A Study of the Structures of Aluminum Complexes with Isopropoxy and Methyl Groups Using Pulsed NMR and Chemical Ionization Mass Spectrometry

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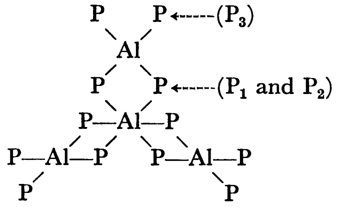
The structures of aluminum complexes formed by the reaction of aluminum isopropoxide with trimethylaluminum was investigated by measuring the spin-lattice relaxation times, T_1 for ^{1}H and T_1^* for ^{27}Al. The motion of the ligand of the complexes reflected upon the value of T_1, which was about twice as long at the terminal position as at the bridge position, and decreased with increasing molecular weight. Coordination symmetry about the aluminum nucleus of the complexes governed the value of T_1^*, which was about ten times as long at the center of the tetrameric complexes as at the wing of the dimeric complexes. The ^{13}C NMR signals of the isopropoxy group varied with the configuration of the ligands, while those of the methyl group were either broad or not observable. Chemical ionization mass spectra of the complexes supported the tetrameric and the dimeric structures determined from the results of NMR measurements.

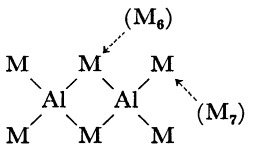
Aluminum alkoxides have a stable structure, while alkylaluminums are so reactive that they are utilized as a reducing reagent in various reactions.[1] A tetrameric structure, T^0, for aluminum isopropoxide was first proposed by Bradley,[2] and a dimeric one, D^2, for trimethylaluminum by Laubengayer *et al.*[3] ^{1}H NMR has been used effectively for the structure determination of these complexes.[4-6]



T^0

$P=(CH_3)_2CHO-$

$M_w=817$

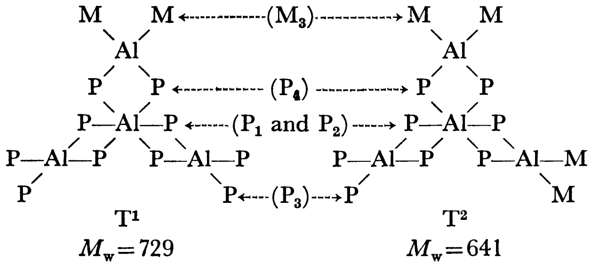


D^2

$M=CH_3-$

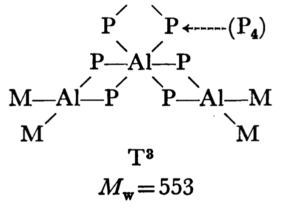
$M_w=320$

M_w indicates the molecular weight of the complexes. Using ^{1}H NMR spectroscopy, it has been found that aluminum isopropoxide reacts with trimethylaluminum to produce three kinds of tetranuclear complexes, T^1, T^2 and T^3, and two kinds of binuclear ones, D^0 and D^1.[7] Chemical shifts, spin-spin coupling constants between the protons, signal intensities and relative values of the spin-lattice relaxation times were measured to confirm the structures reported in a previous publication.[7]



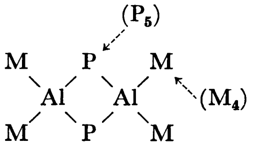
T^1　$M_w=729$

T^2　$M_w=641$



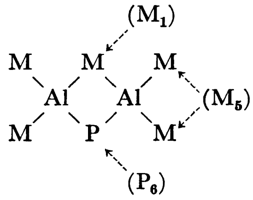
T^3

$M_w=553$



D_0

$M_w=409$



D^1

$M_w=364$

The remaining problems are summarized as follows. a) When ^{1}H NMR signals were obtained in the CW (continuous wave) mode, the spin-lattice relaxation time was measured using the progressive saturation method, so that the absolute values for T_1 could not be obtained, and relative values for T_1 could hardly be determined for NMR signals which are close to each other. b) As a result of overlapping of the NMR signals it was impossible to discriminate between the three kinds of tetranuclear complexes, T^1, T^2 and T^3. c) Since the NMR measurements were performed only on the protons of the ligands, no direct information was obtained concerning the aluminum nucleus of the complexes.

