Mass Spectrometry of Organometallics. II. [Diethyl Aluminum (III) Chloride–Water] System and Aluminum (III) Chloride

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The less volatile components of the [diethyl aluminum (III) chloride–water (20:1)] system were deduced from mass spectrometry. Ions which bear two aluminum atoms were classified to one of the proposed skeletal structures on the basis of several established facts: (1) aluminum atoms hardly change their valence during fragmentations, (2) the stability of bridge bondings increases in the order ethyl < chlorine < oxygen, and (3) even-electron ions are far more abundant than odd-electron ions. Then, the ions which bear two oxygen atoms were classified to the clusters bridged by two oxygen atoms, and the ions which bear only one oxygen atom to the clusters bridged by both oxygen and chlorine atoms. Since the transformation of an electron-deficient oxygen-bridge into a normal oxygen bond did not occur appreciably during fragmentations, the presence of ions of a certain skeletal structure could be taken as a reflect of the presence of species of the same skeletal structure in the mixed components of the sample. Cyclic six-membered skeletal structures were proposed for ions which bear Al_2O_3 . The mass spectrum of aluminum (III) chloride has confirmed the assumption: oxygen-bridged clusters are far more stable than chlorine-bridged clusters.

1. Introduction

There have been increasing number of literatures dealing with a variety of binary catalyst systems which are composed of organo-aluminum compounds. Owing to the scarcity of analytical means which provide informations on the active species of these catalysts, the mechanisms of most of these catalyst systems are still obscure. Mass spectrometry, on the other hand, has been demonstrated to give important informations on the composition and structure of each component in the catalyst, as was described in the studies on [triethyl aluminum–water]¹⁾ and Ziegler catalysts²⁾. It was also noted, however, in these studies that the organo-aluminum compounds gave a number of oxygen-containing ions which made the mass spectra considerably complicated, since the organo-aluminum compounds are very sensitive to air and moisture and are easily susceptible to oxidation

or hydration.

The object of this work was to get the elemental compositions of the ions arising from the [diethyl aluminum (III) chloride–water (20:1)] system which were expected to be present as dimers and trimers through oxygen- and/or chlorine-bridge bondings. The system was selected to get informations on the oxidated species which would be formed in usual operations in industry. The study on aluminum (III) chloride was carried out briefly for the convenience of comparison.

2. Experimental

Diethyl aluminum (III) chloride was purchased from Ethyl Corp., and was used as a dilute solution in n-heptane. Aluminum (III) chloride was purified by sublimation under a reduced pressure. A cumulative exposure technique was applied to detect the less volatile components through the use of a mass

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spectrograph of the Mattauch-Herzog type (JEOL, 0ISG).

The [diethyl aluminum (III) chloride–water (20:1)] system was prepared as a dilute solution in n-heptane under a nitrogen atmosphere and was stored in a sealed capillary. The capillary was broken in a stream of nitrogen just before measurement and was introduced directly into a pre-evacuation chamber of the direct sample-inlet system. The solvent was removed in the chamber and the less volatile components were introduced into the ion source the temperature of which was 80–200°C. The sample was ionized by 100 μ A of 75 eV electrons. Ions were accelerated by an electric field of 8 kV and were collected on a photographic plate (Ilford Q2). The photographic plate was developed by DK-76 for 7 min at 20°C. Perfluorokerosene was used as an internal reference for exact mass determination.

The distance of peaks and their relative densities of the blackening were measured through the use of a comparator of twenty-five magnifications. A part of the data deduction, calculation of exact masses, background subtraction, determination of elemental compositions and fragmentation check were performed according to the procedures described in the preceding papers.^{3–5)} The data processing was carried out in the Computation Center of Kyoto University.

3. Results and Discussion

3.1 Mass Spectrum of [Et₂AlCl–H₂O (20:1)] System

3.1.1 Reduction Procedures of Mass Spectra

The sample was introduced directly into the ionization chamber and was heated gradually in order to detect the ions which would be formed from dimers or trimers. A cumulative exposure technique usually afforded a considerably large number of ions on a photo-

graphic plate together with background peaks and internal reference (PFK) peaks.

