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INVESTIGATIONS OF THE HYDROLYSIS REACTION MECHANISM OF ORGANOALUMINIUM COMPOUNDS. ^{1}H NMR SPECTROSCOPIC STUDIES ON THE R_3Al/H_2O REACTION IN POLAR SOLVENTS

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Summary

The hydrolysis of R_3Al (R = Me, Et, i-Bu) in diethyl ether as a solvent was investigated. The molar ratios of the reagents R_3Al and H_2O were 1 : 1 and 2 : 1, the temperature range −70 to 0°C. The reaction course was followed by ^{1}H NMR spectroscopy.

A several step reaction course was found: in the first step a 1 : 1 complex of R_3Al with H_2O is formed. This complex undergoes intramolecular rearrangement to give dialkylaluminium hydroxide, R_2AlOH. In the next step R_2AlOH forms stable autoassociates (in 1 : 1 systems) or reacts with the excess of R_3Al to give aluminoxanes (in 2 : 1 systems). The selectivity of the whole reaction (in 2 : 1 systems) depends on the stability of the autoassociated dialkylaluminium hydroxide and on the relative rates of the reaction steps.

The main products of the hydrolysis reaction in 2 : 1 systems are alkylaluminoxanes, and in the 1 : 1 systems dialkylaluminium hydroxides. All the intermediates, the starting materials and the final products of the reaction are complexed by diethyl ether, which forms donor-acceptor complexes with hydrogen bondings. This complexation decreases the reaction rate and allows observation of the reaction steps by ^{1}H NMR spectroscopy.

Introduction

Although several methods of controlled hydrolysis of orgaoaluminiums are known, the mechanism of the reaction is not elucidated. Sakharovskaya [1] has proposed a two-step reaction course in which the dialkylaluminium hydroxide is the relevant intermediate:

$$R_3Al + H_2O \rightarrow R_2AlOH + RH$$

$$R_2AlOH + R_3Al \rightarrow R_2AlOAlR_2 + RH$$

Other results confirm the existence of dialkylaluminium hydroxide. Amdurski [2] on the basis of stoichiometry and kinetics of the Et_3Al hydrolysis reaction (1 : 1) has postulated the presence of a hydroxyl group in the final product. Such a possibility was confirmed by radioisotopic investigations of the Et_3Al/T_2O system [3]. Ueyama [4] has even observed the weak resonance signal of the hydroxyl group protons ($\tau = 6$ ppm) in the ^1H NMR spectrum of the products of the reaction of i-Bu_3Al with H_2O (2 : 1). We have also found the dialkylaluminium hydroxide as the intermediate product of the hydrolysis reaction of Me_3Al in dimethoxy methane [5] by IR and NMR. Petrova et al. [6,7] have limited their investigations to the analysis of complex formation between Et_2AlCl and $EtAlCl_2$ with water. The purpose of this study was to elucidate the mechanism of the hydrolysis of R_3Al by ^1H NMR spectroscopy.

Results and discussion

The hydrolysis of R_3Al compounds in the 1 : 1 and 2 : 1 systems was investigated by ^1H NMR spectroscopy in the temperature range −70 to 0°C. Spectra were collected in the six series shown in Figs. 1–6. Each figure shows the changes in the spectrum with the change of temperature.

The hydrolysis of organoaluminium compounds takes place in several steps. The first step is complex formation between R_3Al and water; it does not depend on the Al : H_2O molar ratio.

The complex formation can be described as follows:

$$R_3Al\cdot OEt_2 + H_2O\cdot xOEt_2 \xrightarrow{OEt_2} R_3Al\cdot OH_2\cdot yOEt_2 \tag{1}$$

Evidence for the existence of such a complex is the complete disappearance of crystalline water phase at −70°C when added to the R_3Al solution in ether. Apart from this, the chemical shift of water protons (complexed by R_3Al) differs from that of uncomplexed water (about $\tau = 2$ for complexed to $\tau = 7.50$ for uncomplexed water) *.

