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PHENOXYALUMINIUM COMPOUNDS

VI *. COMPLEX AND REACTION MECHANISM OF METHYLALUMINIUM COMPOUNDS WITH ANISOLE

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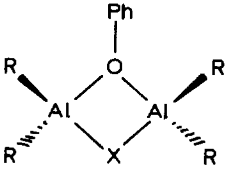
Summary

The reactions of anisole with organoaluminium compounds Me_nAlX_{3-n} have been investigated.

The formation of a complex is the first reaction step, followed by cleavage and elimination of the gases MeX and small amounts of hydrocarbons. The yield of the gases and the cleavage rate decreases in the order: $AlCl_3 \geqslant MeAlCl_2 > Me_2AlCl \gg Me_3Al$ and $Me_2AlI > Me_2AlCl > Me_2AlBr$. For most of the investigated reactions a marked decrease in gas evolution was observed after a short period of time. This is explained by the formation of an almost inactive mixed dimer (I) which at the reaction temperature is more stable than the $Me_2(Cl)Al:O(Me)Ph$ complex. It is suggested that dimer I is formed after the intramolecular reaction of the 2:1 complex II after elimination of MeX.



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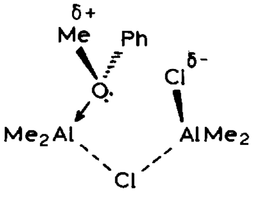

(II)

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* For part V see ref. 11.

Introduction

Many organoaluminium compounds (OAC) form complexes with weak Lewis bases, e.g. anisole, which result in an equilibrium with the substrates [1,2]

$$R'R''O + OAC \rightleftharpoons R'R''O:OAC \qquad (1)$$

The equilibrium also occurs when either weak acids are used or when the bridging substituents of aluminium are strong donors, or when the ligands are bulky [3]. The infrared band of the asymmetric C–O–C stretching vibration of complexed anisole is shifted with respect to free anisole and the values of $\Delta\nu$ were used as a measure of acidity of OAC [3]. When donor-acceptor complexes are formed from $RAlCl_2$ or $AlCl_3$ a small degree of aggregation is observed [1]. Halogen derivatives of OAC when complexed with ethers are unstable at elevated temperatures and eliminate alkyl halogenides [3]. For example during the synthesis of $Pr_3Al_2Cl_3$ from PrCl and aluminium turnings in anisole, minor amounts of methylaluminium sesquichlorides were observed [4].

$$Pr_3Al_2Cl_3 \xrightarrow[\Delta]{\text{anisole}} Pr_3(PhO)_nAl_2Cl_{3-n} + nMeCl \qquad (2)$$

$$3MeCl + 2Al \rightarrow Me_3Al_2Cl_3 \qquad (3)$$

This type of anisole cleavage was not observed by Geisler and Knothe since they treated a mixture of Al and Mg turnings with different alkyl bromides, using anisole as a solvent, to obtain trialkylaluminium [5]. This seems to be a result of the rate of formation of organomagnesium compounds (followed by the alkylation of alkylaluminium sesquibromide) exceeding the rate of formation of the anisolate of alkylaluminium bromide compounds (and the elimination of RBr from the complex).

$$R_3Al_2Br_3 + 3RMgBr \xrightarrow[\text{anisole}]{} R_3Al + 3MgBr_2 \qquad (4)$$

The evolution of HCl postulated for the reaction of Me_nAlCl_{3-n} with anisole was not confirmed by our studies [6]. The aim of this work is to investigate thoroughly the cleavage of anisole by alkylaluminium halogenides at about the temperature used for the synthesis of (OAC) from aluminium and alkyl halogenides.

