Spectroscopic Studies of the Complex Produced by Trimethylaluminum and Diphenylamine*

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In order to make clear the polymerization mechanism of lower olefins and epoxides by the use of a Ziegler-type catalyst, it is most important to know the chemical and physical nature of the catalyst. In our previous work, the structure of trialkylaluminum was studied by infrared spectroscopy.[1] The present papar will report on the structure of the complex obtained by the reaction of trimethylaluminum and diphenylamine. Since trimethylaluminum is the lowest member of the trialkylaluminum series, this compound has been well investigated in spite of its low reactivity toward lower olefins. Until recently only a few compounds of $R_2Al-NR'_2$ type have been reported.

Formerly Brown and Davidson studied a trimethylaluminum and dimethylamine complex.[2] Then Fetter and Bartocha reported on the reaction of trimethylaluminum with various methyl hydrazines.[3] Hoffmann and Tornau described the compound $(Et_2Al\text{-}NC_9H_8)_2$[4] and Murahashi et al. investigated the polymerization of methyl methacrylate by an $EtAl\text{-}N(C_6H_5)$ catalyst.[5] In the publication mentioned above, it was concluded that most of the compounds a covalent aluminum-nitrogen bond was formed by a general reaction scheme:

$$AlR_3 + R'_2NH \rightarrow R_3Al : NHR'_2$$
$$\rightarrow R_2Al-NR'_2 + HR$$

The compound of the $R_2Al-NR'_2$ type has been suggested as associating to form a dimer through nitrogen bridges.[2,3] As the complex was sensitive both to air and to moisture, the reaction and subsequent manipulation were carried out under a high vacuum.

Experimental

Materials. — Trimethylaluminum (Ethyl Corp.) was transferred to several break-sealed ampoules in a dry nitrogen atmosphere and then distilled into storage ampoules under a high vacuum. Diphenylamine was recrystallized from alcohol, and was dried and degassed in vacuo before use. Cyclohexane (optical grade) was dried with calcium hydride and evaporated sodium film and then distilled in vacuo into break-sealed storage ampoules.

Reaction. — The reaction was carried out in a conventional high-vacuum system. Trimethylaluminum was transferred to a cold reactor (−196°C) containing diphenylamine. By warming the reactor toward room temperature, some gas was gradually evolved indicating the commencement of the reaction. After the mixture had been heated to the melting point of the product so as to complete the reaction, the excess trimethylaluminum and evolved gas were pumped out. The product was solid at room temperature and liquid at an elevated temperature. Cyclohexane was distilled into the reactor so as to dissolve the product. Then the solution was led into an NMR tube and a break-sealed capsule (for ultraviolet absorption measurements) previously attached to the reactor. Both NMR tube and break-sealed capsule were sealed and removed from the vacuum line.

Apparatus and Measurements.—The evolved gas was analyzed by a Hitachi Model RMU-5B mass-spectrometer installed at the Institute for Protein Reserch of Osaka University. Measurements of the ultraviolet spectra were made with a Hitachi Model EPS-2 spectrometer using 1-cm. quartz cells at room temperature. Samples were prepared under a high vacuum in a U-tube attached to the ampoule (Fig. 1). At first, the break-sealed capsule was broken, the cyclohexane in the ampoule was then transferred to the capsule, and the solution was introduced into the cell. The sample was diluted by distilling cyclohexane into the cell. The proton resonance spectra were obtained with a Varian Model A-60 high-resolution NMR spectrometer at 60 Mc. The sweep rate was about 1 p.p.m./min. For the measurement of the temperature dependence of the rate of methyl group exchange in the system of trimethylaluminum and the complex, the standard equipment of the spectrometer was used. The solvent was used as an internal reference (8.56 p.p.m. in τ value).

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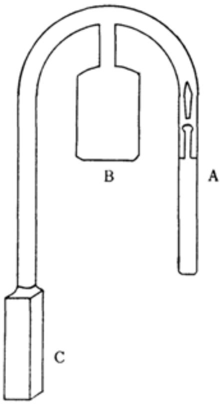
[3] N. R. Fetter and B. Bartocha, *Can. J. Chem.*, **39**, 2001 (1961).

[4] E. G. Hoffmann and W. Tornau, *Z. anal. Chem.*, **186**, 231 (1962).

[5] S. Murahashi, H. Yuki, T. Niki and K. Hatada, The 11th Annual Meeting of the High Polymer Society of Japan, Nagoya, May, 1962; S. Murahashi, H. Yuki and T. Obugata, The Symposium on High Polymers and Rubber, Nagoya, November, 1963.