In addition there were many ions which contained several chlorine atoms, therewith being the mass spectra highly complicated owing to ³⁷Cl-isotope. Although all peaks in the mass spectra are not understood fully at this time, the computer-aided deduction procedures as described in the previous papers^{3,4)} characterized most of the peaks and gave then unambiguous elemental compositions. The ions which can be assigned to combinations of the most abundant isotopes are represented in Table I. A relatively wide allowable difference, 0.006–0.012 amu., was taken in the assignment of elemental compositions because the resolution of the spectra lowered, to some extent, owing to the overlap of Cl-isotopes and owing to the cumulative exposure.

After the elemental compositions were determined for all peaks, the computer sought the ions which carried desired common elemental compositions, such as Al₂O₂, Al₂OCl, Al₂Cl₂, or Al₃O₃, and tabulated the groups which are sticking to the common compositions (skeletons). These procedures performed by the use of the additional subroutine for "classification of cluster" are considerably useful for classifying the ions according to the skeletal structures.

3.1.2 Ions Containing One or Two Aluminum Atoms

Entries 1–6 in Table I show the ions which contain one aluminum atom. Besides the parent and fragment ions of the diethyl aluminum chloride monomer, there are several ions which could arise from disproportionation. Entries 18–22 show the ions which could be from the dimer of diethyl aluminum (III) chloride. The detection of the abundant parent ion of the dimer is in contrast to the spectrum of the [triethyl aluminum–water] system, in which the intensity of the ions corresponding to the

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Table 1. Partial mass spectrum of [Et₂AlCl–H₂O (20:1)].

Entry	R. I.*	(Mass) obsd.	Assign.	(Mass) calcd.	Type
1	7		AlEt ₂		
2	10		AlEtCl		
3	8		AlCl ₂		
4	1	114.093	AlEt ₃	114.099	
5	2	120.023	AlEt ₂ Cl	120.029	
6	3	125.958	AlEtCl ₂	125.958	
7	6	134.973	Al ₂ EtClOH	134.974	V
8	VW	139.896	Al ₂ OCl ₂	139.895	
9	VW	140.906	Al ₂ Cl ₂ OH	140.904	V
10	3	163.004	Al ₂ Et ₂ ClO	163.005	V
11	3	168.931	Al ₂ EtCl ₂ O	168.935	V
12	8	174.865	Al ₂ Cl ₂ O	174.865	V
13	2	150.969	Al ₂ EtClO ₂ H	150.968	II
14	4	156.901	Al ₂ Cl ₂ O ₂ H	156.896	II
15	2	184.927	Al ₂ EtCl ₂ O ₂	184.930	II
16	2	198.989	Al ₂ OEt ₂ Cl ₂ H	198.982	IV
17	5	227.015	Al ₂ Et ₂ Cl ₂ O	227.013	IV
18	7	211.017	Al ₂ Et ₂ Cl ₂	211.018	VI
19	3	239.050	Al ₂ Et ₂ Cl ₂ C ₂ H ₄	239.050	VI
20	3	240.045	Al ₂ Et ₄ Cl ₂	240.057	VI
21	1	244.989	Al ₂ Et ₂ Cl ₂ C ₂ H ₄	244.987	VI
22	2	245.992	Al ₂ Et ₂ Cl ₃	245.994	VI
23	2	248.929	Al ₂ O ₂ Et ₂ Cl ₂	248.938	I
24	3	274.996	Al ₂ Et ₂ Cl ₂ O ₄	274.998	I
25	2	315.033	Al ₃ Et ₄ Cl ₂ O ₃	315.024	VIII
26	3	320.957	Al ₃ Et ₂ Cl ₃ O ₃	320.953	VIII
27	2	326.883	Al ₃ Et ₂ Cl ₄ O ₃	326.883	VIII
28	1	373.098	Al ₃ Et ₄ Cl ₂ O ₃	373.102	VII
29	1	379.030	Al ₃ Et ₂ Cl ₃ O ₃	379.032	VII
30	0.3	257.959	Al ₃ Et ₂ Cl ₂ O ₂ H	257.953	VII
31	1	384.974	Al ₃ Et ₄ Cl ₄ O ₃	384.961	VII

* Relative density of the blackening of the plate judged with the naked eye through the use of a comparator of twenty-five magnifications.
VW refers to "very weak".

dimer was extremely low even when the water was limited to a small quantity. These facts indicate clearly that chlorine-bridges are highly stable compared to ethyl-bridges.

