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PROTON MAGNETIC RESONANCE STUDIES ON THE STRUCTURE OF TETRAETHYLALUMOXANE

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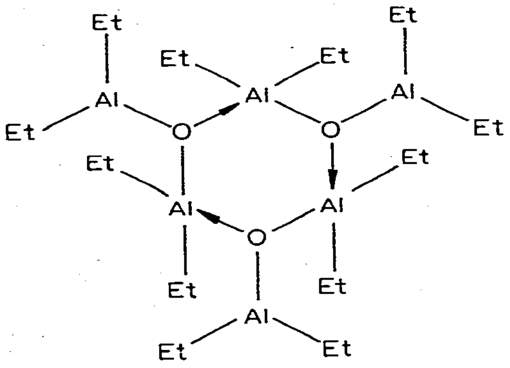
Summary

The structure of tetraethylalumoxane was studied. Comparison of low temperature PMR spectra of $(Et_2Al)_2O$ and Et_3Al suggested that the ethyl groups bridge the aluminium atoms in alumoxane. The investigation of alkyl group exchange between tetraethylalumoxane and tetramethyllead confirm the postulated structure.

Introduction

Tetraalkylalumoxane, general formula $R_2AlOAlR_2$, is one of the key compounds in the study of the positive influence of water on catalytic systems containing organoaluminium compounds [1—7].

The present investigations are concerned with the structure of tetraethylalumoxane, partly described by Storr [8], who found it to be a trimer in benzene solution. According to [8], a cyclic arrangement having oxygen bridging groups seems to be the most likely structure. Storr did not observe bridging ethyl groups in the alumoxane (PMR at —54° C) and proposed structure I.



(I)

Results and discussion

The low-temperature PMR spectrum of tetraethylalumoxane exhibits four groups of signals, whereas the room-temperature spectrum has only two (Fig. 1c, d, Table 1). Integration of room- and low-temperature spectra gives the ratio of protons as 12 : 8 and 9 : 3 : 2 : 6, respectively. This indicates the occurrence of two different ethyl groups in the alumoxane at −70° C.

The room-temperature PMR spectrum of triethylaluminium (Fig. 1a, Table 1) exhibits two groups of signals with a proton ratio of 9 : 6. According to Yamamoto [9] the low-temperature PMR spectrum of triethylaluminium exhibits two