Results

Gas evolution measurements

The gas evolution during the reaction of anisole with organoaluminium compounds was measured. The amount and composition of gases in the reaction, carried out under standard conditions, are shown in Table 1. In Fig. 1 the time-dependent evolution of gases of some of the reactions in Table 1 is shown. As can be seen from Table 1, trimethylaluminium is virtually unreactive, indicating that the halogenide substituent in organoaluminium compounds is responsible for the cleavage of anisole. Methylaluminium dichloride and aluminium trichloride eliminate over 85% of the gases, under standard conditions, according to the general equation (eq. 5),

$$Me_nAlCl_{3-n}:O(Me)Ph \rightarrow Me_n(PhO)AlCl_{2-n} + MeCl \qquad (5)$$

and the reaction is complete after a period of 1–2 h. The reaction of dimethyl-

TABLE 1

THE RATE AND YIELD OF THE ELIMINATION REACTION OF ANISOLE WITH ORGANOALUMINIUM COMPOUNDS [a]

No.	Organoaluminium compound	Ratio of anisole/OAC (mol/mol)	Time (h)	Yield of gases [a] (% mol)	Composition of gases (% vol.)		
					RX	RH	C_2H_4
Binary mixture with anisole							
1	Me_3Al	1/1	6	8.0	–	100	–
2	Me_3Al	1/2	6	12.0	–	100	–
3	Me_2AlCl	1/1	6	50–60	98–99	traces	traces
4	$MeAlCl_2$	1/1	6	85.0	95	4	traces
4a	$AlCl_3$	1/1	6	95.0	–	–	–
5	Me_2AlI	1/1	6	50.0	100	traces	–
6	$MeAlI_2$	1/1	6	45.0	68	30	–
7	Me_2AlBr	1/1	6	31.0	100	traces	–
8	Me/PhO/AlCl [c]	1/1	3	0	–	–	–
9	Me_2AlOPh [c]	1/1	3	0	–	–	–
10	Et_2AlCl	1/1	6	34.0	90	10	–
Ternary mixture with anisole							
11	$Me_2AlCl + Me_2AlOPh$	1/1/1	6	28.0	95	4.5	–
12	$MeAlCl_2$ + Me/PhO/AlCl	1/1/1	6	50.0	98.5	1.5	–
Binary mixture							
13	$Me_2AlCl + Me_2AlOPh$	1/1	3	0	–	–	–
14	$MeAlCl_2$ + Me(PhO)AlCl	1/1	3	0	–	–	–

[a] At 135°C. [b] Yield calculated with respect to anisole. [c] IR spectra do not show even traces of complexes with anisole.

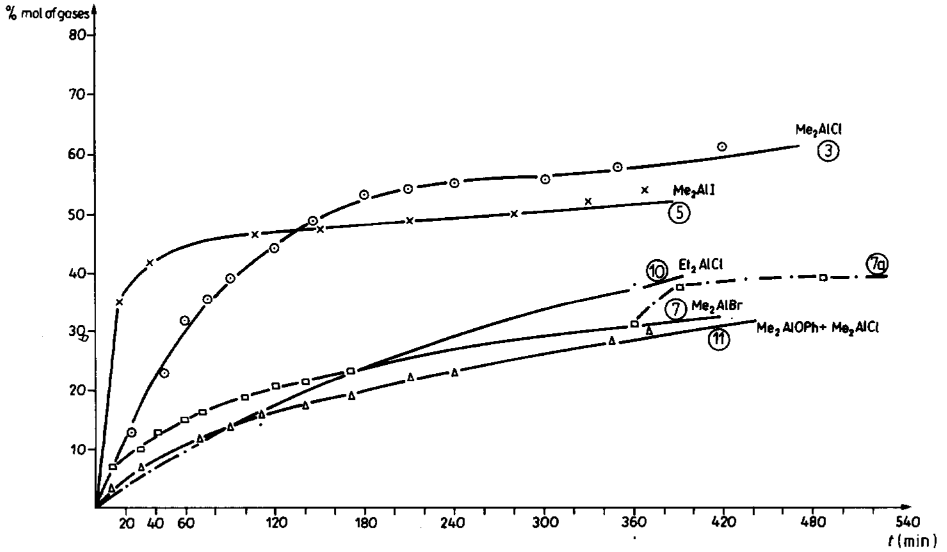


Fig. 1. Reaction rate of anisole with different organoaluminium compounds. Numbers by the curves represent the experiments in Table 1. (7a) repeated heating after 1 d at room temperature.

aluminium chloride and iodide has a rapid initial step but then slows down and after 30–50% of gases have been generated its progress is scarcely visible. Surprisingly the compound Me_2AlBr (reaction 7) reacts more slowly than the compounds previously mentioned. The rate of gas evolution from the complex of anisole and diethylaluminium chloride (reaction 10) is slower but it shows no drastic changes in time. We suggest that steric hindrance in Et_2AlCl decreases the amount of the complex resulting from the equilibrium (eq. 1) thus slowing down the cleavage process.

