

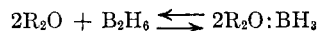
## RAMAN SPECTRA OF SOME ETHER-BORINE ADDITION COMPLEXES

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Raman spectra were obtained for the liquid systems, diborane-tetrahydrofuran, diborane-dimethyl ether and diborane-diethyl ether. The results were in accord with the formation of an  $R_2O:BH_3$  addition complex in each system. Tetrahydrofuran-borine was the most stable and diethyl ether-borine the least stable of these complexes. The Raman frequencies were assigned to the  $BH_3X$  skeletal model, where X represented an ether. Potential constants were calculated for this model of tetrahydrofuran-borine.

## Introduction

The present Raman spectroscopic investigation is a study of the addition complex formed when diborane is dissolved in tetrahydrofuran, dimethyl ether or diethyl ether. Evidence for complex formation in these systems has appeared in the literature.<sup>2</sup> The previous investigators demonstrated, at best, that the complex is formed in a ratio of one mole diborane to two moles of ether. However, from a knowledge of the chemistry of the reactants it seemed reasonable to most investigators to imply that the reaction can be represented by the general equation



Our Raman spectral measurements justify this assumption. The spectral data permit a comparison of the stability of the three ether-borine addition complexes and the determination of force constants for tetrahydrofuran-borine.

## Experimental

**Apparatus and Method.**—A three prism spectrograph (manufactured by Lane-Wells), with an average dispersion of 22 Å./mm. in the range from 4358 to 4916 Å., was used. The diborane-ether solutions were maintained in a closed system and low temperature Raman exposures were obtained by the method described by Lord and Nielsen.<sup>3</sup>

**Chemicals.**—The diborane was prepared by the reaction of lithium borohydride with boron trifluoride. The sample, purified by repeated fractionation, had a vapor pressure of 225 mm. at  $-112^\circ$  in agreement with the literature value.

The tetrahydrofuran, diethyl ether and dimethyl ether were dried and distilled *in vacuo*. The vapor pressure of the purified ethers agreed with the literature values.

**Solutions.**—The Raman spectrum of the diborane-dimethyl ether solution was observed at two temperatures. The diborane-diethyl ether system was treated in a similar fashion. On the other hand, Raman spectra were obtained at the same temperature for two diborane-tetrahydrofuran

solutions which differed in concentration. The concentrations of the solutions and the temperatures at which they were studied are listed in Table I.

**Data.**—In Table II, the Raman frequencies of the most concentrated of the two diborane-tetrahydrofuran solutions studied are listed. For purposes of comparison, the Raman frequencies of pure tetrahydrofuran are also included in the table. The spectrum of the more dilute diborane-tetrahydrofuran solution differs only in the relative intensity of some of the Raman lines.

TABLE II  
RAMAN FREQUENCIES OF A DIBORANE-TETRAHYDROFURAN SOLUTION AND PURE TETRAHYDROFURAN

Diborane-Tetrahydrofuran		Tetrahydrofuran	
Frequency (cm. <sup>-1</sup> )	Intensity	Frequency (cm. <sup>-1</sup> )	Intensity
472	3		
859	7d		
917	8	911	10
976	2	1028	3
1049	5d	1068	1
1173	5	1170	0
1236	4d	1232	8
1364		1364	
1450	6	1445	7
1487	5d	1487	7
2097 <sup>a</sup>	2	2261	0
2284	8		
2398	9		
2523 <sup>a</sup>	1	2717	0
2874	8d	2860	8d
2908	9	2909	9
2948	9d	2954	9d
2994	10d		

<sup>a</sup> Raman lines assigned to unreacted diborane.

The Raman frequencies of the solution of diborane in dimethyl ether at the lower temperature ( $-70^\circ$ ) are reported in Table III, along with the frequencies of the pure ether. The effect of an increase in temperature on the spectrum was again a change in the relative intensities of some of the Raman lines.

