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COMPLEXES OF BIS(CHLOROMETHYL)ALUMOXANE WITH ETHYL ETHER AND BENZONITRILE

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Summary

The partial hydrolysis of dimethylaluminium chloride—ethyl ether and —benzonitrile complexes which gives complexes of bis(chloromethyl)alumoxane with ethyl ether and benzonitrile has been studied. A structure is suggested for bis(chloromethyl)alumoxane on the basis of molecular weight, and IR and NMR spectral studies.

Introduction

The positive effect of small amounts of water in certain catalyzed polymerizations of systems containing organoaluminium compounds had already been observed in the 1960's [1]; however, it was not until the studies of Amdurski, Majdik and Sakharovskaya [2 - 4] had been published that interests in the chemistry of alkylaluminium oxides began to grow steadily. The subject of the studies of Amdurski et al. was the hydrolysis of members of the series $R_{3-n}AlX_n$ (R = Et, Pr, Bu, i-Bu; n = 0, 1). However, data concerning the hydrolysis of methylaluminium compounds only have been described in our earlier studies [5,6].

The present investigation is concerned with the partial hydrolysis of complexes of dimethylaluminium chloride with ethyl ether and benzonitrile.

Results and discussion

The dimethylaluminium chloride—ethyl ether complex in ethyl ether was found to react with water to give methane according to eqn. (1). This reaction was carried out according to the procedure described by Sakharovskaya [7].

$$2(CH_3)_2AlCl\cdot(C_2H_5)_2O + H_2O \xrightarrow{(C_2H_5)_2O} (CH_3AlCl)_2O\cdot(C_2H_5)_2O + 2CH_4 + (C_2H_5)_2O \qquad (1)$$

The reaction mixture was filtered and the solvent evaporated in vacuo, leaving a colourless, highly viscous liquid. During the reaction 4.180 ml of methane was evolved (calcd.: 4.480 ml). Analysis of the resulting complex bis(chloromethyl)alumoxane—ethyl ether is consistent with that expected. (Found: CH_3, 11.2; Al, 22.5; Cl, 27.7. $(MeAlCl)_2O{\cdot}OEt_2$ calcd.: CH_3, 12.2; Al, 22.5; Cl, 28.9%.)

The ethyl ether in the complex could not be displaced even after many hours of heating under vacuum (50°/0.6 mmHg, 50 h).

IR spectral studies on the complex revealed vibrations at ν 808 s and 750 - 770 m(br) cm^{-1} indicative of Al—O—Al bonds. Storr has attributed the 780 - 812 vs(br) and the 755 - 770 cm^{-1} bands in $(Et_2Al)_2O$ and $(EtAlCl)_2O$ to the Al—O—Al vibrations [8]. The original organoaluminium compounds used in this study exhibited no such bands.

Figure 1 presents a comparison of the chemical shifts of corresponding protons in the NMR spectra of dimethylaluminium chloride, ethyl ether, and the ethyl ether complexes of dimethylaluminium chloride and bis(chloromethyl)alumoxane.

The NMR spectrum of the bis(chloromethyl)alumoxane—ethyl ether complex exhibits two bands attributable to the aluminium-methyl group (τ 10.03, 10.32 ppm) and bands attributable to the methyl and methylene groups of the complexed ethyl ether (τ 6.33, 9.10 ppm). Integration of the spectrum is consistent with the ratio of the protons: $C\underline{H}_3{-}Al/(C\underline{H}_3CH_2)_2O/(CH_3C\underline{H}_2)_2O$, 3/3/2.

Cryoscopic molecular weight determinations indicated that the complex is considerably associated in benzene (n = 1.7 - 1.9) (mol.wt. found: 419, 470. $(MeAlCl)_2O{\cdot}OEt_2$ mol.wt., calcd.: 245).

