Structures of Aluminum Complexes with Isopropoxyl and Methyl Groups Studied by Proton Magnetic Resonance

Masao Uetsuki* and Yuzuru Fujiwara

Contribution from the Central Research Laboratories, Kuraray Company, Sakazu 2045, Kurashiki, Japan. *Received December 27, 1972*

Abstract: It was found by measuring proton magnetic resonance that aluminum isopropoxide reacts with trimethylaluminum irreversibly in aromatic solutions to produce three kinds of tetrameric and two kinds of dimeric complexes. The terminal isopropoxyl groups of aluminum isopropoxide are substituted successively by the methyl groups of trimethylaluminum forming the mixed ligand complexes. After all of the terminal isopropoxyl groups are replaced by methyl groups, the resultant tetrameric complex undergoes the decomposition reactions leading to dimeric complexes. In the dimeric complexes isopropoxyl groups form stable bridging bonds without taking the terminal positions, and methyl groups occupy the remaining sites. The magnetic relaxation times of methyl protons showed that the local mobility of ligands is less at bridge positions than at terminal ones and that it varies with the size of complexes.

Aluminum forms complexes with the coordination numbers from three to six showing the singular properties of reducing agents as well as catalysts of a number of reactions.[1] It has been known that aluminum alkoxides have tetrameric structures[2,3] while aluminum alkyls are dimeric.[4-13] Bradley[2] proposed a tetrameric structure for aluminum isopropoxide, in which three pairs of isopropoxyl groups combine three aluminum atoms with a central one. Shiner, Whittaker, and Fernandez[3] supported this structure on the basis of ^{1}H nmr data and the result of molecular weight measurements. Muller and Pritchard[4] and Ramey, O'Brien, Hasegawa, and Borchert[5] examined the ^{1}H nmr of trimethylaluminum at various temperatures in the organic solutions and confirmed a dimeric structure, which had been proposed by Lewis and Rundle[6] for solid state, by Pitzer and Gutowsky[7] for the benzene solution, and by Laubengayer and Gilliam[8] for the gaseous state. The dimeric structure of trimethylaluminum was redetermined by Vranka and Amma[9] who applied single-crystal X-ray diffraction techniques at $-50°$. In order to know the monomer–dimer equilibria of aliminum trialkyls Smith measured the heat of dilution of triethylaluminum[10] and that of triisobutylaluminum[11] obtaining the result that the former is much less in degree of dissociation than the latter. Yamamoto and Hayamizu[12] studied the ^{1}H nmr spectra of the systems composed of trimethylaluminum and one of triethyl-, tri-*n*-propyl-, and triisobutylaluminum observing that the tendency of an alkyl group to occupy the bridge position of the dimeric complex decreases according to the bulkiness of alkyl groups. As a result of ^{1}H nmr measurements Hoffmann[13] suggested a dimeric structure for the reaction product of dimethylaluminum *tert*-butoxyl and trimethylaluminum.

The present work is to investigate the structures of the complexes formed through the reactions of aluminum isopropoxide and trimethylaluminum in aromatic solutions by use of ^{1}H nmr.

Experimental Section

Reagents. Crystalline aluminum isopropoxide, obtained from Wako Pure Chemical Industries, Ltd., was ground into powder and dried for 20 hr under vacuum at room temperature. Trimethylaluminum, manufactured by Ethyl Corp., was used without further purification. Benzene and toluene, commercially purified reagents, were dried in contact with sodium metal for a few days and distilled twice.

Preparation of Samples. Aluminum isopropoxide and trimethylaluminum were dissolved separately in benzene or toluene, and these solutions were mixed at various ratios in nmr sample tubes at 25°. Such a sample preparation was carried out under an atmosphere of nitrogen using a dry box. The concentration was set so that the total amount of solutes was 2.50 mol % in the solution. Since a trace of oxygen in the solution showed no observable effects upon the magnetic relaxation times, all the samples were not degassed.

^{1}H Nmr Measurements. Nmr spectra were observed at 100 MHz with a Varian Associates high-resolution spectrometer, HA-100, equipped with a temperature controlling unit. The signal of methane, which was formed through a side reaction of aluminum isopropoxide and trimethylaluminum, was adopted as an internal reference of chemical shifts. Signal intensities were determined by measuring their chart weights, and the magnetic relaxation times were measured by the progressive saturation technique.

