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TETRAETHYLALUMOXANE—BENZONITRILE COMPLEX

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Summary

Tetraethylalumoxane was found to form a complex with benzonitrile in the molar ratio 1 : 1. This complex is a monomer.

The structure of the complex is proposed on the basis of molecular weight determinations, IR and PMR investigations, and the alkyl group exchange reaction with tetramethyllead. The acidities of tetraethylalumoxane and triethylaluminium are compared.

Introduction

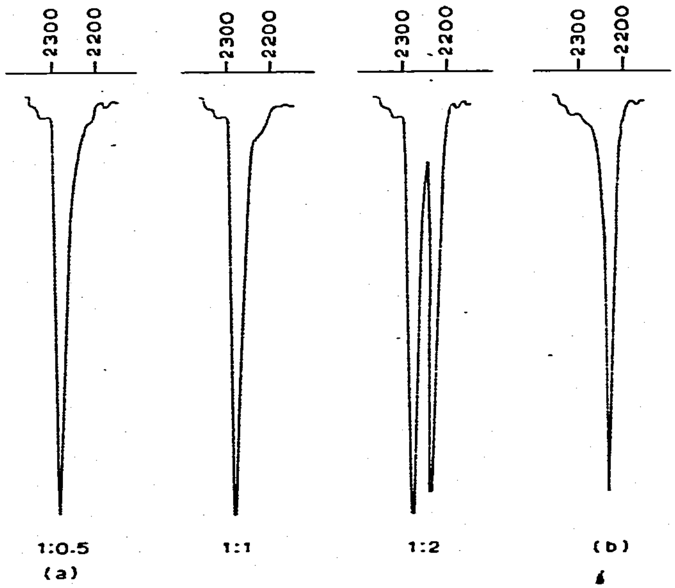
In our previous paper [1] we described the structure of $(Et_2Al)_2O$. It was shown by PMR that the introduction of benzonitrile to the alumoxane solution leads to cleavage of the carbon bridges.

Our present study concerns the formation and structure of the $(Et_2Al)_2O$ benzonitrile complex.

Results and discussion

IR spectra of a mixture of tetraethylalumoxane with benzonitrile show a band at 2270 cm^{-1}, assigned to vibrations of the C≡N group of complexed benzonitrile (Fig. 1). For the $(Et_2Al)_2O$: PhCN molar ratios 1 : 0.5 and 1 : 1, no band of free benzonitrile appears at 2230 cm^{-1}; it only appears when an excess of benzonitrile is present. For the 1 : 2 molar ratios, the bands at 2230 and 2270 cm^{-1} are of the same intensity.

PMR spectra of a mixture of alumoxane with benzonitrile show a shift of signals of the ethyl group protons to a lower field in comparison with signals of the free alumoxane (Fig. 2), and the difference in the internal chemical shift of the CH_2 and CH_3 protons increases. For the $(Et_2Al)_2O$: PhCN molar ratio 1 : 1 and 1 : 2 the chemical shifts of the ethyl groups in both cases are the same and occur at 8.27 and 9.42 ppm.



1:0.5 (a) 1:1 1:2 (b)

Fig. 1. IR spectra of different mixtures of $(Et_2Al)_2O$ with benzonitrile: (a) $(Et_2Al)_2O$: PhCN molar ratio; (b) IR spectrum of free benzonitrile.

The above data indicate the formation of a complex between tetraethylalumoxane and benzonitrile with the molar ratio 1 : 1.

This is also confirmed by the results of molecular weight measurements. For the 1 : 1 mixture, the molecular weight determined by the cryoscopic method in benzene is 286 ($(Et_2Al)_2O \cdot$ PhCN calc. 289), and for the 1 : 2 mixture 198. The calculated average molecular weight of the $(Et_2Al)_2O \cdot$ PhCN + PhCN mixture is 196. These results, besides confirming the 1 : 1 composition of the complex, indicate its monomeric structure in a benzene solution. According to our previous paper [2], the complexes of methylalumoxanes with benzonitrile are not monomeric.