$R_3Al + H_2O$, 1 : 1 systems

The first step of the reaction between R_3Al etherate with water is the exchange reaction (1). Complex I is stable at low temperatures (below about −45°C) and it is possible to observe it in ^1H NMR spectra (Figs. 1–3, −70°C). The stability of complex I at low temperature could be explained by the influence of ether, which

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* The formation of complex I is striking, because of the differences in donor number (DN) of diethyl ether and water: 19.2 and 18.0, respectively [8–10]. These numbers are the negative values of the enthalpy of the complex formation with $SbCl_5$ in the diluted solution of 1,2-dichloroethane. In the presence of a great excess of ether the complex of R_3Al with water should form at least in only very low concentrations. Similar disagreements with the DN scale in relation to $SbCl_5$ were observed in the case of the benzonitrile-diethyl ether competition during complex formation with trimethylchloroaluminoxane [11]. The benzonitrile-aluminoxane complex was found in the solution of diethyl ether, although the DN values are 11.9 and 19.2, respectively. Also the enthalpy of complex formation between trimethylaluminium with benzonitrile (in heptane) and with diethyl ether (in hexane) equal to −25.4 and −20.2 kcal/mol, respectively [12]. The conclusion is, that the DN scale in relation to $SbCl_5$ cannot be apply to predict the complex formation between the organoaluminium compounds and electron donors.

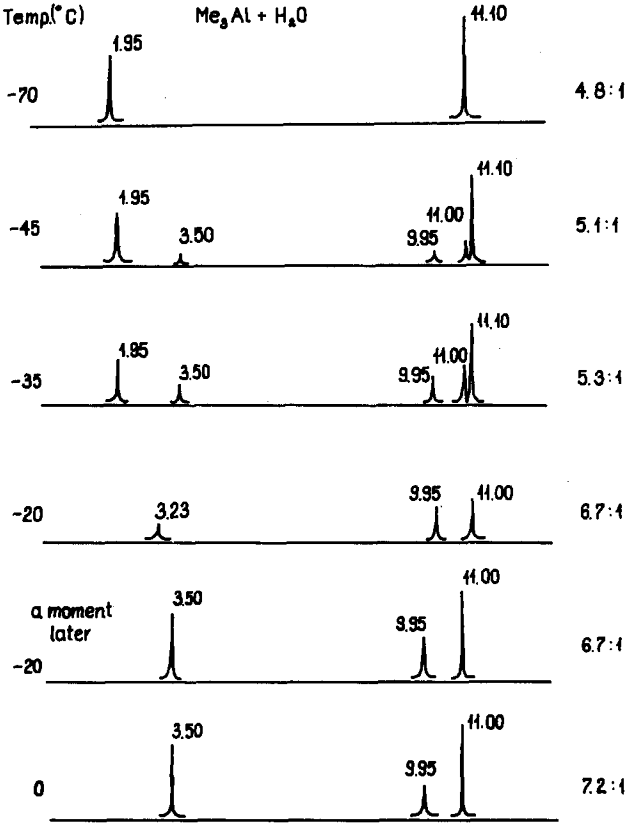
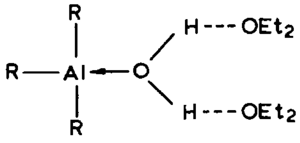


Fig. 1. PMR spectra of protons of CH_3Al, OH and CH_4 in the reaction of Me_3Al with H_2O in diethyl ether. The signals of ether protons are omitted.

forms most probably hydrogen bonds with water protons (the number of ether molecules bonded to water protons is unknown):



(Ia, R = CH_3 ;
Ib, R = C_2H_5 ;
Ic, R = i-C_4H_9)

The integration of the corresponding spectra confirms the existence of I at −70°C (Ia: $Al–CH_3/OH_2 = 9.6:2$, theor: $9:2$; Ib: $Al–CH_2/OH_2 = 6.4:2$, theor: $6:2$; Ic: $6.0:2$, theor: $6:2$).

In complex I a partial negative charge occurs on the Al atom and a partial positive charge on the H atom. As a result of reaction 2 the alkane and diethylaluminium hydroxide are formed.

