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PHENOXYALUMINIUM COMPOUNDS

VI. MASS SPECTRAL INVESTIGATION OF THE ASSOCIATION OF DIMETHYLALUMINIUM PHENOXIDE

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Summary

The mass spectra of Me_2AlOPh dimer and trimer were recorded. A skeleton fragmentation was mainly observed at low temperature. Higher temperature spectra (of the trimer) have many more peaks which were only partly assigned. The spectrum of the trimer indicates the presence of ions with at least 5 aluminium atoms. Based on these ions the existence of higher associated intermediates in the reassociation reaction

trimer → dimer

is proposed.

Introduction

To date several papers concerning mass spectroscopy of organoaluminium compounds have been published. They deal with fragmentation of trialkylaluminium [1,2], alkylaluminium chlorides, aluminium trichlorides [1,3,4], methyl aluminium hydrides [1,2], and oxygen-containing organoaluminium compounds [2,4—6] as well as organoaluminium compounds with an aluminium nitrogen bond [7—10]. In most of these compounds parent ions of associated molecules were either not observed or of low intensity. Usually the strongest peak of the spectrum obeyed the $(3n - 1)$ rule [1] *. On the basis of this, one

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* For the majority of the abundant ions containing aluminium the number of substituents is $3n - 1$, where n is the number of aluminium atoms.

may draw some conclusion about the degree of association by carefully assigning the fragmentation ions.

Most data on the organoaluminium compounds association were obtained using cryoscopic, vapour pressure and NMR measurements [11]. In a series of papers the investigation of degree of association of several phenoxyaluminium compounds was presented [12—14]. Some of them appear to have variable state of association [12,15]. The freshly sublimed compounds were found to be dimers while storage for several days of the solution in hydrocarbons of unhindered compounds led to the formation of nearly or entirely trimeric species. For both types of associated molecules, cyclic structure was proposed. Up till now there has been no attempt to explain how the change of association occurs. One can expect the mass spectroscopic methods of investigation to be useful in monitoring transient species occurring in the process

$$\text{trimer} \rightarrow \text{intermediate} \rightarrow \text{dimer} \qquad (1)$$

Such reaction is likely to proceed under the conditions applied in mass spectrometry apparatus (high temperature, vacuum).

To examine this supposition we carried out investigations of the mass spectra of Me_2AlOPh which, according to previous results, displays a variable state of association.

Results and discussion

The mass spectra of Me_2AlOPh and its ring deuterated analogues are shown in Tables 1, 2 and 3. In Table 1 the spectra of sublimed compounds are collected. Tables 2 and 3 present the spectra of crystals obtained from the seasoned solution after evaporation of the solvent.

Assignment of peaks is given in the tables only in obvious cases and these are confirmed by the ring deuterated analogues. The complex fragmentation of compounds causes difficulty in assigning all peaks, especially with higher *m/e* ratio.

The composition of all possible fragments of Me_2AlOPh with masses ranging from 47 to 800 was calculated, assuming splitting of Al—O—Al, Al—C and C—O bonds only * and furthermore

$$n_{Al} \leqslant n\Sigma \text{ substituents} \leqslant 3n_{Al}$$

$$\text{for } n \leqslant 7$$

where n_{Al} is the number of aluminium atoms in the molecules.

The masses taken into account were those of aluminium atoms, the methyl group, the phenoxy group and oxygen. As an additional parameter we also included the possibility of the existence of Al—H bonds in the ions, but only in order to complete the sum of substituents to $3n_{Al}$.

The calculated data, despite limitations and omitting the presence of hydrogen substituents at the aluminium atom, shown that there are at least two possible compositions for any mass above 200 and 3 to 10 possibilities for

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* The aromatic ring fragmentation and other processes in the ionisation chamber were also observed (see Table 3). They were omitted in the calculation for the sake of clarity.

TABLE 1

MASS SPECTRA OF SUBLIMED $Me_2Al(OC_6H_5)$ AND ITS RING DEUTERATED ANALOGUE [a]