In the present work, the absolute values of T_1 for both ^{1}H and ^{27}Al were measured in the pulsed NMR mode to reconfirm the structures of the aluminum complexes and to study the remaining problems. ^{13}C NMR was also used to study the coordination mode of the ligand. The molecular weight of the complexes was examined using chemical ionization mass spectrometry, which is a useful technique for estimating the molecular size of such unstable compounds.

Experimental

Reagents. All the reagents used were obtained and purified by the same method as that described in Ref. 7.

Preparation of Samples. Aluminum isopropoxide and trimethylaluminum were dissolved separately in benzene, and solutions were mixed at 25 °C in an atmosphere of nitrogen in a dry box. The concentration was set so that the total amount of the solutes was 20 and 5.0 mol % in the solutions used to prepare the samples for pulsed NMR spectroscopy and chemical ionization mass spectrometry, respectively. Since a trace of oxygen in the solution which reacted with trimethylaluminum showed no observable effect upon the magnetic relaxation time, none of the samples were degassed.

Measurements of NMR and Mass Spectra. NMR spectra were measured with a Bruker SXP 4-100 spectrometer operating at 21.14 kG. Spin-lattice relaxation times for ^{1}H and ^{27}Al nuclei were measured at 28 °C using a partial relaxation technique with π- and $\pi/2$-pulses. The length of the π-pulses were 1.3×10^{-5} and 2.4×10^{-5} s for ^{1}H and ^{27}Al, respectively. Mass spectra were recorded using a Finnigan model 3300F quadrupole mass spectrometer equipped with a chemical ionization system. Methane was used as the reactant gas for the chemical ionization.

Results and Discussion

^{1}H NMR. The ^{1}H NMR spectra of the aluminum complexes showed four types of signals with hyperfine structures characteristic of the functional groups of the ligands; the methyl groups displayed a singlet pattern for $\tau=9.96$—10.53, the isopropoxy methyl groups a doublet for $\tau=8.31$—9.04, the isopropoxy methine groups a heptad for $\tau=5.27$—5.70, and methane, a by-product of the reaction of aluminum isopropoxide with trimethylaluminum, a singlet at $\tau=9.85$. For convenience, the signals of the isopropoxy methyl groups are denoted by P_1, P_2, P_3, P_4, P_5, and P_6 in the order of increasing τ values, and those of the methyl groups by M_1, M_2, M_3, M_4, and M_5 at 28 °C. Below −40 °C, the signal due to trimethylaluminum, M_2, splits into two singlet signals, which are designated as M_6 for the smaller value and as M_7 for the larger. On the basis of considerations of chemical-shifts, spin-spin coupling constants and signal intensities, these signals were assigned in Ref. 7 to T^0, T^1, T^2, T^3, D^0, D^1, and D^2.

In the present work, an attempt was made to reconfirm the signal assignments using the spin-lattice relaxation time, T_1. Typical ^{1}H NMR spectra measured using the partial relaxation technique are shown in Fig. 1, where the molar ratio of added trimethylaluminum and aluminum isopropoxide is 0.40: 0.60. The logarithm of the recovery rate of the signals was plotted against the delay time of the $\pi/2$-pulse after the π-pulse, and the linearity was sufficient to determine the T_1 values to within an accuracy of ±5% as listed in Table 1.

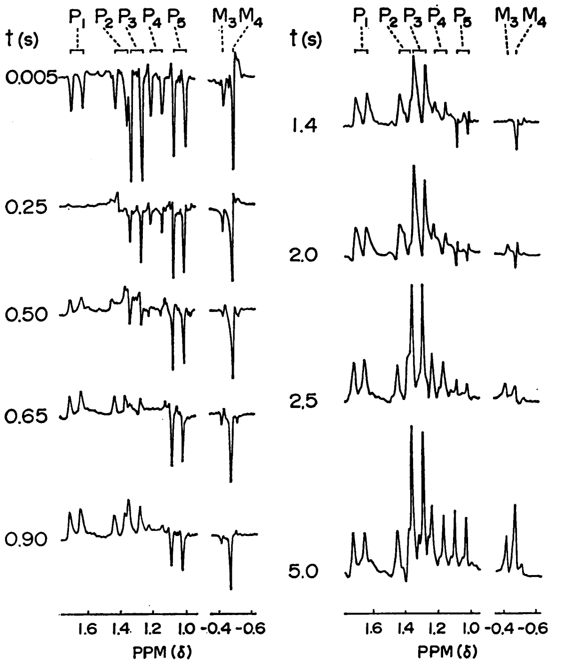


Fig. 1. ^{1}H NMR spectra of the methyl groups of the aluminum complexes in benzene at 28 °C. t is delay time of the $\pi/2$-pulse after the π-pulse. Trimethylaluminum and aluminum isopropoxide were mixed at the molar ratio 0.40: 0.60.