Results and Discussion

^{1}H Nmr Spectra. The nmr spectra of aluminum complexes displayed four types of proton signals with hyperfine structures characteristic of the functional groups of ligands: the methyl groups showed singlet patterns in the lowest frequency range, the isopropoxyl methine groups showed a heptad in the highest range, the isopropoxyl methyl groups showed a doublet in the middle of the above two groups, and methane showed a singlet between two kinds of methyl groups. Methane is supposed to be a by-product, the content of which was less than 2 mol % of the total amount of ligands. For convenience the signals of isopropoxyl methyl groups were designated by P_1, P_2, P_3, P_4, P_5, and P_6 in the decreasing order of resonance frequencies and those of

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[3] V. J. Shiner, Jr., D. Whittaker, and V. P. Fernandez, *J. Amer. Chem. Soc.*, 85, 2318 (1963).

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[6] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, 21, 986 (1953).

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[10] M. B. Smith, *J. Phys. Chem.*, 71, 364 (1967).

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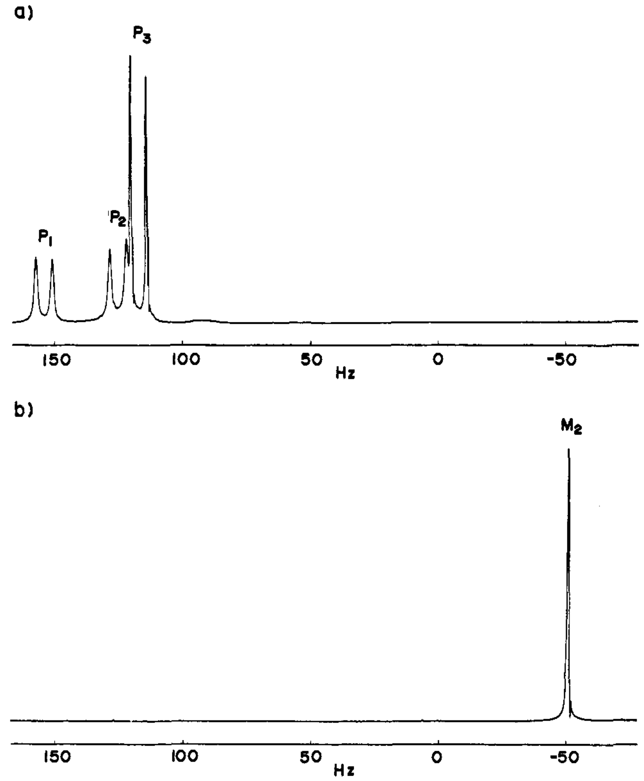


Figure 1. ${}^1H$ nmr spectra of various methyl groups of aluminum isopropoxide (a) and trimethylaluminum (b) in benzene solution at 30°.

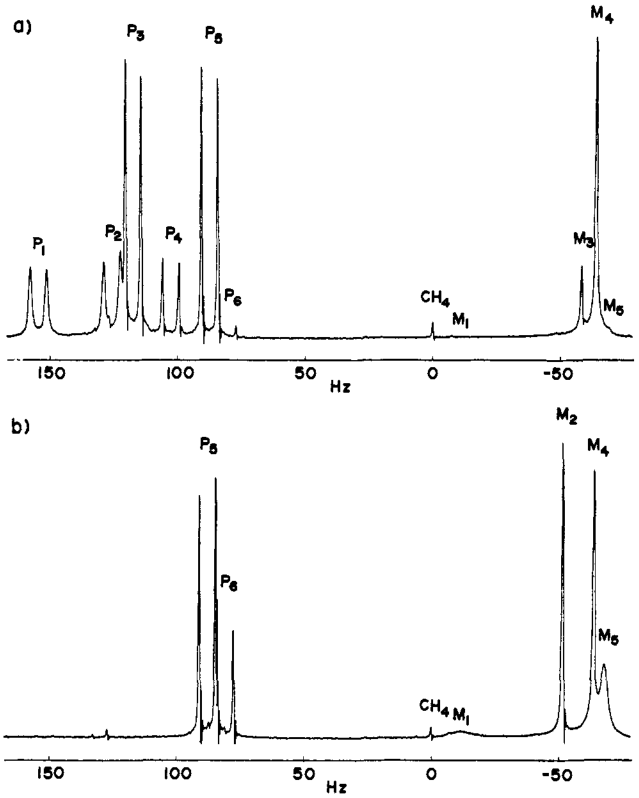


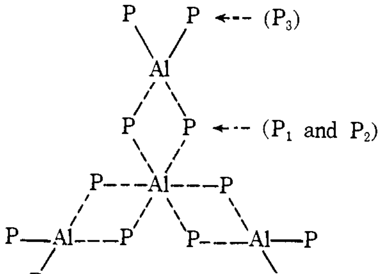
Figure 2. ${}^1H$ nmr spectra of various methyl groups in the mixed system of aluminum isopropoxide and trimethylaluminum in benzene solution at 30°. The prepared molar fraction of trimethylaluminum is 0.399 for a and 0.783 for b.

methyl groups by M_1, M_2, M_3, M_4, and M_5 in the decreasing order at 30° as illustrated in Figures 1 and 2. Below −40° the signal of M_2 split into two singlets, which were designated by M_6 with the higher frequency and by M_7 with the lower.

