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SYNTHESIS AND STRUCTURE OF ALKYLALUMINOXANES

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Summary

The structure of the compounds R_4Al_2O (where R = H or i-Bu) was studied. The occurrence of R groups bridging aluminium atoms (besides the known oxo bridges) is a characteristic feature of these arrangements. The relative stability of H, Me, Et and i-Bu bridges was compared. The influence of steric factors on the aluminoxane association is discussed. A novel technique developing the known hydrolysis method was employed in the preparation of the investigated systems.

Introduction

Although a few papers concerning the preparation and some chemical properties of pure alkylaluminoxanes have been published [1–6], little attention has been given to the structural studies of these compounds. Storr [2] has described the structure of tetraethylaluminoxane, suggesting a trimeric cyclic arrangement with oxygen bridging groups. Ueyama et al. [4] have found this aluminoxane to be a tetrameric aggregate and assigned the discrepancy to the dependence of the association on the concentration. The other workers have limited their investigations to molecular weight determinations to explain the structure of R_4Al_2O compounds. Thus, Et_4Al_2O was found also to be monomeric [1] or dimeric [6], and i-Bu_4Al_2O either to be varying between monomeric and dimeric [3] or dimeric [1,6]. The concentration dependence explanation of the association discrepancies seems to be reasonable; however, no one has investigated the influence of time on the degree of association. It is possible that the measured molecular weight varies also with the age of the aluminoxane solution as the most thermodynamically stable configuration is achieved.

Recently [7], we have described in detail the structure (I) of tetraethylaluminoxane. It was shown by cryoscopy that it exists as a trimer in benzene solution

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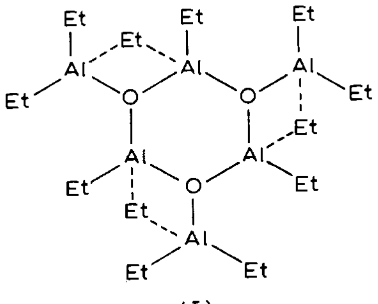
(measurements with time) at a given concentration. The low temperature PMR spectra showed the occurrence of bridging Et groups in aluminoxane. When two of the Et groups were replaced by Me ones, the latter occurred in the bridge, giving evidence of their relative stability in such a system.



(I)

The cyclic structure with oxygen bridges proposed for associated aluminoxanes was finally confirmed by the detection of ions bearing Al_3O_3 species in the mass spectrum of the triethylaluminium-water system [8]. The skeletal cyclic structures were assigned to these ions on the basis of their odd-even electron character.

The present investigations are concerned with the structure of isobutylaluminoxanes and with some synthetic aspects of alkylaluminoxanes.

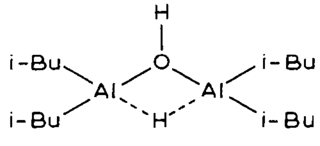
Results and discussion

Tetraisobutyl- and triisobutylhydroaluminoxanes were prepared according to equations 1 and 2 (see Experimental).

$$2\ \text{i-Bu}_3\text{Al} + H_2O \xrightarrow[-70\text{ to }110^\circ\text{C}]{\text{toluene}} \underset{\text{(II)}}{\text{i-Bu}_4\text{Al}_2\text{O}} + 2\ \text{i-BuH} \qquad (1)$$

$$2\ \text{i-Bu}_2\text{AlH} + H_2O \xrightarrow[-70\text{ to }110^\circ\text{C}]{\text{toluene}} \underset{\text{(III)}}{\text{i-Bu}_3\text{HAl}_2\text{O}} + H_2 + \text{i-BuH} \qquad (2)$$

The presence of hydrogen in the aluminoxane molecule III, (eq. 2) surprised us, because it would be expected (based on the relative reactivity of Al–R and Al–H bonds) that reaction 2 should give tetraisobutylaluminoxane. In our case (toluene as a solvent) the reaction proceeds via an intermediate species (IV [9], eq. 3).