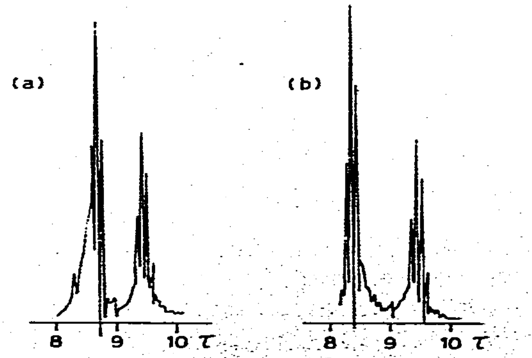


Fig. 2. PMR spectra of (a) tetraethylalumoxane and (b) its complex with benzonitrile. Solvent, toluene, as an internal standard at τ 7.66 ppm, 25°C.

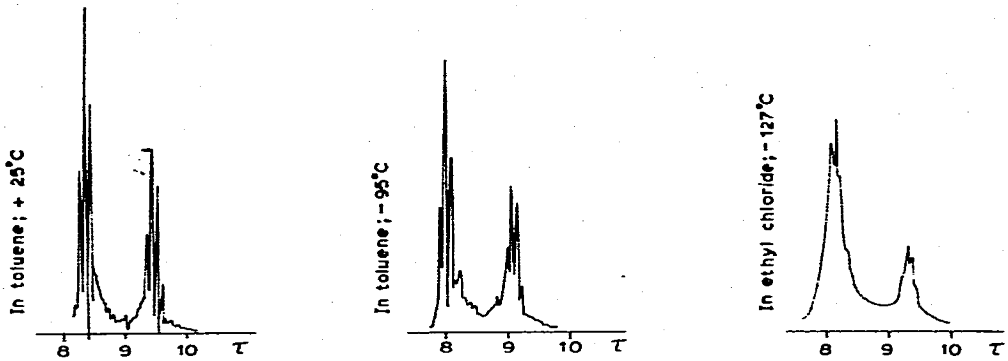


Fig. 3. PMR spectra of the tetraethylalumoxane—benzonitrile complex recorded at various temperatures. Solvents: toluene and ethyl chloride as internal standards at τ 7.66, 6.43 and 8.52, respectively.

To explain the structure of the tetraethylalumoxane—benzonitrile complex, the low-temperature PMR spectra of its toluene solution were recorded in the +25— —95° C range. No changes in the character of the spectrum were observed. A decrease of the temperature to —127° C (in ethyl chloride as solvent) does not change the character of the spectrum (Fig. 3).

Previously we described the alkyl group exchange between tetraethyl-

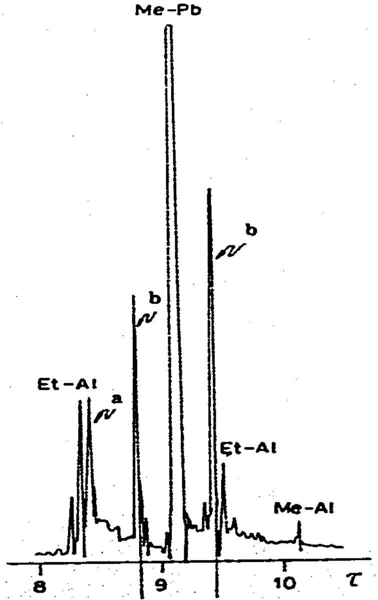


Fig. 4. PMR spectrum of a mixture of $(Et_2Al)_2O \cdot PhCN$ and Me_4Pb in the molar ratio 1 : 3, recorded 9 days after preparation. (a) signal of the Et—Pb group overlapping the CH_3CH_2Al triplet. (b) a strong signal $^2J(^{207}Pb—H)$ overlapping the CH_3CH_2Al quartet. (Solvent, benzene, as an internal standard at τ 2.72 ppm, 25° C.)

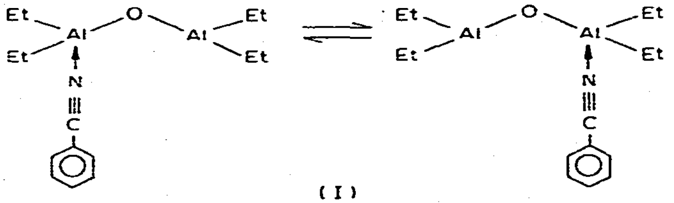
alumoxane and tetramethyllead. It was shown that this reaction proceeds according to eqn. (1).