m/e (H) [b]	Inten-sity	*m/e* (D) [c]	Proposed assignment	*m/e* (H)	Inten-sity	*m/e* (D)	Proposed assignment
15	1.2	15	CH_3^+	177	1.6		$Al_2Me_2(OC_6H_5)^+$
16	1.0	16		191	4.6	195, 196	$Al_2(CH_2)Me_2(OC_6H_5)^+$
27	23.2	27	Al^+				$Al_2Me_3(OC_6H_4)^+$
39	1.6		$C_3H_3^+$	193	4.4	198	$Al_2Me_2(OC_6H_5)O^+$
42	2.5	42	$Al{-}Me^+$	207	1.4	212	$Al_2Me_4(OC_6H_5)^+$
43	2.7	43	$HAlMe^+$ and $Al{-}O^+$	213	2.3	223	$Al(OC_6H_5)_2^+$
51	1.8	54	$C_4H_3^+$	228	5.6	238	$AlMe(OC_6H_5)_2^+$
57	42.7	57	$AlMe_2^+$	229	1.0	239	$M + 1$
58	1.2	58	$M + 1$	253	3.4	261	$Al_2Me(OC_6H_4)_2^+$
61	1.0			255	2.0	265	$Al_2Me(OC_6H_5)_2^+$
65	1.7	70	$C_5H_5^+$	269	3.2	278	$Al_2Me_2(OC_6H_4)(OC_6H_5)^+$
71	1.3	71	Al_2HO^+	281	1.6	286	
77	1.5	82	$C_6H_5^+$	285	100.0	295	$Al_2Me_3(OC_6H_5)_2^+$
85	3.4	85	$Al_2(Me)O^+$	286	17.4	296	$M + 1$
91	6.5	95, 96	$C_7H_7^+$	287	2.0	297	$M + 2$
92	1.1		$C_7H_8^+$	300	1.8	310	$Al_2Me_4(OC_6H_5)_2^+$
115	1.1		$Al_2Me_3O^+$	Above *m/e* = 300 intensities of peaks are below 0.2%			
117	2.5	118	$HAl_2Me_2O_2^+$	*Peaks obtained after heating the sample up to 95°C*			
120	7.7	125	$AlOC_6H_5^+$	301	1.4		$M + 1$ and $Al_2Me_3(OC_6H_5)_2O^+$
121	1.2	126	$M + 1$ and $HAl(OC_6H_5)^+$	302	0.3		$M + 1$
134	1.1	139		316	0.4		$Al_2Me_4(OC_6H_5)_2O^+$ or
135	13.9	140	$AlMe(OC_6H_5)^+$	359	0.5		$Al_3Me_4(OC_6H_5)_2O_2^+$ or
136	1.4	141	$M + 1$				$HAl_3Me_5(OC_6H_5)O^+$
150	1.6	155	$AlMe_2(OC_6H_5)^+$	363	3.0		$Al_2Me_2(OC_6H_5)_3^+$
152	1.1			364	0.6		$M + 1$
163	1.7	168	$Al_2(OC_6H_5)O^+$	373	0.4		$Al_3Me_6(OC_6H_5)_2O^+$
175	1.0			378	0.7		$Al_2Me_3(OC_6H_5)_3^+$
				379	0.3		$M + 1$ and $Al_2Me_2(OC_6H_5)_3O^+$

[a] Up to *m/e* = 300 only peaks of intensity above 1% of the base peak are listed. Sample temp. 40°C; Ion source temp. 60°C; Ionisation potential 75 eV. [b] (H) = Undeuterated compound. [c] (D) = Phenyl ring deuterated compound.