The values of spin–spin coupling constants between methyl and methine protons of isopropoxyl groups were 6.1 Hz for the signals of P_1, P_2, P_4, P_5, and P_6 and 5.9 Hz for P_3 and almost independent of temperature. Through the effects of temperature and the prepared concentrations of aluminum isopropoxide and trimethylaluminum the nmr signals were classified into five sets of peaks, the intensity ratios of which were constant within each set.

As is clear from Figure 1a the nmr spectrum of aluminum isopropoxide showed three kinds of isopropoxyl methyl groups, P_1, P_2, and P_3, with the intensity ratios of 1 : 1 : 2, and two kinds of isopropoxyl methine groups with equal intensities. The signal of the isopropoxyl methine group appeared in the lower frequency range coupled with the signal of P_3 and that in the higher frequency range, which was composed of broader peaks than the former, coupled with the signals of P_1 and P_2. Bradley[2] proposed a tetrameric structure, T^0, for aluminum isopropoxide, and Shiner, Whittaker, and Fernandez[3] supported this structure, assigning the signal of P_3 to the ligand at the terminal position and the signals of P_1 and P_2 to two kinds of isopropoxyl methyl groups of the bridging ligand. Their nmr assignments were based on the intensity ratios of proton signals and on the result of molecular weight measurements.

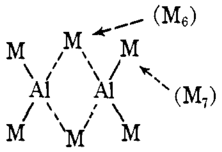
Muller and Pritchard[4] and Ramey, O'Brien, Hasegawa, and Borchert[5] reported a dimeric structure, D^2, for trimethylaluminum in the organic solutions observing that this complex displayed two singlet signals of M_6 and M_7 with the intensity ratio of 1 : 2 below −40° and above this temperature one singlet of M_2 as a result of rapid exchange between the groups M_6 and M_7, as shown in Figure 1b. Hoffmann[13] examined the structures of aluminum complexes in the mixed ligand system of methyl and isobutyl groups by use of ${}^1H$ nmr and found that the mixed aluminum alkyls are associated by virtue of methyl groups. Similar results were obtained by Yamamoto and Hayamizu[12] for the mixed ligand systems of the methyl group and ethyl, *n*-propyl, or isobutyl groups. The nmr spectra of trimethylaluminum were obtained over the temperature range from −70 to +80° in the toluene solution showing no signals other than those of the dimeric complex, D^2.



T^0

P = $(CH_3)_2CHO$-

Three sets of nmr signals, P_4 and M_3, P_5 and M_4, and P_6, M_1, and M_5, were observed in the mixed solutions of aluminum isopropoxide and trimethylalumi-

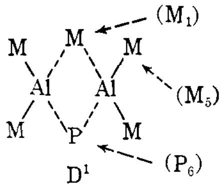


D²

$M = CH_3$-

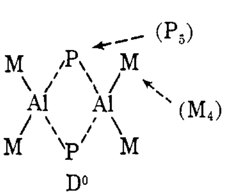
num besides the signals of P_1, P_2, P_3, and M_2 at 30° as illustrated in Figures 2a and 2b. All the values of spin–spin coupling constants of the groups P_4, P_5, and P_6 coincided with those observed for the signals of P_1 and P_2, so that the former are supposed to be bridging ligands.

Intensity ratios of the signals P_6, M_1, and M_5 were 2:1:4 below 50°, which indicate that these signals belong to a dimeric complex designated by D^1. Two aluminum atoms of this complex are bridged by the isopropoxyl group, P_6, and the methyl group, M_1, and the rapid exchange takes place between the terminal methyl group, M_5, and the bridging methyl group, M_1, above 50°. No exchange was observed for the isopropoxyl group, P_6, suggesting that this group holds the dimeric structure of D^1 tightly and does not take the terminal position. Hoffmann[13] proposed a similar dimeric structure for the reaction product of dimethylaluminum *tert*-butoxyl and trimethylaluminum assuming the reaction to be reversible.



