The Low Temperature NMR Spectrum of Triethylaluminum

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In a previous paper,[1)] the author reported on the NMR spectra of triethylaluminum and diethylaluminum monohalides at room temperature and pointed out an anomaly in the δ value of triethylaluminum: in general, the δ value (the internal chemical shift betweeen methyl and methylene protons in the ethyl group) for metal ethyl compounds increases when one of the ethyl groups is replaced by a halogen atom. In contrast with this, the δ value for triethylaluminum (-0.72 p. p. m. for a pure liquid sample) is larger than that for diethylaluminum chloride (-0.81 p. p. m. for pure liquid). In the previous paper it was suggested that this anomaly may be attributed to the rapid exchange of the

1) O. Yamamoto, This Bulletin, 36, 1463 (1963).

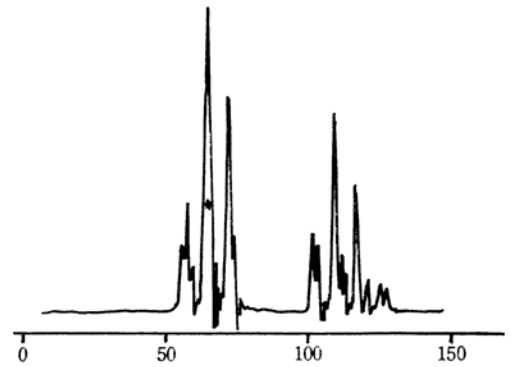
ethyl groups between bridge and terminal positions in the triethylaluminum dimer, so that a weighted mean of two kinds of ethyl spectra is observed as the spectrum of triethylaluminum at room temperature. If this suggestion is valid and if the rapid exchange becomes slower as the temperature is lowered, the NMR spectrum of triethylaluminum at a sufficiently low temperature will show two separate ethyl signals, due to the terminal and bridge groups respectively. To confirm this, the low temperature spectra of triethylaluminum have been studied in this work.

Experimental

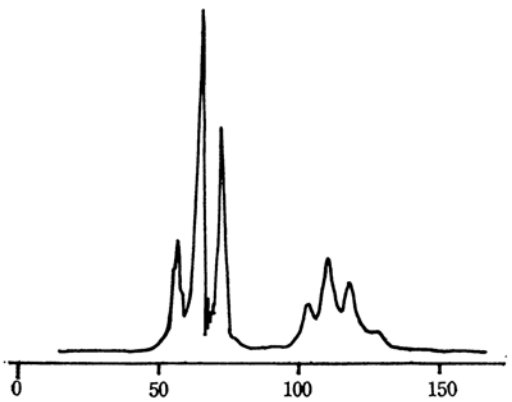
The measurement of the NMR spectea and the preparation of the samples were made in the manner previously reported,[1] except that a Varian-temperature variable cell at 60 Mc. was employed for the low temperature measurements and toluene was used as the solvent. The temperature in the cell was calibrated by the usual technique.

Results and Disussion

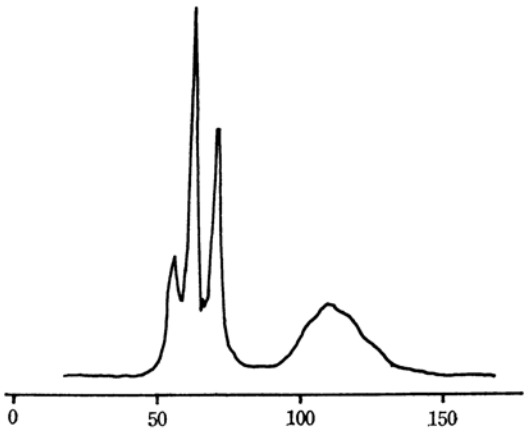
The NMR spectra of triethylaluminum in toluene (a 31.3 mol.% solution) obtained at various temperatures are shown in Fig. 1.



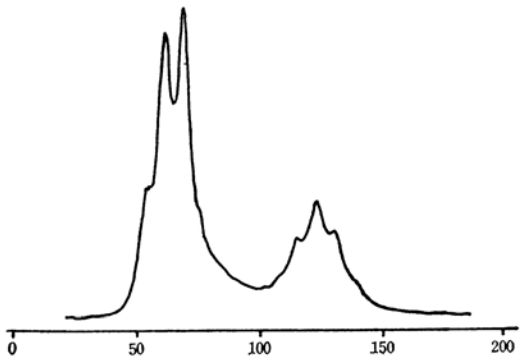
(a) 29.5°C



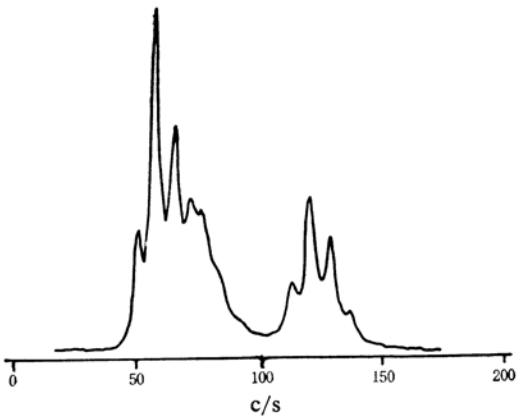
(b) −29°C



(c) −40°C



(d) −61°C



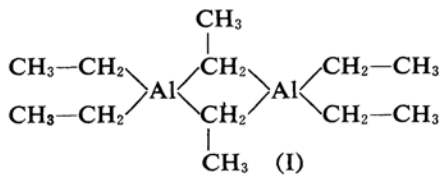
(e) −80°C

Fig. 1(a—e). The NMR traces of triethylaluminum in toluene (31.3 mol.% solution) at various temperatures (chemical shifts are referred to the methyl signal of solvent toluene). The intensity scale was changed arbitrarily from one to the others.