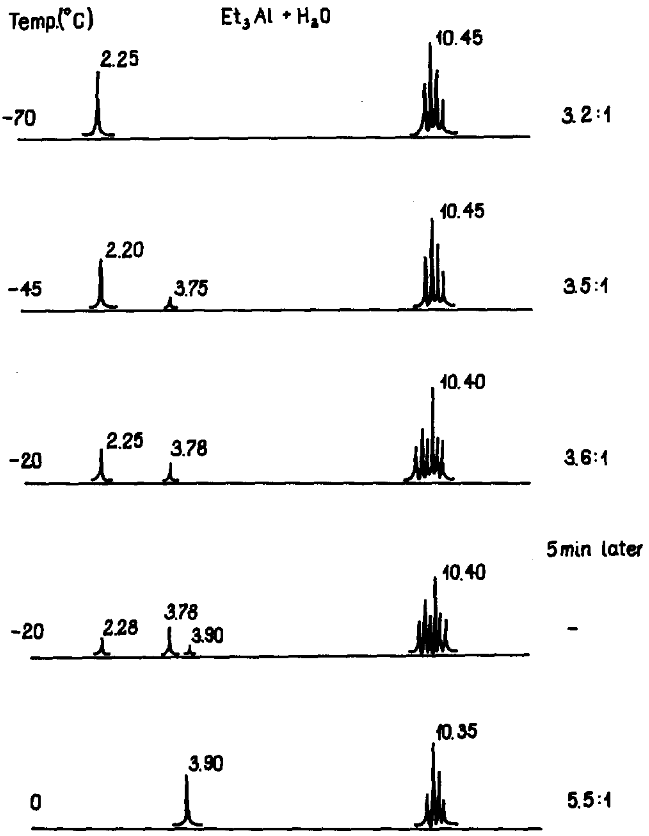
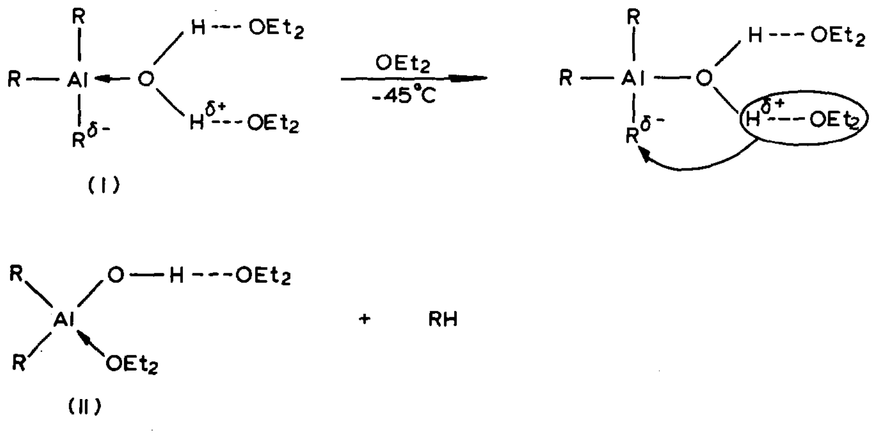


Fig. 2. PMR spectra of protons of CH_2Al and OH in the reaction of Et_3Al with H_2O in diethyl ether. The signals of ether protons are omitted.



(2)

Dialkylaluminium hydroxide should be stabilized by autoassociation [13], probably to form a dimer (III):