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

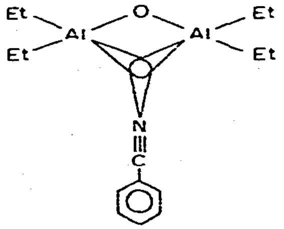
The alkyl group exchange is completely hindered in the case of the reaction between $(Et_2Al)_2O \cdot PhCN$ and Me_4Pb. In the PMR spectrum of this mixture (Fig. 4), even for the molar ratio 1 : 3 very weak signals of ethyl groups bonded to lead (Et-Pb) and of methyl groups bonded to aluminium (Me—Al) are present. GC analysis of the gases and liquid after hydrolysis of the mixture also showed the presence of trace amounts of these bondings.

The hindering of alkyl group exchange can be explained by the fact that both aluminium atoms in the alumoxane molecule are strongly complexed by benzonitrile. Therefore, according to [3], attack of the methyl group initially bonded with lead on the aluminium atom is impossible.

Low temperature PMR studies of the complex and investigations of the alkyl group exchange reaction suggest that the dynamic structure (I) of the complex is the less likely one. It is believed that the hindering of the exchange and the invariant character of the PMR spectra in the +25—127°C range can be caused by the formation of structure (II) in solution.



(I)



(II)

On the basis of IR and PMR spectral studies, the relative Lewis acidities of triethylaluminium and tetraethylalumoxane have been compared. The IR spectrum of the triethylaluminium—benzonitrile complex (1 : 1) shows a strong absorption band $\nu(C{\equiv}N)$ at 2270 cm^{-1}. The band of the benzonitrile C≡N group in complex $(Et_2Al)_2O \cdot PhCN$ has an identical position.

The electronegative values of aluminium in complexes of $Et_3Al \cdot PhCN$ and

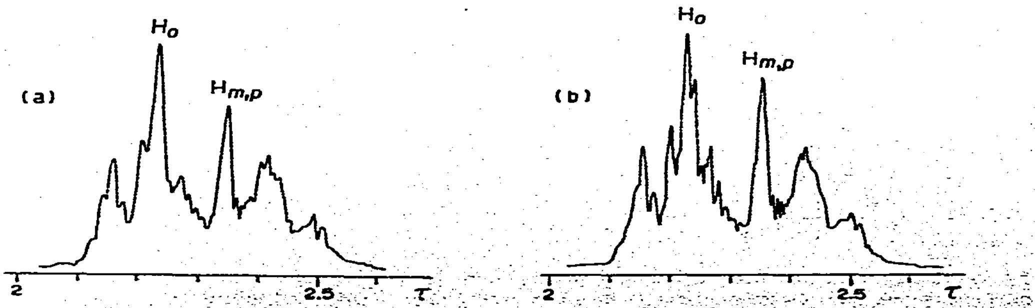


Fig. 5. PMR spectra of the PhCN phenyl group in (a) $Et_3Al \cdot PhCN$ and (b) $(Et_2Al)_2O \cdot PhCN$ complexes. Solvent, methylene chloride, as an internal standard at τ 4.70 ppm, 25°C.

$(Et_2Al)_2O \cdot PhCN$ calculated from the Dayley—Shoolery equation [4] are 1.37 and 1.43, respectively. This suggests that the acidity is similar for both compounds. This conclusion is confirmed by the studied values of chemical shifts of phenyl group protons of benzonitrile in PMR spectra. On the basis of the internal chemical shift of *ortho*, *meta* and *para* protons of the benzonitrile phenyl group in the complex, the electronegativity of the acceptor can be indirectly determined [5] In spectra of the complexes $Et_3Al \cdot PhCN$ and $(Et_2Al)_2O \cdot PhCN$ the internal chemical shifts of *ortho*, *meta* and *para* protons are the same in both cases 0.11 ppm. This confirms the equal electron-accepting ability of the aluminium atoms (Fig. 5).

References

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