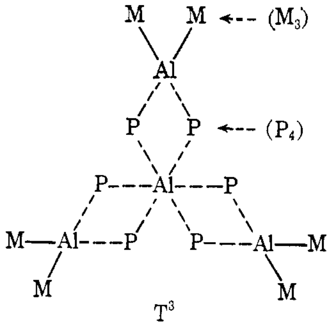
D¹

The signals of P_5 and M_4 have equal intensities, which indicate one of the cyclic complexes bridged by the pairs of isopropoxyl groups with a chemical formula of $[Me_2Al(i\text{-}PrO)]_n$. The degree of polymerization, n, is supposed to be larger than unity because the isopropoxyl group of the dimeric complex, D^1, did not take the terminal position. The observed values of magnetic relaxation times, which will be mentioned below, suggest that $n = 2$, and the signals of P_5 and M_4 are assigned respectively to the bridging and the terminal ligands of the dimeric complex designated by D^0.



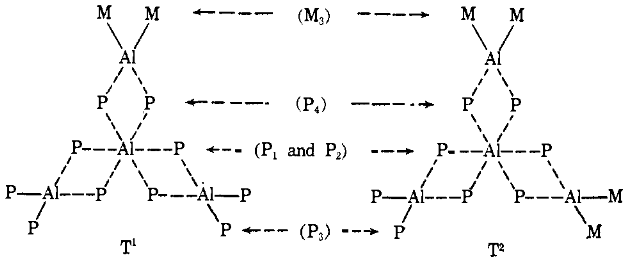
D⁰

Since the intensity ratio of the signals of P_4 and M_3 was 2:1, two kinds of tetrameric structures are assumed as the complexes containing these two groups. One is the case denoted by T^3 that all the terminal isopropoxyl groups of tetrameric aluminum isopropoxide, T^0, were substituted by methyl groups leaving the isopropoxyl groups at the bridge positions unchanged, and another, the opposite case, that the isopropoxyl groups interchanged the coordination positions with the methyl groups in the tetrameric structure of T^3. The former is a reasonable structure since the isopropoxyl group occupies the bridge position in such a mixed ligand system as mentioned above, and hence the latter is not the case.



T³

The difference of chemical shifts was less than 10 Hz for the signals of P_5 and P_6, so that it is appropriate to neglect the long-range effect of terminal groups over six bonds on the chemical shifts of other ligand protons. Therefore, the tetrameric structures T^1 and T^2 are also possible for the complexes showing the signals of P_1, P_2, P_3, P_4, and M_3.



T¹ T²

It should be noted that substitution of terminal isopropoxyl groups by methyl groups caused the collapse of inequality between two kinds of bridging isopropoxyl methyl groups in the tetrameric complexes. This suggests that the terminal isopropoxyl group of tetrameric complexes hinders the free rotation of the adjacent bridging isopropoxyl group about the C–O axis and that the terminal methyl group does not have such a steric effect because of its small size. No signals attributed to monomeric or trimeric complexes were detected in the mixtures of aluminum isopropoxide and trimethylaluminum, and none of the linear or the cyclic structures were observed for the polymeric aluminum complexes except for dimeric ones.

Chemical Shifts. Using the signal of methane as the internal reference the chemical shifts of various methyl signals were measured and plotted in Figure 3. The chemical shifts of ligand protons were not affected by the prepared ratio of aluminum isopropoxide and trimethylaluminum within the accuracy of ±0.3 Hz, but varied with temperature. There are two possible mechanisms through which temperature influenced the chemical shifts; one is the magnetic anisotropy[14] of solvent molecules and another the ligand exchange in the stationary state.

With increasing temperature the signals of terminal ligands shifted toward the higher frequency, while those of bridging ones shifted toward the opposite direction. This is ascribed to the magnetic anisotropy of the solvent molecule which has π electrons. Since the exchange of methyl groups is enhanced sharply above 50° for the dimeric complex D^1 and above −40°

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[14] J. A. Pople, *J. Chem. Phys.*, 24, 1111 (1956).

