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Reactions of Triethylaluminum with Electron Donors

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As a study of the roles of the electron-donor compounds in the three-component Ziegler-type catalysts, the reactions of triethylaluminum with various electron donor compounds, *e. g.*, triethylamine, pyridine, diethyl ether, tetrahydrofuran, dioxane, and triethylstibine, have been investigated by means of the proton magnetic resonance. The internal chemical shifts between the α- and β-protons of the substituent groups bound to key atoms in the reaction mixtures have indicated that (1) each donor gives only one type of complex which is ordinarily expected, and (2) the coordination of the donor to triethylaluminum lowers the electronegativity of the aluminum atom. Qualitative information about the ligand exchange reactions of the donor complexes has also been obtained. All the complexes obtained showed remarkable electrical conductivities, indicating ionic structures.

Many characteristic effects of such electron-donor compounds as tertiary amines, ethers, and stibines on the Ziegler-type catalysts for the polymerization of various monomers have been reported. These compounds promote the rate of polymerization and improve the stereospecificity in the polymerization of α-olefins[1-4] and dienes[5,6].

Furthermore, crystalline polymers of various vinyl monomers[7-14] have been reported to be obtained with these three-component catalysts.

In order to clarify the roles of the electron donors and elucidate the mechanism of the polymerization, studies of the reactions between the catalyst components are important. The reactions of the above ternary systems are very complex; consequently, studies of the reactions and the properties of the reaction products between each of two components, *i. e.*, the electron donors with alkylaluminums and with titanium halides, are necessary.

It is well known that trialkylaluminum or alkylaluminum halides react with these electron donors to give various complexes; for example, trialkylaluminum adds electron donors like ether, thioethers, tertiary amines and tertiary phosphines to form rather stable and, in most cases, distillable complexes ($R_3Al{\cdot}OR_2$, $R_3Al{\cdot}SR_2$, $R_3Al{\cdot}NR_3$ and $R_3Al{\cdot}PR_3$ respectively).[15] Recently, it has been shown that trialkylstibine gives similar complexes.[16]

Several investigations to clarify the properties of these complexes have also been reported. The IR spectra of the complexes have been studied for several systems in detail.[17,3] It has been shown by several authors that some complexes have remarkably high electrical conductivities, indicating that they have ionic structures.[18-21] Brownstein *et al.* studied the NMR spectrum of the 1 : 1 complex of triethylaluminum with diethyl ether.[22] Sakurada *et al.* have also reported on the NMR

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TABLE 1. PROTON CHEMICAL SHIFTS IN THE MIXTURES OF TRIETHYLALUMINUM AND ELECTRON DONOR COMPOUNDS
(60 Mc; room temperature; external standard, $SiMe_4$)

1) Triethylamine

$NEt_3/AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm	NEt_3 τ-Value for $-CH_3$	NEt_3 τ-Value for $>CH_2$	NEt_3 δ ppm	Assignment
0	9.72	8.97	−0.75	—	—	—	Al_2Et_6
0.5	10.20	8.98	−1.22	8.87	7.25	1.62	1 : 1 Complex
	9.73	8.95	−0.78				free Al_2Et_6
1.0	10.20	8.98	−1.22	8.87	7.25	1.62	1 : 1 Complex
2.0	10.20	9.03	−1.17	(8.90)	(7.27)	(1.63)	1 : 1 Complex
				(9.07)	(7.60)	(1.47)	free NEt_3

The values in parentheses were obtained at −55°C.

2) Pyridine

$Py/AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm	Pyridine τ-Value for α-CH	Pyridine τ-Value for β-CH	Pyridine τ-Value for γ-CH	$\delta(\alpha-\beta)$ ppm	$\delta(\alpha-\gamma)$ ppm	$\delta(\beta-\gamma)$ ppm	Assignment
0	9.72	8.97	−0.75	—	—	—	—	—	—	Al_2Et_6
0.5	10.28	9.17	−1.11	1.70	2.67	2.33	0.98	0.63	−0.34	1 : 1 Complex
	9.95	9.17	−0.78							free Al_2Et_6
1.0	10.32	9.25	−1.07	1.76	2.73	2.40	0.97	0.64	−0.33	1 : 1 Complex
2.0	10.37	9.30	−1.07	1.87	3.07	2.77	1.20	0.90	−0.30	1 : 1 Complex + free Pyridine
∞	—	—	—	1.93	3.42	3.15	1.47	1.22	−0.27	Pyridine