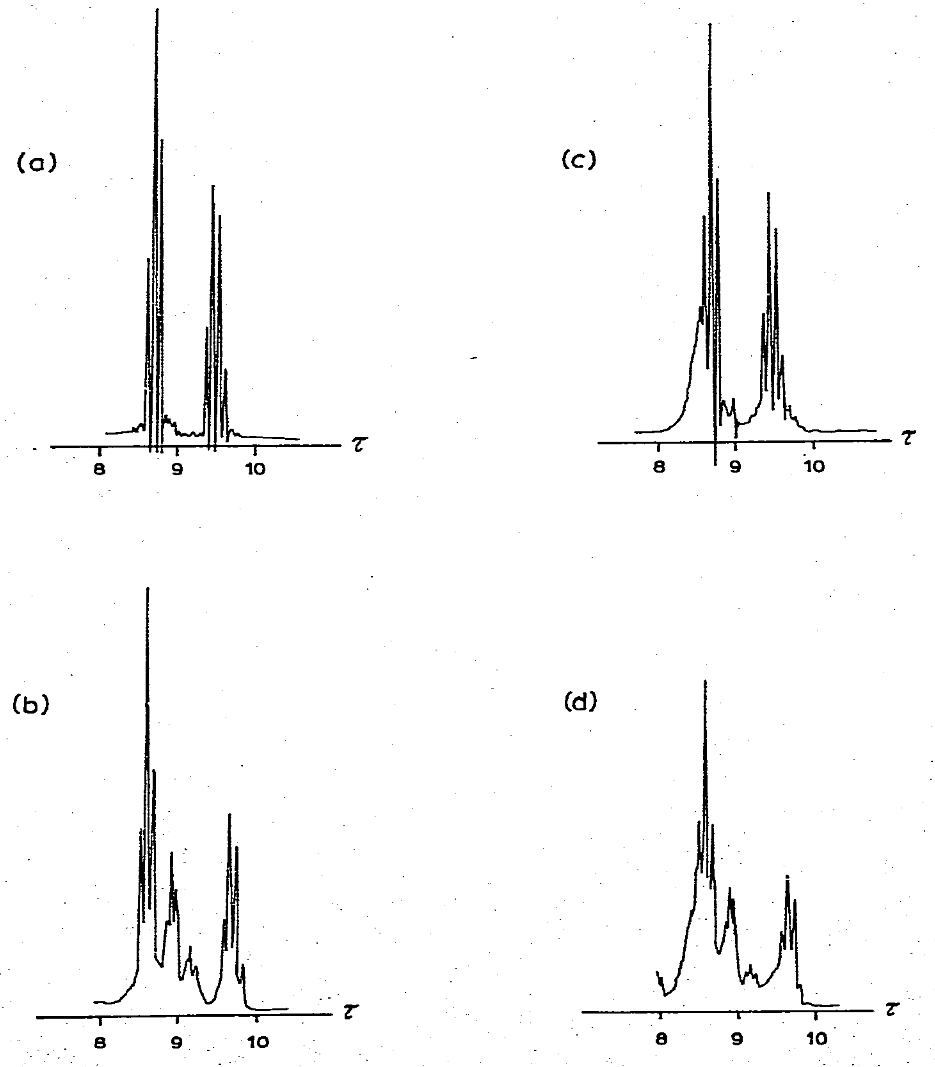


Fig. 1. Comparison of PMR spectra recorded at two different temperatures (toluene as internal standard at τ 7.66 ppm). (a) Et_3Al, +25° C; (b) Et_3Al, −70° C; (c) $(Et_2Al)_2O$, +25° C; (d) $(Et_2Al)_2O$, −70° C.

TABLE 1

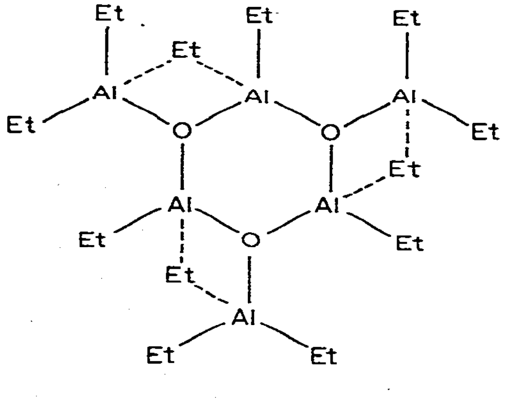
PROTON MAGNETIC RESONANCE SPECTRA. COMPARISON OF THE CHEMICAL SHIFTS OF CORRESPONDING PROTONS AT TWO DIFFERENT TEMPERATURES (TOLUENE AS INTERNAL STANDARD AT τ 7.66 ppm)

Compound	Fig. 1	Temperature (°C)	CH_3 (ppm)	CH_2 (ppm)	δ(Et) (ppm)	δ(CH_3)[a,b] (ppm)	δ(CH_2)[a,b] (ppm)
Et_3Al	a	+25	8.70	9.48	0.78	0	0
	b	—70	8.51[a]	9.61[a]	1.10	0.33	0.50
			8.84[b]	9.11[b]	0.27		
$(Et_2Al)_2O$	c	+25	8.66	9.46	0.80	0	0
	d	—70	8.56[a]	9.59[a]	1.03		
			8.87[b]	9.08[b]	0.21	0.31	0.49

[a] terminal. [b] bridging.

groups of signals attributable to the terminal ethyl groups and a multiplet assigned to the bridging ethyl group (at —80° C). Precise investigations of this multiplet in our PMR spectra of triethylaluminium at —70° C, established that it consisted of two groups of signals (Fig. 1b, Table 1). Integration of the whole spectrum is consistent with the ratio of protons: $CH_{3term}/CH_{3bridge}/CH_{2bridge}/CH_{2term} = 6 : 3 : 2 : 4$. The similar behaviour of tetraethylalumoxane and triethylaluminium in the PMR investigations suggest the occurrence of the bridging ethyl groups in the alumoxane.

Cryoscopic molecular weight determinations (calcd. 558; found 538) indicate that tetraethylalumoxane is a trimer in benzene solution. Proton magnetic resonance and cryoscopic studies lead us to propose structure II for $(Et_2Al)_2O$. In



(II)

the postulated structure each aluminium atom has a coordination number 4. Independence of the character of the spectra on the concentration of alumoxane in toluene solution (2—20 wt.%), indicates that the bridging ethyl groups occur inside the trimer.

Confirmation of structure II was obtained from the investigations of alkyl group exchange between tetraethylalumoxane and tetramethyllead. This reaction yields dimethyldiethylalumoxane and tetraethyllead as the main products, (eqn. 1).

$$2\,(Et_2Al)_2O + Me_4Pb \rightleftarrows 2\,Me_2Et_2Al_2O + Et_4Pb \qquad (1)$$

(mixture A)

Mixture A after hydrolysis was analyzed by GC. The molar ratio of hydrolyzable alkyl groups was found to be MeH/EtH 1 : 1.1, in the organic layer Et_4Pb was the main product. The mechanism of the exchange reaction of alkyl groups, between tetramethyllead and trialkylaluminium has been described previously [10] and it is likely that the mechanism of reaction 1 is quite similar.

