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N.M.R. MEASUREMENT OF THE EQUILIBRIUM CONSTANTS BETWEEN BORON FLUORIDE ETHYL ETHER COMPLEX AND SOME CYCLIC ETHERS.

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The ether exchange reaction between boron fluoride ethyl ether complex and cyclic ether seems to be related to the initiation step in cationic polymerization of cyclic ether with boron fluoride ethyl ether complex as catalyst. Hence, it appears significant to measure the equilibrium constant of the exchange reaction. Recently, some groups of workers (1), (2), (3) have reported the equilibrium constants of the following displacement equilibrium.

$$BF_3 \cdot Et_2O \;+\; R_2O \rightleftharpoons BF_3 \cdot R_2O \;+\; Et_2O$$

However, there have been very few data on the equilibrium constants involving cyclic ethers (3). This short communication describes the results of measurement of the equilibrium constants between boron fluoride ethyl ether complex and some cyclic ethers by means of nuclear magnetic resonance. Nuclear magnetic resonance spectra of a mixture of cyclic ether and boron fluoride ethyl ether complex with varying molar ratios were run without solvent at 20°C. using Japan

Electron Optics JNM C-60 type (60 Mc.) spectrometer with tetramethyl silane as an internal reference. Chemical shifts were determined by the side-band method. The equilibrium constants in Table 1 were calculated from the preliminary determined linear relationship between the chemical shift of methylene protons and the molar fraction of ethyl ether in the mixture of ethyl ether and boron fluoride ethyl ether complex. Gore and Danyluk (4) stated that in dichloromethane solution there occurs to some extent the dissociation of boron fluoride ether complexes. In our calculation of equilibrium constants, however, we neglected the dissociation of boron fluoride ether complexes as was suggested by Craig and Richards (1).

TABLE 1

The equilibrium constants of the displacement equilibrium between cyclic ether and boron fluoride ethyl ether complex.

cyclic ether	K at 20°C.	No. of runs	pK_b*
2-methyl tetrahydrofuran	13 ± 5	4	4.56
tetrahydrofuran	32 ± 9	4	5.00
2-chloromethyl tetrahydrofuran	0.58 ± 0.11	3	5.10
tetrahydropyran	12 ± 0	2	5.42
1,4-dioxane	1.5 ± 0.6	2	5.71
2-methyl-1,3-dioxolane	0.56 ± 0.10	2	7.21
4-methyl-1,3-dioxolane	0.34 ± 0.10	2	7.62
4-chloromethyl 1,3-dioxolane	$(4.1 \pm 1.3)\times10^{-3}$	4	9.05

* See the text.

As is shown in Fig. 1, a good correlation was found to exist between logarithm of equilibrium constant and pK_b value of each cyclic ether which was determined by us (5) from the shift value of O-D band of methanol-D in infrared spectrum of ether solution according to Gordy's method (6). This relationship implies that cyclic ether of higher basicity generally shows a larger affinity towards boron fluoride molecule than that of lower basicity. In some cases, however, steric requirement of cyclic ethers also may be an important factor in determining the equilibrium position, e.g., 2-chloromethyl tetrahydrofuran.

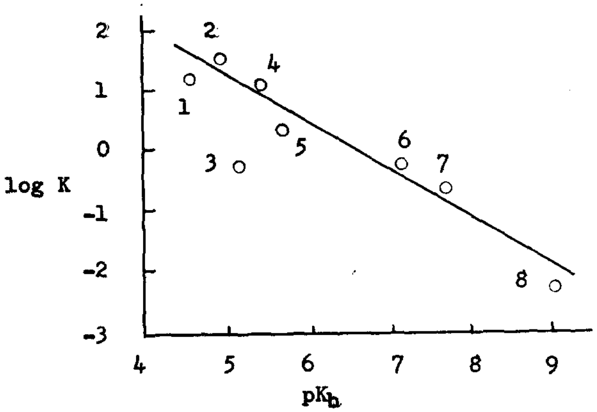

Fig. 1

Plots of logarithm of equilibrium constant vs. basicity (pK_b) of cyclic ether.

1: 2-methyl tetrahydrofuran, 2: tetrahydrofuran, 3: 2-chloromethyl tetrahydrofuran, 4: tetrahydropyran, 5: 1,4-dioxane
6: 2-methyl-1,3-dioxolane, 7: 4-methyl-1,3-dioxolane
8: 4-chloromethyl-1,3-dioxolane

Although it was impossible to measure equilibrium constants of the exchange reactions between boron fluoride ethyl ether complex and easily polymerizable three- or four-membered cyclic ethers, such as propylene oxide, epichlorohydrin or trimethylene oxide, we can estimate their equilibrium constants from the relationship in Fig. 1 using the corresponding pK_b values of these cyclic ethers.

Further details of this work will be published elsewhere in the near future.

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