3) Diethyl ether

$Et_2O/AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm	Et_2O τ-Value for $-CH_3$	Et_2O τ-Value for $>CH_2$	Et_2O δ ppm	Assignment
0	9.72	8.97	−0.75	—	—	—	Al_2Et_6
0.5	10.07	9.07	−1.00	8.78	6.12	2.66	1 : 1 Complex + free Al_2Et_6
1.0	10.34	9.12	−1.22	8.82	6.15	2.67	1 : 1 Complex
2.0	10.47	9.27	−1.20	9.10	6.70	2.40	1 : 1 Complex + free Et_2O
∞	—	—	—	9.25	6.95	2.30	Et_2O

4) Tetrahydrofuran

$THF/AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm	Tetrahydrofuran τ-Value for β $>CH_2$	Tetrahydrofuran τ-Value for α $>CH_2$	Tetrahydrofuran δ ppm	Assignment
0	9.72	8.97	−0.75	—	—	—	Al_2Et_6
0.5	9.92	9.03	−0.89	8.05	6.03	2.02	1 : 1 Complex + free Al_2Et_6
1.0	10.13	9.07	−1.06	8.05	6.03	2.02	1 : 1 Complex
2.0	10.35	9.13	−1.22	8.23	6.30	1.93	1 : 1 Complex + free THF
∞	—	—	—	8.38	6.68	1.70	THF

5) Dioxane

Dioxane/$AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm	Dioxane τ-Value for $>CH_2$	Assignment
0	9.72	8.97	−0.75	—	Al_2Et_6
0.25	9.97	9.00	−0.97	5.87	1 : 2 Complex+free Al_2Et_6
0.50	10.25	9.05	−1.20	5.88	1 : 2 Complex
2.0	10.33	9.10	−1.23	6.38	1 : 2 Complex+free Dioxane
∞	—	—	—	6.57	Dioxane

6) Triethylstibine

$SbEt_3/AlEt_3$ molar ratio	$AlEt_3$ τ-Value for $>CH_2$	$AlEt_3$ τ-Value for $-CH_3$	$AlEt_3$ δ ppm
0	9.72	8.97	−0.75
0.20	9.82	9.00	−0.82
0.50	9.88	9.00	−0.88
1.0	10.03	9.00	−1.03
2.0	10.02	8.97	−1.05
5.0	10.00	8.97	−1.07

spectrum of triethylaluminum in tetrahydrofuran.[23]

In the present paper the reactions of triethylaluminum with various electron donors, such as tertiary amines, ethers, and stibine, were studied; the properties of the complexes obtained were then further studied by means of the nuclear magnetic resonance and measurements of the electrical conductivity.

Experimental

Materials. Commercial ethers and amines (Reagent Grade) were carefully purified as usual, and distilled under a dry nitrogen atmosphere before use. Commercial triethylaluminum (Texas Alkyls Corp.) and triethylstibine (Sankyo Yuki Co.) were used without further purification.

Reaction Procedure. To an aliquot of triethylaluminum was added the electron-donor compound, drop by drop, with stirring at room temperature in most cases. Low-boiling compounds, such as diethyl ether, was added at −70°C in a similar manner. After the addition, the temperature was raised very gradually to room temperature. All the mixtures were allowed to stand at room temperature overnight and were then used for the following measurements.

NMR Measurements. The proton magnetic resonance spectra were obtained using liquid samples in sealed tubes (5 mm o.d.). The spectra were recorded with a Varian A-60 spectrometer operating at 60 Mc. All values are given with tetramethylsilane as an external standard. The determination of the chemical shifts of the ethyl groups was made on the basis of a first-order approximation; *i. e.*, the center line of the methyl triplet and the average of the two center lines of the methylene quartet were chosen as the chemical shifts for CH_3 and CH_2 groups respectively. In the case of complicated signals, a maximum central signal was chosen as an approximate value.

Electrical Conductivities. The specific conductances of the liquid samples was measured at room temperature under a nitrogen atmosphere, using a Toa-Dempa Conductometer Model CM-ID equipped with platinum-black electrodes. The values were corrected by the use of standard aqueous solutions of potassium chloride.