Fi. 1. U-tube for ultraviolet absorption measurement.

A: Break-sealed capsule
B: Ampoule
C: Cell

Results and Discussion

The ultraviolet spectra of diphenylamine, diphenylammonium ion and the complex are shown in Fig. 2. The long wavelength bands of diphenylammonium ion and the complex show the vibrational structure characteristic of weakly-perturbed benzene rings. The spectrum of the complex resembles the spectra of polyphenyl compounds, which have no lone electron pair at the central atom directly bonded to phenyl radicals (for example $(C_6H_5)_3PO$).⁶⁾ The long wavelength band of the complex (274 mμ) is located between the corresponding bands of the diphenylammonium ion (255 mμ) and of diphenylamine (285 mμ). Hence, it may be concluded that the several phenyl rings in the complex are not appreciably conjugated with one another and that, therefore, the nitrogen atom in the complex will take approximately a hybride sp^3 orbital.

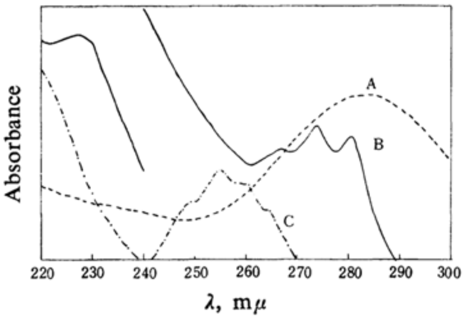


Fig. 2. Ultraviolet absorption spectra.

A: Diphenylamine in cyclohexane
B: The complex in cyclohexane
C: Diphenylammonium ion in water

The proton magnetic resonance spectrum of the complex (Fig. 3) shows two groups of peaks, with chemical shifts (in τ value) of 2.90 p.p.m. and 10.58 p.p.m. The unresolved low field peaks represent all the protons of the phenyl rings. This group of peaks occurs at a lower field position than that of diphenylamine (3.20 p.p.m.). Groenewege et al. have reported a value of 10.67 p. p. m. for the outer methyls in trimethylaluminum dimer and 9.53 p. p. m. for the bridge methyls.⁷⁾ Hoffmann has described a shift of 10.54 p. p. m. of the outer methyls in a dimethylaluminum tertiary-butoxyl dimer.⁸⁾ Compounds of the $(Me_2AlX)_2$ type (with X=OR, NR_2,⋯) form bridges only across X. However, their spectra do not yield the outer-methyl signal position of the trimethylaluminium, because the inductive and co-ordinative influences of the X substituents separately alter the effective electronegativity of the molecule residue,

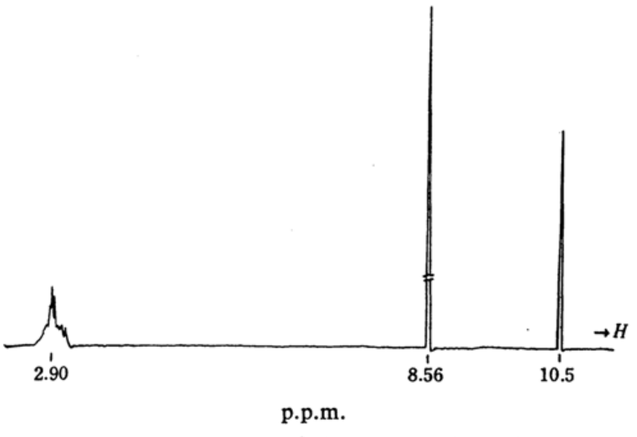


Fig. 3. NMR spectrum of the complex in cyclohexane.

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6) H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1954).

7) M. P. Groenwege, J. Smidt and H. de Vries, *J. Am. Chem. Soc.*, **82**, 4425 (1960).

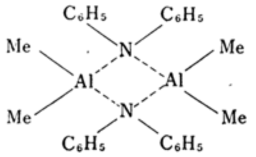
8) E. G. Hoffmann, *Trans. Faraday Soc.*, **58**, 642 (1962).

$Me_2Al\langle$. Negative polarizing substituents which asociate through a lone electron pair (X=OR, NR_2) show the sum of both influences. Thus, the sharp high field peak was assigned to methyl protons in the complex. The intensity ratios of both peaks were found to be approximately 5 : 3 by integration. This suggests that the ratio of phenyl groups to methyl groups in the complex is 1 : 1. The gas evolved in the course of the reaction was found to be methane.