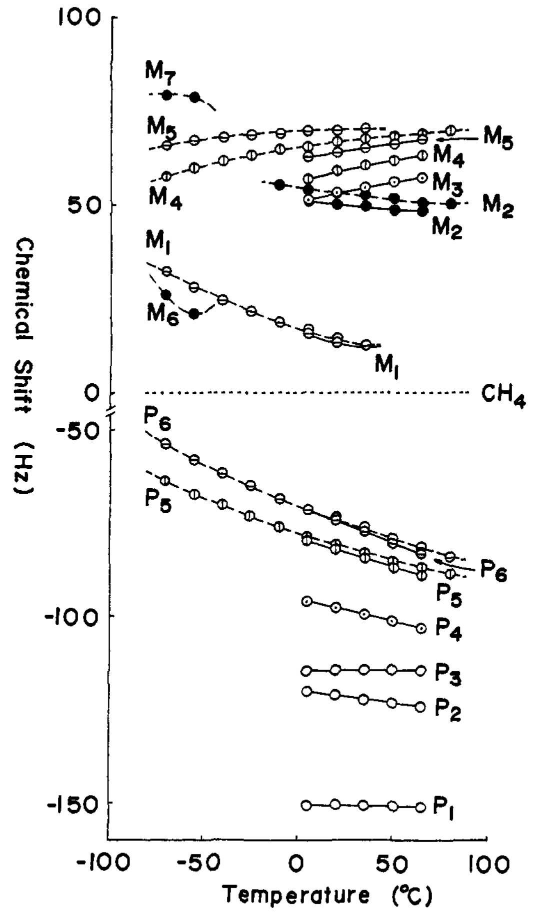

Figure 3. The temperature dependence of chemical shifts of various methyl signals. Solid and broken lines designate benzene and toluene solutions, respectively.

for dimeric trimethylaluminum, D^2, the chemical shifts of terminal and bridging methyl groups approach each other and overlap eventually. Such reactions in the complexes D^1 and D^2 take place independently, so that the methyl groups are supposed to exchange not through intermolecular but through intramolecular reactions. No exchange of ligands was observed for the dimeric complex D^0 and the tetrameric complexes T^1, T^2, and T^3, none of which has the methyl group at the bridge position.

In the unsubstituted wings of the tetrameric complexes T^0, T^1, and T^2, the signal of P_2 showed a significant dependence of chemical shift on temperature; it approaches the signal of P_1 at high temperature and that of P_3 at low temperature. The separation of signals of P_1 and P_2 suggests the steric hindrance due to the terminal group P_3, which is weakened with increasing temperature.

Relaxation Times. The relative values of magnetic relaxation times were measured to make clear the coordination state of ligands. From the steady-state solutions of Bloch equations[15] the relation given by eq 1 holds between the relative value of the spin-lattice relaxation time, T_{1r}, and that of the spin-spin relaxation time, T_{2r}, for the system composed of the spin i and the reference spin 0

$$T_{1r}T_{2r} = (H_i/H_0)^c \qquad (1)$$

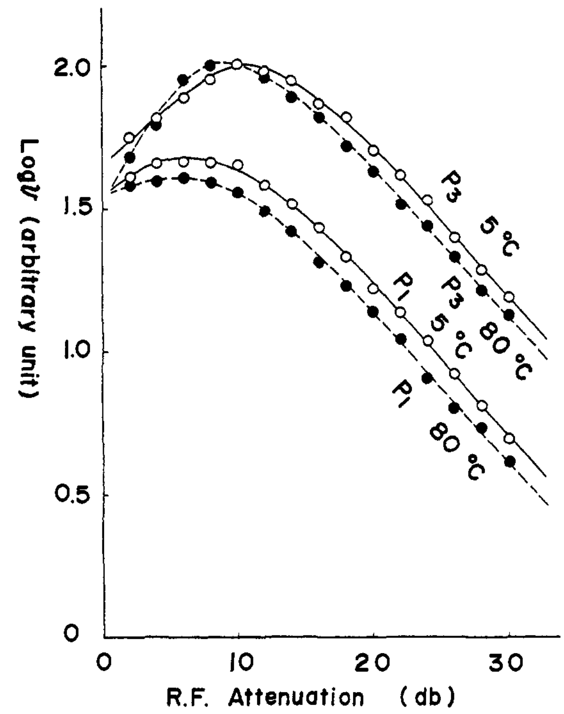

Figure 4. Saturation curves for the isopropoxyl methyl protons of aluminum isopropoxide in benzene solution. ν denotes the signal height.

where c is a constant, $T_{1r} = T_{1i}/T_{10}$, and $T_{2r} = T_{2i}/T_{20}$. H_i and H_0 are the amplitude of the rf field when the nmr signals of spins i and 0 show the maximum height, respectively. The value of T_{2r} is determined from the signal height as a sensitive measure of the line width on applying a weak rf field in the absence of saturation.

