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Spectroscopic Studies of the Mixture of Dialkylaluminum 2-Aminoethoxide $(AlR_2OCH_2CH_2NR'_2)_2$ and Trialkylaluminum $(AlR''_3)_2$*1

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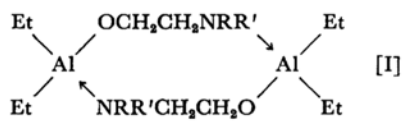
The proton magnetic resonance and infrared spectra of the mixtures of dialkylaluminum 2-aminoethoxide $(AlR_2OCH_2CH_2NR'_2)_2$ and trialkylaluminum $(AlR''_3)_2$ were measured. Special attention was paid to the infrared frequencies of the NH_2 stretching and scissors bands and to the chemical shifts of the methyl groups attached to the aluminum and nitrogen atoms. From the results it was concluded that $(AlR''_3)_2$ reacts with $(AlR_2OCH_2CH_2NR'_2)_2$ to form a 1 : 1 coordination compound $AlR_2OCH_2CH_2NR'_2 \rightarrow AlR''_3$ quantitatively. At the same time, the redistribution and exchange reactions of the alkyl groups were observed.

It is known that trialkylaluminums $(AR''_3)_2$ such as $(AlMe_3)_2$ and $(AlEt_3)_2$ are associated to dimers and that rapid inter- and intramolecular exchanges of alkyl groups take place.[1,2] These exchange reactions are due to the weak bonding between aluminum atom and carbon atom of the bridged alkyls. $(AlR''_3)_2$ also forms 1 : 1 coordination compounds with ethers and amines. Although the bonding between aluminum atom and electron donors seems to be stronger than that between aluminum atom and carbon atom of the bridged alkyls, the alkyl group exchange is still observed in the mixture of such a coordination compound and $(AlR''_3)_2$.[3-5]

One of us obtained the crystals of the dimers of diethylaluminum 2-aminoethoxides $(AlEt_2OCH_2CH_2NRR')_2$ by reacting $(AlEt_3)_2$ with several aminoethanols $HOCH_2CH_2NRR'$; R,R'=H, alkyl, cycloalkyl, and/or aryl groups.[6] We investigated the structures of these comopunds spectroscopically and concluded that their structures could reasonably be repoesented by formula I with two NRR' $\rightarrow$Al coordination bonds.[7]



[I]

The behaviors of the mixture of $(AlR_2OCH_2CH_2NR'_2)_2$ and $(AlR''_3)_2$ seemed to be very interesting in comparison with the mixture of two trialkylaluminums——$(AlR_3)_2+(AlR'_3)_2$——and the mixture of trialkylaluminum and an electron donor, because $(AlR_2OCH_2CH_2NR'_2)_2$ may act as an electron donor ($-NR'_2$ group) and as an electron acceptor ($-AlR_2$ group) simultaneously. Therefore the mixture was studied by IR and NMR spectroscopically.

Experimental

Preparation of the Samples. $(AlEt_2OCH_2CH_2NH_2)_2$ and $(AlEt_2OCH_2CH_2NMe_2)_2$ were prepared by the reaction of $(AlEt_3)_2$ with the corresponding alkanolamine following the synthetic methods described previously.[7] $(AlMe_2OCH_2CH_2NMe_2)_2$ was obtained by the reaction of $(AlMe_3)_2$ with dimethylaminoethanol $HOCH_2CH_2NMe_2$ as white crystals (mp 116.5°C—118.5°C; Found: Al, 18.48%; mol wt, 304.7. Calcd for $Al_2C_{12}H_{32}O_2N_2$: Al, 18.58%; mol wt, 290.4). $(AlEt_3)_2$ and $(AlMe_3)_2$ were purchased from Ethyl Corp. and fractionally distilled before use.

Measurements of IR and NMR Spectra. The IR spectra of the dilute benzene solutions of the samples (the concentrations of the solutions were 1.10 g/100 m*l*) were measured in the 4000—420 cm^{-1} region by using KRS-5 liquid fixed cell of 0.5 mm thickness. A Japan Spectroscopic Co. Model DS-402G infrared spectrophotometer was used.

