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Interaction of Boron Lewis Acids with Polyethers

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Introduction

Recent kinetic studies [1] of crown ether (macrocyclic polyether) effects upon the thermolysis of *p-tert*-butylbenzenediazonium tetrafluoroborate in 1,2-dichloroethane suggested that BF_3 reacts with crown ethers. A literature search revealed that the reactions of boron Lewis acids with crown ethers have apparently not been investigated. In fact, with few exceptions [2], studies of boron Lewis acids with polydentate ligands have generally been neglected. Therefore, an investigation of possible acid–base complexation of BF_3 and B_2H_6 with several crown ethers was undertaken.

Results and Discussion

A tensimetric titration [3] of B_2H_6 and BF_3 with several multidentate ligands was conducted at 0 °C in 1,2-dichloroethane solvent. Interactions of one or both of the Lewis acids with the crown ethers 12-crown-4, 15-crown-5, 18-crown-6, and 1,4-dithia-18-crown-6, and the acyclic multidentate ligand tetraglyme were probed.

Under these experimental conditions, no interaction was observable between B_2H_6 and 18-crown-6 or dibenzo-18-crown-6. If an acid–base reaction did occur, the adduct was so weak, (*i.e.*, the equilibrium lay so far in favor of the free acid and free base) that no pressure drop was noted. This was rather surprising in light of fact that the cyclic ether tetrahydrofuran (THF) reacts readily with B_2H_6 to form the adduct $THF\cdot BH_3$ [4]. It was also observed that a sulfur-containing crown ether, 1,4-dithia-18-crown-6, which should be 'softer' in the Pearson [5] sense, failed to react with B_2H_6.

Unlike B_2H_6, reactions of BF_3 with the polyethers occurred readily. Addition of BF_3 to the cyclic or acyclic polyether in 1,2-dichloroethane caused an immediate precipitation of a white solid. Subsequent increments of BF_3 were added until no further uptake of BF_3 was evident. The mol ratio of BF_3 to multidentate ligand varied with the identity of the polyether (see Table I). The stoichiometries listed are average values from several determinations. Normally only integral values are anticipated in tensimetric titrations involving acid–base reactions. The small deviations from integral values noted in the present investigation probably result from the insolubility of the initial adducts in 1,2-dichloroethane. Reaction of a second equivalent of BF_3 with an initial adduct involves reaction of dissolved BF_3 with a solid. Alternatively, small formation constants could produce the non-integral ratios.

TABLE I. Stoichiometric Values for the Reaction of Boron Trifluoride with Multidentate Ligands in 1,2-Dichloroethane at 0 °C.

Multidentate Ligand	Ratio BF_3/Multidentate Ligand
12-Crown-4	2.1
15-Crown-5	2.9
18-Crown-6	3.9
Dicyclohexano-18-Crown-6	1.7
Dibenzo-18-Crown-6	2.2
Tetraglyme	4.8

The observed stoichiometries for reactions of BF_3 with acyclic and cyclic polyethers are markedly different. For tetraglyme, five molecules of BF_3 coordinate with one molecule of the polyether. Thus, adduct formation occurs at all five ethereal oxygens of tetraglyme. In contrast, for the cyclic polyethers only a fraction of the crown ether oxygen atoms are utilized for acid–base reactions with BF_3.

An examination of CPK space filling models indicates that the stoichiometries of the BF_3 adducts with crown ethers is controlled by steric factors. Thus, 12-crown-4 coordinates two BF_3 molecules, one on the top and one on the bottom of the roughly planar molecule. The models indicate that the further coordination of BF_3 with one of the uncomplexed oxygens would introduce steric repulsions with one of the already-complexed BF_3 moieties. The somewhat larger 15-crown-5 ring allows three BF_3 molecules to be complexed (two on the top and one on the bottom) before steric congestion prevents further coordination. For 18-crown-6, four BF_3 molecules (two on the top and two on the bottom) may be coordinated. With dicyclohexano-18-crown-6 and dibenzo-18-crown-6 only two molecules of BF_3 are complexed. The models indicate that once complexation has occurred at each of the $–CH_2CH_2OCH_2CH_2–$ units, further BF_3 complexation should introduce considerable steric hindrance.

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In conclusion, BF_3, but not B_2H_6, reacts with acyclic and cyclic polyethers to form Lewis acid–base adducts. The adduct stoichiometry for cyclic polyethers is variable and appears to be sterically controlled.

Experimental

The polyethers tetraglyme, 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6, and dibenzo-18-crown-6 (all from Aldrich Chemical Company) and 1,10-dithia-18-crown-6 (Parish Chemical Company) were used directly. The solvent 1,2-dichloroethane (Aldrich, gold label) was used as received. Standard high-vacuum line techniques were used in the titrations, and the tensimeter has been previously described [3]. Diborane was prepared and purified according to literature procedures [6]. Boron trifluoride was purchased (Matheson).

In a typical experiment approximately 5.0 ml of 1,2-dichloroethane was placed in the tensimeter together with a known quantity of a polyoxygen compound (*ca.* 0.25 ml). The system was attached to the vacuum line, and aliquots of the boron Lewis acid (0.1–0.2 mmol) were added. All titrations were made at 0 °C. During the titration, the solution was vigorously, magnetically stirred. The pressure of the system for each aliquot addition was recorded when the system reached equilibrium (about one-half to one hour). Normally, during the first addition of boron trifluoride, a white precipitate formed immediately. Infrared spectroscopic examination of the very air-sensitive solid which resulted from the reaction of BR_3 and 18-crown-6 indicated a normal Lewis acid–base adduct, with no evidence for tetrafluoroborate salt formation.

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