Mass Spectrometry of Organometallics. III. The Detection of Less Volatile Components of [Triethyl Aluminum-Water] System and a Proposal to the Elucidation of Their Skeletal Structures

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Triethyl aluminum and the titled system were studied by mass spectrometry with photographic processings. A number of oxygen-containing ions were detected from the [triethyl aluminum-water] system. A new method is proposed for elucidating the skeletal structures from ion intensity variation according to the number of odd-electron groups which are sticking to the skeleton. The method is based on: (a) invariability of valence of aluminum atoms during fragmentations, (b) relatively high stability of oxygen-bridge bondings, (c) the odd and even electron rule, and (d) high intensity of the ions which come from the parent ion with removal of one radical moiety. Cyclic structures can be assigned to the skeletons of Al_2O_3 , Al_3O_3 and Al_4O_4 , which agree with those suggested in literatures.

1. Introduction

Inasmuch as the aluminum alkyls are very sensitive to air and moisture, the aluminum alkyls prepared in usual procedures are reasonably expected to be contaminated by a small amount of oxidized and/or hydrolyzed species¹⁾. Although the amount of these oxygen-containing species appears relatively small, it is not desirable if the oxygen-containing species can lightly be neglected, because the oxygen-containing species seem to play important roles in a variety of catalysis and because the fraction of active sites has been known to be extremely low in many catalyst systems. In fact, it was reported that the triethyl aluminum treated with a small amount of water has a high catalytic activity for the ring-opening polymerization of cyclic ethers²⁾. It seems important, therefore, to propose a research technique which will shed some light on the composition of less volatile oxygen-containing

components and also on the elucidation of their structures.

There are a few studies on mass spectrometry of aluminum alkyls in literatures^{1), 3-6)}. No information, however, was presented about the less volatile oxygen-containing species. In most of those studies, the aluminum alkyls were introduced into the ion source through a gas-inlet system.

We have studied mass spectrometry of organometallics by cumulating the ions on a photographic plate. The mass spectrograph of the Mattauch-Herzog type fits this purpose. This technique is considerably suitable to the detection of less volatile components of organometallics, as demonstrated by the detection of $(\text{C}_2\text{H}_5)_2\text{TiCl}_2\text{AlC}_2\text{H}_5^+$ from a mixture of the solutions of $(\text{C}_2\text{H}_5)_2\text{TiCl}_2$ and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}^{1)}$.

In the previous paper⁸⁾, we reported mass spectrometry of the $[\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{H}_2\text{O}]$ system and proposed cyclic skeletal structures to the

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ions which had more than two aluminum atoms. In the present article, the results of mass spectrometry of the $[\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}]$ system, as well as $\text{Al}(\text{C}_2\text{H}_5)_3$ itself, are reported. The cyclic structures are proposed to the oxygen-containing aluminum clusters on the basis of variation in the ion intensity. The possibility of transformation of the electron deficient oxygen-bridge bondings into normal oxygen bondings during fragmentations is also briefly discussed.

2. Experimental

Triethyl aluminum was purchased from the Ethyl Corp., and was used as a diluted solution (1.8–2.0 mol/l) in *n*-heptane. Cumulative exposure techniques were applied to the detection of less volatile components through the use of a mass spectrograph of the Mattauch-Herzog type (JEOL, 01SG). The $[\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}(5:1)]$ system was prepared as a diluted solution in *n*-heptane under nitrogen atmosphere and preserved in a sealed capillary. The capillary was cut in a stream of nitrogen just before measurement and introduced directly into the pre-evacuation chamber of the direct inlet system. The solvent was removed in the chamber under a reduced pressure, and the capillary which contained less volatile components was directly introduced into the ion source. The sample was ionized by 100 μA of 75 eV electrons at the temperature range of 100–250°C. Ions were accelerated with 8 kV and were focused 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 the determination of exact masses.

The distance between the peaks and their relative density of blackenings were determined through the use of a comparator of twenty-five magnifications. A part of computer-aided deduction of the spectral data was performed

according to the procedures described previously^{9–10}. The computations were carried out in the Computation Center of Kyoto University (FACOM 230-60).