Raman exposures were taken of the diborane-diethyl ether solutions, maintained at  $-75^\circ$ , until the background on the photographic film became too intense to permit the observation of any more Raman lines. The spectrum contained two weak frequencies, one at 2289 and the other at 2410 cm.<sup>-1</sup> which are not observable in the spectra of the pure components. On the other hand, the spectrum of the diborane-diethyl ether solution maintained at  $0^\circ$  contained only frequencies characteristic of the pure components.

## Discussion

## Raman Frequencies of the Borine Complexes.—

The spectral data were analyzed and found to be consistent with the assumption that ether-borine complexes are formed. The Raman lines which cannot be ascribed to the spectra of the pure components have been abstracted from the solution

TABLE I

SOLUTIONS, CONCENTRATIONS AND TEMPERATURES OF RAMAN DETERMINATIONS

Soln.	Concn. $B_2H_6/R_2O$ (mole ratio)	Temp., °C.
$B_2H_6-C_4H_8O$	1/4	-25
	1/8	-25
$B_2H_6-(CH_3)_2O$	1/6	-70
	1/6	-40
$B_2H_6-(C_2H_5)_2O$	1/10	-75
	1/10	0

(1) Taken in part from a thesis submitted by Henry S. Uchida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1954.

(2) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 290 (1938); J. R. Elliott, W. L. Roth, G. F. Roedel and I. M. Boldebeck, *ibid.*, **74**, 5211 (1952).

(3) R. C. Lord and E. Nielsen, *J. Opt. Soc. Am.*, **40**, 655 (1950).

TABLE III  
RAMAN FREQUENCIES OF A DIBORANE-DIMETHYL ETHER  
SOLUTION AND PURE DIMETHYL ETHER

Diborane-dimethyl ether Frequency (cm. <sup>-1</sup> )	Intensity	Dimethyl ether <sup>a</sup> Frequency (cm. <sup>-1</sup> )	Intensity
387	0	330 (?)	
560	0	412	1
791 <sup>a</sup>	0		
878	4		
921	6	920	5
1044	1		
1092	1	1100	0
1144	1	1150	4
1171	2		
1450	7	1448	6b
2104 <sup>a</sup>	1		
2115	?		
2290	4		
2401	4		
2525 <sup>a</sup>	1		
2812	10	2810	10
2863	6	2863	6
2921	3	2916	5
2951	6	2951	4
2992	6	2986	6

<sup>a</sup> Raman lines assigned to unreacted diborane.

spectra and are listed in Table IV. There appears to be a shift in the positions of some of the non-abstracted frequencies from their positions in the spectra of the pure ethers. However, the diffuse nature of these Raman lines limited the precision with which their positions could be measured and therefore it was not possible to ascribe any significance to these differences. The 1173 cm.<sup>-1</sup> frequency of the tetrahydrofuran solution is listed in our table of abstracted frequencies even though it is coincident with a frequency in the spectrum of the pure ether. This was done because there is a marked increase in the relative intensity of this frequency in the spectrum of the solution as compared to its relative intensity in the spectrum of the pure ether.

TABLE IV  
RAMAN FREQUENCIES OF COMPLEXES ABSTRACTED FROM  
SPECTRA OF SOLUTIONS

Diborane-tetra- hydrofuran Frequencies (cm. <sup>-1</sup> )	Diborane-dimethyl ether Frequencies (cm. <sup>-1</sup> )	Diborane-diethyl ether Frequencies (cm. <sup>-1</sup> )
472	387	
859	560	
976	878	
1049	1044	
1173	1171	
2284	1476	
2398	2290	2289
2994	2401	2410

It should be emphasized that the abstracted frequencies do not represent all the observed Raman frequencies of the addition complexes. The ether parts of the complexes give rise to frequencies so similar to those of the unreacted ethers that these frequencies cannot be abstracted from the spectra of the solutions. One may have anticipated that the carbon-oxygen bonds of an ether would differ

appreciably from the corresponding bonds in a complex in which a borine group also is bonded to the oxygen. However, the solution spectra do not warrant such a conclusion.