Results

The nuclear magnetic resonance spectra of the mixtures of triethylaluminum and various electron-donor compounds over a wide range of molar ratios were measured, and the proton chemical shifts were determined using tetramethylsilane as the external standard. The internal chemical shifts (δ) of various groups were also calculated. The results are summarized in Table 1.

Triethylamine System. An example of the spectra is given in Fig. 1.

Pure triethylaluminum shows triplet signals due to the methyl protons on the lower field side (τ=8.97) and quartet signals due to the methylene protons on the higher filed side (τ=9.72). On the other hand, pure triethylamine shows complicated signals, due to the methyl and methylene protons respectively, on the reverse field sides. However, in the mixtures of two components over a wide range of molar ratios, the ethyl groups bound both to nitrogen and to aluminum showed simple spectra, *i. e.*, triplet signals of the methyl protons and quartet signals of the methylene protons. Each ethyl signal could be easily assigned on the basis of its inverted position, relative signal area, and different coupling constant. At a molar ratio, $NEt_3/AlEt_3$, of 0.5, two types of signals of the ethyl groups bound to aluminum were

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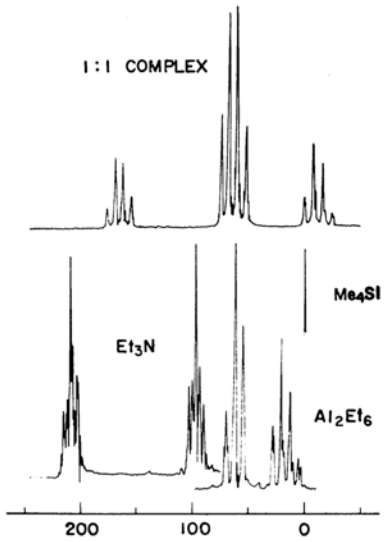

Fig. 1. NMR spectra of $Et_3Al \cdot NEt_3$, NEt_3 and Al_2Et_6.
(60Mc, room temperature, external standard: Me_4Si)

observed; their signal areas were nearly identical. At a molar ratio of 2.0, the signals of the ethyl group bound to nitrogen were broad at room temperature. When measured at a low temperature (−55°C), the above broad signals split into two types of ethyl signals, and their signal areas were nearly identical. The τ values of one of the above two types of the ethyl signals were identical with those of the equimolar mixture.

Pyridine System. Each component (triethylaluminum and pyridine) in the free and co-ordinated states gave similar spectra respectively. When an excess of triethylaluminum was present, two types of signals of the ethyl groups bound to aluminum, which were assigned to those of free and co-ordinated states, were also observed in this system at room temperature. On the other hand, when an excess of pyridine was present, the protons of the pyridine ring showed only one pair of sharp signals at room temperature. Assuming the formation of a 1 : 1 complex, the τ values for α, β and γ protons agreed with the weighed mean values of the 1 : 1 complex and the pyridine.

Diethyl Ether System. Both diethyl ether and triethylaluminum showed clear triplet signals of methyl protons and quartet signals of methylene protons in both free and co-ordinated states. When one component was present in excess, the signal which was assigned to either the complex or the free molecule of the component alone was not observed at room temperature.

Tetrahydrofuran, Dioxane, and Triethylstibine Systems. Each component (triethylaluminum and the electron donor compounds) in the free and co-ordinated states gave similar spectra respectively. When one component was present in excess, results similar to those obtained from the diethyl ether system were obtained.

Electrical Conductivities of the Donor Complexes. All the mixtures of triethylaluminum and various electron donors without any solvent showed remarkably a high electrical conductivity at room temperature over a wide range of molar ratios. Typical results are summarized in Table 2.

Table 2. Specific conductances of the complexes of triethylaluminum with various electron donors (22°C)

Complex	Specific conductance $\mu\Omega$/cm
$Et_3Al \cdot NEt_3$	3.6
$Et_3Al \cdot NC_5H_5$	4.3
$Et_3Al \cdot OEt_2$	8.0
$Et_3Al \cdot OC_4H_8$	13.3
$Et_3Al \cdot O(CH_2)_4O \cdot AlEt_3$	0.1
$Et_3Al \cdot SbEt_3$[16]	52.0

Discussion

Complex Formations between Triethylaluminum and Electron Donors. As for the reactions of triethylaluminum with various electron-donor compounds, the internal chemical shifts (δ) between the α- and β-protons of the substituent groups bound to key atoms give much information.

