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STUDIES OF (CHLOROMETHYL)ALUMOXANES IN COMPLEXES WITH BENZONITRILE

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Summary

The acceptor properties of the alumoxanes $(CH_3)_nCl_{4-n}Al_2O$ (n = 0, 2, 3, 4) have been studied on the basis of their ability to form complexes with benzonitrile. It was found that alumoxanes form equilibrium complexes with benzonitrile. The relative acidity of aluminium in the series of alumoxanes under study was determined.

Introduction

In an alumoxane molecule the two aluminium atoms are strong Lewis acid centres, which are separated by an oxygen atom that is a basic centre. Such a distribution of the electron density in the organometallic molecule is of great interest and it is to be hoped that alumoxanes may be used in homogeneous catalysis, e.g. in polymerization reactions of polar monomers [1]. In order to determine the mechanism of formation of alumoxane complexes with electron donors and the properties of these complexes, we investigated the hydrolysis products of complexes of the methylaluminium compounds.

In a previous paper [2] we described the hydrolysis of the dimethylaluminium chloride—diethyl ether complex (eq. 1).

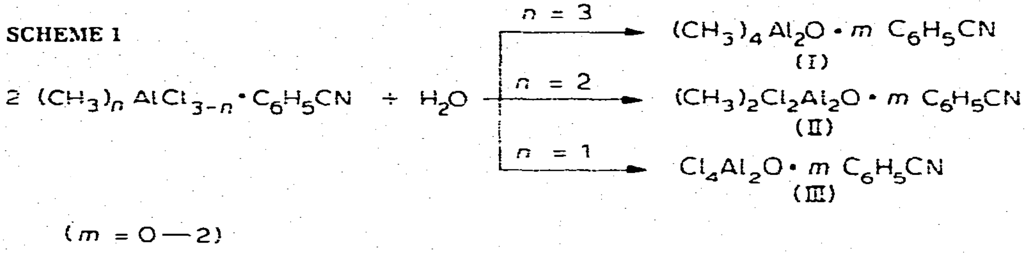
$$2\,(CH_3)_2AlCl \cdot (C_2H_5)_2O + H_2O \rightarrow (CH_3)ClAlOAlCl(CH_3) \cdot (C_2H_5)_2O + 2\,CH_4 + (C_2H_5)_2O \qquad (1)$$

The present investigation is concerned with the hydrolysis products of complexes of methylaluminium compounds with benzonitrile. Unlike complexes with diethyl ether, it was found that alumoxane complexes do not exhibit stoichiometry.

Results and discussion

Complexes of methylaluminium compounds with benzonitrile react with water (at a 2 : 1 molar ratio) according to Scheme 1.

SCHEME 1



The complex $(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN$ (IV) was prepared by exchanging the diethyl ether for benzonitrile in the complex $(CH_3)_3ClAl_2O \cdot (C_2H_5)_2O$ according to eq. 2. The latter complex was obtained from the reaction of lead monoxide with dimethylaluminium chloride by a procedure previously described [3].

$$(CH_3)_3ClAl_2O \cdot (C_2H_5)_2O + 2\ C_6H_5CN \rightarrow \underset{(IV)}{(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN} + (C_2H_5)_2O + (2 - m)\ C_6H_5CN \qquad (2)$$

The products I—IV were isolated under identical conditions (5×10^{-4} Torr, 50°C, 36 h, see Experimental) as yellowish, non-sublimable solids. The content of benzonitrile in the products I—IV was determined and the molar ratios of benzonitrile to alumoxane ($m = C_6H_5CN : 2\ Al$) have been calculated: I, 0.98; II, 1.52; III, 1.86; IV, 0.62.

The composition, observations and results of spectral studies indicate that the complexes have an equilibrium character. It was found that the values of m vary with the time of removal of the volatile components, e.g. for I after 36 h $m = 0.98$ and after 65 h $m = 0.86$.