Reactions 8, 9, 11 and 12 were carried out in order to explain the strong decrease of gas evolution after about 50% of MeCl had been eliminated. The first two reactions with phenoxyaluminium compounds (which as was stated before are products of the reaction 3 and 4) indicate that these compounds are inactive towards elimination and that they do not disproportionate under these conditions. The ternary mixture of $Me_2AlCl/Me_2AlOPh/MeOPh$ reacts inversely, yet slower than the binary mixture (reaction 3). The cooled products of the reaction, after one day at room temperature, after heating, again show a high initial elimination rate (not shown in Fig. 1). After 6 h of heating, storage for 2 at room temperature, and reheating to 130°C reaction of $Me_2AlCl:O(Me)Ph$ (Fig. 1 plot 3) gives rise to the evolution of gases with a rate (but not quantity) similar to that of the ternary mixture (Fig. 1 plot 11). Such an acceleration of reaction after cooling is shown by curve 7a in Fig. 1 for the reaction of $Me_2AlBr:O(Me)Ph$.

^1H NMR investigations

It was expected that more information about the mechanism of the cleavage would be obtained if the reaction course was monitored by ^1H NMR spectroscopy, with time. This is shown in Table 2A for dimethylaluminium chloride. The signals at τ 5.81 ppm of the anisole methyl group decrease and are shifted slightly upfield. A peak at τ 7.15 ppm (apparently of MeCl) is formed, the intensity of which increases in time and also shifts slightly upfield. The only peak in the Me-Al region of the anisole complex (at τ 10.67 ppm) decreases and simultaneously a new peak at τ 10.44 ppm is formed. After heating for 50 min, another peak appears at 10.74. The intensities of both peaks increase during the course of the reaction. Two new minor peaks are also observed. The rate of reaction evaluated from the change of intensities of peaks with time is in agreement with the gas evolution measurements. But probably owing to the increased pressure in the tube, the increasing MeCl concentration, and the very small diameter of the tube, the reaction observed with ^1H NMR spectroscopy was slower than that carried out in a standard reaction vessel under atmospheric pressure.

The ^1H NMR spectrum of the compound assumed to be trimeric Me_2AlOPh [7,8] in cyclohexane at room temperature shows strong absorption at τ 10.85, a weak peak at 10.55 and a number of very weak peaks between 10.60 and 14.00 ppm. At 130°C a very strong peak of the dimer at τ 10.55 ppm is present together with the very weak peaks in the region mentioned above. The sample cooled after 2 d at room temperature, again shows the same spectrum as before it was heated.

In the spectrum of the equimolar mixture of Me_2AlCl and Me_2AlOPh (Table 2C) two signals at room temperature are present: a weaker one at τ 10.29 and a stronger one at 10.45 ppm. There are also three minor peaks at τ 10.63, 10.76 and 10.86 ppm. The spectrum shows a different pattern of peaks to those which are expected from

TABLE 2

CHANGES IN ^{1}H NMR SPECTRA CAUSED BY HEATING OF CYCLOHEXANE (c-hex) SOLUTIONS OF THE SAMPLES IN SEALED TUBES. $(Me_2AlCl)_2$ in (c-hex) τ 10.27 ppm; $(Me_2AlBr)_2$ in (c-hex) τ 10.18 ppm)