(IV)

$$2\ \text{i-Bu}_2\text{AlH} + H_2O \xrightarrow[-70^\circ\text{C}]{\text{toluene}} \underset{\text{(IV)}}{\text{i-Bu}_2\text{AlOH}\cdot\text{i-Bu}_2\text{AlH}} + H_2 \qquad (3)$$

TABLE 1

INFRARED SPECTRA OF ISOBUTYLALUMINOXANES AND PARENT ISOBUTYLALUMINIUMS IN THE RANGE 2000–600 cm^{-1} [a]

$i\text{-}Bu_3Al$	$i\text{-}Bu_4Al_2O$	$i\text{-}Bu_2AlH$	$i\text{-}Bu_3HAl_2O$	Assignments
		1600–1900vs(br)	1600–1900vs(br)	ν(Al–H)
1465s	1465s	1465(sh)	1465s	$\delta_{as}(CH_3)$
1455(sh)	1455(sh)	1455s	1455s	
1396m	1398m	1400m	1399m	$\delta(CH_2\text{–}Al)$
1380s	1380s	1380s	1379s	$\delta_s(CH_3)$
1362s	1362s	1363s	1362s	
1320s	1320s	1320s	1320s	$\gamma,\tau(CH_2)$
		1260w (?)	1260w (?)	
1198(sh)	1200(sh)	1200m	1200(sh)	$\gamma,\tau(CH_2\text{–}Al)$
1182(sh)	1182s			
1173s		1175m	1182s	
1158m	1158m	1156s	1156m	
1064s	1065s	1063s	1062s	$\gamma,\tau(CH_2\text{–}Al)$
1011s	1011s	1005s	1005m	
953(sh)	953(sh)	955(sh)		ν(C–C)
943w	943w	941m	941m	
812m	815s	817s	817s	ν_s(C–C)
	750–780vs(br)		770–800vs(br)	ν(Al–O–Al)
680vs(br)	690vs(br)	700vs(br)	700vs(br)	ν(Al–C)
640s	650s	650s	650s	$\rho(CH_2)$

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

The elimination of isobutane from IV leads to the formation of triisobutylhydroaluminoxane (eq. 4).

$$\text{IV} \xrightarrow[-20 \text{ to } 110^\circ\text{C}]{\text{toluene}} \underset{\text{(III)}}{i\text{-}Bu_3HAl_2O} + i\text{-}BuH \qquad (4)$$

When reaction 2 was carried out in THF as a solvent [10] tetraisobutylaluminoxane (complexed by THF) was formed.

The products obtained (colourless and viscous) were characterized by IR and PMR spectral studies and cryoscopic molecular weight determinations. The IR spectral data of aluminoxanes are shown in Table 1. Table 1 lists also tentative assignments for the absorption bands observed. The spectra of aluminoxanes differ from those of the corresponding parent organoaluminiums in the region 750–800 cm^{-1}, which is characteristic of Al–O–Al linkage vibrations. In the spectrum of $i\text{-}Bu_3HAl_2O$ a strong, broad band in the region 1600–1900 cm^{-1} (attributable to the hydrogen-bridge bond of organoaluminium compounds [11]) is seen, indicating a structure with hydrogen bridges. Addition of tetrahydrofuran reduces this band to a sharper one at a frequency of 1780–1800 cm^{-1}, presumably by formation of a complex with aluminoxane. Diisobutylaluminium hydride displays a similar pattern of behaviour. The assignment of the remaining parts of the spectra follows directly from those of Hoffmann [12].

The room-temperature PMR spectrum of tetraisobutylaluminoxane (Table 2, Fig. 1b) consists of two multiplets with a proton ratio of 7 : 2 (theory 6 : 2), the nonet

TABLE 2

PMR SPECTRA OF ISOBUTYLALUMINOXANES IN COMPARISON WITH THE PARENT ISOBUTYL ALUMINIUMS, RECORDED AT VARIOUS TEMPERATURES [a]