The NMR spectra were run on a Varian A-60A high resolution NMR spectrometer equipped with variable temperature accessories. About 0.5 m*l* of the solution of the sample (10% weight/volume solution) was injected into the sample tube by a hypodermic syringe under nitrogen atmosphere and sealed. Benzene was used as solvent for room temperature measurements

*1 Presented at the Symposium on Organometallic Compounds, Tokyo, October 1968.

1) N. Muller and D. E. Prichard, *J. Am. Chem. Soc.*, **82**, 248 (1960).

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

3) T. Mole, *Aust. J. Chem.*, **16**, 801 (1963).

4) T. Mole, *Chem. Ind. (London)*, **1964**, 281.

5) M. Kawai, T. Ogawa and K. Hirota, This Bulletin, **37**, 1302 (1964).

6) H. Higashi and S. Namikawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 93, 368 (1976).

7) H. Sato, R. Tarao and H. Higashi, This Bulletin, **42**, 1588 (1969).

and toluene for high temperature measurements. The solvents were also used as internal references. The signal intensities were usually measured by an integrator.

Results and Discussion

The IR Spectra of the System $(AlEt_2OCH_2CH_2NH_2)_2+(AlEt_3)_2$. The IR spectrum of the benzene solution of $(AlEt_2OCH_2CH_2NH_2)_2$ is shown in Fig. 1a. The spectra of the mixtures of $(AlEt_2OCH_2CH_2NH_2)_2$ and $(AlEt_3)_2$ are shown in Figs. 1b, 1c and 1d together with the spectrum of triethylaluminum-*n*-propylamine $AlEt_3\cdot n\text{-}PrNH_2$ in Fig. 1e. For $(AlEt_2OCH_2CH_2NH_2)_2$, the bands at 3375 and 3309 cm^{-1} have been assigned to the NH_2 antisymmetric and symmetric stretching vibration and a sharp band at 1590 cm^{-1} to the NH_2 scissors respectively in a previous paper.[7]

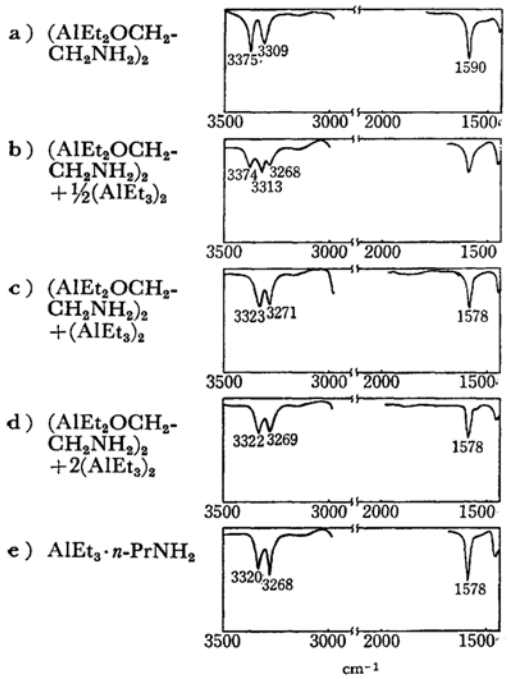


Fig. 1. The IR spectra of the systems $(AlEt_2OCH_2CH_2NH_2)_2+(AlEt_3)_2$.

The spectrum of the 1 : 1 mixture of $(AlEt_2OCH_2CH_2NH_2)_2$ and $(AlEt_3)_2$, Fig. 1c, shows the bands of the NH_2 stretching vibrations at 3323 and 3271 cm^{-1}, and the NH_2 scissors at 1578 cm^{-1}. These frequencies are almost equal to the values of the corresponding bands of $AlEt_3\cdot n\text{-}PrNH_2$, Fig. 1e, 3320, 3268 and 1578 cm^{-1} respectively. This fact is reasonably interpreted by the assumption that the NH_2 group in $(AlEt_2OCH_2CH_2NH_2)_2$ coordinates to the Al atom of $(AlEt_3)_2$. The NH_2 stretching vibrations of the 1 : 0.5 mixture, Fig. 1b, are clearly a superposition of those of Figs. 1a and 1c. The spectrum of the 1 : 2 mixture, Fig. 1d, shows the bands of NH_2 stretching vibrations at the same frequencies as those of the 1 : 1 mixture shown in Fig. 1c.