From the observed T_1 values, the isopropoxyl methyl signals can be classified into two groups, I (P_1, P_2, P_3 and P_4), and II (P_5 and P_6), which represent T_1 values of 0.35—0.97 and 3.2—4.0 s, respectively. In a similar manner, the methyl signals can also be classified into two groups, I (M_3), and II (M_2 and M_4), with T_1 values of 1.9 and 3.2—4.6 s, respectively. Since it is known that aluminum isopropoxide and trimethylaluminum are tetrameric[2] and dimeric,[3] respectively, the signals of groups I and II are referred to the ligands of the tetra- and the binuclear aluminum complexes, respectively.

The M_2 signal, which is a singlet due to the rapid exchange of bridging and terminal methyl groups, M_6 and M_7, of dimeric trimethylaluminum D^2, has the longest T_1 value, 4.6 s. The bridging ligand is supposed to be less mobile and have a shorter value of T_1 than the terminal ligand. Since P_5 and M_4 have shorter T_1 values than P_6 and M_5, the former can be assigned to the ligand of D^0, and the latter to that of D^1. The results agree with those obtained from the change in the signal intensity with the ratio of the trimethylaluminum to aluminum isopropoxide concentrations.[7] The T_1 values of P_5 and P_6 show that the T_1 value of the isopropoxyl methyl group increases by about 0.6 s when the neighboring isopropoxyl group is substituted by a methyl group. The increase in the T_1 value is attributable to a decrease in the number of neighboring protons, which play the role of the energy carriers in the spin-lattice relaxation process.

The T_1 values of P_1 and P_2 are *ca.* 0.35 s, and P_3 has a

TABLE 1. SPIN-LATTICE RELAXATION TIMES FOR METHYL PROTONS OF ALUMINUM COMPLEXES IN BENZENE AT 28 °C

$Al(CH_3)_3$: $Al(isoPrO)_3$[a)]	Spin-lattice relaxation time (s)								
	P_1	P_2	P_3	P_4	P_5	P_6	M_2	M_3	M_4
0.00 : 1.00	0.35	0.35	0.65						
0.40 : 0.60	0.36	0.36	0.79	0.97	3.2			1.9	3.2
0.80 : 0.20					3.4	4.0	4.6		

a) Molar ratio.

T_1 value about twice as long as the former two. Therefore, P_1 and P_2 are assigned to the bridging isopropoxy group of the tetranuclear complexes, and P_3 to the terminal one. The splitting of the signal of the isopropoxy methyl group into the two signals, P_1 and P_2, suggests that the bridging group is less mobile than the terminal group, P_3. P_4 has a T_1 value *ca.* 0.6 s longer than P_1 or P_2, and is equivalent in molar intensity to M_3, which has a T_1 value about twice as long as P_4. Hence, P_4 and M_3 are assigned to the bridging isopropoxy group and the terminal methyl group, respectively, of one of the substituted wings of the tetranuclear structures, T^1, T^2 or T^3. The T_1 values of P_4 and M_3, as well as those of P_1, P_2 and P_3, become longer with an increase in the amount of trimethylaluminum. This phenomenon shows that the T_1 value increases with decreasing proton number of the neighboring ligands, a fact which supports the assumption that all three structures, T^1, T^2, and T^3, exist in the solution. If, for instance, only T^0 and T^3 existed, the T_1 values of P_1, P_2, P_3, P_4, and M_3 would not change with the ratio of the trimethylaluminum and aluminum isopropoxide concentrations.

As long as similar structures are considered, it is seen that the T_1 value is inversely proportional to the molecular weight. For instance, the ratio of the molecular weight of D^0 to that of D^1 is 0.89, while the ratio of the T_1 values of P_5 and P_6 is 0.85 when trimethylaluminum and aluminum isopropoxide are mixed at a molar ratio of 0.80: 0.20. When the ratio of the trimethylaluminum and aluminum isopropoxide concentrations is 0.40: 0.60, the mean molecular weight of the tetranuclear complexes is calculated from the T_1 value of P_3 to be 672 in comparison with that for a pure solution of aluminum isopropoxide, while from the T_1 values of M_3 and M_4, it is 689. The mean molecular weight decreases with an increase the number of methyl groups.

