be pointed out that the dynamic equilibria present in aluminoxanes are still far from being understood fully, but it seems relevant to note an analogy with the well-known Schlenk equilibrium in organomagnesium compounds [6].

$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg \cdot MgX_2 \qquad (10)$$

Finally, the solubility of oligoaluminoxanes in Lewis acids allows the use of oligoaluminoxanes II or III as an active component or carrier of Ziegler—Natta type catalysts. Our preliminary results [7] reveal significant catalytic properties for the oligoaluminoxanes.

Details of the structures of the oligoaluminoxanes obtained and of the mechanism of reactions of Et_3Al with water will be published elsewhere.

Experimental

Synthesis of ethyloligoaluminoxane

To a solution of 2.89 g (25 mmol) of Et_3Al in 30 cm^3 of Et_2O, a solution of 0.45 g (25 mmol) of H_2O in 85 cm^3 of Et_2O was added dropwise at —70°C. The mixture was stirred and warmed slowly to room temperature. After complete literation of ethane the solvent was distilled off under reduced pressure. The residue was dried in vacuo to give a white amorphous powder insoluble in organic solvents. The amorphous nature of the product was confirmed by X-ray analysis. Similar results were obtained from the reaction between a toluene solution of Et_3Al and neat H_2O (Al/H_2O 1/1). The Al content of the product was 33.5—34.5%.

Reactions of ethyloligoaluminoxane with Lewis acids

(A) Ethyloligoaluminoxane—triethylaluminium complex. To the ethyloligoaluminoxane obtained as described above, an equimolar amount of neat Et_3Al (2.85 g) was added at room temperature. The mixture was warmed up slightly, and the white powder dissolved after about 24 h with evolution of a small amount of ethane. The ^1H NMR, IR spectra, molecular weight and elemental analysis of the obtained oily liquid product were identical to those for tetraethylaluminoxane Et_4Al_2O [1—3].

(B) Ethyloligoaluminoxane—trimethylaluminium complex. To the ethyloligoaluminoxane obtained as above, 1.8 g (25 mmol) of Me_3Al was added without solvent at room temperature. The mixture was warmed up and the white powder dissolved after several hours with evolution of CH_4. The product was a dense, colourless, opalescent liquid. The ^1H NMR spectrum in PhH τ (ppm) = 2.73—8.88 (CH_3) very broad triplet, 9.88 (CH_2) quartet and 10.28 (CH_3) singlet. Nearly 25 mmol of Me_3Al could be distilled off reversibly from the product. The distillate showed no traces of the ethyl groups.

(C) Ethyloligoaluminoxane—trifluoroboron complex. To the ethyloligoaluminoxane an equimolar amount of $BF_3 \cdot OMe_2$ was added (Al/B 1/1) without solvent at room temperature. The mixture warmed up to about 70° C and the powder was dissolved immediately. The liberated gas was identified chromatographically as Me_2O. Gaseous BF_3 evolved slowly at room temperature from the obtained ethyloligoaluminoxane—trifluoroboron complex during several hours. After complete liberation of BF_3 a white powder, containing no boron was left.

Reaction of ethyloligoaluminoxane—triethylaluminium complex with benzonitrile

To the 2.32 g of ethyloligoaluminoxane—triethylaluminium complex in 10 cm^3 of cyclopentane, 1.28 g of benzonitrile was added at —20° C (Al/PhCN 2/1). The mixture was slowly warmed to room temperature and the solvent was distilled off under reduced pressure. The physical, chemical, and spectroscopic properties of the product were identical with those reported for the tetraethylaluminoxane—benzonitrile complex ($Et_4Al_2O \cdot PhCN$) [3b].

All experiments were carried out under purified nitrogen. The reactants and solvents were deoxygenated and dried before use.

References

1 G.B. Sakharovskaya, N.N. Korneev, A.F. Popov, E.I. Larikov and A.F. Zhigach, Zh. Obshch. Khim., 34 (1964) 3435.

2 A. Storr, K. Jones and A.W. Laubengayer, J. Am. Chem. Soc., 90 (1968) 3173.

3 (a) M. Bolesławski, S. Pasynkiewicz, A. Kunicki and J. Serwatowski, J. Organometal. Chem., 116 (1976) 285; (b) A. Kunicki, J. Serwatowski, S. Pasynkiewicz and M. Boleslawski, ibid., 128 (1977) 21; (c) M. Bolesławski, J. Serwatowski and S. Pasynkiewicz, ibid., 161 (1978) 279; (d) A. Pietrzykowski, S. Pasynkiewicz and A. Wolińska, ibid., 201 (1980) 90; (e) A. Piotrowski, A. Kunicki and S. Pasynkiewicz, ibid., 153 (1978) 123; (f) A. Piotrowski, A. Kunicki and S. Pasynkiewicz, ibid., 186 (1980) 185; (g) A. Piotrowski, A. Kunicki and S. Pasynkiewicz, ibid., 201 (1980) 105.

4 S. Amdurski, C. Eden and H. Feilchenfeld, Inorg. Nucl. Chem., 23 (1961) 133.

5 A. Wolińska, J. Chem. Soc. Chemical Communications, submitted.

6 J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, McGraw-Hill, 1968.

7 A. Wasilewski and A. Wolińska, to be published.