There are noticeable similarities between the frequencies abstracted for the different complexes. Where differences are observed, reasonable explanations may be advanced for their occurrence. For example, the arithmetic mean of the 387 and 560 cm.<sup>-1</sup> frequencies, which occur in the diborane-dimethyl ether spectrum, is 473 cm.<sup>-1</sup>. This is almost identical with the 472 cm.<sup>-1</sup> frequency of the diborane-tetrahydrofuran spectrum. Later, in the section on assignments of frequencies, this correspondence is made significant when a possibility for Fermi resonance in the diborane-dimethyl ether complex is proposed.

There are no frequencies in the diborane-dimethyl ether spectrum similar to the two that occur at 976 and 2944 cm.<sup>-1</sup> in the diborane-tetrahydrofuran spectrum. The absence of the first line may be simply a question of intensity. The diborane-dimethyl ether spectrum had an intense continuous background which made the detection of weaker lines more difficult. The second frequency corresponds to an absorption band of the same magnitude in the infrared spectrum of tetrahydrofuran and therefore it may arise in the Raman spectrum of the complex. A similar conclusion may be reached for the 1476 cm.<sup>-1</sup> frequency of the diborane-dimethyl ether spectrum which corresponds to strong absorption band in the infrared spectrum of the pure ether.

Although only two weak lines were abstracted from the diborane-diethyl ether spectrum, they also fit into the trend and correspond to the most intense abstracted frequencies in the Raman spectra of the two other ether solutions.

**Assignment of Frequencies.**—The Raman frequencies listed in Table IV are most easily discussed in terms of a postulated molecular model for the R<sub>2</sub>O:BH<sub>3</sub> complex. Consider the ether group as a point particle, X, attached to one of the terminal positions of a tetrahedral boron atom. This postulated model for the H<sub>3</sub>BX molecule would belong to point group C<sub>3v</sub>. All six normal modes of vibration of this model give rise to Raman active fundamental frequencies. Most of the abstracted frequencies (Table V) are assigned to normal modes of vibration of this postulated molecular model of the ether-borine complexes.

TABLE V  
ASSIGNMENT OF FREQUENCIES TO THE H<sub>3</sub>BX MOLECULAR  
MODEL

Designation	Description	C <sub>4</sub> H <sub>9</sub> O: BH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> O: BH <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O: BH <sub>3</sub>
ν <sub>1</sub>	B-H stretching (in phase)	2284	2290	2289
ν <sub>2</sub>	H-B-H deformation (in phase)	1049	1044	
ν <sub>3</sub>	B-O stretching	859	878	
ν <sub>4</sub>	B-H stretching (out-of-phase)	2398	2401	2410
ν <sub>5</sub>	H-B-H deformation (out-of-phase)	1173	1171	
ν <sub>6</sub>	H <sub>3</sub> ≡B-O bending	976		

(4) B. L. Crawford, Jr., and L. Joyee, *J. Chem. Phys.*, **7**, 307 (1939).

There appears to be very little question about the assignment of the boron-hydrogen stretching frequencies,  $\nu_1$  and  $\nu_4$ . The magnitudes of the frequencies assigned to  $\nu_1$  are in good agreement with a frequency of 2290  $\text{cm}^{-1}$  observed in the Raman spectrum of an aqueous solution of sodium borohydride<sup>5</sup> and assigned to the symmetrical boron-hydrogen stretching mode of vibration of the borohydride ion. These frequencies are considerably lower than those characteristic of terminal hydrogen stretching in diborane and aluminum borohydride (2500 to 2600  $\text{cm}^{-1}$ ). In the latter two cases the terminal boron-hydrogen bonds are most likely of the  $\text{sp}^2$  type while in the ether-borine complexes and the borohydride ion they are probably  $\text{sp}^3$  type bonds.

The intense Raman lines at 859 and 878  $\text{cm}^{-1}$  of tetrahydrofuran-borine and dimethyl ether-borine, respectively, were assigned to boron-oxygen stretching on the basis of the expected magnitude of the frequencies characteristic of bonds between atoms of such mass. The spectral data available for comparison with our boron-oxygen stretching frequency are limited; however, comparable assignments at 754 and 947  $\text{cm}^{-1}$  have been made for symmetrical and antisymmetrical boron-oxygen stretching, respectively, of the aqueous borate ion,<sup>6</sup>  $\text{B}(\text{OH})_4^-$ .