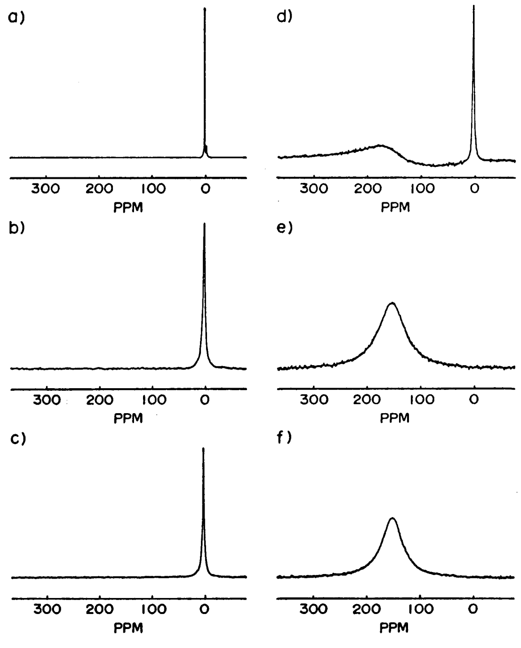


Fig. 2. ^{27}Al NMR spectra of a) aluminum sulfate in water, and the mixture of trimethylaluminum and aluminum isopropoxide at the molar ratios b) 0.00: 1.00, c) 0.40: 0.60, d) 0.60: 0.40, e) 0.80: 0.20, and f) 1.00: 0.00 in benzene at 28 °C.

Table 2. Chemical shifts, ν, half-height widths, $\Delta\nu$, and spin-lattice relaxation times, T_1^*, for ^{27}Al NMR signals in benzene at 28 °C

$Al(CH_3)_3$: $Al(isoPrO)_3$[a)]	ν (ppm)	$\Delta\nu$ (Hz)	T_1^* (s)
$Al_2(SO_4)_3$[b)]	0	1.35×10	2.2×10^{-3}
0.00 : 1.00	2.69	1.02×10^2	4.3×10^{-4}
0.40 : 0.60	3.75	8.75×10	4.5×10^{-4}
0.60 : 0.40[c)]	2.30	7.19×10	7.2×10^{-4}
0.80 : 0.20	5.37×10^2	1.48×10^3	2.3×10^{-5}
1.00 : 0.00	5.37×10^2	1.04×10^3	3.2×10^{-5}

a) Molar ratio. b) Saturated water solution. c) The narrower of the two signals.

^{27}Al NMR. The aluminum nucleus forms the skelton of the polynuclear complexes, but little work has so far been undertaken on the structure of the complexes based on information about the aluminum nucleus itself. For this reason ^{27}Al NMR spectroscopy is an indispensable technique. However, ^{27}Al NMR signals are usually broad because of the $I=5/2$ spin and the large electric quadrupole moment,[8)] so that they are not easily used to obtain detailed information. After the work of O'Reilly,[9)] most studies using ^{27}Al NMR, which is a sensitive probe of the environment of the aluminum nucleus, have been developed by measuring line widths instead of direct measurements of the spin-lattice relaxation times.

^{27}Al NMR spectra of the reaction products of aluminum isopropoxide with trimethylaluminum are shown in Fig. 2, where aluminum sulfate dissolved in water is used as a chemical shift standard. Values of the chemical shift, ν, and the half-height width, $\Delta\nu$, are listed in Table 2. Aluminum sulfate shows up as a sharp line with a half-height width of 13.5 Hz indicating the formation of a monomeric structure involving six ligands in water. A single line of aluminum isopropoxide appeared at a frequency 2.69 ppm higher than that of aluminum sulfate with a half-height width of 102 Hz, although the tetrameric structure T^0 contains two kinds of the aluminum nuclei. Trimethylaluminum, the dimeric structure D^2 of which was determined from ^{1}H NMR spectra,[5,6)] showed a broad signal with a half-height width of 1042 Hz at a frequency 537 ppm higher than that of aluminum sulfate. No signals other than those corresponding to the tetrameric or the dimeric structures were observed at molar ratios for trimethylaluminum and aluminum isopropoxide of 0.40: 0.60 and 0.80: 0.20, respectively. When trimethylaluminum and aluminum isopropoxide were mixed at a molar ratio of 0.60: 0.40, the ^{27}Al NMR spectrum displayed both narrow and broad lines corresponding to the tetra- and binuclear complexes, respectively. The coordination number of the aluminum nucleus of the tetranuclear complexes is six at the center and four in the wing. Hence, the aluminum nucleus at the latter position should show an NMR signal with a frequency close to that of the binuclear complexes, but no such signal was observed. As a result, the aluminum nuclei that represent the NMR signals are attributable to the central nucleus of the tetranuclear complexes, T^0, T^1, T^2 and T^3, and to the nuclei forming the binuclear complexes, D^1 and D^2. The spin-lattice relaxation time for the aluminum nuclei situated in the wings of all the tetranuclear complexes and for those of the binuclear complex D^0 is believed to be too short to exhibit this NMR signal because of the low symmetry of the coordination structures.

