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ALKYL INTERCHANGE IN THE MIXTURE OF TRIETHYL ALUMINUM AND DIETHYLALUMINUM CHLORIDE

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Rapid exchange of alkyl groups in mixtures of trialkyl aluminums (1~3) or of trimethyl aluminum and methyl aluminum halides (4,5) have been studied mainly by NMR spectroscopic measurements. Sakurada et al. (5) have measured the NMR spectra of Al_2Me_5Cl prepared from trimethyl aluminum and methyl aluminum sesquichloride at 26 and -94°C and considered Al_2Me_5Cl to be primarily an equimolar mixture of dimeric forms of trimethyl aluminum and dimethylaluminum chloride.

Here, we investigated the NMR spectra of the mixtures of triethyl aluminum and diethylaluminum chloride at room temperature as well as at low temperatures.

The NMR spectra were obtained with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.,) at 100 Mc/sec by using a sample containing a few per cent of toluene as an internal standard. The chemical shifts were measured relative to a methyl signal of toluene.

The NMR spectra of triethyl aluminum-diethylaluminum chloride mixtures were measured at room temperature with varying the ratio of the two. Each spectrum consisted of only a single methyl and methylene signal, and the chemical shifts of methyl and methylene protons varied as a nearly linear function of the fraction of ethyl groups on triethyl aluminum as shown in Fig. 1. This result indicated that the rapid intermolecular exchange of ethyl groups occurred at room temperature in the mixtures of triethyl aluminum and diethylaluminum chloride.

The temperature dependence of the spectrum of an equimolar mixture of triethyl aluminum and diethylaluminum chloride was shown in Fig. 2.

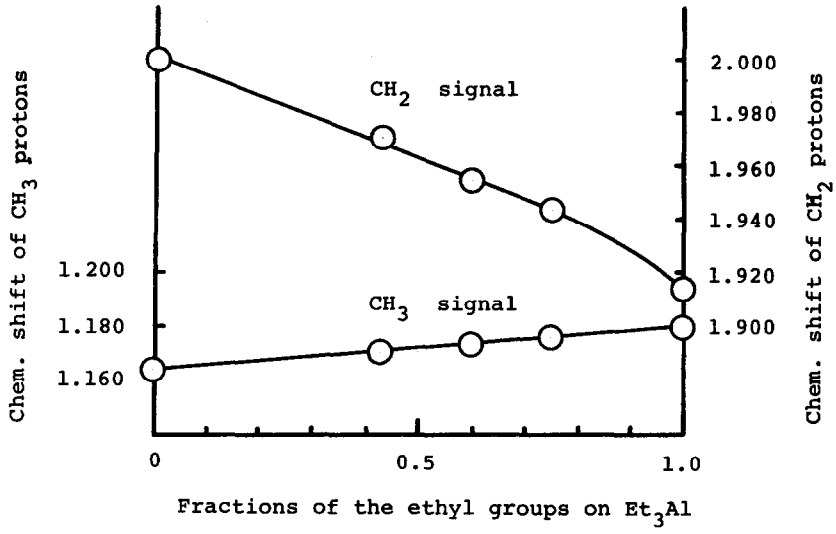


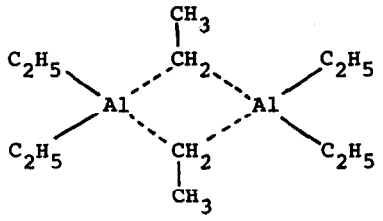
FIG. 1

NMR Spectra of the Mixtures of Triethyl Aluminum and Diethylaluminum Chloride at Room Temperature

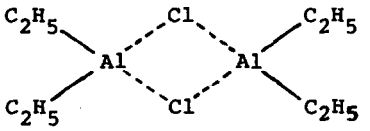
At room temperature the spectrum exhibited only one methyl and methylene resonance. On cooling the mixture to 2°C the spectrum showed some broadening of signals, especially of the methylene signals. On further cooling the resolution of the spectrum again improved gradually. At -22°C the methyl signals split into a pair of triplets and the methylene signals also became to be a superposition of two quartets. At the same time a new signal appeared on the higher-field side of the methyl signals as a shoulder. In considering the chemical shifts of the signals, the pair of triplets and the two quartets must correspond to the methyl and terminal methylene resonances ,respectively, of triethyl aluminum and diethylaluminum chloride and the shoulder must be the bridging methylene signals of triethyl aluminum. As the temperature decreased furthermore, the mixture became too viscous to give a good resolution and the measured spectrum showed only two broad peaks.

These results show that at room temperature in an equimolar mixture of triethyl aluminum and diethylaluminum chloride the ethyl groups are involved in

a rapid exchange which seems to cease at about -20°C, and at the lower temperatures only an equimolar mixture of I and II exists.



