

The Molecular Structure of Trimethylaluminium Monomer

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UNDER equilibrium conditions trimethylaluminium gas at 215° and a vapour pressure of 30 mm. consists of more than 98% monomer.¹ If the gas is allowed to expand into a vacuum, the amount of dimer should be even lower. We have recorded the electron diffraction pattern from gaseous trimethylaluminium with the reservoir at 40° (v.p. ~ 30 mm.) and the nozzle heated to 215°.

Exposures were made at nozzle-to-photographic-plate distances of about 50 and 30 cm. The results cited here are based only on the plates obtained with the larger distance. Six apparently faultless plates were photometered and the data processed in the usual way.² The final modified molecular intensity curve extended from $s = 2$ to 19.5 Å⁻¹. The data were found to be consistent with a concentration of 100% monomer.

The radical distribution curve obtained by Fourier inversion of the modified molecular intensity curve is consistent with a D_{3h} AlC₃ skeleton with freely rotating methyl groups. The structure is therefore analogous to the structure of trimethylboron as determined by Bartell and Carroll.³ The main molecular parameters, determined by least-squares calculations on the intensity data,² are given in the Table. The distances are given as r_a ,⁴ and the angle has not been corrected for shrinkage. The standard deviations obtained from the least-squares calculations have been multiplied by a factor of 3.0 to compensate for

correlation in our data⁵ and further expanded to include uncertainty in the electron wavelength.

In crystalline trimethylaluminium dimer the two crystallographically nonequivalent terminal Al-C distances are 1.96 (0.01) Å and 1.98 (0.01) Å.⁶ There is therefore at this point no evidence that the terminal bonds in the dimer are longer than the bonds in the monomer. A difference of the order of 0.012 Å, however, cannot be ruled out. This is the difference between the (terminal) B-C bonds in tetramethyldiborane and the B-C bonds in trimethylboron.⁷

Molecular parameters at trimethylaluminium monomer with estimated standard deviations

| | |
|---------|-----------------|
| Al-C | 1.964 (0.003) Å |
| C-H | 1.113 (0.003) Å |
| Al...H | 2.593 (0.012) Å |
| ∠Al-C-H | 111.8° (0.7°) |

Similarly, there is no evidence for an increase in the Al-C bond distance on complex formation; in the 2:1 complex of trimethylaluminium with dioxan, the two crystallographically nonequivalent Al-C distances are 1.96 (0.01) and 1.98 (0.02) Å, respectively.⁸

(Received, April 17th, 1969; Com. 528.)

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