Compound	Temp. (°C)	Solvent	PMR resonances			
			CH_3	CH_2	δ(i-Bu) (ppm)	Al–H (ppm)
i-Bu_3Al	25	toluene	8.74d	9.47d	0.73	–
	–70	toluene	8.62d	9.39d	0.77	–
i-Bu_4Al_2O	25	toluene	8.63d 8.56br	9.51d 9.31br	0.88	–
	–70	toluene	8.59d 8.54br	9.51d 9.30br	0.92	–
	25	benzene	8.70d 8.63br	9.62d 9.41br	0.88	–
	70	benzene	8.69d 8.61br	9.60d 9.40br	0.91	–
i-Bu_2AlH	25	toluene	8.62d	9.32d	0.70	6.74s,br
	–70	toluene	8.62d	9.32d	0.70	6.74s,br
i-Bu_3HAl_2O	25	toluene	8.56m	9.30m	0.77	5.85s,br
	–70	toluene	8.55m	9.30m	0.75	5.85s,br

[a] Toluene and benzene as internal standards at $\tau = 7.66$ and $\tau = 2.72$. s = singlet, d = doublet, br = broad, m = multiplet.

attributable to the CH proton of the isobutyl group lies in the region of the toluene CH_3 protons and therefore was not detected in the spectra. These multiplets can be finely resolved as two doublets (coupling constant 7 Hz) superimposed on the two multiplets of smaller intensities. These observations are in agreement with those reported by Ueyama et al. [3]. The relative intensities of the doublets and corresponding overlapped multiplets cannot be determined from the spectra. The room temperature PMR spectrum of triisobutylaluminium (Table 2, Fig. 1a) consists of two doublets with a proton ratio of 7 : 2.

Triisobutylhydroaluminoxane displays a similar behaviour in PMR spectra as i-Bu_4Al_2O does regarding the signals of the i-Bu group protons. Additionally a weak but broad resonance signal at $\tau = 5.85$ (Table 2, Fig. 1d) appears, attributable to the Al–H proton. A similar signal occurs in the spectrum of diisobutylaluminium hydride (Table 2, Fig. 1c) at $\tau = 6.74$. Integration of these spectra gives a ratio of protons $CH_3 : CH_2 :$ Al–H of 21 : 6 : 1 for i-Bu_3HAl_2O and 14 : 4 : 1 for i-Bu_2AlH. The PMR spectra do not change with variation of temperature in the –70 to 25°C range.

The cryoscopic molecular weight determinations (Table 3) indicate a dimeric structure for i-Bu_4Al_2O and a trimeric one for i-Bu_3HAl_2O as the most stable in benzene solution.

The observed behaviour of the two aluminoxanes studied in IR, PMR and cryoscopic investigations is a consequence of their structural features. Tetraisobutylaluminoxane appears to be a dimer, as shown by cryoscopic data, associated through strong oxygen bridges. The large steric effect in the associated molecule of i-Bu_4Al_2O causes significant rotational restrictions around the Al–C bond. The consequence of this is the disturbance of its PMR spectrum. Such hindrances do not occur in