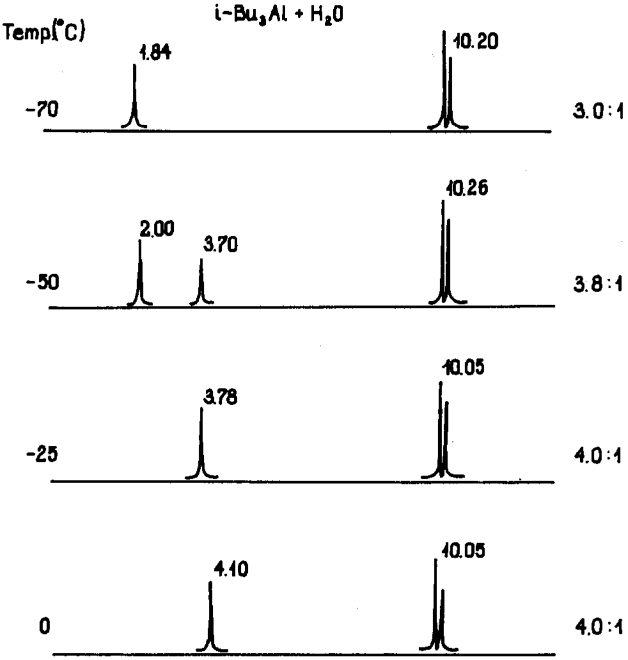
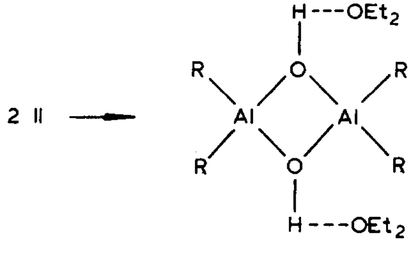


Fig. 3. PMR spectra of protons of CH_2Al and OH in the reaction of i-Bu_3Al with H_2O in diethyl ether. The signals of ether protons are omitted.



(III)

(3)

The proposed reaction (eq. 1–3) is based on the ^1H NMR spectra (Figs. 1–3). The elimination of methane (Fig. 1) in the reaction of $Me_3Al/H_2O = 1:1$ begins at −45°C. Besides the signal of the methane protons ($\tau = 9.95$) the signal of the hydroxyl group protons in IIIa ($\tau = 3.50$) and the corresponding signal of the aluminium-bonded methyl group protons in IIIa ($\tau = 11.00$) appear. With increasing temperature the intensity of the signal $\tau = 3.50$ increases and the intensity of water protons signal in Ia ($\tau = 1.95$) decreases. Simultaneously, the intensity of the signal of CH_3-Al protons in IIIa ($\tau = 11.00$) increases and the intensity of CH_3–Al protons signal in Ia ($\tau = 11.10$) decreases. At −20°C the signal ($\tau = 1.95$) disappears very quickly. At that temperature, after a short time, one broad signal at $\tau = 3.23$ appears. At that moment is present in the reaction mixture only the dimethylaluminium hydroxide (the signal of Ia protons: τ 1.95 and 11.10 are not observed in the spectrum). The nature of the signal at $\tau = 3.23$ suggest rapid hydroxyl proton exchange between IIa and IIIa. After a short time only signals at $\tau = 3.50$ and 11.00 remain (with ratio of protons 6.7 : 1). The signals correspond to the stable structure IIIa (theor: 6 : 1). A similar reaction course can be observed in the $Et_3Al/H_2O = 1:1$ system. The reaction begins at −45°C: at −45°C a signal at $\tau = 3.75$ appears, which corresponds to the hydroxyl group protons in IIb. The intensity of this signal increases rapidly with increasing temperature. At −20°C three signals corresponding to protons bonded to oxygen in compounds Ib ($\tau = 2.25$), IIb ($\tau = 3.78$) and IIIb ($\tau = 3.90$) occur. At 0°C only one sharp signal of hydroxyl group protons at $\tau = 3.90$ and methylene group protons signal (Al–CH_2; quartet $\tau = 10.35$) are observed.

The reaction in $i\text{-}Bu_3Al/H_2O = 1:1$ system is shown in Fig. 3. The reaction begins at −50°C and is completed at −25°C. At that temperature the signal $\tau = 2.00$ attributed to water protons in Ic disappears. Also one signal of hydroxyl group protons ($\tau = 3.78$) and the doublet of Al–CH_2 protons in IIc are present. The molar ratio of these protons proves that the reaction is completed (Al–CH_2-/OH = 4 : 1, theor. 4 : 1). In the range of −25 to 0°C the etherate diisobutylaluminium hydroxide stabilizes by autoassociation. In the stable autoassociated form the hydroxyl group protons signal appears at $\tau = 4.10$ (IIIc).