When the relaxation times of isopropoxyl methyl protons of P_1 were used as standards in the benzene solution of aluminum isopropoxide, the relative values of relaxation times of the isopropoxyl methyl protons of P_3 were obtained from the saturation curves shown in Figure 4 as $T_{1r} = 1.8$ and $T_{2r} = 1.5$ at 5° and $T_{1r} = 1.7$ and $T_{2r} = 1.6$ at 80°. All these values are larger than unity suggesting that the group P_1 is less in the local mobility than the group P_3 and that there exist spins with different resonance frequencies at a close distance to the group P_1. The spins of the group P_2 are to play the role of energy carrier enhancing the magnetic relaxation from the resonant spins of the group P_1 to the lattice. The saturation curve for the group P_1 is located lower than that for the group P_3 in Figure 4, and these two curves tend to cross each other as the rf field increases. This indicates that the group P_1 has an exchange reaction with the group P_2, the rate of which is slow and hardly shows the observable effect on the temperature dependence of chemical shifts. The signal of P_2 behaved in a similar manner as that of P_1, though precise measurements were impossible because of overlapping with the big signal of P_3. These results support the nmr assignments done by Shiner, Whittaker, and Fernandez.[3]

Table Ia displays the relative values of relaxation times at 5° for various isopropoxyl methyl protons in the mixed system of the complexes T^0, T^1, T^2, T^3, D^0, and D^1, when the relaxation times of the isopropoxyl methyl protons of P_1 are used as standards. The spin-lattice relaxation times increase in the order of P_1, P_3,

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[15] A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, London, 1961, p 44.

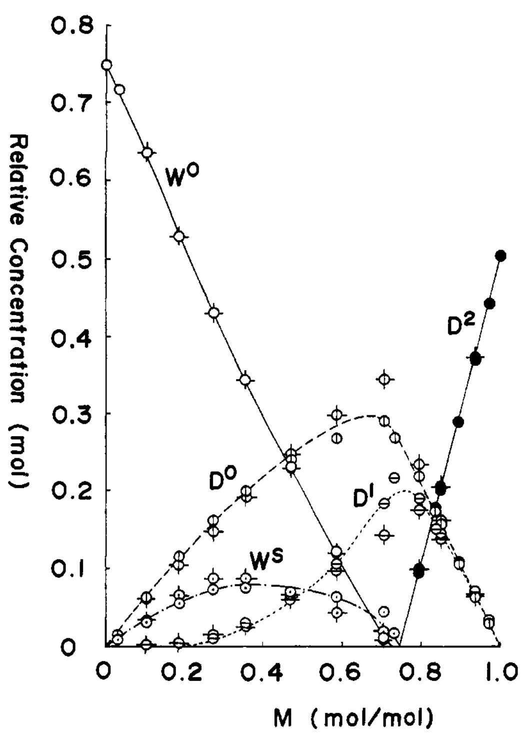

Figure 5. Relative molar concentrations of aluminum complexes produced through the reactions of aluminum isopropoxide and trimethylaluminum in benzene solution at 25°. Circles show experimental values, and circles with a cross designate simulated values.

Table I. Relative Relaxation Times of Various Methyl Protons of Aluminum Complexes in Benzene Solution

(a) Mixed System of Tetrameric Complexes T^0, T^1, T^2, T^3, D^0, and D^1, at 5° [a]

Signal	Mol ratio	T_{1r}	T_{2r}
P_1	1.0	1	1
P_3	2.0	1.6	1.7
P_4	0.90	1.9	1.4
P_5	2.6	2.5	2.9
P_6	0.36	3.6	2.0

(b) Mixed System of Dimeric Complexes D^0, D^1, and D^2 at 20° [b]

	Mol	T_{1r}			T_{2r}		
Signal	ratio	5°	20°	35°	5°	20°	35°
P_5	1.0	1.0	1	1.0	1.0	1	1.0
M_4	2.0	0.91	1.7	3.1	0.67	0.59	0.53
P_6	0.88	1.3	1.3	1.3	0.77	0.77	0.77
M_1	0.88	0.83	*c*	*c*	0.26	*c*	*c*
M_5	3.5	1.6	2.7	4.5	0.37	0.29	0.15
M_2	6.4	2.0	1.1	1.0	0.40	0.91	1.0

[a] Standards: T_1 and T_2 of P_1. [b] Standards: T_1 and T_2 of P_5. [c] The saturation curve did not attain the maximum within the experimental rf field.