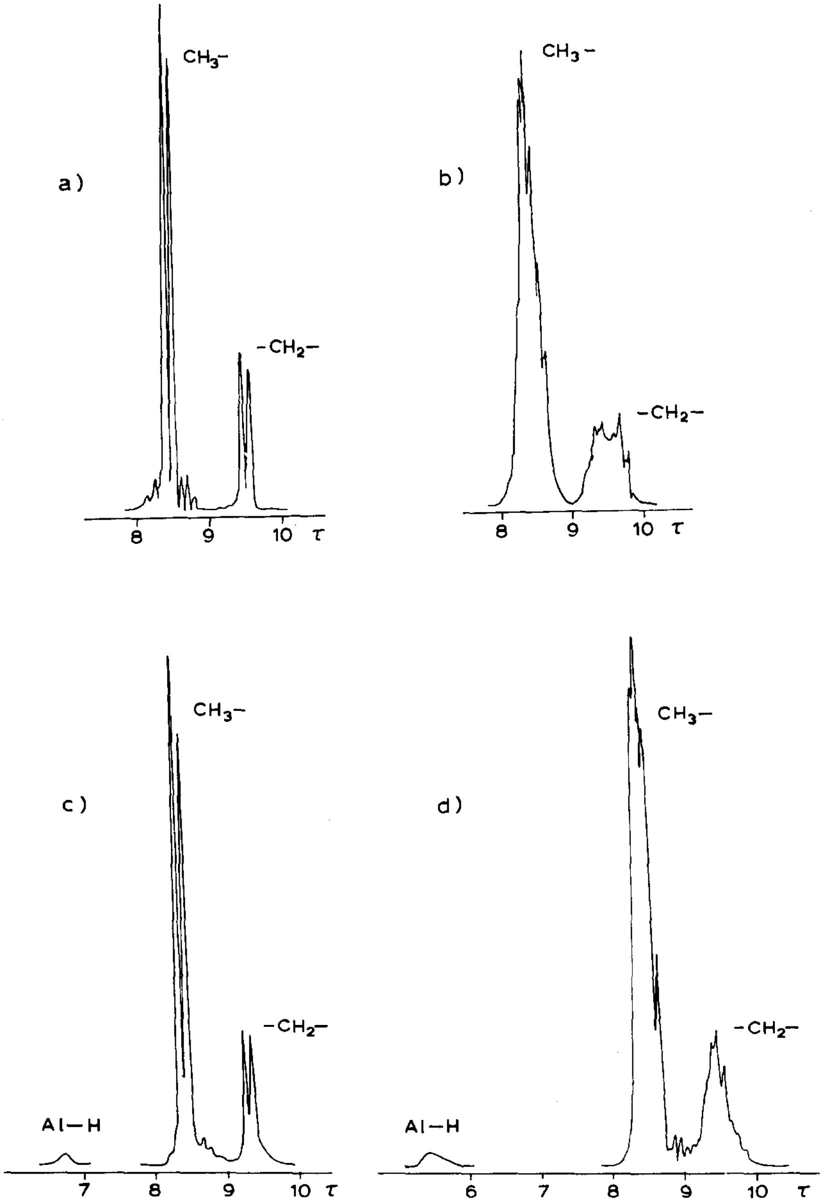


Fig. 1. Proton magnetic resonance spectra: (a) i-Bu_3Al; (b) i-Bu_4Al_2O; (c) i-Bu_2AlH; (d) i-Bu_3HAl_2O. Toluene as internal standard at $\tau = 7.66$, temp. 25°C.

triisobutylaluminium, which is practically not associated in solution [13] and has a trigonal planar AlC_3 skeleton [12]. A small percentage of i-Bu bridges was observed only for the pure i-Bu_3Al [14]. The energy of the formation of the i-Bu bridge in solution is too small to overcome the steric factors. Thus it should be expected that i-Bu bridges would not occur in the investigated solutions of aluminoxanes, what is

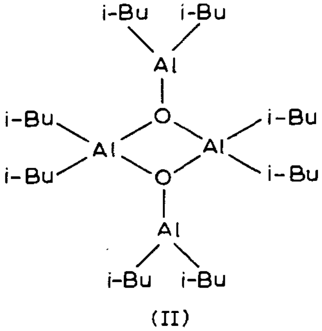
TABLE 3

CRYOSCOPIC MOLECULAR WEIGHT MEASUREMENTS (Benzene, 5°C)

Aluminoxane	Time[a] (h)	Measured molecular weight	Theoretical value for monomer	Degree of association
i-Bu_4Al_2O	2–3	536	298	1.81
	24	603		2.03
	~	611		2.05
i-Bu_3HAl_2O	2–3	670	242	2.77
	24	680		2.81
	~	706		2.92

[a] The time after which the measurement was performed.

actually confirmed by PMR spectral results (the lack of variation of the spectra from −70 to 25°C).

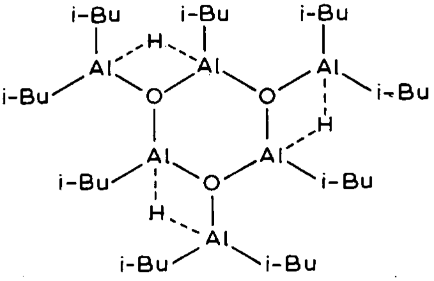


(II)

Proton magnetic resonance and cryoscopic studies lead us to propose structure II for i-Bu_4Al_2O. In the postulated structure two aluminium atoms have a coordination number of 4 and the remaining two a coordination number of 3. The two resolved doublets in its PMR spectrum (with coupling constant 7 Hz) are attributable to the protons of the less hindered i-Bu groups attached to tricoordinated aluminium atoms. Both multiplets are assigned to these i-Bu group protons which are bonded to four-coordinated aluminiums. The spectrum does not change with temperature to 70°C, indicating that a large steric effect is involved in the formation of the dimeric molecule.