(I)



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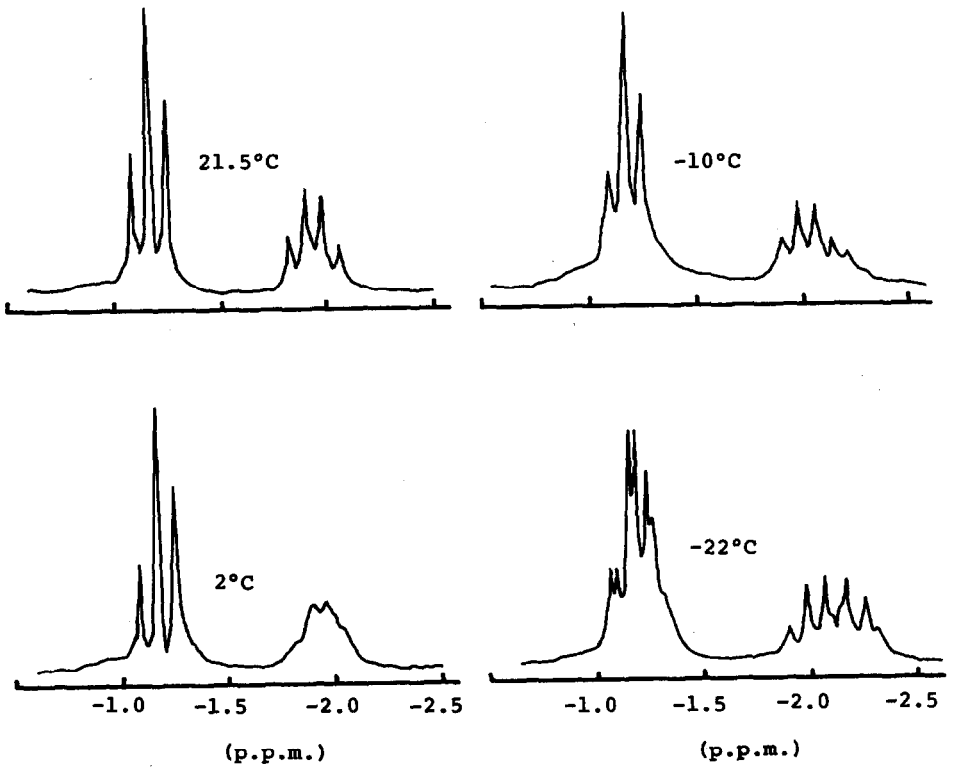


FIG. 2

NMR Spectra of A Equimolar Mixture of Triethyl Aluminum and Diethylaluminum Chloride at Various Temperatures

TABLE 1

Temperature Dependence in NMR Spectra of the Mixtures of Triethyl Aluminum and Diethylaluminum Chloride

Mol. fraction of Et_3Al	Temp. (°C)	Chem. shift of ethyl group[a]		Intensity ratio[b]	
		CH_3 signal	CH_2 signal	Obsd.	Calcd.
0.67	21.5	-1.176	-1.944	0.64	0.67
"	-20	-1.133 -1.168	-2.029 -2.212	0.41	0.43
0.50	21.5	-1.173	-1.955	0.67	0.67
"	10.0	-1.170	-1.945	0.64	0.67
"	2.0	-1.178	-1.927	0.64	0.67
"	-10	-1.168	-2.024	0.49	0.47
"	-22	-1.158 -1.183	-2.029 -2.234	0.49	0.47
"	-30	-1.170 -1.198	-2.037 -2.235	0.47	0.47
"	-40	1.183[c]	-2.117[c]	—	—
0.33	21.5	-1.170	-1.971	0.64	0.67
"	-20	-1.140 -1.168	-2.012 -2.224	0.52	0.52

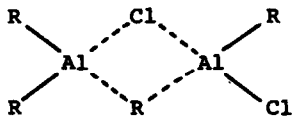
[a] Chemical shifts in p.p.m. are referred to the methyl signal of toluene.

[b] Ratio of signal area between the higher-field methylene signals and the remainder in the spectrum.

[c] A poor resolution of spectrum gave only two broad peaks.

The intensity ratios between the higher-field double quartet and the remainder in the spectra of triethyl aluminum-diethylaluminum chloride mixtures at various ratios of the two were measured at low temperatures. The observed values were in good agreement with the expected values for the above assignment as shown in Table 1. This seems to confirm the above conclusion about the alkyl interchange in the mixtures of triethyl aluminum and diethylaluminum chloride.

Ziegler (6) has suggested that the mixed dimer III exists to a certain



(III)

extent in an equilibrium state and that the intramolecular exchange of alkyl group in III is possible. Our NMR data concerning the mixtures of triethyl aluminum and diethylaluminum chloride showed that at low temperature only two symmetrical dimers I and II exist and gave no evidence for the existence of the unsymmetrical mixed dimer III. From these results it may be said that even at room temperature the rapid intermolecular exchange of ethyl groups between I and II can be expected in the mixture and the mixed dimer III must have only a transitory existence, if present at all.

References

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