These observations lead to the conclusion that $(AlEt_3)_2$ forms a 1 : 1 coordination compound with $(AlEt_2OCH_2CH_2NH_2)_2$ quantitatively.

The NMR Spectra of the System $(AlMe_2OCH_2CH_2NMe_2)_2+(AlMe_3)_2$. The NMR spectra of the benzene solutions of the mixtures of $(AlR_2OCH_2CH_2NR'_2)_2$ and $(AlR''_3)_2$ (R=Me, Et, R'=H, Me, Et, R''=Me, Et) support the above conclusion obtained from the IR spectra. The result for the particular case where R, R' and R'' are methyl group will be described in detail, although similar conclusions are reached for all other cases. In Fig. 2a, the spectrum of the benzene solution of $(AlMe_2OCH_2CH_2NMe_2)_2$ is given. The 7.83 and the 5.28 ppm peaks are due to the methyl group attached to the Al atom and the N atom (hereafter abbreviated as the Al-Me group and the N-Me group) respectively. Two triplets at 5.14 and 3.67 ppm are assigned to the N-methylene group and O-methylene group respectively by taking the assignments given in Ref. 7 into consideration.

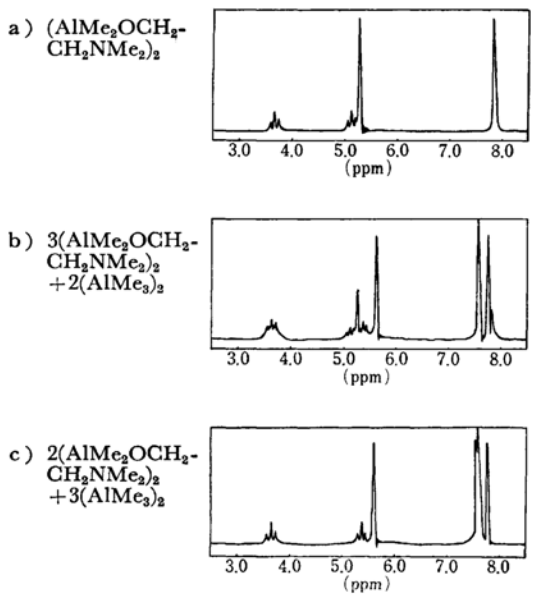


Fig. 2. The NMR spectra of the mixtures of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$.

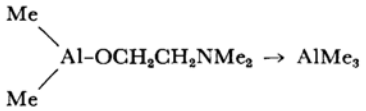
The NMR spectrum of the 3 : 2 mixture of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$ is shown in Fig. 2b. There appear two new peaks due to the Al-Me group at 7.77 and 7.56 ppm, and also one new peak due to the N-Me group at 5.63 ppm.

The areas of the 7.77 ppm and the 5.63 ppm peaks are equal and the ratio of the areas of the 7.77 ppm and the 7.56 ppm peaks is 2 : 3. Thus the 7.56 ppm peak is assigned to the Al-Me group of $(AlMe_3)_2$ which is coordinated by the N atom in $(AlMe_2OCH_2CH_2NMe_2)_2$. The spectrum of

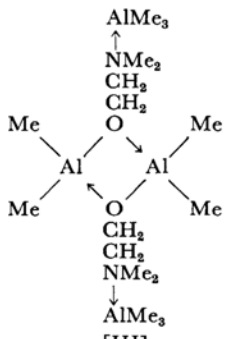
the 2 : 3 mixture is shown in Fig. 2c. The 7.83 ppm peak due to the Al-Me group and the 5.28 ppm peak due to the N-Me group of $(AlMe_2OCH_2CH_2NMe_2)_2$ disappear and excess $(AlMe_3)_2$ gives the peak at 7.53 ppm.

These observations support the conclusion that $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$ form a 1 : 1 coordination compound quantitatively.

The Molecular Weight of the 1 : 1 Coordination Compound of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$. As to the structure of this coordination compound, there are two possible formulas II (monomeric) and III (dimeric).

