

PROTON MAGNETIC RESONANCE EVIDENCE FOR THE DIMETHYLALUMINIUM HYDROXIDE

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Summary

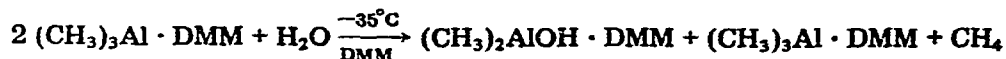
The reaction of trimethylaluminium with water has been studied. It was carried out in ethereal solvents with a 2 : 1 mol ratio of reactants. The resonance of protons of the hydroxyl groups bonded to aluminium was observed. On the basis of the properties of hydrogen bonding the structures of complexes between dimethylaluminiumhydroxide and the solvent have been proposed.

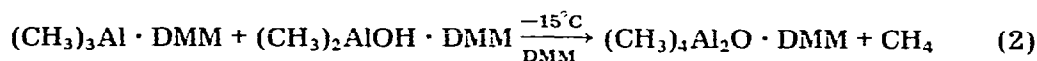
Introduction

The controlled reactions of organoaluminium compounds with water (mol ratio 2 : 1) lead to the formation of aluminoxanes, compounds containing the $\text{>AlOAl}<$ linkage and very probably proceed via an intermediate unstable organoaluminium molecule containing a hydroxyl group.

In the literature we can find only a few papers reporting the presence of hydroxyl groups in the final reaction product. Amdurski et al. [1], on the basis of the stoichiometry and kinetics of the reaction between Et_3Al and H_2O (1 : 1) postulate the presence of hydroxyl groups bonded to aluminium. Such a possibility is confirmed by Ueshima's et al. [2] radioactivity measurements of the $\text{Et}_3\text{Al}/\text{T}_2\text{O}$ reaction product. Ueyama et al. [3] even observed a weak resonance of the hydroxyl protons ($\tau \sim 6$ ppm) in the PMR spectra of the product of the $i\text{-Bu}_3\text{Al}/\text{H}_2\text{O}$ reaction (2 : 1). However the intermediate stage of the hydrolysis was not the object of these previous investigations.

While studying the reaction of Me_3Al with H_2O (mol ratio 2 : 1) in dimethoxymethane (DMM) at -35°C we observed a two-step reaction. At -35°C about 1/2 of the stoichiometric amount of methane was evolved. The rest of methane evolved above -15°C . The two-step course of the reaction can be presented by eq. 1 and 2.





When trimethylaluminium is not present in the medium of reaction 2, the Me_2AlOH molecules react with each other to form polyaluminumoxanes.

Results and discussion

In order to establish dimethylaluminiumhydroxide as the intermediate in the hydrolysis of trimethylaluminium, comparative PMR studies were carried out.

In the spectra of the reaction mixture (eq. 1) at -45°C resonance signals at τ 2.0 and 3.6 ppm appeared. They were not present in the spectrum of the $\text{Me}_3\text{Al} \cdot \text{DMM}$ solution in dimethoxymethane and the $\text{H}_2\text{O} \cdot \text{DMM}$ solution gave an OH resonance signal at τ 7.0 ppm. The ratio of the summarized intensity of signals at 2.0 and 3.6 ppm (Fig. 1a) to the intensity of the CH_3Al signal (10.9 ppm) was about 1 : 15.



Fig. 1. PMR spectra of the products of the $\text{Me}_3\text{Al}/\text{H}_2\text{O}$ reaction: a, Spectrum of the products mixture of the first step of hydrolysis carried out in DMM (eq. 1); τ 2.0, OH; 3.6, OH; 8.6, cyclohexane; 9.8, CH_4 ; 10.9 ppm, Al-CH_3 . b, Spectrum of the hydrolysis final products; τ 8.6, cyclohexane; 10.8 ppm, $\text{CH}_3\text{-Al}$. c, Spectrum of the products mixture of the first step of hydrolysis carried out in ethyl ether; τ 1.7, OH; 8.6, cyclohexane; 11.0 ppm, $\text{CH}_3\text{-Al}$.

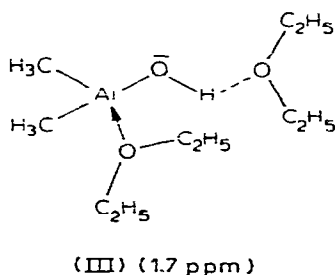
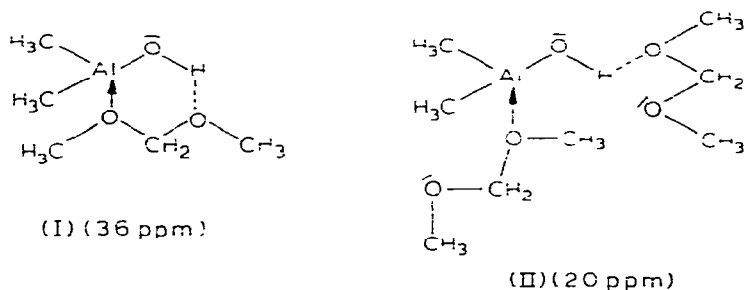
* Solvent, dimethoxymethane; temp. -45°C ; cyclohexane was used as the internal standard of concentrations and τ scale.