Our assignment of frequencies to the  $\text{BH}_3$  deformation modes of vibration is consistent with similar assignments in sodium borohydride<sup>7</sup> and borine carbonyl.<sup>8</sup> The weak Raman line that occurs at 976  $\text{cm}^{-1}$  in the tetrahydrofuran-borine spectrum was assigned to H-B-O bending; however, we do not have similar frequencies of other compounds for comparison.

The 472  $\text{cm}^{-1}$  frequency abstracted from the tetrahydrofuran-borine spectrum was not assigned to the  $\text{H}_3\text{BX}$  skeletal model but could be characteristic of B-O-C bending, while the 387 and 560  $\text{cm}^{-1}$  frequencies abstracted from the dimethyl ether-borine spectrum may arise from a Fermi resonance between B-O-C and a C-O-C bending modes of vibration. As mentioned in the previous section, the 2994  $\text{cm}^{-1}$  frequency of tetrahydrofuran-borine and the 1476  $\text{cm}^{-1}$  frequency of dimethyl ether-borine may arise from the ether parts of the complexes. Thus we account for all the abstracted frequencies. Of course, the possibility exists that reasonable assignments could be made for an entirely different molecular model. However, we were not able to find another model for which the frequencies could be assigned in a reasonable fashion.

#### Potential Constants of Tetrahydrofuran-Borine

A normal coordinate treatment, based on the  $\text{H}_3\text{BX}$  skeletal model, was carried out for tetrahydrofuran-borine. A similar treatment was not made for dimethyl ether-borine, since one of the anticipated frequencies ( $\nu_6$ ) was missing.

(5) W. J. Lehmann, Ph.D. Thesis, Saint Louis University, 1954.

(6) J. O. Edwards, G. C. Morrison, V. F. Ross and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 266 (1955).

(7) W. C. Price, H. C. Longuet-Higgins, B. Rice and T. F. Young, *J. Chem. Phys.*, **17**, 217 (1949).

(8) R. D. Cowan, *ibid.*, **18**, 1101 (1950).

The valence force potential function used (similar to one proposed by Cleveland and Meister for methyl chloride<sup>9</sup>) was

$$2V = f_d \Sigma (\Delta d_i)^2 + f_D (\Delta D)^2 + f_{\alpha} \Sigma (d \Delta \alpha_i)^2 \\ + f_{\beta} \Sigma (d \Delta \beta_i)^2 + 2f_{\alpha\beta} [(d \Delta \beta_1)(d \Delta \alpha_{12} + d \Delta \alpha_{23}) \\ + (d \Delta \beta_2)(d \Delta \alpha_{12} + d \Delta \alpha_{23}) + (d \Delta \beta_3)(d \Delta \alpha_{13} + d \Delta \alpha_{12})] \\ + 2f_D \Sigma (d \Delta D \Delta \alpha_i) + 2f_{D\beta} \Sigma (d \Delta D \Delta \beta_i)$$

In this equation  $d$  and  $D$  represent the boron-hydrogen and boron-oxygen distances, respectively, while  $\alpha$  and  $\beta$  designate the hydrogen-boron-hydrogen- and hydrogen-boron-oxygen angles, respectively. The significance of the potential constants, the  $f$ 's in the equation, can be determined from the subscripts used.