TABLE 2

MASS SPECTRA OF $Me_2Al(OC_6H_5)$, AND ITS RING DEUTERATED ANALOGUES, CRYSTALLIZED FROM HEPTANE, UP TO 101 m/e

m/e (H)[a]		Ion assignment	Int. measured (H)	m/e (D)	m/e (H)		Ion assignment	Int. measured (H)	m/e (D)
Measured	Calculated				Measured	Calculated			
14		CH_2^+	1.0	14	58.000	58.000	$AlCH_3O^+$	1.3	
15		CH_3^+	4.4	15	58.032	58.032	$M + 1$, $Al^{13}CCH_6^+$		
16		CH_4^+	5.3	16	59.024	59.008	$AlCH_4O^+$	2.0	
26.981	26.981	Al^+	16.9	27	60.984	60.987	$AlH_2O_2^+$	1.5	
28.999	28.997	AlH_2^+	1.9	29	63			2.2	
31.015	31.012	AlH_4^+	1.3		65		$C_5H_5^+$	6.3	70
31.019	31.018	CH_3O^+			66		$C_5H_6^+$	5.6	71
32.026	32.026	CH_4O^+			69.957	69.958	Al_2O^+		
38			18.0		70.959	70.958	Al_2HO^+	2.0	
39		$C_3H_3^+$	7.1	42	73.018	73.023	$AlC_2H_6O^+$	9.4	78
39.991	39.989	$AlCH^+$	1.9		75.026	75.024	$C_6H_3^+$	1.4	
40.999	40.997	$AlCH_2^+$	1.5		77		C_6H_5	6.3	82
42.005	42.005	$AlCH_3^+$	2.9		78		$C_6H_6^+$	1.6	
43.015	43.013	$AlCH_4^+$	6.6	43	84.983	84.982	$Al_2CH_3O^+$	7.3	85
50		$C_4H_2^+$	2.2		86.970	86.961	$Al_2HO_2^+$	2.0	
51.989	51.989	AlC_2H^+			87.003	87.003	$AlC_2H_4O_2^+$		
53.002	53.003	C_3HO^+			89			1.4	
53.964	53.963	Al_2^+			91		$C_7H_7^+$	15.2	95
54.008	54.005	$AlC_2H_3^+$			92		$M + 1$	1.8	96
55.026	55.013	$AlC_2H_4^+$	1.2		93		$C_6H_5O^+$	1.0	
55.027	56.021	$AlC_2H_5^+$, $C_3H_4O^+$	1.0		94		$C_6H_6O^+$	4.6	99
57.028	57.028	$AlC_2H_6^+$	35.6	57					

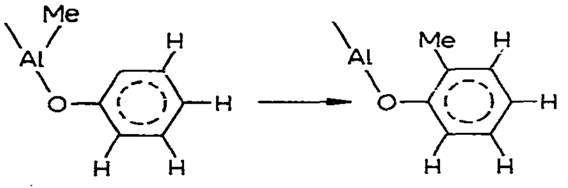
[a] (H) undeuterated compound. [b] (D) phenyl ring deuterated compound.

m/e above 300. Many of these can be excluded immediately as for example Al_4O_{11} but it is still difficult to choose the correct peak composition. Nevertheless the results of calculation have proved useful in cases where peaks of deuterated and undeuterated compounds were compared.

The spectrum of sublimed Me_2AlOPh indicates the presence of a species with degree of association not higher than that of the dimer of Me_2AlOPh. Although the very weak peaks detected above the parent ion of the dimer (300) increase in intensity at elevated temperature (95°C) they are still weak and in all but two cases do not exceed 0.7% of the base peak. These peaks correspond with the $Me_3Al_2(OC_6H_5)_3$ and $Me_2Al_2(OC_6H_5)_4$ ions formed. Since sublimation does not cause any other alternation than change of degree of association, it can be suggested that $Me_3Al_2(OPh)_3^+$ and $Me_2Al_2(OPh)_3^+$ are formed in a disproportionation process occurring in the ionization chamber *. In spectra recorded at 120°C these ions are still more abundant. At higher temperatures the fragmentation becomes more complex as indicated by increased numbers of peaks in the spectra. The new peaks arise mainly from three processes: (i) aromatic ring fragmentation; (ii) formation of an Al—H bond; and (iii) loss of protons from methyl groups (Table 3). Other processes were also found to occur in the ionisation chamber. The isotopic change of peaks with *m/e* ratio 191, 253 and 369 was 4 and 8 mass units. This could be explained by formation of methane from the methyl group and from hydrogen of the aromatic ring in a secondary process (eq. 2).

$$\underset{285}{Al_2Me_3(OC_6H_5)_2^+} \xrightarrow{-CH_4} \underset{269}{Al_2Me_2(OC_6H_4)(OC_6H_5)^+} \xrightarrow{-CH_4} Al_2Me(OC_6H_4)_2^+ \qquad (2)$$

In all spectra a reasonably strong peak of tropylium ion is present. The formation of hydrocarbon ion with 7 carbon atoms indicates that methylation of the



(3)

phenyl ring with subsequent fragmentation is taking place. At room temperature the trimeric species are thermodynamically more stable than the dimers.

$$(Me_2AlOPh)_3 \rightleftharpoons (Me_2AlOPh)_2$$

The spectrum of the trimer differs drastically from that of the dimer. A large number of peaks with *m/e* up to about 850 was observed. Assignment of peaks occurring at above 450 (molecular weight of the trimer) based mainly on the comparison of the spectra of aromatic ring deuterated and undeuterated compounds proved the presence of ions with at least 5 aluminium atoms. The occurrance of these peaks apparently cannot be attributed to crystal lattice interaction

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* Disproportionation was also observed in the spectrum of Et_2AlDMP run at 120°C where even the parent ion of $EtAl(DMP)_2$ dimer was observed (DMP = 2,6-dimethylphenoxy group).