In order to evaluate the spin-lattice relaxation time from the ^{27}Al NMR data, it is necessary to formulate an equation that describes the nuclear magnetization of aluminum in terms of the time interval t between the π- and $\pi/2$-pulses. The master equations for a nucleus with a spin quantum number I are expressed as

$$\mathrm{d}P_1/\mathrm{d}t = -W_{12}(P_1-P_2-\delta_{12})$$

$$\mathrm{d}P_i/\mathrm{d}t = W_{i-1,i}(P_{i-1}-P_i-\delta_{i-1,i}) - W_{i,i+1}(P_i-P_{i+1}-\delta_{i,i+1})$$

and

$$\mathrm{d}P_n/\mathrm{d}t = W_{n-1,n}(P_{n-1}-P_n-\delta_{n-1,n}), \quad (1)$$

where n is the total number of spin states given by $n=2I+1(=6)$, and i can take any integer between unity and n. P_i and $W_{i,i+1}$ denote the spin population of the i-th state and transition probability of the spin from the i-th state to the next higher state, respectively. $\delta_{i,i+1}$ denotes the difference in the spin populations between the i-th and $(i+1)$-th states at thermal equilibrium. For simplicity, it is assumed that both $W_{i,i+1}$ and $\delta_{i,i+1}$ are constants independent of i, and that the apparent value of the spin-lattice relaxation time is given by T_1^*, one half of the reciprocal of the transition probability. Then, the normalized value of the magnetization M for the ^{27}Al nucleus is given by

$$\begin{aligned} M &= M(t)/M(\infty) \\ &= 1-(2/105)(A+B+C), \end{aligned} \quad (2)$$

where $A=\exp(-t/T_1^*)$, $B=2(26+15\sqrt{3})\exp[-(2-\sqrt{3})t/(2T_1^*)]$ and $C=2(26-15\sqrt{3})\exp[-(2+\sqrt{3})t/(2T_1^*)]$. A and C have smaller values than B, so that they are negligible within the practical accuracy of M. Hence Eq. 2 can be simplified to

$$M = 1-2\exp[-(2-\sqrt{3})t/(2T_1^*)]. \quad (3)$$

Experimental values of $\log 2(1-M)^{-1}$ lie along a straight line when plotted against the value of t. For a sample composed of a mixture of D^1 and D^2, it was difficult to obtain a straight line as a result of the overlapping of the broad signals, so that the apparent value of T_1^* was determined from the line width upon comparison with that of D^2. The T_1^* values are listed in the last column of Table 2.

Aluminum sulfate dissolved in water provided the longest T_1^* value, 2.2×10^{-3} s, of all the samples. T_1^* of the signal due to the tetranuclear complexes gradually increased with an increase in the amount of trimethylaluminum. This corresponds to a decrease in the molecular weight, as well as to a slight change in the coordination symmetry about the observable aluminum nucleus, supporting the assumption that it is the central nucleus alone that produces the NMR signal of the tetranuclear complexes. The T_1^* value is much shorter for the aluminum nucleus with the coordination number six, as can be seen from the following results of the binuclear complexes. When trimethylaluminum and aluminum isopropoxide were mixed at a molar ratio of 0.80: 0.20, the ^{27}Al NMR spectrum displayed a T_1^* value of 2.3×10^{-5} s, which was shorter than that for a pure solution of trimethylaluminum. This indicates that the aluminum nucleus of the binuclear complex D^1 produces an NMR signal at the same position as dimeric trimethylaluminum D^2. The T_1^* value would be too short to allow detection of the NMR signal of the aluminum nucleus between a pair of bridging isopropoxy groups and a pair of terminal methyl or isopropoxy groups.