The [diethyl aluminum (III) chloride–water] system itself is expected to be complicated matters by mixing a number of components which will be bridged by oxygen and/or chlorine. It was the initial object of this work to see the possibility if the ions which contain two aluminum atoms can reflect, to some extent, on the composition and relative abundance of each component in the complicated mixture. It seems an important question if the mass spectral data will afford informations on the skeletal structures of the mixture because of the paucity of analytical means for such a complicated mixture.

We will now attempt to assign the ions entered as 7–24 in Table 1 to one of the proposed skeletal structures, thereby shedding some light on the structure and relative abundance of each component in the original complicated mixture. These attempts are based on several established facts: (1) aluminum atoms in the ions hardly change their valence during fragmentations, (2) the stability of bridge bondings increases in the order ethyl-bridge < chlorine-bridge < oxygen-bridge, and (3) even-electron ions are far more abundant than odd-electron ones.

From the relative stability of the bridge bondings, we can reasonably assume that the ions which carry two oxygen atoms may preferably form the clusters bridged by two oxygens (I, II and III), that the ions which carry only one oxygen atom possibly form the clusters bridged by both oxygen and chlorine (IV and V), and that the ions which carry no oxygen atom possibly form the cluster bridged by two chlorines.

Inasmuch as the valence of aluminum atoms does not change through fragmentations, the fragmentations of aluminum-containing ions should be rather simple; and an apparent loss of two radical moieties from the oxygen-containing cluster could be possibly explained by the transformation of electron-deficient oxygen bridges into normal oxygen bonds ($I \rightarrow II \rightarrow III$, and $IV \rightarrow V$). The transformation of oxygen bridges could be assumed by detection of abundant ions which could be led by loss of three radical moieties from the skeletal structure I or IV, whereas the appearance of abundant ions with loss of three radical moieties seemed rather improbable.

The well-known odd-even electron rule for the ion intensity limits the number of ethyls plus chlorines plus hydrogens which are sticking to the skeleton for abundant ions. There are several ions which bear ethylene or oxygen other than used as clusters. The ethylene and oxygen, however, have even electrons, and, therefore, do not change the odd-even character of the ions in question. The odd-even electron character can be, then, discussed by the number of groups of odd electrons which are sticking to the skeleton. In view of these deductions we can anticipate that the following ions should be abundant:

1. Al_2O_2 (skeleton I) + five groups of odd-electron.
2. Al_2O_2 (skeleton II) + three groups of odd-electron.
3. Al_2O_2 (skeleton III) + one group of odd-electron.
4. Al_2OCl (skeleton IV) + four groups of odd-electron.
5. Al_2OCl (skeleton V) + two groups of odd-electron.
6. Al_2Cl_2 (skeleton VI) + three groups of odd-electron.

The ions entered as 7–24 in Table I evidently show that the ions which fall under I,

2, and 4–6 are detected abundantly, whereas the ions which fall under 3 can not be observed. The fact that the ions which have skeletal structure III can not be detected clearly indicates that the ions which have skeletal structure III were not produced appreciably during the fragmentations. These facts may point out that the transformation of oxygen bridges proposed above is hardly due to the fragmentation. The failure to observe the ions of structure III may be due to the limited amount of water, since the ion, such as $[Al_2O_2Et]^+$, was observed in the case of [triethyl aluminum–water (5:1)] system.^{11,6)} If we assume that the transformation of oxygen bridges does not proceed appreciably during the fragmentation, the presence of the ions which have skeletal structures II and V can possibly reflect on the presence of species of the same skeletal structures in the mixed components of the sample. The proposed types of the skeletal structure are represented in the last column in Table I.

Many other skeletal structures can be assumed for each ion if we deduce from the elemental composition only on the basis of the odd-even electron rule. For example, the following skeletal structures can be proposed for $[Al_2O_2Cl_2Et]^+$ (entry 15 in Table I).

However, the contribution of structure (1) is reasonably expected to be actually great by taking the stability of the bridged bondings into consideration.

3.1.3 Ions containing Three Aluminum Atoms

Ions which have three aluminum atoms are entered as 25–31 in Table I. As may be

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seen in Table 1, these ions carry three oxygen atoms without exception. The following skeletal structures, VII and VIII, could conceivably be assigned to these ions on the basis of the total

number of odd-electron groups and of the relative stability of bridged bondings. Analogous cyclic skeletal structure was also proposed for Al_3 -ions arising from the [triethyl aluminum–water] system.