No.	Recording temperature	(Chemical shift): integration						
		MeOPh	MeCl	Me–Al region				
				(10.46)	(10.56)	(10.66)	(10.75)	(10.92)
A Mixture of Me_2AlCl + PhOMe. Reaction temp. 130°C								
1. after mixing	r.t.	(5.90)–	–	–	–	89	–	–
2. 0.5 h heating	r.t.	(5.88)44	(7.18)21	2	–	88	–	–
3. 1 h heating	r.t.	(5.86)40	(7.18)4	8	1	81	1	–
4. 2 h heating	r.t.	(5.90)38	(7.18)5	14	1	66	6	1
5. 4 h heating	r.t.	(5.97)33	(7.12)10	18	1	53	19	1
6. 12 h heating	r.t.	(6.04)22	(7.25)22	36	1	30	24	1
7. after 3 d at r.t.	r.t.	(6.02)20	(7.20)23	25	2	31	31	2
8. after 3 d at r.t.	80°C	(6.02)20	(7.20)23	(10.52) 42	5	39	15	1
9. 0.5 h heating	130°C	(6.12)18	(7.23)16		(10.52) 92		5	–
10. after cooling	r.t.	(6.04)21	(7.23)21	40	2	25	24	2
B Mixture of Me_2AlCl + Me_2AlOPh + PhOMe. Reaction temp. 130°C								
1. after mixing	r.t.	(5.88)–	–	26	7	44	22	2
2. 0.5 h heating	130°C	(6.12)–	–		(10.52) 96		3	–
3. 4.5 h heating	r.t.	(6.06) 76	(7.24) 24	37	1	27	27	5
C Mixture of Me_2AlCl + Me_2AlOPh heated to 130°C								
1. after mixing	r.t.		(10.22)30	64	–	2	4	2
2. 1 h heating	130°C	–		(10.46) 95			5	–
3. 24 h after cooling	r.t.		(10.27)14	64	–	8	6	7
D Mixture of Me_2AlBr + Me_2AlOPh heated to 130°C								
		–		(10.18)	(10.30)	(10.38)	(10.60)	(10.89)
1. after mixing	r.t.			52	9	27	6	3
2. after mixing	56°C			42	12	42	2	2
3. after mixing	80°C	–		30	15	50	2	2
4. after mixing	130°C			–		99br	1	1
5. after cooling	r.t.			49	12	30	5	3

the physical dissolution of the starting compounds. At 130°C there is one very strong peak at τ 10.46 ppm, which is formed by a change in intensity of peaks during the elevation of temperature and not by coalescence. Two other very weak peaks lie upfield. After only one day at room temperature the intensities of peaks are the same as before heating. The pattern of peaks of the spectrum of the mixture of Me_2AlBr and Me_2AlOPh (Table 2D) is also different from the sum of these two spectra. There are two strong bands at τ 10.18 of $(Me_2AlBr)_2$ and 10.38 ppm with an intensity ratio of about 2/1 and three of minor intensity. The intensity ratio changes rapidly when the temperature is elevated. At 130°C there is only one strong broad peak at 10.36 and two hardly discernable peaks upfield. Upon cooling the sample once more gives the starting spectrum contrary to the chloro-containing mixture described.

The ternary mixture of Me_2AlCl, Me_2AlOPh and MeOPh (Table 2B) shows a multi-peak signal spectrum which is similar to that of the reaction shown in Table 2A after 4 h of heating. Increasing the temperature of the mixture to 130°C gives a spectrum with a very strong peak at 10.51. The spectra recorded at lower temperatures show that the peak which simultaneously increases in intensity and shifts upfield without broadening is the peak of τ 10.45 ppm. This mixture, contrary to the $Me_2AlCl : Me_2AlOPh$ system, shows, immediately after cooling, the position and intensity of peaks of the starting spectrum. The rapid rearrangement in the mixture is explained by the influence of the larger amount of free anisole (more basic solvent). When the sample is heated, further elimination of MeCl takes place (Fig. 1 Curve 11).