^{13}C NMR. The coordination state of the ligand was examined by ^{13}C NMR, too, as is shown in Fig. 3, where tetramethylsilane was used as the chemical shift standard. The isopropoxy methyl and methine carbons produced ^{13}C NMR signals higher in frequency and narrower in width than those of the methyl carbons attached to the aluminum nucleus.

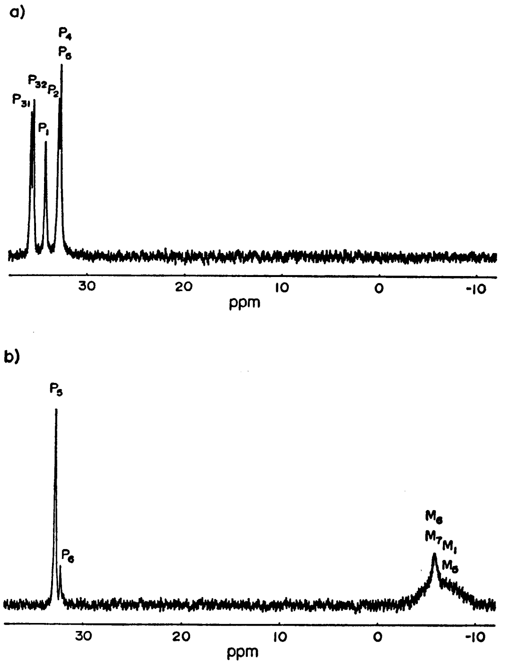


Fig. 3. ^{13}C NMR spectra of the mixture of trimethylaluminum and aluminum isopropoxide at the molar ratios a) 0.40: 0.60, and b) 0.80: 0.20 in benzene at 28 °C.

Four kinds of signals from the isopropoxyl methyl of the benzene carbon at 128.60 ppm, were observed in the ^{13}C NMR spectrum of a pure solution of aluminum isopropoxide. The signals at 34.27 and 33.00 ppm are assigned to the bridging ligand of tetrameric aluminum isopropoxide, T^0, and are designated by P_1 and P_2, respectively, in a similar manner to the case of ^{1}H NMR. The two signals at 35.75 and 35.53 ppm, which are close to each other in comparison with the other two signals, are assigned to the terminal ligand P_3 of T^0, and are indicated by P_{31} and P_{32}, respectively. The ^{1}H NMR signal from P_3 was, however, lower in frequency than the signals from P_1 and P_2, and did not split. On the other hand, the isopropoxy methine