P_4, P_5, and P_6. This suggests the increasing order of motion of these groups according to the size of complexes. The degree of polymerization of the complex D^0, which was ambiguous in the investigation of signal intensities, is determined as 2 considering that the spin–lattice relaxation time of isopropoxyl methyl protons is extended on substituting the adjacent isopropoxyl groups by methyl groups. The reason why the spin–lattice relaxation time of the group P_4 is longer than that of the group P_1 is ascribed to the increase of the local mobility of the former accompanied by the disappearance of inequality in the bridging isopropoxyl methyl groups and to the decrease of the proton number at the terminal position.

Table Ib shows the relative values of relaxation times for various methyl protons in the mixed system of the complexes D^0, D^1, and D^2, when the relaxation times of the group P_5 at 20° are used as standards. No dependence on temperature from 5 to 35° is observable for the spin–lattice relaxation time of the bridging isopropoxyl methyl groups P_5 and P_6 reflecting the stable bonds. The saturation curves for the methyl groups M_1 and M_5 displayed a slower decrease in the signal height than others upon increasing the rf field. This is interpreted in terms of the exchange reaction of these two groups; when the ligands exchange between the coordination sites with different resonance frequencies and the rate of the reaction is of a comparable order of magnitude with the reciprocal of the spin–lattice relaxation time, this reaction helps the magnetic relaxation from the resonant spin to the lattice through the off-resonant site. Such an effect was not observed at room temperature for the saturation behavior of dimeric trimethylaluminum, the methyl groups of which exchanged so rapidly between terminal and bridge positions that these coordination sites were not distinguished.

Reaction Mechanism. In order to know the reaction mechanism kinetic analyses were carried out for the yields of reaction products formed from the known amounts of aluminum isopropoxide and trimethylaluminum in the benzene solution. A symbol M is used to denote the prepared fraction of trimethylaluminum, which is equivalent to the total fraction of methyl groups in the summed amount of all the ligands given by $M = \Sigma[\mathrm{Me}]/(\Sigma[\mathrm{Me}] + \Sigma[i\text{-PrO}])$. Concentrations of aluminum complexes varied with the value of M as plotted in Figure 5.

It is seen from Figure 5 that the dimeric complex D^0 was detected in the whole region of M, though the dimeric complex D^1 appeared in $0.2 < M < 1$. The substituted and the unsubstituted wings of tetrameric complexes were observed in the region of $0 < M < 0.75$ in contrast to dimeric trimethylaluminum, D^2, which appeared in $0.75 < M < 1$. D^0 appeared together with either aluminum isopropoxide or trimethylaluminum, while these two complexes did not coexist. Therefore, present reactions take irreversible mechanisms, where D^0 and D^1 are the reaction products.

D^1 was not observed in the region of $0 < M < 0.2$, where D^0 was detected in fair amount. As a result it is expected in the early stage of the reactions that the dimeric complex D^0 and the tetrameric complexes T^1, T^2, and T^3 are produced through successive reactions I, which take place at the terminal positions of the

$$T^{i-1} + D^2 \xrightarrow{k_{ti}} T^i + D^0 \qquad \text{(I)}$$
$$i = 1\text{–}3$$

tetrameric complexes. After all the terminal isopropoxyl groups of tetrameric complexes are substituted by the methyl groups, the resultant tetrameric structure of T^3 is supposed to be decomposed through one of the competitive reactions II forming two kinds of dimeric

$$T^3 + jD^2 \xrightarrow{k_{bj}} (4 - j)D^0 + 2(j - 1)D^1 \qquad \text{(II)}$$
$$= 1\text{–}4$$

complexes, D^0 and D^1. k_{ti} and k_{bj} denote the rate constants for the ith terminal and the jth bridge reactions, respectively.

The relative values of rate constants are estimated on assumptions as follows. The prepared fractions of aluminum isopropoxide and trimethylaluminum are expressed as $0.25(1 - M)$ and $0.5M$, respectively, and it requires $0.75(1 - M)$ of trimethylaluminum to substitute all the terminal isopropoxyl groups of tetrameric aluminum isopropoxide by methyl groups. If the mean value of rate constants for the terminal reactions, k_{ti}'s, was extremely larger than the mean value of those for the bridge reactions, k_{bj}'s, the dimeric complex D^1 would be observed only in the region $0.6 < M < 1$, where the relation of $0.75(1 - M) < 0.5M$ holds. On the other hand, if the mean value of k_{ti}'s was extremely small compared with that of k_{bj}'s, D^1 would appear in the whole region of M accompanying no signal due to the substituted wings of tetrameric complexes. Experimentally, D^1 was detected in the region $0.2 < M < 1$, suggesting that these extreme conditions are not the case. Hence it is assumed that the mean value of k_{ti}'s is of a similar order of magnitude as that of k_{bj}'s.

