Hydrogen Bond Formation with Saturated Cyclic Ethers[1]

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The electron donor ability of a series of ethylene oxides, trimethylene oxides, tetrahydrofurans, tetrahydropyrans and acylic ethers in hydrogen bonding has been measured by both a calorimetric and a spectroscopic method. The two methods are compared. In contrast to published reports, the results showed that all the cyclic ethers, except the ethylene oxides, were as good or better electron donors than comparable acyclic ethers. The order with regard to ring size was 4- > 5- > 6- > 3-members. The explanation offered by Brown and Gerstein for a similar order in the basicity of cyclic imines does not seem applicable here.

Introduction

Studies of hydrogen bonding usually have been concerned with determining the effects of resonance, electronegativity and steric hindrance on the strength of bond formation. It may be suspected that ring strain in cyclic compounds can affect the ability of donor molecules to form hydrogen bonds. Consequently an investigation of a series of saturated three-, four-, five- and six-membered cyclic ethers was undertaken, and the results may be compared with those for several open-chain ethers.

A further reason for this work was to check Gordy and Stanford's[3] conclusion that saturated cyclic ethers are less effective electron donors in hydrogen bonding than the open-chain analogs. Unpublished work in this Laboratory on the reactivity of certain cyclic ethers had suggested that this generalization, which has been accepted by others[4] although based on spectroscopic measurements on only three cyclic ethers, might be incorrect.

Two methods widely used for hydrogen-bonding investigations are to determine the heat of mixing with chloroform and to determine the frequency shift of the OD band in the infrared spectrum of methanol-d solutions. Both methods were used in this work in order to give independent checks on the hydrogen-bonding measurements and to provide data on the correlation of these two methods with ethers.

Experimental

Apparatus and Methods.—Infrared spectra were determined with a Perkin–Elmer Model 12B spectrometer equipped with a lithium fluoride prism. The instrument was calibrated using the grating data of Plyler and Barker[5] on the rotational fine structure of hydrogen bromide. The accuracy of determining the apparent band centers was limited mainly by the broadness of the bands. The values cited are reproducible to ±1 cm.$^{-1}$ with the exception of propylene oxide, cyclohexene oxide, 1,1-dimethyltrimethylene oxide and 1,1-diethyltrimethylene oxide where the greater breadth of the bands increased the range of separate measurements to ±3 cm.$^{-1}$. However, in cases of overlapping and asymmetrical bands, the apparent band maximum is undoubtedly shifted,[3] so that the total uncertainty in the location of the true band center is somewhat greater than the experimental reproducibility. The spectroscopic method has been described by Gordy[6] and consists of comparing the position of the monomeric OD band in a 0.1

molar solution of methanol-d in a reference solvent with the OD band in 1.0 molar solutions of methanol-d in various ethers. Gordy used benzene as his reference liquid whereas carbon tetrachloride was chosen for this work.

The apparatus and method employed for the heat of mixing determinations were essentially as described by Zellhoefer and Copley,[7] except for a slight modification in the procedure used at 25° with the more volatile ethers, such as ethyl ether and trimethylene oxide. In such cases the volatile ether was sealed in a thin-walled glass ampoule which was placed in the copper calorimeter containing the calculated quantity of chloroform, and mixing was accomplished by crushing the ampoule.

Several determinations were made of the heat of mixing of each ether with an equimolecular amount of chloroform (and also of dioxane with a 1.50-molecular portion of chloroform). The average deviation of the mean of the results was 10–15 calories per mole of solution. The maximum deviations of the mole percentage of ether from 50 mole % (0.4 mole % at 25° and 0.8 mole % at 3°) does not appreciably affect the heat of mixing value at this concentration.