IR investigations

The IR spectrum of the 1:1 mixture of Me_2AlCl^+MeOPh shows two strong bands of $\nu(C{-}O{-}C)_{as}$ of anisole, one for free anisole at 1252 and the second at 1152

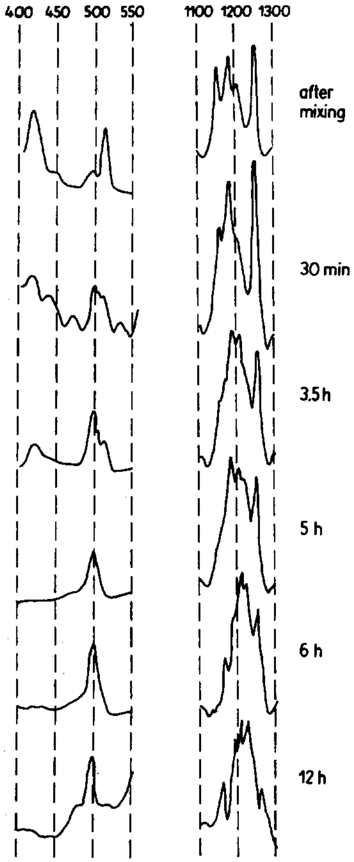
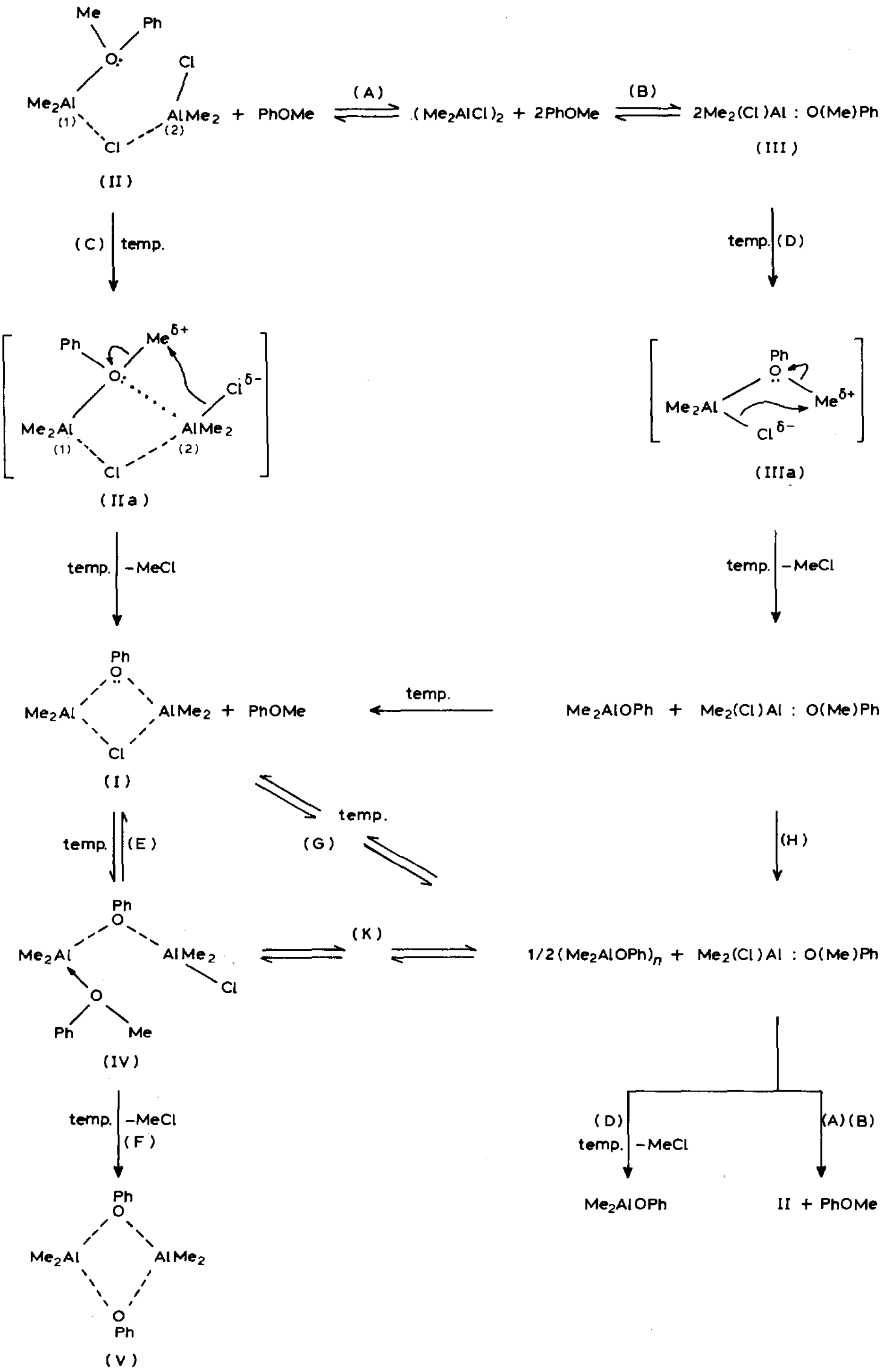