The variations in the δ values for the ethyl groups bound to aluminum as a function of the molar ratios of the electron-donor compounds to triethylaluminum are shown in Figs. 2—4.

In various ether systems, the δ value decreases as the molar ratio increases, attaining a constant value at the molar ratio which corresponds to the composition of the complex, namely, at $AlEt_3 \cdot Et_2O$, $AlEt_3 \cdot C_4H_8O$, or $2AlEt_3 \cdot C_4H_8O_2$, as is illustrated in Fig. 2. This indicates that only one

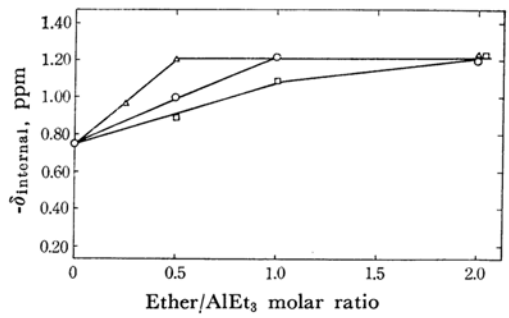

Fig. 2. Internal chemical shifts of the ethyl groups bound to aluminum in the mixtures of triethylaluminum and various ethers.
(60 Mc, room temperature)
○, $AlEt_3$-Et_2O △, $AlEt_3$-Dioxane
□, $AlEt_3$-THF

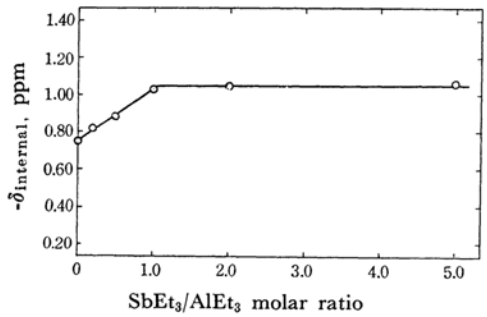

Fig. 3. Internal chemical shifts of the ethyl groups bound to aluminum in the mixtures of triethylaluminum and $SbEt_3$.
(60 Mc, room temperature)

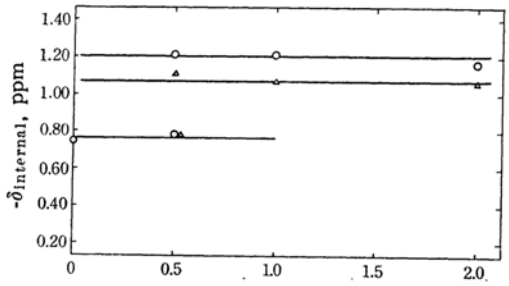

Fig. 4. Internal chemical shifts of the ethyl groups bound to aluminum in the mixtures of triethylaluminum and amines.
(60 Mc, room temperature)
○, $AlEt_3$-NEt_3 △, $AlEt_3$-pyridine

complex is formed in each system, as has been expected, and that the complex formation is almost quantitative. In the tetrahydrofuran system, however, this reaction does not appear as quantitative as in the cases of the other systems, since the δ value slightly decreased when the molar ratio exceeded unity. The author believes that the common discussion mentioned above is also applicable to this system on the basis of the similar chemical properties of the ethers.

As is shown above, the δ value can be used as a convenient parameter for the identification of the complex formation. The complex of triethylstibine with triethylaluminum is not distillable, and its composition has been postulated from the conductometric study.[16] Figure 3 clearly shows that the 1 : 1 complex is formed almost quantitatively.

In contrast with the above weak electron-donor systems, the mixtures of the amines show constant δ values in the resulting complexes over a whole range of molar ratios, as is illustrated in Fig. 4. The presence of free triethylaluminum can be detected only at molar ratios lower than unity. Thus, it appears that the formations of the 1 : 1 complexes, $AlEt_3$·NEt_3 and $AlEt_3$·Py, proceed almost quantitatively.

Ligand-exchange Reactions. When one of the ligand components is present in a free state together with the complex, a ligand exchange reaction occurs. The reaction rates can be estimated qualitatively from the present NMR data. When this rate is sufficiently high, only one type of signals should be observed, and the δ value is expected to correspond to the weighed mean value of the complex and the ligand component in a free state. The linear dependency of the δ values on the molar ratios of the electron-donor compounds to triethylaluminum, as shown in Figs. 2 and 3, indicates a high rate of ligand-exchange reactions. On the other hand, two types of signals, which are assigned to the free ligand component and the complex respectively, are observed in the cases of slow reactions, as Fig. 4 shows. A summary of these estimations is given in Table 3.