Materials.—Methanol-d was prepared by the method of Redlich and Pordes,[8] b.p. 65° (750 mm.). The ethers listed in Table I were purified by drying over sodium metal,

TABLE I

MEASUREMENTS OF HYDROGEN BONDING OF ETHERS

	Compound	OD Band in CH₃OD Solutions Position, cm.$^{-1}$	Shift, cm.$^{-1}$	Heat of mixing with chloroform per mole of solution, cal./mole 25°	3°
	Carbon tetrachloride	2689	Reference		
1	Epichlorohydrin	2609	80	190	...
2	Styrene oxide	2604	85	215	...
3	Propylene oxide	2590	99	443	461
4	Cyclohexene oxide	2590	99	566	...
5	Diethyl ether	2593	96	597	650
6	Methyl n-butyl ether	2594	95	...	...
7	Ethyl n-butyl ether	2592	97	...	...
8	Di-n-butyl ether	2588	101	412	480
9	Dioxane	2578	111	453	...
				482^a	...
10	Tetrahydropyran	2574	115	600	640
11	Diisopropyl ether	2579	110	678	740
12	Tetrahydrofuran	2572	117	677	750
13	2,2-Dimethyltetrahydrofuran	2569	120	720	...
14	Trimethylene oxide	2569	120	703	760
15	Cineole	2564	125	835	...
16	1,1-Dimethyltrimethylene oxide[b]	2564	125	...	915
17	1,1-Diethyltrimethylene oxide[c]	2564	125	847	...

^{a} 40.2 mole % dioxane used in this experiment. ^{b} S. Searles, unpublished work. ^{c} C. Moreau and G. Barrett, *Bull. soc. chim.*, **29**, 993 (1921).

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(3) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); *ibid.*, **9**, 204 (1941).

(4) For example: M. Gordon, J. G. Miller and A. R. Day, THIS JOURNAL, **71**, 1245 (1949).

(5) E. K. Plyler and E. F. Barker, *Phys. Rev.*, **44**, 984 (1933).

(6) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

(7) G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

(8) O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936).

followed by fractional distillation in a six-inch column with a heated jacket and high reflux ratio and packed with glass helices. Only the middle fractions, boiling within 0.2° were employed (except with numbers 4, 13, 16 and 17 in Table I, where 0.5° cuts were used). Carbon tetrachloride and chloroform were purified in the manner described by Fieser.[9]

Results

The measurements of the shifts of the OD vibrational frequency in solutions of methanol-d in the ethers, and of the heats of mixing of the ethers with chloroform are listed in Table I. The heats of mixing of the ethers with chloroform were measured at 25°, the temperature of the spectroscopic measurements, and also at 3° in most cases, for comparison with earlier data.[10] The heats of mixing at 25° were consistently lower than those at 3°, as expected. A definite trend may be noted in the plot of the molar heat of mixing at 25° versus the OD shift (Fig. 1), and this may be represented by the straight line drawn using the method of least squares. The deviations from linearity, however, are more than can be attributed to experimental error.

It is not surprising that this should be so, for not only are we comparing different electron acceptors (CH_3OD and $CHCl_3$), but the heat of mixing should be a function of both the strength or energy of the hydrogen bond formed and the fraction of the molecules involved at one time, whereas the OD shift should be a "semiquantitative" measure of the strength of the hydrogen bond.[6,11] Also, heat effects upon mixing liquids may be caused by factors other than the formation of hydrogen bonds. The much lower heat of mixing of chloroform with di-n-butyl ether as compared with ethyl ether suggests that a steric factor may be involved in hydrogen bonding with chloroform. Thus, the OD frequency shift would seem to be the more reliable method of the two for estimating the strength of the hydrogen bond.

It may be noted that dioxane possesses two bonding sites, and it was shown that the maximum heat of mixing is obtained at more than 50 mole % chloroform. Consequently it was not included in the plot of Fig. 1.

The use of the OD frequency in carbon tetrachloride solutions of methanol-d as a reference rather than that in benzene may have some merit since unpublished results of this Laboratory indicate that hydrogen bonding occurs between methanol-d and aromatic hydrocarbons such as benzene. The higher frequency of 2689 cm.$^{-1}$ for the OD band in carbon tetrachloride as compared to Gordy's value[3] of 2681 cm.$^{-1}$ in benzene is perhaps indicative of such bonding. The observed value of 2689 cm.$^{-1}$ for the OD band in carbon tetrachloride as compared to its position[12] at 2720.4 cm.$^{-1}$ in methanol-d vapor seems reasonable since the percentage shift between solution and vapor is the same for ordinary methanol. The OH band for monomeric methanol in the vapor[11] is at 3680 cm.$^{-1}$ and is shifted to 3640 cm.$^{-1}$ in carbon tetrachloride.[13]

(9) Fieser, "Experiments in Organic Chemistry, second ed., D. C. Heath, Boston, Mass., 1941, p. 365.