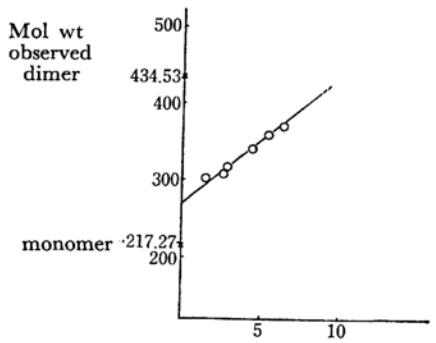


[II]



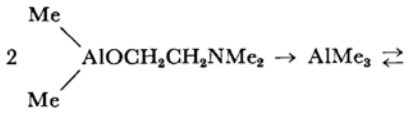
[III]

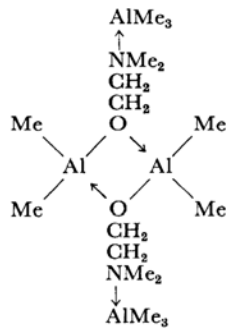
In order to determine which formula is preferable, the freezing point depression of the benzene solution of the 1 : 1 mixture of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$ was measured. The results are shown in Fig. 3. The molecular weight obtained by extrapolation to the infinite dilution is a little larger than the value calculated by assuming the monomeric formula II. If the coordination compound is a mixture of species represented by formulas II and III, two triplets due to the *O*-methylene group should be expected, but only one triplet is observed. Therefore the coordination compound might exist in an equilibrium represented by Eq. (1) in the benzene solution.



$AlMe_2OCH_2CH_2NMe_2 \rightarrow AlMe_3$ wt%
$(AlMe_2OCH_2CH_2NMe_2\ 50 \pm 2$ mol%)

Fig. 3. Concentration dependence of molecular weight of the coordination compound $AlMe_2OCH_2CH_2NMe_2 \rightarrow AlMe_3$.

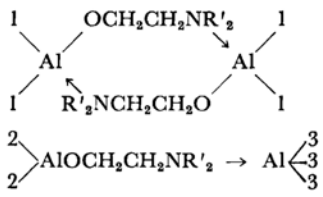




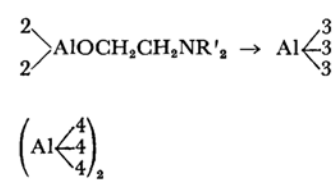
(1)

Although the possibility of the existence of the dimeric species could not be completely excluded, the molecular weight extrapolated to infinite dilution apparently suggests the predominance of monomeric species; so, in the following discussion, the structure of the coordination compound will be considered as given by formula II (monomeric).

The Redistribution Reactions of the Alkyl Groups. As described previously, there exist the following species in the mixture of $(AlR_2OCH_2CH_2NR'_2)_2$ and $(AlR''_3)_2$ depending on the molar ratio.



when $(AlR_2OCH_2CH_2NR'_2)_2$ is in excess



when $(AlR''_3)_2$ is in excess

(The numbers 1, 2, 3 and 4 mean the sites to be occupied by the Al–R groups. For example, the methyl group at site 1 will be hereafter abbreviated as 1-Me.)

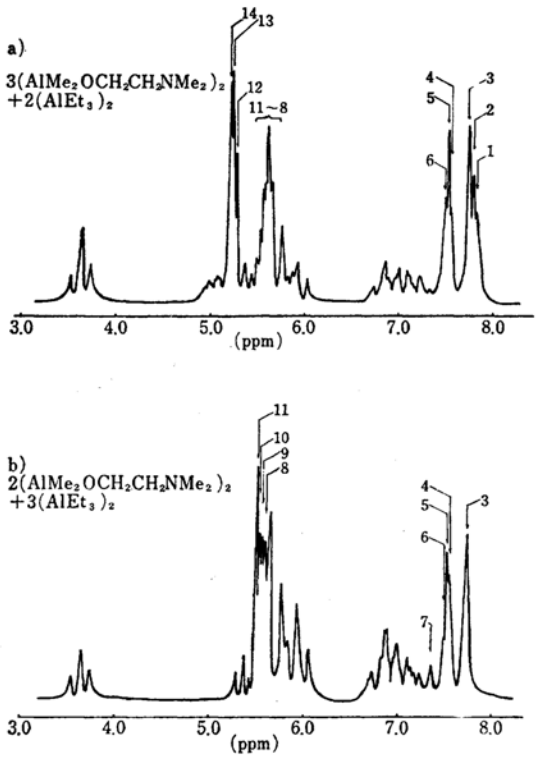
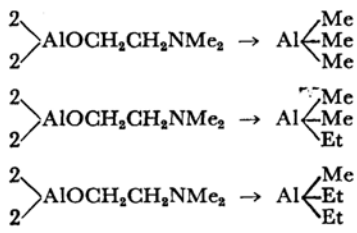