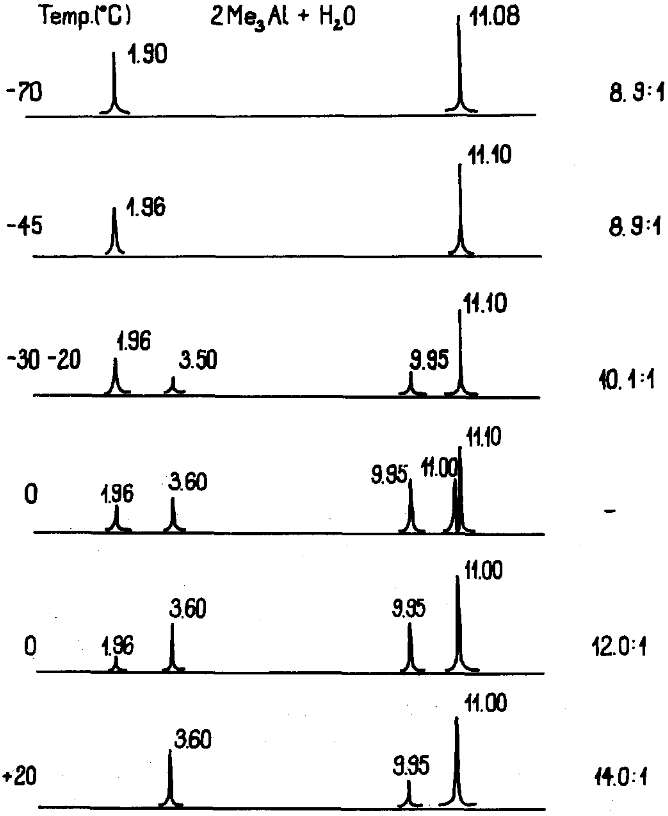


Fig. 4. PMR spectra of protons of CH_3Al, OH and CH_4 in the reaction of $2Me_3Al$ with H_2O in diethyl ether. The signals of ether protons are omitted.

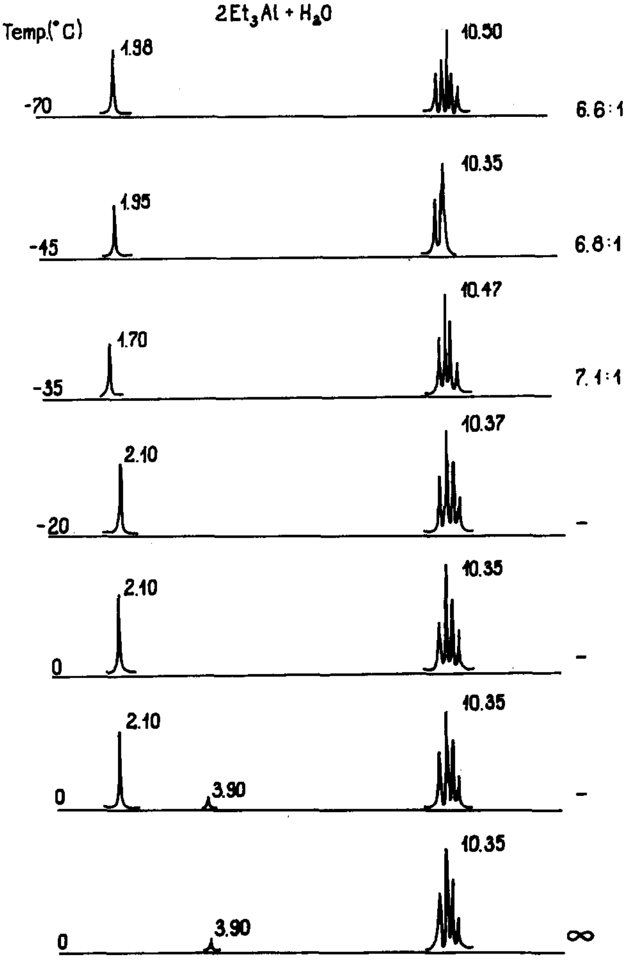


Fig. 5. PMR spectra of protons of CH_2Al and OH in the reaction of $2Et_3Al$ with H_2O in diethyl ether. The signals of ether protons are omitted.