TABLE 3

MASS SPECTRA OF $Me_2Al(OC_6H_5)$ AND ITS RING DEUTERATED ANALOGUE, CRYSTALIZED FROM HEPTANE [a]

m/e (H) [b]	Intensity	*m/e* (D) [c]	Proposed assignment	*m/e* (H)	Intensity	*m/e* (D)	Proposed assignment	*m/e* (H)	Intensity	*m/e* (D)	Proposed assignment
101	3.9			213	9.0	223	$Al(OC_6H_5)_2^+$	365	2.6		
103	1.2			214	2.0			373	2.8	388	$Al_3Me_6(OC_6H_5)_2O^+$
105	3.4			223	37.3	228	$Al_2Me_4(OC_6H_5)O^+$	375	9.0		$Al_3Me(OC_6H_5)_3^+$
115	2.3		$Al_2Me_3O^+$	224	5.1		*M* + 1	376	2.1		
117	6.1	118	$HAl_2Me_2O_2^+$	225	2.4			377	1.7		
119	1.5			227	1.2			378	11.8	393	$Al_2Me_3(OC_6H_5)_3^+$
120	16.7	125	$Al(OC_6H_5)^+$	228	13.4	238	$AlMe(OC_6H_5)_2^+$	379	15.3		
121	8.0		$HAl(OC_6H_5)^+$	229	4.3			380	3.9		
129	2.6		$Al_2Me_3CH_2O^+$	235	2.6		$Al_3Me_3(OC_6H_5)O^+$	389	13.7	399	$Al_3Me_6(OC_6H_5)_2O_2^+$
131	6.3	131	$Al_2Me_3O_2^+$	237	2.0			390	3.8		
133	2.5			238	2.1			391	2.1		$Al_3Me(OC_6H_5)_3O^+$
134	3.9			239	33.3	244	$Al_2Me_4(OC_6H_5)O_2^+$	394	5.9		
135	28.4	140	$AlMe(OC_6H_5)^+$	240	4.2			395	1.8		
136	3.7	141	*M* + 1	241	1.2			405	7.4	420	$Al_3Me_3(OC_6H_5)_3^+$
137	1.7			244	5.5			406	1.8		
147	3.4		$Al_2(OC_6H_5)^+$	245	1.2			421	2.6	436	$Al_3Me_3(OC_6H_5)_3O^+$
149	3.3			251	1.9		$Al_3Me_3(OC_6H_5)O_2^+$	435	1.4	450	$Al_3Me_5(OC_6H_5)_3^+$
150	3.0	155	$AlMe_2(OC_6H_5)^+$	253	27.7	261	$Al_2Me(OC_6H_4)_2^+$	437	4.3		
$150\frac{1}{2}$	1.1	$155\frac{1}{2}$	301^{2+}	254	5.8			438	1.8		
151	4.3		$AlMe(OC^6H_5)O)$	255	4.9	265	$Al_2Me(OC_6H_5)_2^+$	441	3.1	461	$Al_2Me(OC_6H_5)_4^+$
152	3.7			267	1.6		$Al_3Me_3(OC_6H_5)O_3^+$	451	9.3	466	$Al_3Me_5(OC_6H_5)_3O^+$
153	1.4			269	12.4	278	$Al_2Me_2(OC_6H_4)(OC_6H_5)^+$	452	3.0		
159	1.4		$Al_3Me_2O_3^+$	270	2.4			453	2.2		
				271	4.5	281	$Al_2Me(OC_6H_5)_2O^+$				
				281	2.2	286	$Al_3Me_5(OC_6H_5)O_2^+$				
				283	2.4						
				285	89.4	296	$Al_2Me_3(OC_6H_5)_2^+$				