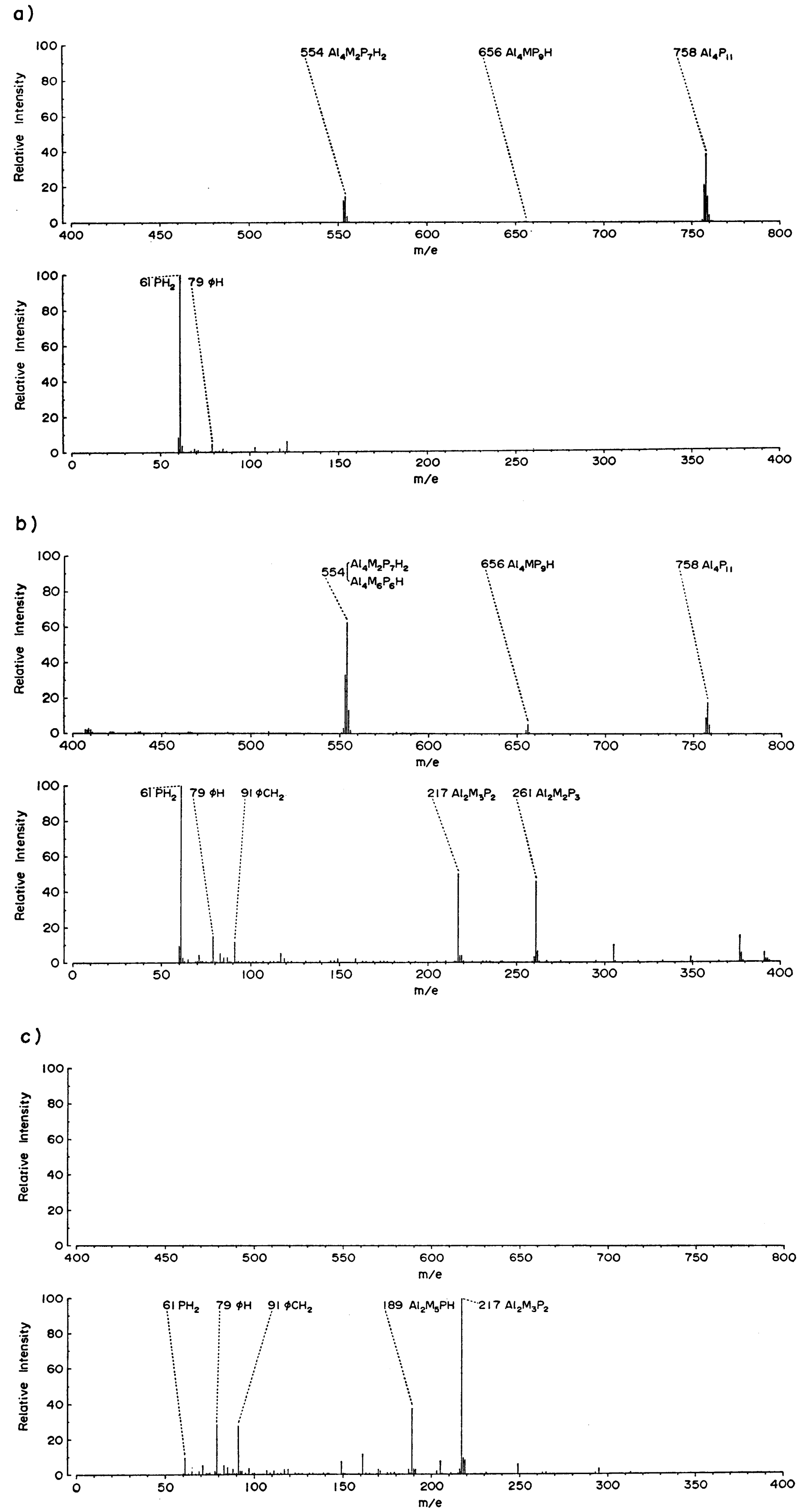


Fig. 4. Chemical ionization mass spectra of the mixture of trimethylaluminum and aluminum isopropoxide at the molar ratios a) 0.00: 1.00, b) 0.30: 0.70, and c) 0.90: 0.10 in benzene.

carbons of aluminum isopropoxide display only the two signals with equimolar intensity at 73.70 and 70.83 ppm, which are assigned to the terminal and bridging ligands respectively, so that splitting of the isopropoxy methyl, signal is attributed to the steric difference of the two methyl groups bonded to a methine carbon.

When trimethylaluminum was added to aluminum isopropoxide in benzene, a new signal from the isopropoxy methyl carbon appeared at 32.80 ppm, which was assigned to a mixture of the bridging ligands, P_4 of the substituted wing of the tetranuclear complexes T^1, T^2, and T^3, and P_5 of the binuclear complex D^0. However, the methyl groups of M_3 and M_4 attached to the aluminum nuclei bearing P_4 and P_5, respectively, produced no ^{13}C NMR signal. This phenomenon coincides with the result of the ^{27}Al NMR experiments that no NMR signal was detected due to these aluminum nuclei.

When the amount of trimethylaluminum exceeded 75.0 mol % in the benzene solution, signals from the tetranuclear complexes diminished to the point of disappearing, and a signal due to the isopropoxy methyl carbon, assigned to P_6 of the binuclear complex D^1, appeared at 32.21 ppm accompanied by the signals from the corresponding to methyl groups M_1 and M_5, which overlapped each other at -7.0 ppm with a half-height width of *ca.* 140 Hz. The methyl groups, M_6 and M_7, of dimeric trimethylaluminum D^2 also displayed an overlapping of the carbon signals at -5.9 ppm with a half-height width of *ca.* 20 Hz. Line broadening of the methyl carbons bonded to the aluminum nucleus corresponds to the exchange of the methyl groups and to the electric quadrupole moment of the adjacent aluminum nucleus, as well as to the spin-spin coupling between the ^{13}C and ^{27}Al nuclei.[10] Since the carbons of the ligands are located at positions closer to the aluminum nucleus in comparison with the protons, the ^{13}C NMR spectrum exhibits an intermediate character between the ^1H NMR and the ^{27}Al NMR data supporting these results.

Chemical Ionization Mass Spectrometry. In order to verify the NMR results mentioned above, it is desirable to determine the molecular weight of the aluminum complexes. However, these complexes are so unstable that it is very difficult to measure their molecular weights using ordinary methods. CIMS (chemical ionization mass spectrometry) is a useful technique for the molecular weight measurements of such unstable compounds, since ions are produced under a milder condition in CIMS than in electron impact mass spectrometry.