3. Results and Discussion

3.1 Triethyl Aluminum

Introduction of triethyl aluminum vapor into the ion source through the gas-inlet system gave a relatively simple mass spectrum, which could be explained by successive eliminations of ethyl, ethylene, and hydrogen moieties from its parent peak ($m/e=114$)⁵. The abundant ions which bear more than two aluminum atoms were detected in the mass spectrum of trimethyl aluminum⁹, and NMR studies confirmed the presence of bridged methyl groups^{12, 13}. No appreciable peak which could be assigned to the dimer of triethyl aluminum was detected in our measurements. The possibility if any ions corresponding to the dimer could be detected was reexamined by introducing triethyl aluminum directly into the ion source, the temperature of which varied at a range of 80–150°C. Several peaks appeared at a region of 120–250 a.m.u. However, any peaks which could be assigned to the dimer of triethyl aluminum, $\text{Al}_2(\text{C}_2\text{H}_5)_6^+$, and the ions which corresponded to $\text{Al}_2(\text{C}_2\text{H}_5)_n^+$ ($n=1-5$) were not found in the spectrum. Most of the peaks of this region could be assigned to oxygen-containing ions which probably came from the oxidized and/or hydrolyzed species of triethyl aluminum.

The ion corresponding to the dimer, $\text{Al}_2(\text{CH}_3)_6^+$, was detected in the case of trimethyl aluminum^{10, 11}, and more abundant ions which had Al_2Cl_2 clusters were reported in the cases of diethyl aluminum chloride and ethyl aluminum dichloride¹¹. These results indicate that ethyl-bridges are less stable than methyl-bridges, which, in turn, are far more unstable than chlorine-bridges.

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3.2 [Triethyl Aluminum-Water (5:1)] System

The oxygen-containing ions of relatively high mass unit were accompanied by mass spectrometry of triethyl aluminum. The detection and structural elucidation of these ions seemed to provide important informations for deduction of contaminants and active sites of the $[\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}]$ catalyst system. A mixture of triethyl aluminum with water was then measured by direct introduction of the samples into the ion source, the temperature of which varied at a range of 100–250°C. A considerably large number of peaks were detected on the photographic plate. The spectra were extremely complicated at a range of 120–250 a.m.u. Although the peaks detected on the photographic plate are not fully understood at the present time, many peaks can be assigned to the ions which come from partly ethoxylated species of triethyl aluminum in the forms of dimer, trimer, tetramer, and so on. The abundant peaks which are considered to originate from the ethoxylated species are summarized in Table 1.

3.3 Intensity Variation of Ions Which bear Al_2O_2 Cluster

The ions entried as 6–13 in Table 1 are those which can be considered to originate from the dimer of diethyl aluminum ethoxide. The fact that these ions bear Al_2O_2 as a common elemental composition shows clearly that the dimer has a skeletal structure bridged by ethoxy and hydroxy moieties⁽⁴⁾. Chambers and his co-workers⁽⁵⁾ reported the mass spectrum of pure diethyl aluminum ethoxide. Their spectrum contained a large number of ions which carried several hydrogen atoms. The intensity variation of the ions entried as 6–13 is illustrated in Scheme 1.

Scheme 1. Suggested fragmentation of $\text{Al}_2\text{O}_2\text{Et}_6$. Numbers in parenthesis refer to relative density and "n" refers to the number of odd-electron groups sticking to the skeleton (Al_2O_2).

The eliminations of hydrogen, ethyl and ethylene may be major processes of the fragmentation. It has been known that the terminal alkyl groups in organometallics are much more subject to cleavage than bridged groups and that hydroxy bridges are more stable than ethoxy bridges⁽⁴⁾. The eliminations of ethyl groups and ethylene moieties are, therefore, considered to occur at terminal ethyl groups and at bridged ethoxy groups respectively, and hydroxy bridges may be formed in the latter process. The elimination of hydrogen gives relatively abundant ions which carry the ethylene moiety, which may presumably be stabilized as even-electron ions by localizing the positive charge as carbonium ions.

3.4 Application of Odd and Even Electron Rule

A remarkable feature of the ions represented in Scheme 1 is that the relative intensities of the ions which carry even numbers of (ethyls plus hydrogens) are always high. The tendency can be reasonably explained by the odd and

Table 1. Partial mass spectrum of $[\text{AlEt}_3\text{-H}_2\text{O} (5:1)]$ system.