In the IR spectra of complexes 1—4 (Table 1), besides a $\nu(C{\equiv}N_c)$ band corresponding to the valential frequency of the benzonitrile C≡N bond, a $\nu(C{\equiv}N_f)$ band of the free benzonitrile always occurs. The $\nu(C{\equiv}N_f)$ band occurs even in the spectra of complexes I and IV where the molar ratio of benzonitrile to alumoxane is less than one. The NMR spectra of complexes I, II and IV, in the range of resonance of protons of methyl groups bonded with aluminium (τ = 10.20—10.80 ppm), show several signals with different intensities. Their number increases at lower temperatures (−70°C).

This suggests the occurrence of different forms of complexes or associated forms. With some of these forms rapid (in NMR time scale) exchange reactions at room temperature take place. Japanese investigators [4] observed that the 1 : 2 complex of tetraethylalumoxane with 5,6-benzoquinoline transforms at room temperature over a period of time to the 1 : 1 complex. This may be

TABLE 1

IR SPECTRA IN THE FREQUENCY RANGES 400—1300 cm^{-1} AND 1500—2400 cm^{-1}

$(CH_3)_4Al_2O \cdot m\ C_6H_5CN$	$(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN$	$(CH_2)_2Cl_2Al_2O \cdot m\ C_6H_5CN$	$Cl_4Al_2O \cdot m\ C_6H_5CN$	Assignment
2274s	2278s	2279s	2281s	$\nu(C{\equiv}N_c)$
2228w	2228w	2228w	2228w	$\nu(C{\equiv}N_f)$
1208s	1206s	1202s		$\sigma(CH_3Al)$
1019w	1028w	1020w	1030w	
888w	885w	884w		
800vs(br)	798vs(br)	809vs(br)	813vs(br)	$\nu(Al—O—Al)$
760vs	761vs	759vs	760vs	(C—C)
689vs(br)	695vs(br)	685vs(br)		$\nu_{as}(Al—C)$
559s	560s	562s		$\nu_s(Al—C)$
548m	550w	548m	549m	$\omega(C—H)$
	443w	445w	435w	$\nu(Al—Cl)$
	417m	413m	410m	$\nu(Al—Cl)$

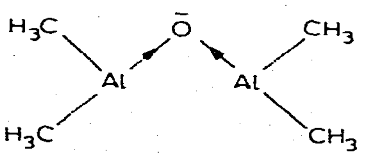
caused by steric hindrances in the 1 : 2 complex. Consideration of steric hindrances can be ignored in the case of complexes with benzonitrile described here.

Products I—IV are, therefore, mixtures of alumoxane—benzonitrile complexes of molar ratios 1 : 1 and 1 : 2 in equilibrium with the substrates. The formation and dissociation of alumoxane complexes is shown in eq. 3.

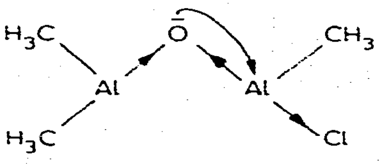
$$>\!\text{AlOAl}\!< + 2\ C_6H_5CN \rightleftharpoons\ >\!\text{AlOAl}\!< \cdot\ C_6H_5CN + C_6H_5CN \rightleftharpoons\ >\!\text{AlOAl}\!< \cdot\ 2\ C_6H_5CN \quad (3)$$

In our previous studies [5] on the complexing abilities of monophenoxyaluminium compounds with benzonitrile, we found that most of the complexes formed exist in equilibrium with the substrates. It was found that the equilibrium state is due to the comparable basicity of bridging oxygen atoms in phenoxyaluminium compounds and nitrogen in benzonitrile.

