A Proton Magnetic Resonance Study of Boron Trihalide Complexes with Diethyl Ether

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A ROOM-TEMPERATURE proton magnetic resonance ^{1}H n.m.r. spectrum of a solution of a boron trihalide in an organic base consists of one set of signals, displaced to lower field from their positions in the pure solvent spectrum.[1] The one set of signals results from a rapid exchange which averages the resonance peaks arising from bulk and complexed solvent molecules. In addition to complex formation, the positions of the signals in such a system are influenced by factors such as temperature and the extent of solvent–solvent interactions.

Our low-temperature ^{1}H n.m.r. studies of solutions of boron trihalides in diethyl ether (Et_2O) have revealed separate resonance signals for bulk and complexed ether molecules. A spectrum of a 1 : 5 molar ratio of BCl_3 to Et_2O, recorded at −45° in a Varian A60 Spectrometer, along with a recording of the electronic integration of all peaks, is shown in the Figure; the peaks corresponding to bulk (*B*) and complexed (*C*) Et_2O are identified. At this temperature, similar spectra are observed for solutions of BF_3 and BBr_3 in Et_2O. The integrations are rapid and result in co-ordination numbers of one, within 10%, for BF_3 and BCl_3 ether complexes. This rules out the existence of the dietherates in these systems. Some evidence for slight decomposition in the BBr_3 solution was apparent, but the chemical shifts of the bulk and complexed ether signals were easily discernible and accurately measured. An accurate co-ordination number measurement was not possible in this solution.

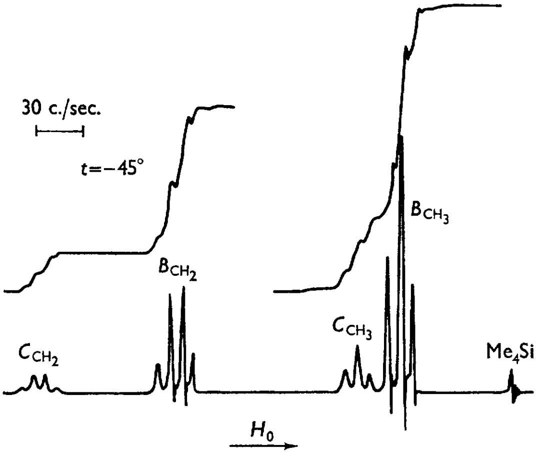

FIGURE 1. *The proton magnetic resonance spectrum of a* 1 : 5 *mole ratio solution of* BCl_3 *to diethyl ether, recorded at* −45° *on a Varian A*60 *Spectrometer. The peaks are identified as bulk* (B) *or complexed* (C) *ether signals.*

The separations between the bulk and complexed methylene proton signals are 54, 82, and 89 c./sec., respectively, for BF_3, BCl_3, and BBr_3

solutions. The methyl signal separations for the corresponding complexes are 15, 27, and 30 c./sec. The observed trend, $BBr_3 > BCl_3 > BF_3$, is opposite to what one would predict on the basis of electronegativities of the halogen atoms. Also, for these tetrahedral boron complexes, any correlation between the observed chemical shift differences and Lewis acidities[2] of the reagent boron halides is to be regarded presently as merely coincidental. Another approach is to assess how the separations observed between bulk and complexed solvent molecules reflect all possible electronic changes in the solvent molecule. These changes could include the charge withdrawal and decreased shielding resulting from complex formation along with changes in any paramagnetic effect which may be operative at the oxygen atom. In addition, the possibility of a similar anisotropic effect in the B–X bond should be considered.

To permit more definitive statements regarding the cause of the observed chemical shifts, investigations of boron trihalide complexes with a wide variety of organic bases are under way, using low-temperature n.m.r. techniques. Temperature studies are also in progress to obtain kinetic data for the ligand-exchange processes occurring in these systems.

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