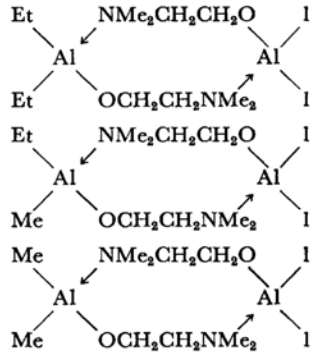
Fig. 4. The NMR spectra of the mixtures of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlEt_3)_2$.

When R differs from R″, the redistribution of the alkyl groups is observed in the NMR spectra. The NMR spectra of the benzene solutions of the mixtures of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlEt_3)_2$ are shown in Figs. 4a and 4b. If the redistribution of the alkyl groups does not take place, 3-Me peak would not be observed. In Figs. 4a and 4b, however, the 7.56 ppm peak is reasonably assigned to the 3-Me by taking the assignments of the spectrum of the mixture of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$ into consideration. These observations show clearly the existence of the redistribution of the Al-R groups.

The 3-Me group gives a fine structure of three peaks corresponding to the following formulas respectively as the result of the redistribution of



the alkyl groups. Also, the 5.28 ppm peak due to the N-Me group in $(AlRR'OCH_2CH_2NMe_2)_2$ gives a fine structure of three peaks corresponding to the following formulas respectively.



These fine structures of the N-Me group owing to the redistribution of the Al-R groups provide a strong evidence that N atom in $(AlR_2OCH_2CH_2NR'_2)_2$ coordinates to the Al atom and supports the conclusion reported as to the structures of these compounds in Ref. 7. The assignments of the N-Me and Al-Me groups in Figs. 4a and 4b are summarized in Table 1.

TABLE 1. THE ASSIGNMENTS OF THE Al-Me AND N-Me PEAKS IN THE NMR SPECTRA OF THE MIXTURES OF $(AlMe_2OCH_2CH_2NMe_2)_2$ AND $(AlEt_3)_2$

No. of peak	Assignment	Chemical shift*
1	1-Me (AlEtMe)	7.85
2	1-Me ($AlMe_2$)	7.83
3	2-Me ($AlMe_2$+AlEtMe)	7.77
4	3-Me ($AlEt_2Me$)	7.58
5	3-Me ($AlEtMe_2$)	7.57
6	3-Me ($AlMe_3$)	7.56
7	4-Me	7.38
8	N-Me (NMe_2 → $AlMe_3$)	5.63
9	N-Me (NMe_2 → $AlEtMe_2$)	5.60
10	N-Me (NMe_2 → $AlEt_2Me$)	5.58
11	N-Me (NMe_2 → $AlEt_3$)	5.55
12	N-Me (NMe_2 → $AlMe_2O$-)	5.28
13	N-Me (NMe_2 → AlEtMeO-)	5.26
14	N-Me (NMe_2 → $AlEt_2O$-)	5.24

* ppm from benzene peak.

In the mixture of $(AlMe_3)_2$ and $(AlEt_3)_2$, a rapid exchange of the alkyl groups is observed, and it has been shown that the methyl group prefers to occupy the bridge position from six to seven times as much as the ethyl group.[8] In the system under investigation, there are four sites to be occupied by the alkyl groups. To see if such a selectivity exists among the four sites as observed in the system of $(AlMe_3)_2$ and $(AlEt_3)_2$, the distribution of the methyl group among the four sites was measured. The results are shown in Figs. 5a and 5b. The dotted lines are theoretical curves obtained by as-

8) O. Yamamoto and K. Hayamizu, *J. Phys. Chem.*, **72**, 822 (1968).