161	3.9			286	15.7	296	$M + 1$	456	1.5	476	$Al_2Me_2(OC_6H_5)_4^+$
163	5.9	168	$Al_2(OC_6H_5)O^+$	287	5.2	297	$M + 2$	467	13.9	482	$Al_3Me_5(OC_6H_5)_3O_2^+$
165	2.5			297	4.2	302	$Al_3Me_5(OC_6H_5)O_3^+$	468	3.9		
166	4.7		$AlMe_2(OC_6H_5)O^+$	299	1.7			483	3.8		
167	2.9			301	100.0	311	$Al_2Me_3(OC_6H_5)_2O^+$	513	1.8	533	$Al_3Me_4(OC_6H_5)_4^+$
168	1.7			302	19.0	312	$M + 1$	529	3.8	549	$Al_3Me_4(OC_6H_5)_4O^+$
175	2.2			303	2.8	313	$M + 2$	530	1.4		
177	10.5	182	$Al_2Me_2(OC_6H_5)^+$	306	1.1			545	2.4	565	
178	1.8			311	1.6			585	1.3	605	$Al_4Me_7(OC_6H_5)_4^+$
179	6.5		$Al_2(OC_6H_5)O_2^+$	313	3.9		$Al_3Me_2(OC_6H_5)_2O^+$	601	2.3	621	$Al_4Me_7(IC_6H_5)_4O^+$
$181\frac{1}{2}$	1.1	$188\frac{1}{2}$		315	1.2			617	1.1		$Al_4Me_7(OC_6H_5)_4O_2^+$
182	1.9			316	12.8	326	$Al_2Me_4(OC_6H_5)_2O^+$	663	1.0	688	$Al_4Me_6(OC_6H_5)_5^+$
191	5.4	195, 196	$Al_2(CH_2)Me_2(OC_6H_5)^+$	317	11.9			679	-	604	$Al_4Me_6OC_6H_5O^+$
			$Al_2Me_3(OC_6H_4)^+$	318	2.3			689			
192	1.5			327	4.4	337	$Al_3Me_4(OC_6H_5)_2^+$	695			
193	12.7	198	$Al_2Me_2(OC_6H_5)O^+$	329	1.0		$Al_3Me_2(OC_6H_5)_2O_2^+$	705			$Al_5Me_7(OC_6H_5)_5^+$
194	1.4		$M + 1$	332	4.4			721			$Al_5Me_7(OC_6H_5)_5O^+$
195	2.7			333	1.2			737			
207	11.8	212	$Al_2Me_4(OC_6H_5)^+$	343	3.1	353	$Al_3Me_4(OC_6H_5)_2O^+$	741			$Al_4Me_5(OC_5H_6)_6^+$
208	1.2		$M + 1$	347	1.5			751	<1	776	$Al_5Me_9(OC_6H_5)_5O^+$
209	6.1	214	$Al_2Me(OC_6H_5)O_2^+$	349	1.4			757			$Al_4Me_5(OC_5H_6)_6O^+$
210	1.0			359	6.3	369	$Al_3Me_4(OC_6H_5)_2O_2^+$	767			$Al_5Me_9(OC_6H_5)_5O_2^+$
211	4.3			360	1.4			783			
212	2.6			361	1.3						
				363	73.9	378	$Al_2Me_2(OC_6H_5)_3^+$				
				364	18.3	379	$M + 1$				

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[a] At m/e from 101 to 660 only peaks of intensity above 1% of the base peak are included. Ion source temp. 180°C; Sample temp. 120°C; Ionisation voltage 75 eV.

[b] (H) = Undeuterated compound. [c] (D) = Phenyl ring deuterated compound.

because at least some of them should then also be observed in the spectrum of the dimeric species. Since the change of association from trimer to dimer was found to occur at elevated temperature the presence of ions with high *m/e* value can be rationalised as products of fragmentation of highly associated intermediates formed in the trimer-dimer process. The opposite process does not take place at elevated temperatures and therefore the spectrum of the dimer is (nearly) clean above the molecular ion. The change of association to the dimer at elevated temperature was also observed for $(Me_2AlH)_3$ [16]. In the mass spectra of these trimeric compounds Tanaka and Smith observed ions with clear-cut termination at the mass of the hexametric species [1]. They suggest the existence of stable hexametric units with a cyclic or cluster arrangement. Our data show that peaks with higher masses correspond rather to the high molecular weight associates formed as intermediates in the process trimer → intermediate → dimer. The life time of these aggregates has to be longer than their presence in the ionisation chamber. Their structure can be linear but the existence of a cyclic-linear or cluster arrangement is also possible.

Experimental

The investigated dimethylaluminium phenoxide was prepared according to the method given in the literature [12,13]. The trimeric compound was obtained from the sublimed dimer which after dissolving in heptane was kept at least 6 days in solution. After evaporation of the solvent under vacuum the Me_2AlOPh obtained displays a cryoscopically measured molecular weight of 445 (calc. for trimer, 450). Mass spectra were obtained using a JEOL JMS-01 SG double focussing mass spectrometer. Ionisation voltage 75 V, ionisation current 100 A, accelerating voltage 6 kV. For high resolution measurements Ilford Q-2 photo plates were used. The glass capillaries containing the investigated compounds were broken in a helium stream and introduced into the ion source by a direct inlet system.

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