Fig. 2. The IR changes of $Me_2AlCl + MeOPh$ during heating of the mixture at 135°C.

cm^{-1} which is assigned to the complexed form [3]. In this region a strong band at 1184 cm^{-1}, which could not be assigned, is also observed. The bands of the dimethylaluminium chloride dimer are rather weak, indicating a low concentration of the free aluminium compound. Within the reaction time (Fig. 2) the intensities of both $\nu(C-O-C)_{as}$ bands of anisole decrease, whereas that of the unassigned band increases, and after 5 h of heating, it becomes the strongest band in the region. There are two new bands which appear during the reaction course, one at 1208 and the second at 1223 cm^{-1}. Both are assigned to $\nu(C-O{=}Al_2)$. The band at 1223 cm^{-1} appears for both dimeric and trimeric Me_2AlOPh. It is important to note that the band of lower wavenumber is formed first and the other appears in the spectrum only after 3.5 h of heating. After 12 h these two bands dominate this region of the spectrum. Other bands, discussed earlier, are either weak of form shoulders after 12 h. A very distinct new absorption is observed at about 500 cm^{-1}. It is broad and corresponds to the skeletal stretching vibrations of the Al–O bonds of the associated molecule [9]. The spectra of the equimolar mixture of $Me_2AlCl + Me_2AlOPh + PhOMe$ are very similar to those of the reaction mixture after 3.5 h of heating. The spectra of the ternary mixture after 6 h of heating, and of the binary mixture after 12 h of reaction, are also similar.

Discussion

From studies of the reaction of anisole with OAC (Table 1) and from the IR spectra of the mixtures one can assume that the first step of the reaction must be the formation of a donor-acceptor complex. Phenoxyaluminium compounds are the only OAC investigated which do not react, yet are strongly associated, and also the only compounds which do not form complexes with anisole. It has been stated that attack of a donor on OAC (with a strongly basic bridge substituent, (halogen, oxygen, alkynyl group) takes place in the bridge plane [10]. It initiates the splitting of only one Al–X bond with the simultaneous formation of an $Al \leftarrow O$ bond (structure II in the Scheme 1). The basicity of the anisole oxygen is low and comparable with that of Cl in Me_2AlCl (presence of free anisole in the 1 : 1 mixture). The 1 : 2 complex formed can therefore be reasonably stable and exists in equilibrium with the substrates and the 1 : 1 complex (A and B in Scheme 1). The small intensities of the IR bands of free $(Me_2AlCl)_2$, and the strong $\nu(C-O-C)_{as}$ signal of free anisole in the 1 : 1 mixture suggests that more than stoichiometric amounts of OAC are required for the formation of the complex, in agreement with equilibrium A. Moreover, Smith's investigations provide evidence for structure II [1]. The only explanation for the lack of substrates elucidated from molecular weight measurements [1] and the existence of free anisole in the 1 : 1 mixture, which we observed in the IR spectra is the formation of II which is in equilibrium with complex III. The low temperature ^1H NMR spectra (at $-75°C$) in toluene showed only one broad peak for the methylaluminium protons. The low basicity of anisole and thus formation of a weak complex, and the aromatic solvent can in this case be the factors which allow the fast exchange to proceed even at that temperature. Furthermore, the complex of type II was proposed on the basis of low temperature ^1H NMR spectra of the $(Me_2AlCCMe)_2/Et_2O$ system in hydrocarbon solvents between -60 and $-80°C$ [11]. The calculation indicates that $(Me_2AlCCMe)_2$ and $(Me_2AlCl)_2$ undergo a nucleophilic attack in the same way forming in the first step