The observed differences in the chemical shifts of hydroxyl group protons in the stable autoassociates (IIIa, IIIb and IIIc: τ 3.50, 3.90, 4.10, respectively) could be explained by the shift of the equilibrium of hydrogen bonding between Al–OH protons and ether. The increasing steric hindrance in the series Me, Et, i-Bu decreases the possibility of hydrogen bonding in these systems. Also the comparison of the transformation process II → III in the investigated trialkylaluminiums series shows, that the relative rates of the autoassociation reaction (eq. 3) decrease with increasing bulkyness of the alkyl group attached to aluminium. These facts are of the great relevance in the reaction course in the 2 : 1 systems.

$R_3Al + H_2O$, 2 : 1 systems

The excess of R_3Al influences the reaction mechanism and the reaction products. The first step of the reaction (the formation of complex I) is similar to that of 1 : 1

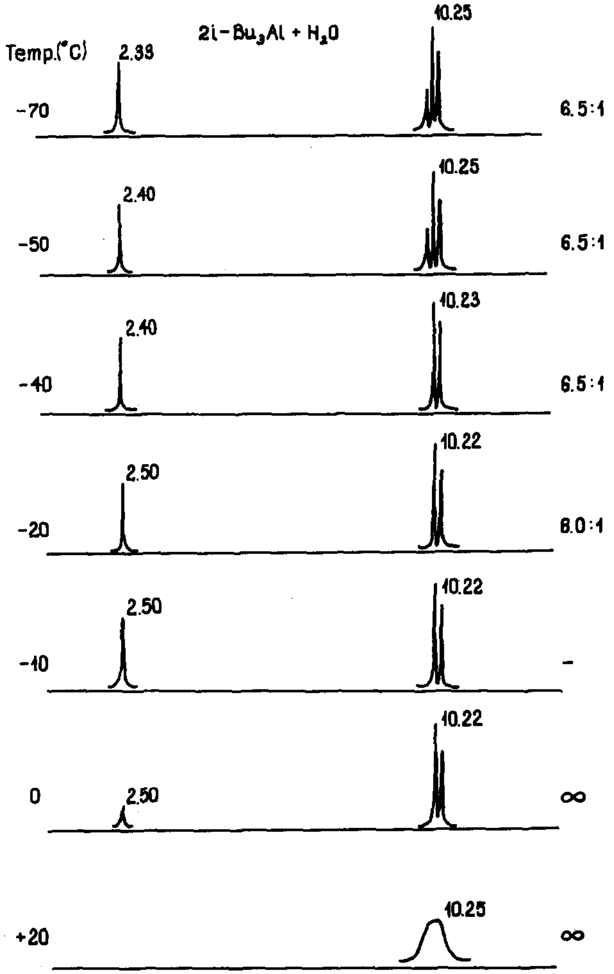
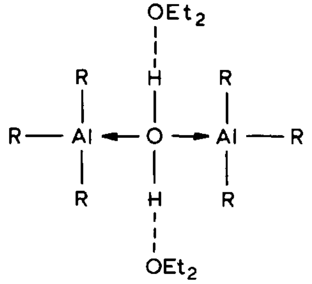


Fig. 6. PMR spectra of protons of CH_2Al and OH in the reaction of 2i-Bu_3Al with H_2O in diethyl ether. The signals of ether protons are omitted.

systems. However, the second step requires higher temperatures than −45°C. Not before −30 to −20°C (for Me_3Al) or about 0°C (for Et_3Al and i-Bu_3Al) are the first signals of hydroxyl protons bonded to aluminium observed in the spectra. The increasing activation energy of reaction 2 in the 2 : 1 systems is probably connected with a change in mechanism.

Both complex I and the etherate of trialkylaluminium ($R_3Al \cdot OEt_2$) exist in the reaction sphere. The ^1H NMR spectra show splitting of signals of the alkyl group protons: one group of signals attributable to the protons of the etherate alkyl group and another one of complex I (Figs. 4–6). At about −45°C this splitting disappears. Two simple hypothesis can be proposed based on the ^1H NMR results. Either complex I attaches the second R_3Al molecule to form the 2 : 1 type complex (IV) or a fast exchange between I and the etherate occurs (on the NMR time scale, reaction 4).