When other samples with different concentrations were also measured, they were found to give similar spectra, with only slight differences in the chemical shift due to the dilution effect. As is shown in the figures, the signals of an A_3B_2 pattern, which are quite sharp at room temperature, broaden as the temperature decreases, especially for methylene signals (the higher-field side ones). At $-40°C$, the methylene signals are almost collapsed. As the temperature decreases further, the signals become slightly sharper; at the same time, a group of new signals appears on the higher-field side of the methyl signals. At $-80°C$, the temperature which seems to be the lowest limit for the apparatus used, the spectrum of triethylaluminum consits of three groups: a triplet with the strongest intensity at the lowest field, a quartet at the highest field, and a group of new signals in the middle portion. The quartet signal is found to be at a higher field than the methylene quartet at room temperature, while the triplet is at only a slightly lower field than the methyl signals at room temprature.

Muller and Pritchard[2] and Growenewege and others[3] observed two singlet signals for trimethylaluminum at $-75°C$, but only one singlet signal at room temperature. The two singlet signals were separated by about 1 p. p. m. from one another and were positioned at either side of the original signal found at room temperature. They concluded from their NMR studies that, in a dimeric structure for trimethylaluminum with a bridged form[4] similar to the I shown below, the rapid exchange of the methyl group occurs between bridge and terminal positions at room temperatune. Judging from a consideration of the intensity of the $-75°C$ spectrum, the higher-field side singlet was due to terminal methyl groups, and the lower-side one, to bridge methyl groups, in the dimer.

In a similar way, if the following methylene-bridged structure I is assumed for triethylaluminum, an assignmet of the signals will be obtained rather straightforwardly:



(I)

In model I, the bridge-forming group is the methylene group. By analogy with the methyl compound, the signals of the protons in the bridge-forming group at a sufficiently low temperature will appear at a lower field when the group is in the bridge position, and at a higher field when it is in the terminal position, than the averaged signals at room temperature. On the other hand, the signals of the protons which do not directly take part in the bridge formation are expected to show only a small change in their resonance position through the exchange process. In the spectrum obtained at $-80°C$, the methylene signals show a considerable shift (about 12 c. p. s. to a higher field) from the position at room temperature, while the methyl signals show only a small shift (about 6 c. p. s. to a lower field). Thus, the methylene-bridge model I seems to be reasonable for the structure of triethylaluminum.

Since the bridge methylene signals are at a lower field than for the terminal methylene, the higher field quartet of triethylaluminum at $-80°C$ must be responsible for the terminal methylene, and, correspondingly, the triplet at a lower field, for the terminal methyl, and the middle portion, for the bridge ethyl group. It is considered that a group of signals with a complex appearance in the middle portion results from the fact that the δ value in the bridge ethyl group becomes comparable to the coupling constant (presumably about 8 c. p. s.) between the methyl and methylene protons.

To confirm this assignment, the intensity ratio between the highest side quartet and the remainder of the signals was measured and found to be 0.39, while the expected value for the formula I is 0.37. This agreement between the observed and the expected values is very good.

Thus, as in the case of trimethylaluminum, triethylaluminum gives a single ethyl spectrum at room temperature because of a rapid exchange between the terminal and the bridge ethyl groups, and a compound spectrum of two kinds of ethyl groups at a sufficiently low temperature because of the decreased exchange rate.[5] In contrast with the methyl compound, however, the bridge-forming group in triethylaluminum is the methylene group.

This seems to be the first positive experimental evidence that triethylaluminum forms a dimer bridged *through the methylene group*, although formula I has been used for the triethylaluminum dimer in the literature.[6]

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

3) M. P. Growenewege, J. Smidt and H. de Vries, ibid., **82**, 4425 (1960).

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

5) Unfortunately the rate and the activation energy for the exchange process can not be found because of the complex nature of the spectrum.

6) For example, see H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corportaion, New York (1960), p. 207.

The σ values for the terminal and bridge ethyl groups are calculated from the $-80°C$ spectrum to be -1.11 p. p. m. and about -0.2 p. p. m. respectively. Since the monohalogen derivatives of triethylaluminum are halogen-bridged dimer,[7] the ethyl groups are always at the terminal position. Thus, in comparing the δ values of triethylaluminum and diethylaluminum monohalides, the value for the terminal group should be used. Since the δ value of diethylaluminum monochloride in benzene (at almost the same concentration of aluminum compound as that in the present work) is about -0.85 p.p. m.,[1] triethylaluminum has a smaller δ value in its terminal ethyl group than do diethylaluminum monohalides. Therefore, the general trend for the δ values of metal ethyl compounds stated at the beginning of this paper still holds for the case of aluminum compounds, and the origin of the anomaly mentioned in the previous paper is elucidated satisfactorily.

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7) O. Yamamoto, This Bulletin, 35, 619 (1962), and the references cited therein.