The values chosen for the bond distances were:  $d = 1.31 \times 10^{-8}$  cm. and  $D = 1.52 \times 10^{-8}$  cm. These values were supplied to us by Dr. George W. Schaeffer of St. Louis University, who calculated them from covalent bond radii corrected for the difference in electronegativity of the bonded atoms. The angles  $\alpha$  and  $\beta$  were assumed to be tetrahedral for lack of more precise information. A problem was presented in the choice of mass for the group represented by the symbol X. The value obtained for the force constant  $f_D$ , characteristic of the boron-oxygen bond, is very sensitive to the mass assigned. A minimum value for  $f_D$  would perhaps be obtained if the mass of an oxygen atom was used for X, while the result obtained if the entire tetrahydrofuran mass was used could be considered a maximum. Both masses were tried in separate calculations. Clearly, calculations of this type would be improved if it were possible to select, "a priori," an effective mass for a group treated as a point particle.

The six frequency equations were solved by a method of approximation, whereby the force constants were adjusted until the left-hand and right-hand sides of each equation differed by only a few tenths of a per cent. The results of our calculations are listed in Table VI. As can be observed, the magnitude of the boron-oxygen stretching potential constant  $f_D$  is very sensitive to the choice of mass of X. The only other term which differs appreciably in the two sets of values is  $(f_{D\alpha} - f_{D\beta})$ . However, the significance of this "correction" term is not too apparent. Our lower value of  $3.29 \times 10^5$  dyne  $\text{cm}^{-1}$  for  $f_D$  appears to be closest to the "best" value. This can be seen by application of Gordy's rule,<sup>10</sup> which relates force constants to the bond distance and electronegativity of the bonded atoms. On the basis of this rule, a value of  $3.74 \times 10^5$  dynes  $\text{cm}^{-1}$  is obtained for this force constant. We may consider this value as the magnitude of the force constant for a normal covalent boron-oxygen bond. Since our skeletal treatment of tetrahydrofuran-borine left us with a choice somewhere between  $3.3$  and  $5.4 \times 10^5$  dynes  $\text{cm}^{-1}$  for the boron-oxygen force constant, we can speculate that the donor-acceptor boron-oxygen bond in this molecule is comparable in strength to a normal covalent boron-oxygen bond.

(9) F. F. Cleveland and A. G. Meister, "Molecular Spectra II," Illinois Institute of Technology, 1948.

(10) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

TABLE VI

POTENTIAL CONSTANTS OF  $\text{BH}_3\text{X}$  MODEL OF TETRAHYDROFURAN-BORINE,  $\times 10^5$  DYNES CM.<sup>-1</sup>

Mass of X	$f_D$	$f_A$	$f_\alpha$	$f_\beta$	$f_{\alpha\beta}$	$f_{D\alpha} - f_{D\beta}$
X = 16.00	3.29	3.01	0.300	0.474	0.0415	-0.320
X = 72.10	5.40	3.01	.306	.488	.0406	-.502

## Relative Stabilities of Ether-Borine Complexes

A quantitative measure of the apparent equilibrium constants was not attempted, but an estimate can be made of the relative stabilities of the ether-borines. The intensity,  $I$ , of a Raman line characteristic of a particular substance is proportional to the concentration of that substance, hence

$$\frac{[R_2OBH_3]}{[B_2H_6]} = \frac{k_1 I_{R_2OBH_3}}{k_2 I_{B_2H_6}}$$

The ratio of the proportionality constants,  $k_1/k_2$ , should depend primarily on the nature of the two species in solution. The intensities of the lines at 2524, 2284, 2290 and 2289 cm.<sup>-1</sup> were chosen as indicative of the concentration of diborane, tetrahydrofuran-borine, dimethyl ether-borine and diethyl ether-borine, respectively.

If we assume that the ratios  $k_1/k_2$  are almost the same for all the diborane-ether systems investigated, a comparison of the stabilities of the complexes can be obtained. The above assumption appears to be reasonable, since the magnitude of the boron-hydrogen stretching frequency, whose intensity we have chosen to be indicative of the concentration of the complex, remains almost unchanged in the three ether-borines. Thus this bond is only slightly affected by the nature of the ether parts of the complexes and similarly the intensities of vibrations characteristic of this bond may be only slightly affected.

The solutions for which we were able to calculate "intensity ratios" are listed in Table VII. Calculations were not made for the diborane-diethyl ether system, since the observed lines characteristic of the complex in this system were too weak. We can conclude, therefore, that diethyl ether-borine is the least stable of the complexes.