Likewise, in the studied series of complexes, the reason for the existence of equilibrium states shown in eq. 3 is the comparable basicity of the oxygen atom in the alumoxanes and nitrogen in benzonitrile. The existence of different molar ratios of benzonitrile to alumoxane is probably caused by the variable basicity of oxygen, depending on the number of chlorine substituents in alumoxane. The replacement of the aluminium methyl group by chlorine (A, B) causes an increase in the electronegativity of aluminium and a partial shift of the electrons back from oxygen to aluminium, which, in effect, decreases the basicity of oxygen. The formation of a donor—acceptor bond between the



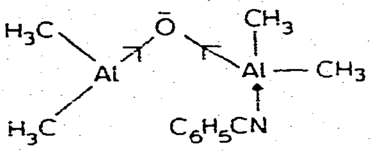
(A)



(B)

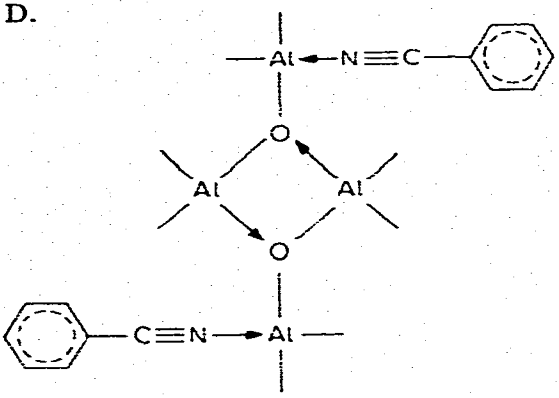
benzonitrile molecule and one of the alumoxane aluminium atoms (C) enriches the alumoxane molecule in electrons and, in effect, increases the basicity of oxygen in the alumoxane.

In products I and IV the molar ratio of benzonitrile to alumoxane is 0.98 and



(C)

0.62, respectively. The 1 : 1 forms of the complexes, i.e. $(CH_3)_4Al_2O \cdot C_6H_5CN$ in I and $(CH_3)_3ClAl_2O \cdot C_6H_5CN$ in IV are dominant. Cryoscopic molecular weight determinations for products I and IV, carried out in benzene, gave a degree of association of 1.7—1.9. These results indicate that I and IV exist to a significant degree as dimers *. The most probable structure of such dimers is D.



(D)

The basicity of the oxygen atom in the 1 : 1 complexes is probably higher than the basicity of nitrogen in benzonitrile and the 1 : 2 complexes are only minor products.

For products II and III, where the value of *m* are 1.52 and 1.86, respectively, the 1 : 2 complexes predominate, i.e. $(CH_3)_2Cl_2Al_2O \cdot 2\ C_6H_5CN$ in II and $Cl_4Al_2O \cdot 2\ C_6H_5CN$ in III. The formation of 1 : 2 complexes indicates that the oxygen atom basicity decreases considerably due to the induction effect of chlorine substituents bonded to the aluminium atom.

As was mentioned previously, the acidity of aluminium atoms in the alumoxanes depends on the number of chlorine substituents bonded to the aluminium atom. The values of $\Delta\nu$ shown in Table 2 represent the difference between the valential vibration IR frequences in the complexed benzonitrile C≡N bond and that corresponding to the free benzonitrile, and may be an indication of the

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* We recently found that the 1 : 1 complex between tetraethylalumoxane and benzonitrile does not undergo bridging through oxygen atoms and is monomeric, unlike methylalumoxanes complexes. Steric factors seem to be the only explanation of this.

TABLE 2

FREQUENCY OF VALENTIAL VIBRATIONS IN IR SPECTRA OF THE C≡N BOND OF BENZONITRILE COMPLEXES WITH ORGANOALUMINIUM COMPOUNDS (cm^{-1}) (in benzonitrile $\nu(C{\equiv}N_f)$ = 2228)

Complex	$\nu(C{\equiv}N_c)$	$\Delta\nu$ [a]
$(CH_3)_4Al_2O \cdot m\ C_6H_5CN$ (I)	2274	46
$(CH_3)_3Al \cdot C_6H_5CN$	2269	41
$(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN$ (IV)	2278	50
$(CH_3)_2AlCl \cdot C_6H_5CN$	2274	46
$(CH_3)_2Cl_2Al_2O \cdot m\ C_6H_5CN$ (II)	2279	51
$CH_3AlCl_2 \cdot C_6H_5CN$	2278	50
$Cl_4Al_2O \cdot m\ C_6H_5CN$ (III)	2281	53
$AlCl_3 \cdot C_6H_5CN$	2286	58