Room-temperature PMR spectrum of mixture A also shows that the reaction has occurred as shown in eq. 1. This spectrum exhibits signals attributable to the Me and Et groups bonded to the Al atom and the Et groups bonded to the Pb

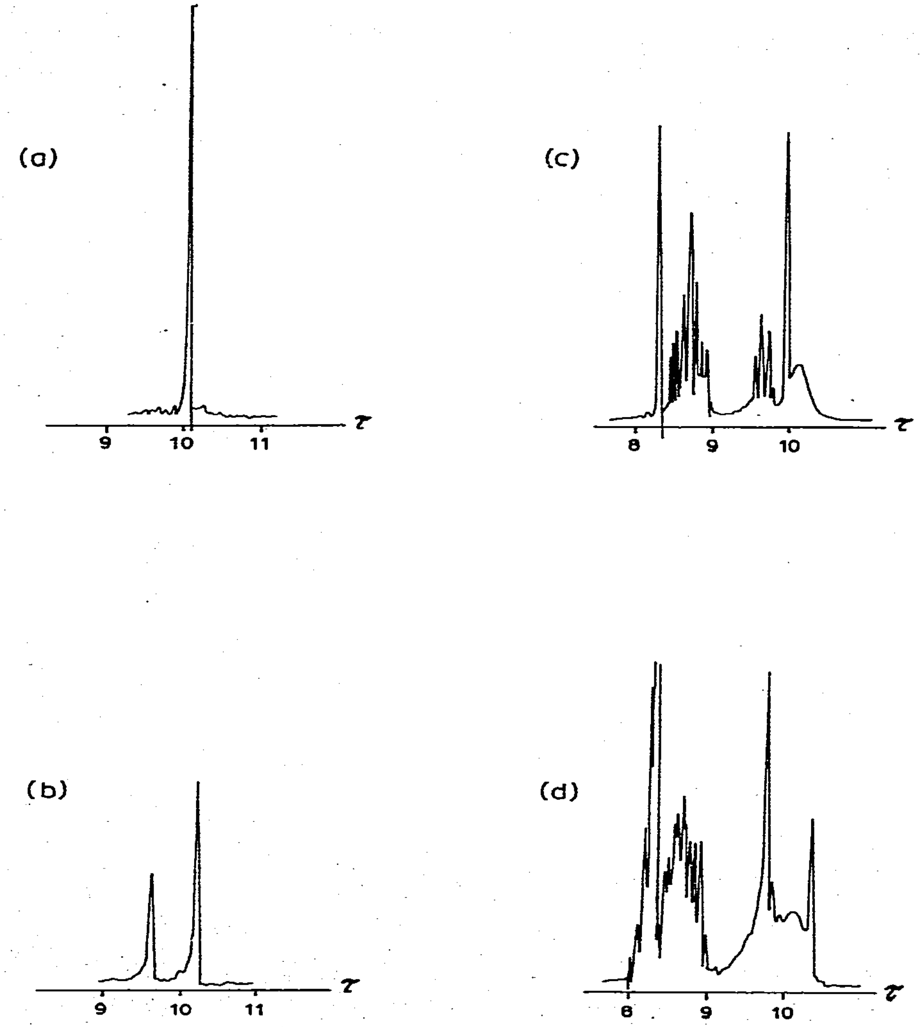


Fig. 2. Comparison of PMR spectra recorded in two different temperatures (toluene as internal standard at τ 7.66 ppm). (a) Me_3Al, +25°C; (b) Me_3Al, −70°C; (c) $Me_2Et_2Al_2O$, +25°C; (d) $Me_2Et_2Al_2O$, −70°C.

TABLE 2

PROTON MAGNETIC RESONANCE SPECTRA. COMPARISON OF THE CHEMICAL SHIFTS OF CORRESPONDING PROTONS AT TWO DIFFERENT TEMPERATURES (TOLUENE AS INTERNAL STANDARD AT τ 7.66 ppm)

Compound	Fig. 2	Temperature (°C)	CH_3 (ppm)	$\delta(CH_3)$ [a,b] (ppm)
Me_3Al	a	+25	10.09	0
	b	—70	9.71 [b]	0.59
			10.30 [a]	
$Me_2Et_2Al_2O$	c	+25	9.94	0
	d	—70	9.66 [b]	
			10.26 [a]	0.60

[a] terminal. [b] bridging.

atom (Fig. 2c, Table 2). The low-temperature PMR spectrum of the investigated mixture A (Fig. 2d, Table 2) exhibits two signals attributable to the methyl groups, caused by the splitting of the methyl group signal observed at room-temperature. It proves that in the case of $Me_2Et_2Al_2O$, the methyl group is the bridging one. The structure of $Me_2Et_2Al_2O$ is probably similar to II but with methyl groups in the bridges.

These facts are in agreement with the general conclusion that a methyl bridge is stronger than an ethyl one. This was also indicated by the PMR spectra of mixed methyl and ethyl aluminium compounds. A methyl group preferentially displaces the ethyl group in the bridging position; e.g. in $Al_2Me_2Et_4$ 74% of the methyl groups are in the bridge and 26% in the terminal position [11,12].

Addition of benzonitrile to a solution containing tetraethylalumoxane or the mixture A causes a cleavage of the carbon bridges. This is due to complex formation between alumoxane and benzonitrile. The low-temperature PMR spectra of $(Et_2Al)_2O \cdot PhCN$ or $Me_2Et_2Al_2O \cdot PhCN$ in toluene failed to show the presence of two different ethyl or methyl groups, respectively. Formation of complexes between alumoxanes and electron donors have been described previously [13—16].

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