(IV)

(4)

$$R_3Al\cdot OH_2\cdot nOEt_2 + R_3Al\cdot OEt_2 \xrightleftharpoons[\text{exchange}]{\text{fast}} R_3Al\cdot OH_2\cdot nOEt_2 + R_3Al\cdot OEt_2$$

In both cases the aluminium–oxygen interaction is weaker in comparison to that in complex I. The weakness of the aluminium–oxygen interaction decreases the rate of evolution of alkane; hence a higher temperature is necessary for reaction 2 in 2 : 1 systems. Dialkylaluminium hydroxide (the product of reaction 2) is stabilized in 1 : 1 systems by autoassociation (eq. 3). In the case of Me_3Al this was the major reaction, connected probably with the high dimerization energy [13]. Both Et_3Al and i-Bu_3Al gave their hydroxyl derivatives, which were in equilibrium between their two forms (II and III). This fact influences the next reaction step in 2 : 1 systems.

In the ^1H NMR spectra of the $Me_3Al/H_2O = 2:1$ system, in the range -30 to -20°C, disappearance of the signal at $\tau = 1{,}96$ attributable to the water protons in the complex Ia and increasing signal at $\tau = 3.60$ attributable to the hydroxyl group protons in the complex IIIa is observed (Fig. 4). The simultaneous changes in the intensities of the signals at $\tau = 3.60$ and 11.10 (the latter is attributable to the aluminium-attached methyl group) prove the formation of dimethylaluminium hydroxide (8.9 : 1 at the beginning to 14 : 1 at the end, theor. 9 : 1 and 15 : 1, respectively). The inhibition of the last reaction step (eq. 5) proves the high stabilization of the Me_2AlOH autoassociate and the high activation energy of this reaction:

$$(R_2AlOH \cdots OEt_2)_n + nR_3Al\cdot OEt_2 \rightarrow nR_2AlOAlR_2\cdot OEt_2 + nRH \qquad (5)$$

In such a situation the selectivity of the whole reaction is very low, because of the parallel reactions of dimethylaluminium hydroxide itself.

In the case of Et_3Al and i-Bu_3Al in 2 : 1 systems, reaction 2 requires a temperature of about 0°C. At that temperature fast disappearance of the signal of water protons in complex I ($\tau = 2.10$ and 2.50 for Et_3Al and i-Bu_3Al, respectively) is observed. Practically no signals of hydroxyl protons in complexes II or III are seen in the spectra. This proves the higher rate of reaction 5 in comparison with that of reaction 3 for more bulky alkyl groups. The product of the second step of the reaction (R_2AlOH), reacts immediately with an excess of R_3Al without stabilization (autoassociation). As a result, high selectivity (regarding aluminoxane synthesis) can be expected in the 2 : 1 systems if R is larger than Me.

Conclusions

1) Dialkylaluminium hydroxide, as the intermediate product of the partial hydrol-

ysis of trialkylaluminiums, may be obtained in diethyl ether solution at low temperatures.

2) The rate of autoassociation of R_2AlOH depends on the aluminium-bonded alkyl group, and decreases in the series Me > Et > i-Bu.

3) The rates of autoassociation and the energies of oligomerization of R_2AlOH influence the selectivity of the hydrolysis reaction in 2 : 1 systems.

4) High selectivity for aluminoxane can be obtained in the systems where R is larger than Me.

Experimental

All the experiments were carried out in a purified nitrogen atmosphere. The reactants and solvent were deoxidized and dried before use.

Preparation of complexes

The reaction mixtures were prepared in a standard NMR tube. Small amounts of R_3Al (about 0.03 g) were weighed in the NMR tube and cooled to $-70°C$. Then, a saturated solution of water in diethyl ether (1.22 wt. % at room temperature) was slowly introduced into the tube with the aid of a Hamilton syringe in 1 : 1 or 2 : 1 molar ratios (R_3Al/H_2O). The mixture in the tube was mixed until a homogeneous. The tube was then cooled in liquid nitrogen before recording the NMR spectra. The spectra were recorded on a Jeol JNM-4H-100 apparatus at various temperatures. Cyclohexane was used as internal standard ($\tau = 8.60$).

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