The fact that the ions composed of (Al_3O_3 + four odd-electron groups) were not detected seems to indicate, again, that the transformation of oxygen-bridges does not proceed during fragmentations, thereby providing a support to the assumption that the ions of skeletal structures VII and VIII may reflect on the presence of species of the same skeletons in a mixed sample.

3.2 Mass Spectrum of Aluminum (III) Chloride

It seemed important to see the difference in the fragmentation processes of ions which contain two or three aluminum atoms bridged by oxygen or chlorine in order to prove the assumption: oxygen-bridged bondings are more stable than chlorine-bridged bondings. There are several reports which dealt with mass spectrometry of aluminum (III) chloride.⁷⁻⁹⁾ It seemed necessary, however, to measure the mass spectrum under the same conditions employed for the [$AlEt_2Cl-H_2O$] system, providing the partial mass spectrum shown in Table 2.

Ions which contain two aluminum atoms can be considered to be formed from chlorine-bridged aluminum (III) chloride dimers, and the intensity variation can be explained by the

Table 2. Partial mass spectrum of aluminum (III) chloride.

Entry	I. R. *	(Mass) _{obsd.}	Assign.	(Mass) _{calcd.}
1	2	96.918	$AlCl_2^+$	96.919
2	6	131.889	$AlCl_3^+$	131.888
3	1	166.855	$AlCl_4^+$	166.857
4	3	88.931	Al_2Cl^+	88.932
5	2	193.839	$Al_2Cl_2^+$	193.839
6	5	228.808	$Al_2Cl_3^+$	228.807
7	1.5	263.775	$Al_2Cl_4^+$	263.776
8	3	80.948	Al_3^+	80.945
9	1	115.912	Al_3Cl^+	115.914
10	**	360.682	$(Al_3Cl)_2^+$	360.695
11	VW	247.798	$Al_4Cl_4^+$	247.802

* Same as Table I.

** Peak was extremely broad.

number of chlorine atoms which are sticking to the skeleton. Entries 8–10 show ions which contain three aluminum atoms. Porter and Zeller⁹⁾ also observed these ions and they considered the origin of these ions was ion–molecule reactions. However, they also detected less abundant parent ions of trimers, which seems to indicate the cyclic skeletal structure. The $Al_3Cl_8^+$ peak was considerably broad in our measurement, presumably owing to an instability of the cyclic skeleton or owing to the ion–molecule reaction.

Besides the ions of chlorine-bridged clusters, several ions which can be assumed to have direct aluminum–aluminum bonds, such as Al_2Cl^+ , Al_3^+ and Al_3Cl^+ , were also observed. These ions could be formed by loss of chlorine atoms from the chlorine-bridged cluster. Since the loss of bridged-oxygen was not observed appreciably, the apparent loss of chlorine atoms can be taken as an evident support to the assumption of the relative stability of bridged-bondings which enabled us to classify the skeletal structures as described in 3. 1. 2.

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References

- 1) T. Ueno and Y. Takegami, unpublished.
- 2) Y. Takegami, T. Ueno, T. Suzuki and Y. Fuchizaki, *Bull. Chem. Soc. Japan*, **41**, 2637 (1968).
- 3) T. Ueno, T. Sueyoshi and Y. Takegami, *Mass Spectroscopy Japan*, **22**, 95 (1974).
- 4) T. Ueno, T. Sueyoshi, K. Ashida and Y. Takegami, *ibid.*, **22**, 103 (1974).
- 5) T. Ueno, T. Sueyoshi, E. Tanaka, R. Jinkawa, A. Hamada and Y. Takegami, *ibid.*, **22**, 109 (1974).
- 6) T. Ueno, K. Ashida, E. Tanaka and Y. Takegami, *Mass Spectroscopy Japan*, to be published.
- 7) J. Tanaka and S. R. Smith, *Inorg. Chem.*, **8**, 265 (1969).
- 8) T. Imanaka, *Bull. Chem. Soc. Japan*, **40**, 2182 (1967).
- 9) R. F. Porter and E. E. Zeller, *J. Chem. Phys.*, **33**, 858 (1960).