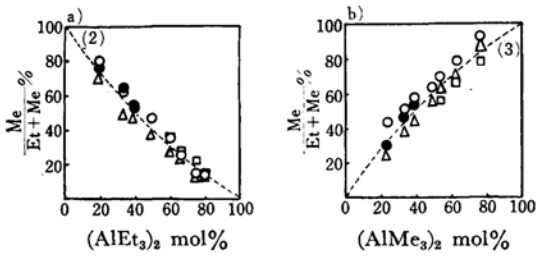


Fig. 5. The distribution of the methyl group.

a) $(AlMe_2OCH_2CH_2NMe_2)_2+(AlEt_3)_2$
b) $(AlEt_2OCH_2CH_2NMe_2)_2+(AlMe_3)_2$
● 1-Me ○ 2-Me △ 3-Me □ 4-Me

suming that the methyl and ethyl groups distribute to the four sites at random and expressed by the following equations. We have for the mixture of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlEt_3)_2$

$$y = \frac{200x}{300-x}, \tag{2}$$

and for the mixture of $(AlEt_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$

$$y = \frac{300(100-x)}{300-x}, \tag{3}$$

where x is molar ratio (per cent) of $(AlR_2OCH_2CH_2NMe_2)_2$ and y is the ratio (per cent) of the methyl group. The agreement of the experimental data with the theoretical curves (Fig. 5) shows that the methyl and ethyl groups distribute to the four sites at random.

The Exchange Reactions of the Alkyl Groups. After the redistribution reaction took place, the rapid exchange of the alkyl group is not observed at room temperature except for the 4-alkyl group. Chemical shifts of the 4-Me signals in the mixture of $(AlR_2OCH_2CH_2NMe_2)_2$ and $(AlR''_3)_2$ are shown in Fig. 6. These tendencies observed in Fig. 6 could be explained according to the fact that the methyl group prefers to occupy the bridge position from six to seven times as much as the ethyl group in the mixture of $(AlMe_3)_2$ and $(AlEt_3)_2$.

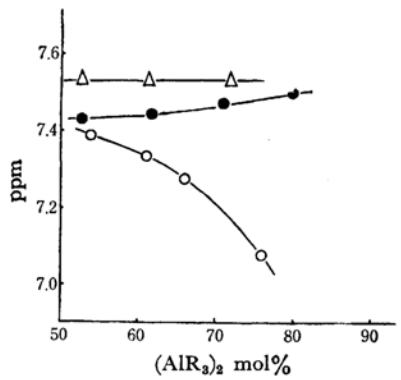
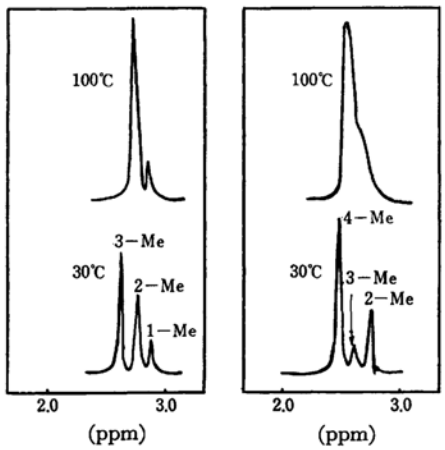


Fig. 6. Chemical shifts of the 4-Me signals in the mixture of $(AlR_2OCH_2CH_2NMe_2)_2$ and $(AlR''_3)_2$.

△ $(AlMe_2OCH_2CH_2NMe)_2+(AlMe_3)_2$
● $(AlEt_2OCH_2CH_2NMe_2)_2+(AlMe_3)_2$
○ $(AlMe_2OCH_2CH_2NMe_2)_2+(AlEt_3)_2$

When the temperature of the system is raised to 100°C, the rapid exchanges of the alkyl groups are observed except for the 1-alkyl group. The NMR spectra of the Al-Me group of the mixtures of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$ are shown in Figs. 7a and 7b. In Fig. 7a, the 2-Me



a) $3(AlMe_2OCH_2CH_2NMe_2)_2 + 2(AlMe_3)_2$
b) $(AlMe_2OCH_2CH_2NMe_2)_2 + 4(AlMe_3)_2$

Fig. 7. Temperature dependence of signal shape of the Al-Me group in the system of $(AlMe_2OCH_2CH_2NMe_2)_2$ and $(AlMe_3)_2$.

and the 3-Me peaks coalesce into a single peak, while the 1-Me peak only broadens slightly. This fact suggests that the 1-alkyl group is less mobile than the alkyl groups at any other site.

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