[a] $\Delta\nu = \nu(C{\equiv}N_c) - \nu(C{\equiv}N_f)$.

relative acidities of aluminium in the molecules [6]. The results obtained confirm that the acidity of alumoxanes increases when the number of chlorine substituents increases. It appears also from these results that alumoxanes are stronger acids than the corresponding methylaluminium compounds. It should be noted that the values of $\Delta\nu$ for the alumoxane complexes are probably

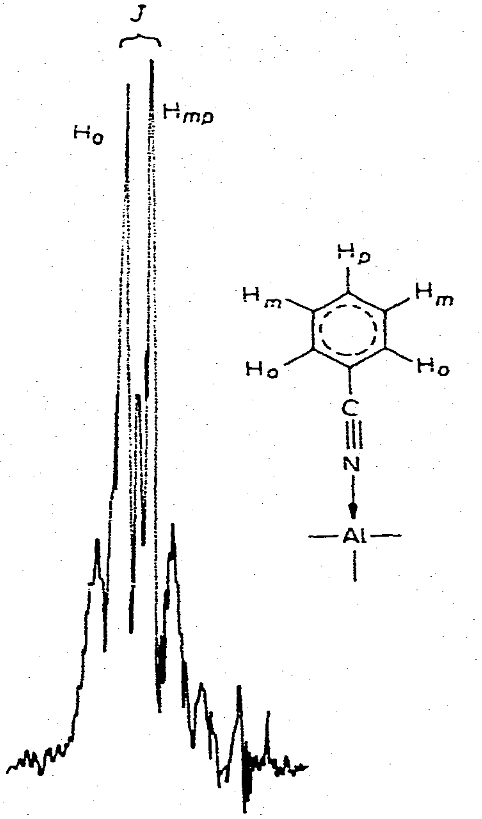

Fig. 1. Multiplet in the NMR spectrum of complexed benzonitrile.

TABLE 3

NMR COUPLING CONSTANTS BETWEEN PROTONS IN COMPLEXED BENZONITRILE

Compound	*J* (Hz)
C_6H_5CN	4.0
$(CH_3)_4Al_2O \cdot m\ C_6H_5CN$	12.5
$(CH_4)_3Al \cdot C_6H_5CN$	11.0
$(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN$	14.5
$(CH_3)_2AlCl \cdot C_6H_5CN$	14.5
$(CH_3)_2Cl_2Al_2O \cdot m\ C_6H_5CN$	16.0
$(CH_3)AlCl_2 \cdot C_6H_5CN$	16.5

relatively underrated due to the action of the "mass effect". Quantitative conclusions about the differences in acidity of aluminium in alumoxanes and in methylaluminium compounds are given also from the NMR spectra of the benzonitrile complexes. A complicated multiplet corresponds to the benzonitrile protons, of which the two more intensive signals (Fig. 1) correspond to the *ortho* and the *meta* and *para* protons of the ring. The coupling constant, *J*, between these two signals is proportional to the electron withdrawing effect from the ring by the C≡N substituent [7]. Indirectly then, the value of *J* is proportional to the acidity of the organoaluminium acceptor bonded to the C≡N group of benzonitrile. The values of the coupling constants, *J*, described above, are presented for different complexes in Table 3.

On the basis of data presented in Table 2 and 3, the following order of the relative acidity of alumoxanes and other aluminium compounds can be established: $(CH_3)_3Al < (CH_3)_4Al_2O \leqslant (CH_3)_2AlCl < (CH_3)_3ClAl_2O < CH_3AlCl_2 \leqslant (CH_3)_2Cl_2Al_2O < Cl_4Al_2O < AlCl_3$.