From these observations of the complex, as well as from the results of previous works, the reaction of trimethylaluminum with diphenylamine may be expressed by Eq. I.

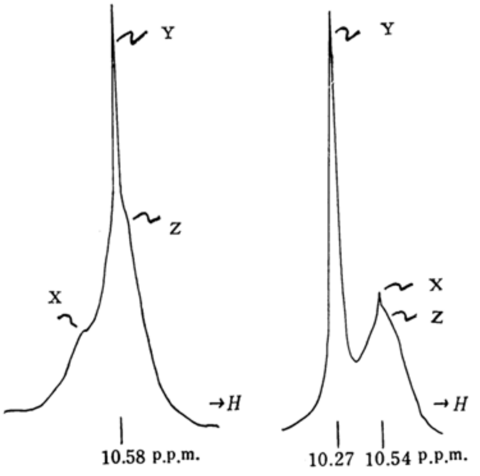
$$Al_2Me_6 + 2(C_6H_5)_2NH \rightarrow [(C_6H_5)_2NAlMe_2]_2 + 2CH_4 \qquad \text{(I)}$$

The structure of the complex may be a dimer through nitrogen bridges, which are perpendicular to the plane of four methyl groups.



(II)

The dimer shown in formula II may be called a aluminum diphenylamide complex. In order to confirm this structure of the complex, the NMR spectra of the mixtures of the complex and trimethylaluminum at various ratios were measured in cyclohexane. Figure 4 shows methyl group signals of mixtures at room temperature. The molar ratios of the complex to trimethylaluminum are about 1 : 1 and 1 : 3.2. In the molar ratio 1 : 1, there is no sharp methyl group signal of trimethylaluminum at 10.29 p.p.m., but a sharp methyl group signal (X) and broadened signals are superposed. The position of the former signal coincides with that of the complex. In the mixture, (1 : 3.2) there are two broad and one sharp signals of the methyl group, as is shown in Fig. 4(b). A broad signal with a chemical shift of 10.27 p.p.m. (Y) and a sharp signal (X) with one of 10.54 p.p.m. are assigned to trimethylaluminum and the complex respectively. The broadened signals in those systems show that some exchange takes place in the system.



(a) (b)

Fig. 4. NMR spectra of mixtures at the molar ratio of (a) 1 : 1 and (b) 1 : 3.2 (the complex : trimethylaluminum) at room temperature.

Each sample was measured at various temperatures to make clear the mechanism of this exchange. The temperature dependences of the NMR spectra of the mixture of the complex and trimethylaluminum in the molar ratios of 1 : 1 and 1 : 3.2 are shown in Fig. 5 and Fig. 6 respectively. The figures illustrate the broadening and coalescence of NMR peaks when they pass through the transition region between slow and fast exchange.

All the results and assignments are summarized in Table I. In the mixture, (1 : 3.2) two broadened signals (Y and Z) at room temperature move together as the temperature rises and coalescence into a single peak (T) at about 50°C. The sharp signal (X) decreases

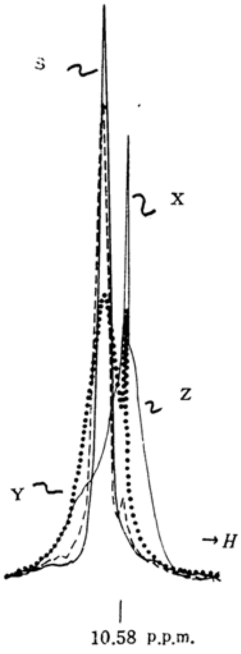


Fig. 5. The temperature dependence of the NMR spectrum of the mixture 1 : 1 ; (the complex : trimethylaluminum).

—— room temperature ······ 50°C
- - - 70°C ━━ 90°C

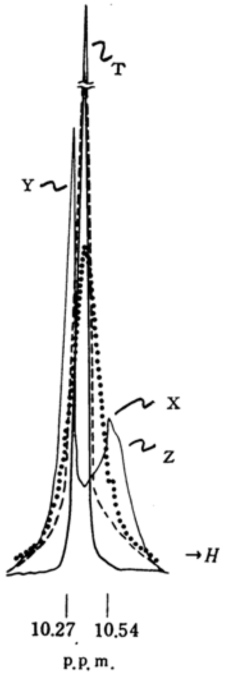


Fig. 6. The temperature dependence of the NMR spectrum of the mixture 1 : 3.2 ; (the complex : trimethylaluminum).