Entry	(Mass) _{obsd.}	R.I. ^{a)}	Assignment	(Mass) _{calcd.}	Type of skeleton
1	69.959	1	Al_2O^+	69.958	
2	70.967	2	Al_2OH^+	70.966	
3	72.016	0.3	AlOEt^+	72.016	
4	113.096	0.3	$\text{AlEt}_2\text{C}_2\text{H}_4^+$	113.091	
5	114.094	3	AlEt_3^+	114.099	
6	114.991	2	$\text{Al}_2\text{O}_2\text{Et}^+$	114.992	III
7	144.032	1	$\text{Al}_2\text{O}_2\text{Et}_2^+$	144.031	III
8	173.071	4	$\text{Al}_2\text{O}_2\text{Et}_3^+$	173.070	II
9	175.086	4	$\text{Al}_2\text{O}_2\text{Et}_3\text{H}_2^+$	175.086	I
10	203.119	5	$\text{Al}_2\text{O}_2\text{Et}_4\text{H}^+$	203.117	I
11	231.147	4	$\text{Al}_2\text{O}_2\text{Et}_5^+$	231.149	I
12	259.182	3	$\text{Al}_2\text{O}_2\text{Et}_5\text{C}_2\text{H}_4^+$	259.182	I
13	260.180	0.3	$\text{Al}_2\text{O}_2\text{Et}_6^+$	260.188	I
14	189.064	3	$\text{Al}_2\text{O}_3\text{Et}_3^+$	189.065	II + OEt
15	247.145	5	$\text{Al}_2\text{O}_3\text{Et}_5^+$	247.143	I + OEt
16	276.175	2	$\text{Al}_2\text{O}_3\text{Et}_6^+$	276.183	I + OEt
17	263.137	4	$\text{Al}_2\text{O}_4\text{Et}_3^+$	263.138	I + 2 OEt
18	292.179	0.1	$\text{Al}_2\text{O}_4\text{Et}_6^+$	292.177	I + 2 OEt
19	275.134	4	$\text{Al}_3\text{O}_3\text{Et}_3\text{H}^+$	275.133	VI
20	361.243	8	$\text{Al}_3\text{O}_3\text{Et}_8^+$	361.242	V
21	389.275	4	$\text{Al}_3\text{O}_3\text{Et}_8\text{C}_2\text{H}_4^+$	389.275	V
22	319.153	8	$\text{Al}_3\text{O}_4\text{Et}_6^+$	319.160	VI + OEt
23	347.187	4	$\text{Al}_3\text{O}_4\text{Et}_8\text{C}_2\text{H}_4^+$	347.191	VI + OEt
24	348.197	2	$\text{Al}_3\text{O}_4\text{Et}_7^+$	348.198	VI + OEt
25	377.237	10	$\text{Al}_3\text{O}_4\text{Et}_8^+$	377.237	V + OEt
26	406.273	2	$\text{Al}_3\text{O}_4\text{Et}_9^+$	406.276	V + OEt
27	433.257	2	$\text{Al}_4\text{O}_4\text{Et}_9^+$	433.260	VII
28	461.290	2	$\text{Al}_4\text{O}_4\text{Et}_9\text{C}_2\text{H}_4^+$	461.291	VII
29	489.323	1	$\text{Al}_4\text{O}_4\text{Et}_9(\text{C}_2\text{H}_4)_2^+$	489.321	VII
30	533.346	1	$\text{Al}_4\text{O}_5\text{Et}_9(\text{C}_2\text{H}_4)_3^+$	533.347	b)
31	561.334	2	$\text{Al}_3\text{O}_5\text{Et}_{10}(\text{C}_2\text{H}_4)_2^+$	561.336	b)
32	577.285	1	$\text{Al}_4\text{O}_5\text{Et}_{11}^+$	577.289	b)

a) Relative density of blackening judged with the naked eye through the use of a comparator of twenty-five magnifications.

b) Cyclic skeletal structure could be assumed, but remained to be confirmed.

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even electron rule which can be summarized: the ions of even electrons should be more abundant than those of odd electrons.

Although there are several ions which carry hydrogen and/or ethylene moieties as can be seen in Table 1, the ethylene moiety itself has even electrons, and, therefore, the number of ethylene groups which are sticking to the skeleton does not change the odd-even electron character of the ions subjected. Therefore, the odd-even electron character can be discussed by the total number of ethyls plus hydrogens (number of odd-electron groups) which are sticking to the skeleton.