Experimental

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

Preparation of the studied complexes

$(CH_3)_4Al_2O \cdot m\ C_6H_5CN$ (I). $(CH_3)_3Al$ 7.43 g and 10.6 g of C_6H_5CN were stirred in 30 ml of toluene at −20°C. The $(CH_3)_3Al \cdot C_6H_5CN$ complex was hydrolyzed, without isolation, for 3 h at −20°C by adding a solution of 0.90 g of H_2O in 110 ml of diethyl ether. The solution was stirred until its temperature reached room temperature and the evolution of gases stopped. The solvents were evaporated under reduced pressure, and then the volatile components were removed under a pressure of 5×10^{-4} Torr at 50°C over 36 h to give 8.6 g of product. (Analysis: found: CH_3, 25.0; Al, 23.0; C_6H_5CN, 43.9%; CH_3/Al, 1.96; C_6H_5CN/Al, 0.49. $(CH_3)_4Al_2O \cdot 0.98\ C_6H_5CN$ calcd. taking into account the effective contents of benzonitrile: CH_3, 25.9; Al, 23.3%.)

$(CH_3)_2Cl_2Al_2O \cdot m\ C_6H_5CN$ (II). $(CH_3)_2AlCl$ 7.40 g, 8.40 g of C_6H_5CN and 0.72 g of H_2O were reacted under the same conditions described for I and 6.7 g of product was isolated in an identical manner. (Analysis: found: CH_3, 8.3; Al,

15.7; Cl, 22.6; C_6H_5CN, 45.0%; CH_3/Al, 0.95; Cl/Al, 1.09; C_6H_5CN/Al, 0.76. $(CH_3)_2Cl_2Al_2O \cdot 1.52\ C_6H_5CN$ calcd.: CH_3, 9.1; Al, 16.4; Cl, 21.6%.)

$Cl_4Al_2O \cdot m\ C_6H_5CN$ (III). CH_3AlCl_2 8.36 g, 60 ml of toluene, 7.65 g of C_6H_5CN and 0.67 g of H_2O were reacted under the same conditions described for I. During the hydrolysis a precipitate was isolated which was collected and dried in vacuo. The yield of product was 8.6 g. (Analysis: found: Al, 12.8; Cl, 34.4; C_6H_5CN, 45.8%; Cl/Al, 2.07; C_6H_5CN/Al, 0.93. $Cl_4Al_2O \cdot 1.86\ C_6H_5CN$ calcd.: Al, 13.3; Cl, 35.1%.)

$(CH_3)_3ClAl_2O \cdot m\ C_6H_5CN$ (IV). In the exchange reaction of the donor 7.33 g of $(CH_3)_3ClAl_2O \cdot (C_2H_5)_2O$ and 6.87 g of C_6H_5CN were used. The reaction was carried out in toluene for 4 h at 50°C. After isolation by the method described for I, 7.8 g of product was obtained. (Analysis: CH_3, 19.1; Al, 25.4; Cl, 14.8; C_6H_5CN, 30.4%; CH_3/Al, 1.35; Cl/Al, 0.46; C_6H_5CN/Al, 0.31. $(CH_3)_3ClAl_2O \cdot 0.62\ C_6H_5CN$ calcd.: CH_3, 20.9; Al, 25.1; Cl, 16.5%.)

Complexes of benzonitrile with $(CH_3)_3Al$, $(CH_3)_2AlCl$, CH_3AlCl_2 and $AlCl_3$

An excess of benzonitrile was introduced to the respective aluminium compound at −196°C. After the mixture reached room temperature excess of donor was distilled off in vacuo.

Analysis methods of the studied compounds

Weighed samples of compounds were decomposed with n-hexanol, and then with diluted nitric acid. The volume of gases resulting from the methyl groups bonded to aluminium was measured. Aluminium and chlorine were determined from the solutions, after hydrolysis, complexometrically and argentometrically, respectively. Benzonitrile was determined chromatographically from the toluene layer, after hydrolysis, by the internal standard method.

Spectral measurements

IR spectra were recorded in the 400—2400 cm^{-1} range on a Zeiss UR-10 spectrometer as Nujol mulls enclosed in polyethylene bags between KBr plates. NMR spectra were recorded using a Jeol-JNM-100MH apparatus from ca. 20 wt. % methylene chloride solutions.

Acknowledgements

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