(10) C. S. Marvel, M. J. Copley and E. Ginsberg, THIS JOURNAL, **62**, 3109 (1940).

(11) R. M. Badger and S. H. Bauer, J. Chem. Phys., **5**, 839 (1937).

(12) E. F. Barker and G. Bosschieter, ibid., **6**, 563 (1938).

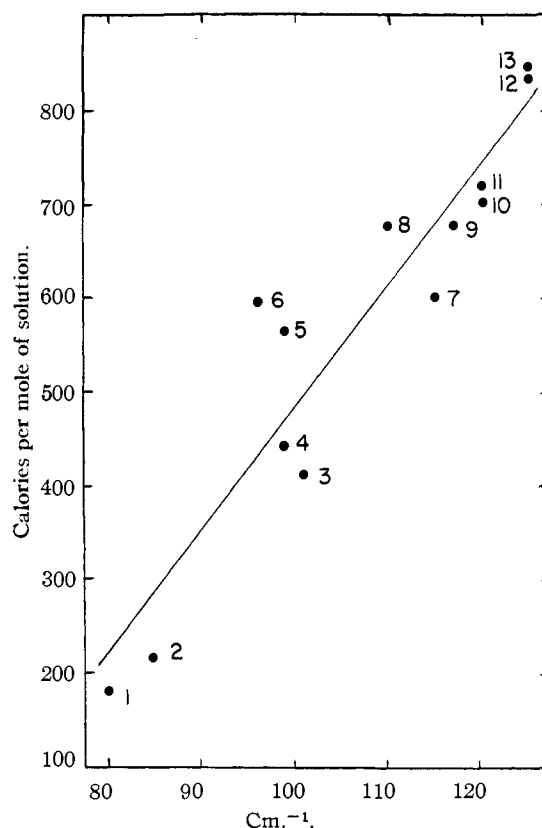(13) J. Errera and P. Mollet, Nature, **138**, 882 (1936).

Fig. 1.—Heat of mixing at 25° of chloroform with ethers (50 mole %) vs. shift in vibrational frequency of OD band of CH_3OD in ethers: 1, epichlorohydrin; 2, styrene oxide; 3, di-n-butyl ether; 4, propylene oxide; 5, cyclohexene oxide; 6, diethyl ether; 7, tetrahydropyran; 8, diisopropyl ether; 9, tetrahydrofuran; 10, trimethylene oxide; 11, 2,2-dimethyltetrahydrofuran; 12, cineole; 13, 1,1-diethyltrimethylene oxide.

The positions and shifts of the OD bands of methanol-d, in several ethers, differ appreciably from those reported by Gordy.[3,6] With the exception of diethyl ether, the differences are probably within limits of the combined calibration and band center location errors of the two sets of data. For instance, preliminary frequencies we obtained with sodium chloride optics, somewhat similar to those used by Gordy, were 5–10 cm.$^{-1}$ lower than the final data with lithium fluoride optics, and the experimental reproducibility of band center location was no better than ±5 cm.$^{-1}$. For the data reported herein, considerable care was taken to insure the purity of the compounds and the calibration of the spectrometer. Gordy[14] has suggested that the larger diethyl ether discrepancy may have arisen from the fact that his measurements were carried out at an appreciably higher temperature. Evaporation of the ether would increase the methanol-d concentration, shifting the OD band toward that for pure methanol-d at 2494 cm.$^{-1}$.

Discussion

Both the spectral data and the heats of mixing show that the four- and five-membered ring ethers, trimethylene oxide and tetrahydrofuran, are ef-

(14) W. Gordy, personal communication.