CIMS spectra of the reaction products of aluminum isopropoxide with trimethylaluminum are illustrated in Fig. 4. In the CIMS spectrum of aluminum isopropoxide, the large peak at an *m/e* of 758 corresponds to an ion of $[Al_4(isoPrO)_{11}]^+$, which is a fragment from a $Al_4(isoPrO)_{12}$ molecule. This indicates a tetrameric structure for aluminum isopropoxide, although no molecular ion $[T^0H]^+$ was detected at an *m/e* of 818. The peaks at *m/e* of 656 and 554 are assigned to $[Al_4(CH_3)(isoPrO)_9H]^+$ and $[Al_4(CH_3)_2(isoPrO)_7H_2]^+$, respectively, which are produced by the partial substitution of the isopropoxyl groups of T^0 by methyl groups of methane, the reactant gas. The isopropoxyl group of the ligand produces a peak at an *m/e* of 61, which is assigned to $[isoPrOH_2]^+$.

When trimethylaluminum and aluminum isopropoxide were mixed at a molar ratio of 0.30: 0.70, the peaks at *m/e* of 656 and 554 were enhanced indicating the progress of the substitution reaction of the isopropoxyl group by the methyl group for trimethylaluminum. The peak at an *m/e* of 554 might include a molecular ion $[Al_4(CH_3)_6(isoPrO)_6H]^+$ from the tetranuclear complex T^3, but no molecular ions were produced from the tetranuclear complexes, T^1 and T^2, as well as from T^0. The peaks at *m/e* of 261 and 217 are attributable to $[Al_2(CH_3)_2(isoPrO)_3]^+$ and $[Al_2(CH_3)_3(isoPrO)_2]^+$ binuclear ions, respectively. The former corresponds to the reaction product of D^0 with the isopropoxyl ion or to a fragment from T^1, T^2, or T^3, and the latter to a fragment from D^0.

At a molar ratio of trimethylaluminum and aluminum isopropoxide concentrations of 0.90: 0.10, no tetranuclear ions were detected in the CIMS spectrum, which displayed large peaks for binuclear ions at *m/e* of 217 and 189. The peak at an *m/e* of 189 is assigned to the $[Al_2(CH_3)_5(isoPrO)H]^+$ molecular ion from D^1. These results agree with the data obtained in the NMR experiments.

Conclusion

The structure of aluminum complexes formed by the reaction of aluminum isopropoxide with trimethylaluminum was investigated from three different angles: the ligand was examined using ^1H NMR and ^{13}C NMR, the central nucleus using ^{27}Al NMR, and the molecular weight employing chemical ionization mass spectrometry.

The spin-lattice relaxation time of ^1H is sensitive to the motion of the ligand; T_1 was shorter at the bridge position than at the terminal position, and inversely proportional to the molecular weight. This was used to estimate the mean molecular weight of the mixture of tetranuclear complexes, which were indistinguishable from one another using the chemical shift of the ^1H and ^{13}C NMR signals.

The coordination symmetry about the aluminum nucleus was reflected on the spin-lattice relaxation time of ^{27}Al, which was defined as one half of the reciprocal of the transition probability of the spin, T_1^*. The T_1^* value was longer at the center of the tetranuclear complex than at the binuclear complex, and was too short to produce an NMR signal for the aluminum nucleus between a pair of bridging isopropoxy groups and a pair of terminal methyl or isopropoxy groups.

The ^{13}C NMR data for the ligand represented an intermediate character between the data for ^1H NMR and ^{27}Al NMR; the ^{13}C NMR signal due to the isopropoxyl group reflected the configuration of the ligand in a manner similar to the ^1H NMR, while that of the methyl group was broad and was not observed with a methyl group attached to the aluminum nucleus that showed no NMR signal.

The chemical ionization mass spectra of the products of the reaction of aluminum isopropoxide with trimethylaluminum showed fragment ions from both the tetra- and the binuclear complexes as predicted from the NMR study. However, no molecular ions of tetrameric aluminum isopropoxide were observed.

All the results support the conclusions of previous work⁷⁾ that the terminal isopropoxy groups of tetrameric aluminum isopropoxide are replaced successively by the methyl groups of dimeric trimethylaluminum to form three kinds of tetranuclear and two kinds of binuclear complexes, and that, after the reactions, the resultant tetranuclear complex undergoes decomposition reactions leading to two kinds of binuclear complexes.

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