Triisobutylhydroaluminoxane forms a trimeric molecule, as shown by cryoscopic data. The replacement of one i-Bu group in i-Bu_4Al_2O by hydrogen decreases the steric hindrance sufficiently to form a trimer. However, the nature of the PMR spectrum in the part characteristic of i-Bu group protons indicates again significant rotational restrictions around the Al–C bond.

The band at 1600–1900 cm^{-1} in the IR spectrum of i-Bu_3HAl_2O, attributable to Al–H stretching vibrations, indicates the presence of hydrogen bridges (Table 1). This is also confirmed by the Al–H proton signal in the PMR spectrum. Spectral and cryoscopic studies lead us to suggest structure III for i-Bu_3HAl_2O. In this structure each aluminium atom has a coordination number of 4. The two observed multiplets in its PMR spectrum (Fig. 1d) are attributable to the i-Bu group protons and the weak and broad singlet to the bridging hydrogen atom. The latter is shifted to lower field in comparison with i-Bu_2AlH, probably because of the vicinity of the electronegative oxygen atom and its inductive effect transfered through the O–Al–H



(III)

bonds. The spectrum does not change with a decrease of temperature to −70°C, indicating that only hydrogen bridges occur in the trimer. This is as expected, since there is no competition between hydrogen and alkyl groups regarding the bridge formation in organoaluminium hydrides [11].

The existence of structures I, II and III in solutions affords a new evidence of the relative bridge stabilities involving hydrogen or alkyl groups [7]; this order is the same as in the case of simple organoaluminium compounds

H > Me > Et > i-Bu

Finally it seems to be proved that the occurrence of alkyl or hydrogen bridges in the associated aluminoxane aggregates is a general characteristic feature for these arrangements.

Experimental

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

Hydrolytic methods

Both periodical and continuous methods depend generally on the introduction of disperced water (in toluene) to a dilute toluene solution of R_3Al (R = H, Et, i-Bu). In the first case the condensed vapors of toluene-water azeotrop (44.2 mole % of water) are introduced into a vigorously stirred, cooled solution of R_3Al to cause the slow hydrolysis reaction. The continuous method depends on the simultaneous combination of two streams: a dilute R_3Al solution with the water-toluene emulsion (0.5 wt % of water) in a very small reaction vessel, and immediate removal of this mixture from the reaction sphere. The method avoids direct contact between water and hydrolysis product (aluminoxane).

Analysis

Weighed samples of compounds were dissolved in toluene and decomposed with methanol (at −20°C) and then with diluted nitric acid (at room temperature). The volume of gases resulting from hydrolyzable alkyl groups or hydrogen was measured using a gaseous burette. The composition of gases was detected by GC. Aluminium

was determined complexometrically from the solution. Et_4Al_2O: Found: Al, 28.2; Et, 59.2; Et/Al = 1.96. Calcd.: Al, 29.05; hydrolyzable Et, 62.4%; Et/Al = 2. $i\text{-}Bu_4Al_2O$: Found: Al, 17.8; i-Bu, 74.7; i-Bu/Al = 1.99. Calcd.: Al, 18.1; hydrolyzable i-Bu, 76.5%; i-Bu/Al = 2.
$i\text{-}Bu_3HAl_2O$: Found: Al, 20.5; i-Bu, 68.7; i-Bu/Al = 1.58; i-Bu/H = 2.9. Calcd.: Al, 22.3; hydrolyzable i-Bu, 70.6%; i-Bu/Al = 1.5; i-Bu/H = 3.

Spectral measurements

IR spectra were recorded in the 2000–600 cm^{-1} range on a Perkin-Elmer Model 577 spectrometer as liquid films (of ca 10 wt.% benzene solutions) between KBr plates. NMR spectra were recorded using a Jeol JNM-4H-100 apparatus in ca. 10 wt.% benzene or toluene solutions.

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