Tetrahedron Letters No. 27, pp. 25-26, 1960. Pergamon Press Ltd. Printed in Great Britain

RAPID INTERMOLECULAR EXCHANGE OF METHYL GROUPS[1]

A. L. Allred and C. R. McCoy

Department of Chemistry, Northwestern University
Evanston, Illinois

(Received 23 November 1960)

The bridge structure[2,3,4] of trimethylaluminum was confirmed recently[5] for the liquid state by the observation of two peaks in the nuclear magnetic resonance (NMR) spectrum of trimethylaluminum dissolved in cyclopentane at -75°C. At room temperature only one NMR peak appears due to either inter- or intramolecular exchange of methyl groups. In this communication, evidence for intermolecular exchange is presented, and calculations of pre-exchange lifetimes and reaction rates are summarized.

Solutions of trimethylaluminum in dimethylcadmium exhibit only one NMR absorption peak. The variation of the chemical

---

[1] This research was supported by grants from the Research Corporation and from the Esso Education Foundation.

[2] A. W. Laubengayer and W. F. Gilliam, J. Am. Chem. Soc. 63, 477 (1941).

[3] K. S. Pitzer and H. S. Gutowsky, J. Am. Chem. Soc. 68, 2204 (1946).

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

[5] N. Muller and D. E. Pritchard, J. Am. Chem. Soc. 82, 248 (1960).

shift of this peak as a function of concentration, from pure trimethylaluminum to pure dimethylcadmium, is linear. The appearance of only one peak must be the result of rapid intermolecular exchange; magnetic equivalence due to some other process, for instance, formation of complexes, would give a non-linear variation of chemical shift with concentration. From equation 6 of reference 6 and the chemical shifts of three solutions, dimethylcadmium (0.097 M) in benzene, trimethylaluminum (0.062 M) in benzene, and both dimethylcadmium (0.097 M) and trimethylaluminum (0.062 M) in benzene, the upper limit of the average time τ_A before exchange was found to be 0.09 sec.

For solutions of dimethylzinc in dimethylcadmium, the NMR spectrum consists of a single peak the chemical shift of which varies linearly with concentration. Dilution of the dimethylzinc-dimethylcadmium system with inert solvents decreases the average pre-exchange lifetimes of methyl groups and leads to a separation of the nuclear resonance components. Methods discussed in ref. 6 were employed in the calculation of τ_A for 1M dimethylzinc and 1M dimethylcadmium in five solvents: 0.127 sec in cyclohexane, 0.118 sec in benzene, 0.081 sec in ether, 0.087 sec in pyridine, and 0.102 sec in nitrobenzene. The order of the exchange process is approximately 1.7, and the apparent-order rate constants are approximately 10 $(\text{moles/l})^{0.7}$ sec^{-1} for cyclohexane, benzene, pyridine, and nitrobenzene solutions.

All NMR spectra were observed at 40 Mc and at 25°C. A more complete discussion of this research will be presented later.

---

[6] H. S. Gutowsky and C. H. Holm, J. Chem. Phys. 25, 1228 (1956).