According to this rule, the weak ions, $\text{Al}_2\text{O}_2(\text{C}_2\text{H}_5)_6^+$, $\text{Al}_2\text{O}_2(\text{C}_2\text{H}_5)_4^+$, and $\text{Al}_2\text{O}_2(\text{C}_2\text{H}_5)_2^+$ can be taken as ions of odd electrons. The fact that these ions give weaker peaks than those of even electrons indicates that the aluminum atoms in these ions hardly change their valence during the fragmentation process. The invariability of aluminum valence was also demonstrated in the fragmentation of tris (acetylacetonato) aluminum¹⁵⁾. These considerations can be taken, in turn, as another support to confirm that $\text{Al}_2\text{O}_2(\text{C}_2\text{H}_5)_6^+$ originated from $\text{Al}_2\text{O}_2(\text{C}_2\text{H}_5)_6$ species which were contained in the $[\text{Al}(\text{C}_2\text{H}_5)_3\text{-H}_2\text{O}]$ system as such.

Although the intensities of the ions entried as 6–13 obey the odd and even electron rule, the number of odd-electron groups of abundant ions ranges five, three, and one. The change in the number of odd-electron groups seems important in the interpretation of the spectrum and in the deduction of composition and relative abundance of each component in the mixed sample. In view of the established fragmentation processes of organic^{16, 17)} and organometallic^{4), 6)} compounds, the appearance of abundant ions with loss of three or five radical moieties from the parent ion seems

rather improbable, if valence of central metal(s) does not change. Furthermore, the “ $(3n-1)$ rule”^{*} proposed for organo-¹⁾ or inorganic¹⁸⁾ aluminum compounds demonstrates clearly that the ion which can be produced from the parent ion by removing one radical moiety should be abundant.

Therefore, the ions which bear three or one odd-electron groups can reasonably be assumed to originate from the species which bear four or two odd-electron moieties, respectively. These species can be produced by transformation of electron-deficient oxygen bridges into normal oxygen bonds (I $\rightarrow$ II $\rightarrow$ III). The transformations are reasonably considered to proceed mostly during the reaction of triethyl aluminum with water rather than during the fragmentation of ions on the basis of the “ $(3n-1)$ rule”, whereas some degree of the transformation accompanied by the fragmentation can not be entirely ruled out. Thus, it seems reasonable to assign the ions to one of the proposed skeletal structures, which is shown in the last column of Table 1.

Ions entried as 14–16 and ions entried as 17 and 18 are those which can originate from the mixed dimer of diethyl aluminum ethoxide with ethyl aluminum diethoxide and from the dimer of ethyl aluminum diethoxide, respectively. The skeletal structures of these ions are assigned to I or II which carried one or two

* As to aluminum compounds, most of the abundant ions obey the rule that the number of substituents is $3n-1$, where n is the number of aluminum atoms in the ions.

ethoxy group(s), on the basis of the variation of intensity with the number of ethyl groups.

3.5 Proposal of Cyclic Structure to Al_3O_3 and Al_3O_4 Skeletons

Ions entered as 19–21 and 22–26 in Table I are those which bear Al_3O_3 and Al_3O_4 as common elemental compositions, respectively. In these ion series, more abundant ions are observed when the number of odd-electron groups is even whereas the opposite was true for the ion series of Al_2O_2 and Al_2O_3 . These results can not be rationalized if the ions came from the species which had a skeletal structure such as IV. The skeletal structures V and VI can be then assigned to these ions on the basis of the odd-even electron character.

Entries 27–30 show the ions which bear Al_4O_4 and Al_4O_5 as common elemental compositions. These ions can be assumed to originate from the species whose skeletal structure is such as VII on the basis of the same consideration as mentioned above.

Similar cyclic structures can be proposed to the ions of Al_5O_5 and Al_6O_6 skeletons, but remain to be confirmed because of the paucity of fragment ions.

There are several publications^{14), 19, 20)} which confirmed the dimeric or trimeric form of monoalkoxide of aluminum alkyls. The dimers have been formulated with four-membered cyclic structures bridged by alkoxy groups¹⁴⁾. A six-membered cyclic structure has been proposed for the trimer of dimethyl aluminum methoxide^{19, 20)}. These cyclic structures agree with the conclusion of the present deduction from mass spectral data, thereby indicating the validity of the method presented in this paper.

Apparently the catalyst system itself is so complicated that a number of species of different skeletal structures are mixed. The method presented in this paper is based on four established facts: (a) invariability of valence of aluminum atoms during fragmentations, (b)

relatively high stability of oxygen-bridged bondings, (c) the odd and even electron rule, and (d) high intensity of the ions which come from the parent ion with removing one radical moiety (the “ $3n-1$ ” rule). The new method for deriving the skeletal structure from variation of intensity with the total number of the odd electron groups (substituents) which are sticking to the skeleton will certainly provide important informations in the elucidation of the structure in many organometallic compounds.

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