For convenience the observed concentrations of the complexes and the wings are denoted by the square brackets. The substituted and the unsubstituted wings of tetrameric complexes are shown by W^s and W^0, respectively. The consumed amount of dimeric trimethylaluminum, D^2, is given by $0.75(1 - M) - [W^0]$ in the terminal reactions I and by $0.25(5M - 3) + [W^0] - [D^2]$ in the bridge reactions II. The former is equivalent to the amount of the dimeric complex D^0 produced through the terminal reactions. The total amounts of isopropoxyl and methyl groups are expressed by eq 2 and 3, respectively

$$3(1 - M) = 2\sum_{i=1}^{4}(7 - i)[T^{i-1}] + \sum_{j=1}^{2}(3 - j)[D^{j-1}] \quad (2)$$

$$3M = 2\sum_{i=1}^{3}i[T^{i}] + \sum_{j=1}^{3}(3 + j)[D^{j-1}] \quad (3)$$

where the concentrations of tetrameric complexes, $[T^i]$'s, are related to those of the substituted and the unsubstituted wings of them, $[W^s]$ and $[W^0]$, as

$$[W^s] = \sum_{i=1}^{3}i[T^{i}] \quad (4)$$

$$[W^0] = \sum_{i=1}^{3}(4 - i)[T^{i-1}] \quad (5)$$

Equations 2–5 yield

$$4[W^0] + 2[W^s] = 3(1 - M) - 2[D^0] - [D^1] \quad (6)$$

$$2[W^s] + 6[D^2] = 3M - 4[D^0] - 5[D^1] \quad (7)$$

Assuming that the unsubstituted wing of tetrameric complexes, W^0, and dimeric trimethylaluminum, D^2, do not coexist, the relative values of the rate constants, k_{bj}'s, are calculated from these equations.

By numeric simulation the relative values of rate constants for the bridge reactions II were determined as $k_{b1} = k_{b2} = 1.0 \times 10^{-2}$, $k_{b3} = 1.0$, and $k_{b4} = 1.4 \times 10^{-1}$. The simulated values of the concentrations of aluminum complexes agreed fairly well with the observed ones as shown in Figure 5. These results suggest that the tetrameric structure of T^3 is decomposed most easily when it is attacked by three molecules of dimeric trimethylaluminum.

Since none of the tetrameric complexes having the odd number of terminal methyl groups was observed, such complexes are unstable compared with those having the even number of terminal methyl groups. However, it was impossible to determine the individual values of rate constants for the terminal reactions I.

Conclusion

By use of proton magnetic resonance it was found that aluminum isopropoxide reacts with trimethylaluminum forming three kinds of tetrameric and two kinds of dimeric complexes in aromatic solutions. The structures of these complexes were determined from their signal intensities by the aid of the temperature dependence of chemical shifts, the spin–spin coupling constants of isopropoxyl protons, and the magnetic relaxation times of various methyl protons.

The chemical shifts of proton signals display a significant dependence on temperature reflecting the coordination state; with increasing temperature the signals of bridging ligands shift toward the higher frequency, while those of terminal ones shift toward the opposite direction. The spin–spin coupling constants of isopropoxyl protons are classified according to the coordination state; the bridging groups are larger in coupling constants than the terminal ones. The relative values of magnetic relaxation times of methyl protons were useful as a measure of the size of complexes as well as the motional state.

Two kinds of methyl protons in the bridging isopropoxyl group of tetrameric aluminum isopropoxide have different resonance frequencies, and this difference disappears when the neighboring terminal groups are replaced by methyl groups. In the dimeric complexes the isopropoxyl group bridges two aluminum atoms tightly and does not take the terminal position. The methyl groups occupy the remaining sites and exchange rapidly at room temperature between the terminal and the bridge positions if the latter is not taken by the isopropoxyl group.

All the reactions, except for the exchange of ligands in the stationary state, occur irreversibly. The terminal isopropoxyl groups of tetrameric aluminum isopropoxide are substituted by the methyl groups of dimeric trimethylaluminum successively. After these reactions the resultant tetrameric structure is decomposed through four kinds of competitive reactions. The decomposition reaction takes place most easily when attacked by three molecules of dimeric trimethylaluminum.