TABLE 3. RATE OF THE LIGAND EXCHANGE REACTIONS OF THE DONOR COMPLEXES OF TRIETHYLALUMINUM WITH TRIETHYLALUMINUM AND WITH ELECTRON DONORS

Complex	Ligand component	
	$AlEt_3$	Electron donor
$AlEt_3$·NEt_3	slow	fast
$AlEt_3$·NC_5H_5	slow	rapid
$AlEt_3$·OEt_2	rapid	rapid
$AlEt_3$·OC_4H_8	rapid	rapid
$AlEt_3$·$O(CH_2)_4O$·$AlEt_3$	rapid	rapid
$AlEt_3$·$SbEt_3$	rapid	rapid

Electronegativities of the Aluminum Atoms in the Donor Complexes of Triethylaluminum. Dailey and Shoolery have shown the direct dependency of the internal chemical shifts of the ethyl derivatives on the electronegativity of the substituent.[24] For these correlations several equations have been proposed for many ethyl compounds.[25,26] Here, the electronegativities of the aluminum atoms in the complexes of triethylaluminum with various electron donors were evaluated by Narashimhan's equation:[26]

$$x = 0.62\,\delta + 2.07 \qquad (1)$$

where x is electronegativity and δ is the internal chemical shift between methylene and methyl protons of the ethyl group. The results are summarized in Table 4. The reliability of the absolute value evaluated from such an equation depends

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25) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
26) P. J. Narashimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 5983 (1960).

Table 4. Electronegativities of the aluminum atoms in the complexes of triethylaluminum with various electron donors

Complex	Internal δ ppm	Electronegativity
$Et_3Al{\cdot}OEt_2$	−1.22	1.31
$Et_3Al{\cdot}OC_4H_8$	−1.22	1.31
$Et_3Al{\cdot}O(CH_2)_4O{\cdot}AlEt_3$	−1.23	1.31
$Et_3Al{\cdot}NEt_3$	−1.22	1.31
$Et_3Al{\cdot}NC_5H_5$	−1.07	1.41
$Et_3Al{\cdot}SbEt_3$	−1.07	1.41
$AlEt_3$	−0.75(−0.79)*	1.60

* Yamamoto's data obtained by extrapolating to infinite dilution using benzene as a solvent.

on the experimental conditions and other unknown factors. Narashimhan's equation (1) has been established for liquid samples consisting of metals with rather low electronegativities. Yamamoto has reported that the electronegativity of aluminum in triethylaluminum, which was evaluated from the same equation (1), agreed approximately with the value expected from the IR spectral data for trimethylaluminum.[27] Although we can not discuss quantitatively the results obtained here, the values shown in Table 4 are thought to be reliable, at least qualitatively.

Table 4 shows that the electronegativities of aluminum decreased remarkably when the triethylaluminum formed complexes with various electron donors, as reported by Brownstein *et al.*[22] In these complexes, the ethyl group bound to the aluminum atom may be more polarized than that of free triethylaluminum. Triethylaluminum is known to consist of a dimeric bridge structure. Yamamoto has reported that the δ values for the terminal and bridge ethyl groups are −1.11 ppm and about −0.2 ppm respectively as calculated from the spectrum obtained at −80°C, using toluene as a solvent. The above polarization of the ethyl groups in the donor complexes may be caused by both the absence of the bridged ethyl groups and the inductive effect of the electron-donating ligands in the complexes.

Electrical Conductivity of the Donor Complexes. All the mixtures show remarkably high electrical conductivities over a wide range of molar ratios, as has been reported previously for the diluted systems of triethylaluminum with diethyl ether,[18] diisobutyl ether,[18] isoquinoline,[18] quinoline,[19] and pyridine.[21] The ionic structures of all the donor complexes of triethylaluminum were supported by these results. The specific conductances of various donor complexes are summarized in Table 2.

The ionic properties of the electron-donor complexes and the polarized nature of the ethylaluminum linkage in these complexes might significantly affect the reactions of the components of the three-component catalysts.

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