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THE CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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OBJECTIVE

The research reported here had as its objective the fundamental study of the chemistry of the hydrides of boron.

ABSTRACT

Evidence is presented to show that B_4H_{10} reacts with NH_3 to form $B_4H_{10}\cdot 7\ NH_3$, $B_4H_{10}\cdot 3\ NH_3$, and $B_4H_{10}\cdot 2\ NH_3$. The product formed is dependent upon experimental procedures. No evidence for $B_4H_{10}\cdot 4\ NH_3$ has been found. The addition product formed by B_4H_{10} in liquid ammonia at -77°C reacts with excess sodium to give 1/2 mole H_2 per B_4H_{10} and the solid NaB_3H_8. Results are interpreted in terms of bridge cleavage in B_4H_{10}.

A Raman Study of H_3BCO is described in detail.

I. THE REACTIONS AND STRUCTURE OF THE DIAMMONIATE OF DIBORANE

A. REVIEW OF PREVIOUS WORK

All preceding work on the ammonia addition compounds of diborane has been reviewed. The vacuum line for this system has been reconditioned. H_3BNH_3 has been prepared for further Raman study. Work now proceeding on the ammonia-diborane system is directed toward the larger-scale production of salts of the $[H_2B(NH_3)_2]^+$ cation.

B. THE PREPARATION OF SALTS OF $H_2B(NH_3)_2^+$

The compound $[NH_4][AsF_6]$ was prepared from laboratory stocks of $KAsF_6$* by the following reactions.

$$KAsF_6 + CdCl_2 + 6NH_4OH \longrightarrow \downarrow[Cd(NH_3)_6[AsF_6]_2 + 2KCl$$

$$[Cd(NH_3)_6][AsF_6]_2 \xrightarrow[H_2S]{EtOH} CdS \downarrow + 2NH_4AsF_6 + 4NH_3 \quad .$$

The NH_4AsF_6 was allowed to react with $[H_2B(NH_3)_2][BH_4]$ according to methods developed by Shultz and described in earlier reports. A solid which gave a powder pattern, definitely not NH_4AsF_6, was obtained. Further characterization is still incomplete.

The same process with NH_4PF_6 produces a solid which still contains some NH_4PF_6 lines. Such solids are under more thorough study.

II. RAMAN SPECTRAL STUDIES ON H_3BCO

A normal coordinate treatment of the H_3BCO molecule which was carried over from the earlier contract has been completed and a formal report on the Raman spectra of H_3BCO and D_3BCO has been written. A copy is submitted with

*H. M. Dess, Doctoral Dissertation, The University of Michigan, Ann Arbor, 1955.

this report. Permission to submit this work to a technical journal for publication is requested.

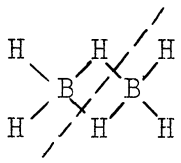
III. THE REACTIONS AND STRUCTURES OF THE AMMONIA ADDITION COMPOUNDS OF B_4H_{10}

A. BACKGROUND

Although the structure of the diammoniate of diborane has long been a question for debate, the stoichiometry of its formation has been well established and easily reproduced in any laboratory, if proper precautions were taken. In contrast, both the stoichiometry for the formation, and the structures of the ammoniates of B_4H_{10} have been uncertain. Stock, Wiberg, and Martini* reported that four ammonia molecules add to one molecule of B_4H_{10} to give $B_4H_{10}\cdot 4NH_3$. Since their observations on stoichiometry have not been tested in other laboratories, the original work must be considered uncertain until it is confirmed.

In previous studies of the diborane ammoniates, compounds were identified which suggested that reactions of the diborane molecule involve cleavage of the hydrogen bridges. Such cleavage can be symmetrical or nonsymmetrical, depending upon the conditions of the experiment. If symmetrical cleavage occurs, H_3B groups are liberated and their primary reaction is that of a Lewis acid.

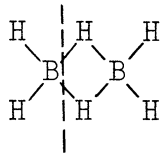
Symmetrical Cleavage



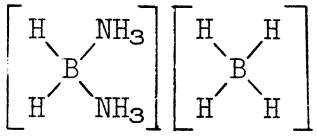
$$+ \qquad 2NR_3 \longrightarrow 2H_3BNR_3$$

If nonsymmetrical cleavage occurs, the reactions are formally analogous to those observed with some bridge-type coordination compounds and typical Werner coordination compounds of boron result.