fective electron donors in hydrogen bonding and are better than the unbranched open-chain ethers. The spectral data indicate that the six-membered ring ethers, tetrahydropyran and dioxane, are approximately comparable to the open-chain ethers, although the molar heat of mixing with chloroform may modify this conclusion in the case of dioxane. Both methods agree in showing that the three-membered ring ethers, propylene oxide and the other substituted ethylene oxides, are much poorer donor molecules than the other cyclic ethers. As seen in Fig. 2, both methods agree in showing that the extent of hydrogen bonding of cyclic ethers varies with the number of atoms in the ring in the following order: 4- > 5- > 6- > 3-members.
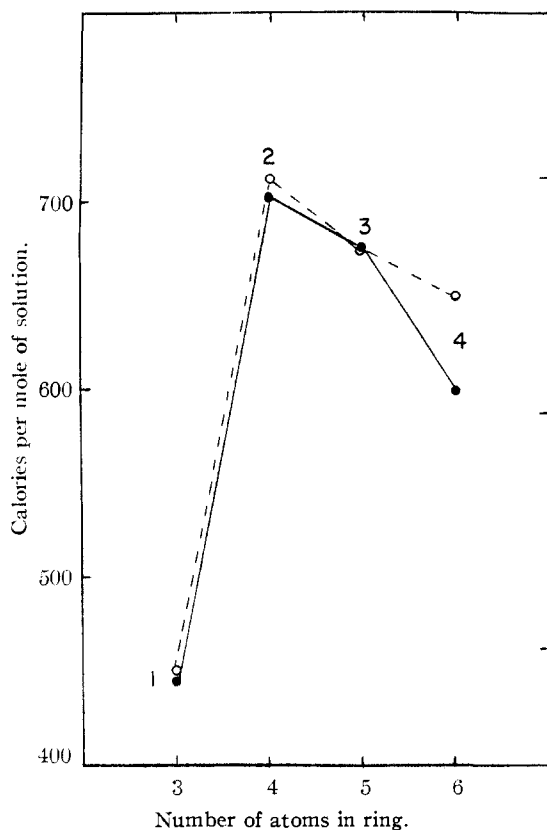

Fig. 2.—Solid line: heat of mixing at 25° of chloroform with 50.0 mole % of: 1, propylene oxide; 2, trimethylene oxide; 3, tetrahydrofuran; 4, tetrahydropyran. Broken line: shift in vibrational frequency of OD band of CH_3OD with the same ethers.

The results with the substituted ethers, both cyclic and acyclic, are in agreement with expected effects of substitution of a hydrogen atom in an ether by an atom or group of different electronegativity. This has been discussed by Gordy and Stanford[3] in terms of electronic theory. This substitution

caused a pronounced change in the heats of mixing with chloroform and a similar but less pronounced change in the OD shift. An outstanding example is the strongly basic cineole, which may be considered an $\alpha,\alpha,\alpha',\alpha'$-tetraalkyl substituted tetrahydropyran. In comparing the substituted ethylene oxides (ethylene oxide itself was unsuitable for this study because of its low boiling point) with open-chain ethers, one must bear in mind the electronic effects of α-alkyl groups. Thus, it appears that the three-membered ring structure causes a slight decrease in basicity, whereas the four-membered ring causes a definite increase in basicity.

The same effect of ring size has been reported recently by Brown and Gerstein[15] for the basicity of the unsubstituted three- to six-membered cyclic imines toward trimethylboron. The relation to our results seems significant because of the correlation between basicity and donor ability in hydrogen bonding. These workers have proposed an explanation for this order based on a combination of "F-strain" and "I-strain." The low basicity of ethylenimine was ascribed to an increase of internal strain (I-strain) which might be expected to occur when the base coördinates with an acid, and the decrease of basicity in going from the five-membered to the six-membered cyclic imine was ascribed to an increase in the steric effects of the α-methylene groups (F-strain). The high basicity of the four-membered ring compound trimethylene imine, was explained as due to the I-strain being of low magnitude and more than compensated for by a large decrease in F-strain (as compared with pyrrolidine).

A similar explanation seems unlikely for the cyclic ethers for two reasons. First, α-substitution by alkyl groups definitely increases the donor ability (and hence basicity) of all ethers regardless of ring structure. Therefore, F-strain cannot be a factor. Secondly, I-strain as defined by Brown and Gerstein,[15] should not be an important factor with the cyclic ethers because the hydrogen bond is much weaker than the nitrogen–boron bond and should not greatly increase the strain in the molecule. We prefer to ascribe the effects in the small ring compounds as being due to an alteration of electron distribution with ring size. We hope that studies in progress on the ability of cyclic imines and sulfides to form hydrogen bonds with acceptor molecules will clarify the interpretation.

(15) H. C. Brown and M. Gerstein, THIS JOURNAL, 72, 2926 (1950).