—— room temperature ······ 50°C
- - - 70°C ━━ 90°C

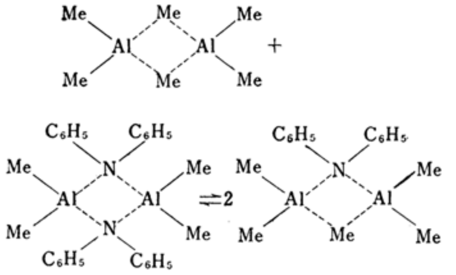
TABLE I. CHEMICAL SHIFTS OF METHYL GROUPS (p.p.m.)

Signal*	Assignment	Obs.		Calcd.
		Room temp.	90°C	90°C
X	Dimer complex	10.58	—	—
Y	Trimethylaluminum, B_2	10.29	—	—
Z	Outer methyls of mixed dimer, AB	~10.58	—	—
S	Mixed dimer,** AB	—	10.40	—
T	Mixture, 1 : 3.2	—	10.34	10.34

* See Fig. 4, Fig. 5 and Fig. 6.
** An averaged position for all protons of AB.

its intensity as the temperature is elevated and finally disappears at about 70°C. At 90°C, the spectrum becomes sharp and narrow. Figure 5 shows the same behavior of methyl group signals in mixture (1 : 1). These results reveal behavior of methyl group signals in the mixture (1 : 1). These results reveal the presence of three chemical species in the system.

The dimer structure of the complex suggested above permits us to interpret the three species and also these exchange phenomena by assuming the following reaction :



(III)

i. e. $B_2 + A_2 \rightleftharpoons 2AB$

where A stands for $AlMe_2N(C_6H_5)$ and B, for $AlMe_3$. The broad signal (Z) is assigned to the outer methyl groups of the mixed dimer AB. The existence of the three species could not be explained by a monomer structure. There are five different sites which can be occupied by the methyl groups. In the previous study of trimethylaluminum by proton resonance, it was concluded that the exchange between B_2 and B_2 (including intramolecular exchange) was fast at room temperature.[8] At room temperature, the NMR spectrum of Fig. 5 shows a sharp methyl group signal at 10.58 p.p.m. (X) corresponding to A_2 and broadened methyl group signals, which originate from a slow exchange between AB and B_2 and between AB and AB. At 50°C the rate of this exchange is probably fast enough for the two broadened peaks to coalescence into a single peak (S), as is shown in Fig. 6. A sharp methyl group signal (X) corresponding to A_2 decreases with the increasing temperature and disappears at 90°C. This shows that reaction III proceeds toward the right side with the increasing temperature. At 90°C, therefore, AB is the predominant species in the system and shows a sharp signal (S), which indicates a fast exchange between AB and AB. This observation shows that the rate of the three exchanges between B_2 and B_2, between AB and AB, and between AB and A_2 are in the observable region of proton resonance.

Using the value, 10.40 p.p.m. of AB and 10.29 p.p.m of B_2, the τ-value of the mixture (1 : 3.2) at 90°C was calculated** shown in Table I. The agreement of the observed and the calculated τ-values for the mixture (1 : 3.2) at 90°C supports the present assignment of proton magnetic resonance spectra.

Ziegler et al. reported that the mixtures of dialkylaluminum amide $(R_2AlNR'_2)_2$ and trialkyl aluminum do not polymerize ethylene, and that a mixed dimer of the type

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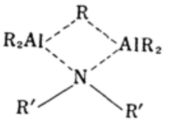
** This τ-value was the weighted average of the τ-values of B_2 and AB, assuming that reaction III proceeded completely towards the right side at 90°C.



(IV)

is not produced in the system.[9]

The results of the present NMR study clearly show the existence of the mixed dimer (IV) in the present case. A similar system was reported to polymerize methyl methacrylate.[5] Aliphatic amines and aromatic amine might be different in activity in forming a complex.

Summary

The reactive complex produced by the reaction of trimethylaluminum with diphenylamine has been studied by the ultraviolet absorption and proton magnetic resonance methods. The ultraviolet absorption of the complex has shown two bands, at 228 mμ and 274 mμ, in cyclohexane. Proton magnetic resonance spectrum of the complex has been shown to consist of two groups of peaks, with an intensity ratio of approximately 5 : 3 and with chemical shifts of 2.90 p.p.m. and 10.58 p.p.m. These shifts have been assigned to phenyl protons and methyl protons respectively. In the mixture of trimethylaluminum and the complex, an exchange of methyl groups occurs. The structure of the complex has been concluded to be dimeric through two nitrogen bridges, as is shown in formula II.

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