Nonsymmetrical Cleavage



$$+ \qquad 2NH_3 \longrightarrow$$

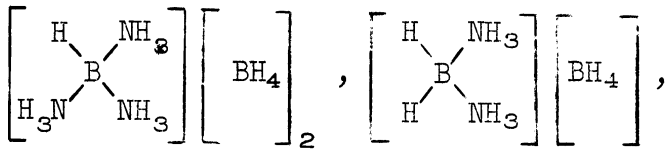


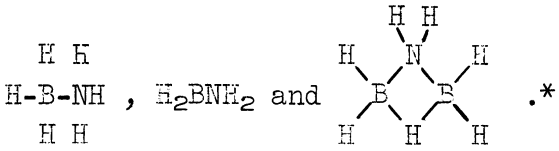
Certain reagents such as trimethylamine promote symmetrical cleavage. Molecular-weight studies on the addition compounds of H_3B with mono- and dimethylamines indicate that these reagents also promote symmetrical cleavage,

*Ber., 63, 2927 (1930).

while ammonia promotes nonsymmetrical cleavage under the usual conditions of the interaction.

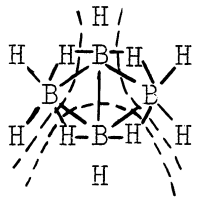
Not only the reagent but the conditions of the experiment seem to be important in determining the type of interaction to be expected. Gas-phase reactions of B_2H_6 seem to favor symmetrical cleavage as the initial process. Reactions in a solvent such as ether, likewise seem to favor symmetrical cleavage, although with reagents such as ammonia, which strongly favor nonsymmetrical cleavage, reactions in ether may also give the nonsymmetrical cleavage product. Reactions involving solid phases usually give nonsymmetrical cleavage for those reagents such as ammonia which are capable of producing nonsymmetrical bond rupture. The reactions of NH_3 and B_2H_6 produce a variety of products, the formation of which has been associated with localized heating during the reaction process. Formulas which are supported by significant evidence are:





Obviously, the reaction of ammonia with diborane is a complex process which is strongly dependent upon the details of the experimental procedure.

An extrapolation of the observations on the ammonia-diborane reaction suggests that the ammonia-B_4H_{10} reaction should be at least as complex as that involving the simpler diborane molecule. From the known structure for B_4H_{10} one can make a number of predictions as to the expected products of reaction with amines and ammonia. For example, since $N(Me)_3$ is known to favor symmetrical cleavage of double bridges, one might expect interaction as follows:



$$+ \quad xNR_3 \longrightarrow 3H_3BNR_3 + BH(NR_3)_{(x-3)}$$

Three molecules of H_3BNR_3 per molecule of B_4H_{10} have been recovered from the foregoing process. Agreement between theory and observation is excellent.

*See Final Report from this laboratory for Project 1966, 1956.

The more complex possibilities with ammonia are considered in connection with the discussion of experimental results.

B. THE REACTION BETWEEN B_4H_{10} AND NH_3

The B_4H_{10}-ammonia reaction, like the ammonia-B_2H_6 process, is strongly dependent upon experimental conditions. Reactions in ether and in the absence of solvent were studied.

1. Reaction in the Absence of Solvent.—Stock, Wiberg, and Martini* reported that B_4H_{10} and excess NH_3, frozen together with liquid air will form $B_4H_{10}\cdot 4NH_3$ when warmed up to -78°C for one hour. All attempts to reproduce their work have been unsuccessful. There appears to be a reasonable doubt as to the validity and generality of their observations.

Data summarized in Table A and Fig. 1 suggest that equilibrium in the reaction is not reached in one hour at -78°C. If ample time is allowed at -78°C, the compound $B_4H_{10}\cdot 7NH_3$ appears to form. This loses four molecules of ammonia when the temperature is raised to -63.5°C. The resulting compound $B_4H_{10}\cdot 3NH_3$ appears to be stable up as high as -23°C. Above this temperature hydrogen evolution becomes vigorous. The above conclusions are being tested further by construction of a phase diagram for the system B_4H_{10}-NH_3.

Symmetrical cleavage of the double-bridge bond in B_4H_{10} would yield BH_3 and B_3H_7 as fragments. These might add a base such as NH_3 to give H_3BNH_3 and other products (e.g., $NH_3B_3H_7$). Although the conditions used in this NH_3-B_4H_{10} reaction were not those which should favor symmetrical cleavage, the residue was leached with diethyl ether in the vacuum system to extract any H_3BNH_3 from the solid reaction products. No BH_3NH_3 was detected; it was concluded that symmetrical cleavage did not occur under the conditions of this experiment.

2. Reaction of the NH_3-B_4H_{10} Addition Product with Sodium in Liquid Ammonia.—To the product from Run No. 1, Table A, 3 ml of liquid ammonia was added; then a bulb containing sodium metal was crushed and added to the frozen system. The temperature was permitted to rise slowly to -78°C and then held at this temperature. Hydrogen evolution as a function of time is shown in Fig. 2. Similar data for Run No. 2, Table A, are also shown. It is significant that one-half mole of hydrogen per B_4H_{10} is liberated rapidly, then another one-half mole is liberated more slowly.