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TABLE VII

"INTENSITY RATIOS" OF DIBORANE-ETHER SOLUTIONS

Solution	Initial mole ratio $B_2H_6/R_2O$	Temp., °C.	$I_{R_2OBH_3}/I_{B_2H_6}$
$B_2H_6-C_4H_8O$	1/4	-25	8
$B_2H_6-(CH_3)_2O$	1/6	-40	2
$B_2H_6-(CH_3)_2O$	1/6	-70	4

The "intensity ratio" of dimethyl ether-borine at -70° is twice as large as its value at -40°. As anticipated, complex formation is favored by a drop in temperature. Even at -25° the "intensity ratio" of the diborane-tetrahydrofuran system is four times as great as the value for the diborane-dimethyl ether system at -40°. It would be best to compare "intensity ratios" of both solutions at the same temperature and concentration of diborane. However, if the initial mole ratio of diborane to tetrahydrofuran was reduced from 1/4 to 1/6 and the temperature decreased from -25 to -40°, the "intensity ratio" for the diborane-tetrahydrofuran system should be still greater than 8. Therefore, we can conclude that the tetrahydrofuran-borine complex is the most stable of the ether-borines.

Thus the order of stabilities of the ether-borines is:  $C_4H_8OBH_3 > (CH_3)_2OBH_3 > (C_2H_5)_2OBH_3$ . This is the same order observed<sup>11</sup> for the analogous ether-boron trifluoride complexes in the vapor phase. This order emphasizes the predominance of steric to inductive effects.

(11) H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **64**, 2557 (1942).

THERMODYNAMICS OF SODIUM CARBONATE IN SOLUTION<sup>1</sup>

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Contribution from The Institute of Paper Chemistry, Appleton, Wisconsin

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The thermodynamics of sodium carbonate in aqueous solution has been studied from 15 to 95°. From electromotive force measurements of the concentration cells  $\text{Ag}-\text{Ag}_2\text{CO}_3, \text{Na}_2\text{CO}_3(0.1) \text{NaHg} \text{Na}_2\text{CO}_3(m_2) \text{Ag}_2\text{CO}_3-\text{Ag}$  and determinations of solution vapor pressures, the activity coefficients have been calculated over a concentration range of 0.1 to 1.5 *m* below 65° and 0.1 to 2.5 *m* at 65° and above. The relative partial molal enthalpies have been calculated between 25 and 80°.

## Experimental

**Concentration Cell Measurements.**—The equilibrium e.m.f.s of the concentration cells were measured at 15, 25, 37.5, 50 and 65°. The reference solution was 0.1 *m* and drawn from a large reservoir of constant composition. The value of  $m_2$  was varied from 0.2 to 1.5 *m*. The solutions were prepared using weighed amounts of reagent grade sodium carbonate and twice-distilled water. The sodium carbonate analyzed 99.8 to 99.9% using constant-boiling hydrochloric acid diluted to 0.5 *N* after heating at 140° for an hour. The dissolved oxygen in the solutions was

removed by stripping with nitrogen at reduced pressure, and the solutions were stored under a positive nitrogen pressure. The reference solution was stored in an 18-liter bottle lined with a plastic bag to eliminate attack on the glass by the solution. Analyses of each solution were run in triplicate using weighed samples and standard hydrochloric acid.

The silver-silver carbonate electrodes were similar to the type 2 electrodes of Harned.<sup>2</sup> Due to the higher solubility of silver carbonate, the electrodes were electrolyzed in 0.5 *m* sodium bicarbonate at 200 ma./cm.<sup>2</sup> for two hours. It was necessary to form very fine porosity silver on the platinum spirals to obtain equilibrium potentials. These electrodes are apparently less stable than other silver electrodes, but with care in preparation they were usually reproducible to 0.1 mv.

(1) This communication contains material from a dissertation presented to The Institute of Paper Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy from Lawrence College, June, 1954. The work was done under the direction of Roy P. Whitney.

(2) H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).