** Solvent, diethyl ether; temp. -40°C ; cyclohexane as the internal standard.

$(I(2.0) + I(3.6))/I(10.9) = 8/122$. After heating the PMR sample to room temperature methane evolved. In a repeated spectrum of the previously heated sample at -45°C (Fig. 1b) disappearance of the signals at τ 2.0 and 3.6 ppm was observed. Additionally, in spectrum b the intensity of the CH_3Al signal at τ 10.8 ppm decreased in comparison to that in spectrum a. $I(10.8) = 96$; $I(10.9) = 122$. The ratio of the sum of intensities of the τ 2.0 and 3.6 ppm signals to the difference of intensities of the CH_3Al signals in spectra a and b is about 1 : 3. $(I(2.0) + I(3.6))/(I(10.9) - I(10.8)) = 8/26$. This ratio is consistent with the stoichiometry of eq. 2. Therefore, the signals at τ 2.0 and 3.6 ppm can be attributed to the resonance of protons of the hydroxyl groups bonded to aluminium.

In analogous PMR spectra for the deuterolysis reaction ($\text{Me}_3\text{Al}/\text{D}_2\text{O}$) the signals at τ 2.0 and 3.6 ppm were not observed at all, while the signals of CH_3Al , after heating the sample, reduced their intensity as in the previous case ($\text{Me}_3\text{Al}/\text{H}_2\text{O}$).

The pair of resonance signals of the hydroxyl group in the PMR spectra can be explained by the existence of two forms (I and II) of the complex between dimethylaluminiumhydroxide and dimethoxymethane, differing in the kind of hydrogen bonding. The assignment of signals is based on an inversely proportional relation between the value of chemical shift (τ scale) of the hydrogen bonded hydroxyl group and the strength of this bond. The strength of hydrogen bond should depend in the first place on the basicity of the etheral oxygen [4].



In form I the participation of the oxygen of dimethoxymethane in the donor-acceptor bond significantly decreases the basicity of the second oxygen atom, which takes part in the hydrogen bond. Form II should therefore contain a stronger hydrogen bond.

These conclusions were supported by results of the trimethylaluminium hydroxol-

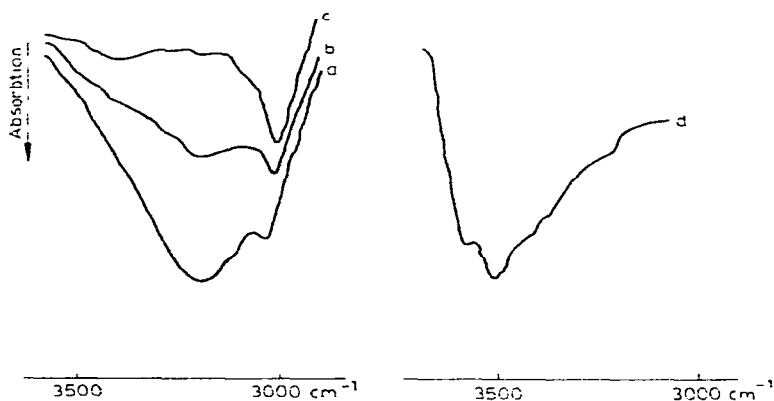


Fig. 2. IR OH Stretching vibration region: a, 70% of the expected volume of methane evolved in the course of hydrolysis; b, 90%, c, 100%, d, absorption of water. Solvent, diethyl ether; conc. 0.2 M, l 0.1 mm.

ysis performed in diethyl ether. In the low-temperature PMR, spectrum c, only one resonance signal of the hydroxyl proton at about 1.7 ppm was observed. It corresponds to form III. Diethyl ether cannot form an intramolecular hydrogen bond. And since dimethoxymethane can be removed from the complex $\text{Me}_3\text{Al} \cdot \text{DMM}$ by treating with diethyl ether, the latter is slightly more basic than dimethoxymethane.

The hydroxyl groups bonded to aluminium have also been observed using IR spectroscopy. The spectra of the reaction mixture $\text{Me}_3\text{Al}/\text{H}_2\text{O}$ (2 : 1, diethyl ether as a solvent, second step of the reaction) exhibited the strong and broad absorption band at 3180 cm^{-1} . The intensity of this band diminished during the course of hydrolysis, (Fig. 2: a, b, c). Water in a similar concentration in diethyl ether absorbed at 3510 cm^{-1} (Fig. 2d).

Experimental

All operations were carried out under a blanket of purified nitrogen. Trimethylaluminium was distilled prior to use through a glass helix packed column. The ethers and cyclohexane were distilled from sodium and then over a potassium phenolphthalein ketyl. Redistilled water was used.

(i) dimethylaluminiumhydroxide/dimethoxymethane

0.20 g of H_2O (11 mmol) dissolved in 15 ml of dimethoxymethane was added during 40 min to a cooled (-35°C) and vigorously stirred mixture of 1.58 g of Me_3Al (22 mmol) in 25 ml dimethoxymethane and 1 ml of cyclohexane. When about 250 ml of methane (11 mmol) had evolved, a sample of the mixture was taken into an NMR tube placed in a liquid nitrogen.

(ii) dimethylaluminiumhydroxide/diethyl ether

0.16 g of H_2O (9 mmol) dissolved in 30 ml of ethyl ether was added during 1 h to a cooled (-25°C) mixture of 1.26 g of Me_3Al in 10 ml of ethyl ether and 1 ml

of cyclohexane. When about 190 ml of methane (9 mmol) had evolved, a sample was collected as in previous case.

A JEOL-JNH-100 MHz spectrometer was used for recording PMR spectra at reaction conditions given under Fig. 1. IR spectra were recorded with Perkin-Elmer 527 apparatus.

References

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