SCHEME 1. Proposed scheme for the cleavage of anisole by dimethylaluminium chloride.

a 1 : 2 complex with only one split bridging-bond [10], this is further evidence for the existence of such a complex.

Complex II as postulated seems to have a lower activation energy to anisole cleavage (C). The geometry of the complex should favour the rearrangement to IIa in which Al^{II} attacks oxygen, which in turn causes the increased polarisation of the O–Me and Al–Cl bonds. Simultaneous action of attracting forces should decrease the bond energy of the split bonds and as a result should also decrease the activation energy. The dimer I is characterised in that it has at least a 20 kcal/mol lower energy of activation than the expected monomeric species, provided the reaction proceeds according to D in the four centre system (IIIa).

From the results described in the ^1H NMR investigations and from the data collected in Table 2, it can be stated that the peak at 10.45 ppm corresponds to the protons of methyl groups in I. This peak first appears in the spectrum when the reaction is carried out in an NMR tube. It is followed by the Me-Al peak in $(Me_2AlOPh)_3$. This confirms our suggestion that I is the first product formed and suggests that other associates such as symmetric dimers and trimers result from the disproportionation reaction of I (reaction G). Complex II is the most likely source of dimer I since it is presumed that it is the first product formed in the reaction. It is suggested that the band at 1209 cm^{-1} in the IR spectra of the mixture corresponds to $\nu(C{-}OAl_2)$ in I, since the intensity increases during the entire reaction period. Moreover, the band at 1223 cm^{-1} assigned to $(Me_2AlOPh)_3$ appears after some time, which is in agreement with the various changes in the ^1H NMR spectra. Complex I predominates at elevated temperatures as can be seen from the ^1H NMR spectra of the equimolar mixture of dimethylaluminium chloride and bromide with dimethylaluminium phenoxides (Table 2C No. 2 and 2D No. 4). From the above it is evident that at about 50% gas evolution, dimer I and free anisole are present in the mixture at the reaction temperature. The very slow evolution of gases from such a mixture can result from two mechanisms; (i) from complexes which could be formed according to equilibrium G (and possibly further, through B and A). This equilibrium must be a multistep process. Structure IV is very likely to be the first intermediate (E and K), (ii) from the proposed structure, complex IV, which could be an intermediate in the cleavage reaction (F). The mechanism of the proposed reaction should then be similar to the cleavage (C) from the complex II.

The ^1H NMR spectrum of the ternary mixture at 130 °C, furthermore, indicates the existence of only I, free anisole and possibly IV presumed from the upfield shift of $Al{-}CH_3$ and downfield shift of $CH_3{-}O$. But the decrease in temperature shifts the equilibrium G to the right. The rate of this shift depends on the rate at which the temperature decreases, on the solvent and on the type of OAC. This is much greater for the bromide substituted compound than for the chloride substituted one (Table 2). Me_2AlX ($X = Cl, Br$) was cleaved from I at room temperature (G) from the complex(es) with free anisole, which gave rise to the accelerated cleavage after repeated heating (Fig. 1 curve 7a).