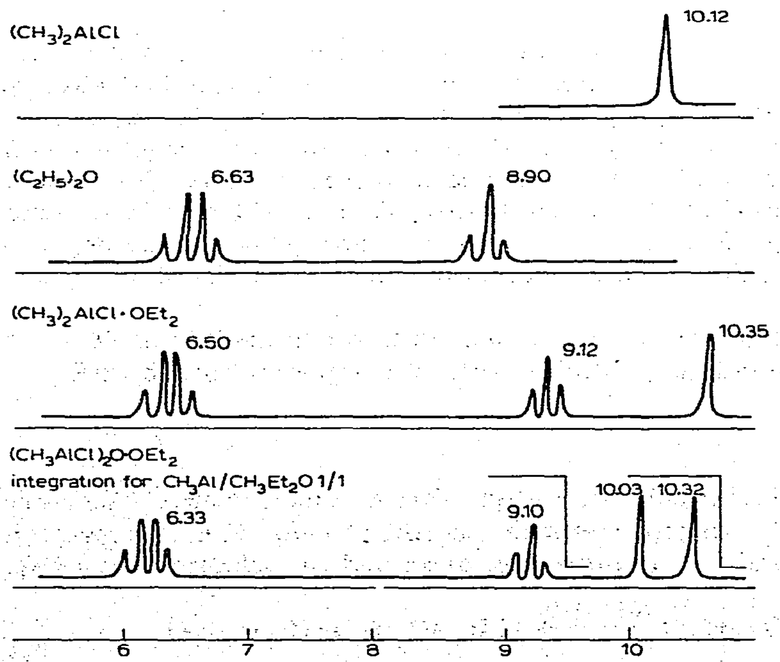
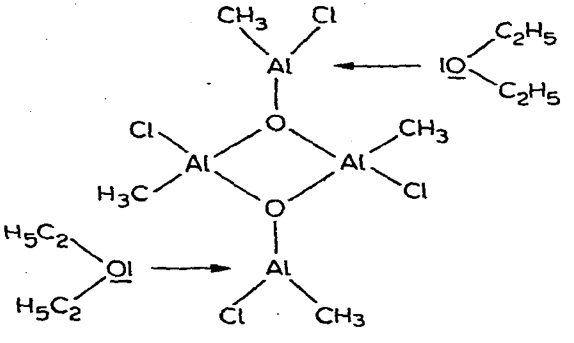


Fig. 1. Comparison of NMR spectra recorded at room temperature. (Toluene as internal standard at τ 7.66 ppm.)

The spectroscopic and cryoscopic studies lead us to suggest the dimeric structure (I) for the bis(chloromethyl)alumoxane—ethyl ether complex. In the



(I)

structure postulated each aluminium atom has a coordination number of 4, and the molecular ratio of the different methyl groups bonded to the aluminium atom is 1/1, in agreement with the NMR data.

Heating the $(CH_3AlCl)_2O\cdot Et_2O$ complex with excess benzonitrile, followed by prolonged evaporation in vacuo, results in complete displacement of ethyl ether from the molecule according to eqn. (2). The NMR spectrum of the

$$(CH_3AlCl)_2O\cdot(C_2H_5)_2O \xrightarrow[50^\circ]{C_6H_5CN} (CH_3AlCl)_2O\cdot 2C_6H_5CN + (C_2H_5)_2O \tag{2}$$

resulting complex exhibits no ethyl group, thereby supporting complete displacement of the ligand. (Found: CH_3, 6.60; Al, 14.45; Cl, 18.13. $(CH_3AlCl)_2O\cdot 2C_6H_5CN$ calcd.: CH_3, 7.90; Al, 14.30; Cl, 18.83%).

The complex bis(chloromethyl)alumoxane—benzonitrile was also obtained by hydrolyzing the complex of dimethylaluminium chloride and benzonitrile (eqn. 3). (Analysis found: CH_3, 7.15; Al, 13.9; Cl, 18.85. $(CH_3AlCl)_2O\cdot 2C_6H_5CN$ calcd.: CH_3, 7.90; Al, 14.30; Cl, 18.83%.)

$$2(CH_3)_2AlCl\cdot C_6H_5CN + H_2O \xrightarrow{C_6H_6} (CH_3AlCl)_2O\cdot 2C_6H_5CN + 2CH_4 \tag{3}$$

Sakharovskaya [7] has observed the formation of donor - acceptor complexes of bis(diethyl)alumoxane and ethyl ether $[(Et_2Al)_2O\cdot OEt_2]$, and Storr [8] has described the complex with trimethylamine $[(Et_2Al)_2O\cdot NMe_3]$.

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