The methyldichloroaluminium anisolate is more stable to dissociation (reaction 1) than $Me_2AlCl : O(Me)Ph$ [1,10a] because of the higher acidity of $MeAlCl_2$ and lower basicity of the Cl substituent *. The decreased donor ability of Cl substituents

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* The basicity of substituents was discussed in more detail in [12]. Similarly, Smith's investigation indicated the change of the donor ability of aluminium ligands [1].

will thus lower the tendency to maintain the chlorine bridges in the dimer and in the 1 : 2 complex. The higher concentration of the complex(es) and decreased stability of $MeAlCl_2 : O(Me)Ph$ at elevated temperature causes fast evolution of gases with nearly 100% yield, without the time-dependent strong slowing down of the reaction observed for dimethylaluminium halides. At reaction temperature the resulting Me(Cl)AlOPh can also associate with $MeAlCl_2$ to form a dimer with mixed bridges similar to I. Because the basicity of the Cl bridging atom is lower than in (the similar) dimer I one expects a shift to the right of the equilibrium of eq. 1. The possible complexes thus formed, like II, III and IV in the scheme, also readily undergo cleavage reactions.

A high concentration of complex(es) is visible in the IR spectra of ternary mixtures of $MeAlCl_2$/Me(PhO)AlCl/MeOPh (a strong ν(C–O–C) of complexed anisole and a weak band of free anisole). This is reversed in the IR spectrum of the ternary mixture Me_2AlCl/Me_2AlOPh/MeOPh.

Experimental

The solvents were dried over a sodium-potassium alloy, then distilled, and were stored over this alloy under oxygen-free nitrogen. Anisole was dried using 4Å molecular sieves followed by distillation over freshly prepared molecular sieves under nitrogen.

All organoaluminium compounds were prepared by methods given in the literature [7,13,14].

The reactions were carried out in a vessel connected to a gasometer (or cooled flask for collecting liquid RX) through a bubbler. The liquids in the bubbler (Nujol) and in the gasometer were saturated with corresponding alkyl halides. The reaction mixture was prepared by very slow introduction of anisole to the stirred OAC at about −10°C.

IR spectra were recorded in the range 400–1400 cm^{-1} with a UR-10 Carl Zeiss, Jena spectrometer using 3% solutions in benzene. The 0.15 mm cell was adapted for recording the spectra in an inert atmosphere.

^1H NMR spectra were recorded with a JEOL I-NM-C-6OH spectrometer using 15% solutions in cyclohexane. However, when Me_2AlCl was treated with anisole, the reaction was carried out in 5 mm sealed tubes in a 50% cyclohexane solution.

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References

1 G.H. Smith and F.J. Hamilton, J. Phys. Chem., 72 (1968) 3567.
2 K.B. Starowieyski, S. Pasynkiewicz and E. Jankowska, J. Organomet. Chem., 19 (1970) 283.
3 K.B. Starowieyski, Prace Naukowe Politechniki Warszawskiej, Chemia, z. 9, Warszawa, 1973.
4 S. Pasynkiewicz, W. Dahlig and K. Starowieyski, Roczniki Chem., 36 (1962) 1583.
5 G. Geisler and W. Knothe, Chem. Ber., 81 (1958) 2446.
6 K.B. Starowieyski and S. Pasynkiewicz, J. Organomet. Chem., 19 (1969) 249.
7 K. Starowieyski, S. Pasynkiewicz and M.D. Skowrońska, J. Organomet. Chem., 31 (1971) 149.

8 E.A. Jeffery and T. Mole, Aust. J. Chem., 21 (1968) 2683.
9 S. Pasynkiewicz, K.B. Starowieyski and D. Skowrońska-Ptasińska, J. Organomet. Chem., 52 (1973) 269.
10 A. Okniński, (a) Prace naukowe Politechniki Warszawskiej, Chemia z. 31, Warszawa, 1983; (b) J. Mol. Liq., 28 (1984) 25.
11 K.B. Starowieyski, A. Bęcalska and A. Okniński, J. Organomet. Chem., 293 (1985) 7.
12 K.B. Starowieyski, S. Pasynkiewicz and D. Skowrońska-Ptasińska, J. Organomet. Chem., 65 (1974) 155.
13 S. Pasynkiewicz and M. Bolesławski, J. Organomet. Chem., 25 (1970) 29.
14 Houben Weyl, Methoden der Organischen Chemie XIII/4, Georg Thieme Verlag, Stuttgart, 1970.
15 K.B. Starowieyski, M. Skowrońska-Ptasińska and J. Muszyński, J. Organometal. Chem., 157 (1978) 379.