The product formed in the reaction of sodium with the diammoniate of diborane is sodium borohydride. If one assumes similar unsymmetrical cleavage of the double-bridge bond in the B_4H_{10}-ammonia system, the reaction should be:

*Loc. cit.

TABLE A. SUMMARY OF ALL RUNS ON B_4H_{10} AND AMMONIA

Run No.	Millimoles B_4H_{10}	Millimoles NH_3 at Start	Reaction Temp. (°C)	Reaction Time (hr)	Temp. NH_3 Removal (°C)	Time for NH_3 Removal (hr)	NH_3/B_4H_{10} Ratio Approached by System	Millimoles H_2 / Millimoles B_4H_{10}
1	1.04	12.58	-196 to -78	5	-78	8-1/2	7.05	nil
					-63.5	6	3 to 3.2	nil
2	1.12	8.34	-165 to -65	12+	-63.5		3.2	.053
3	0.325	4.66	-78	1	-78	24	3.2	0.15
					-63	6	2.91	0.15
					-45	3	2.83	0.15
					-23	8	2.34	0.17
					0	25	2.16	0.70
					25	6	2.16	0.76
4	0.337	5.17	-78	24	-23	3.3	3.03	0.016
					25	18	2.14	0.72
					70-80	5	2.14	0.81
					25	24	2.14	0.82
Comparable Data of Stock *et al.*								
1S	0.445	4.7	-165 to -78	1	-75	About 3	4.0	Not Reported
2S	0.455	4.8	-165 to -75	1	-75	About 3	4.0	Not Reported
3S	0.442	4.6	-165 to -78	1	-75	About 3	4.0	Not Reported

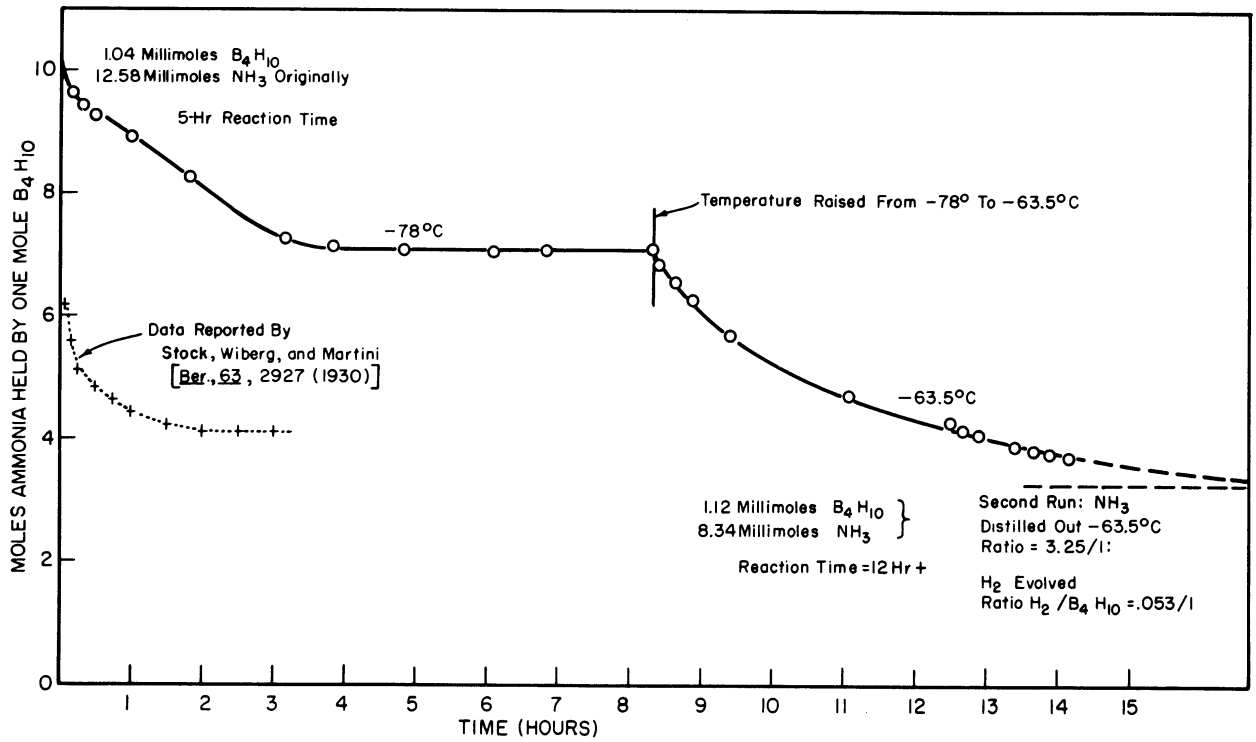


Fig. 1. Initial runs on stoichiometry of reaction between B_4H_{10} and NH_3 at -78.5°C and below and -63.5°C and below.

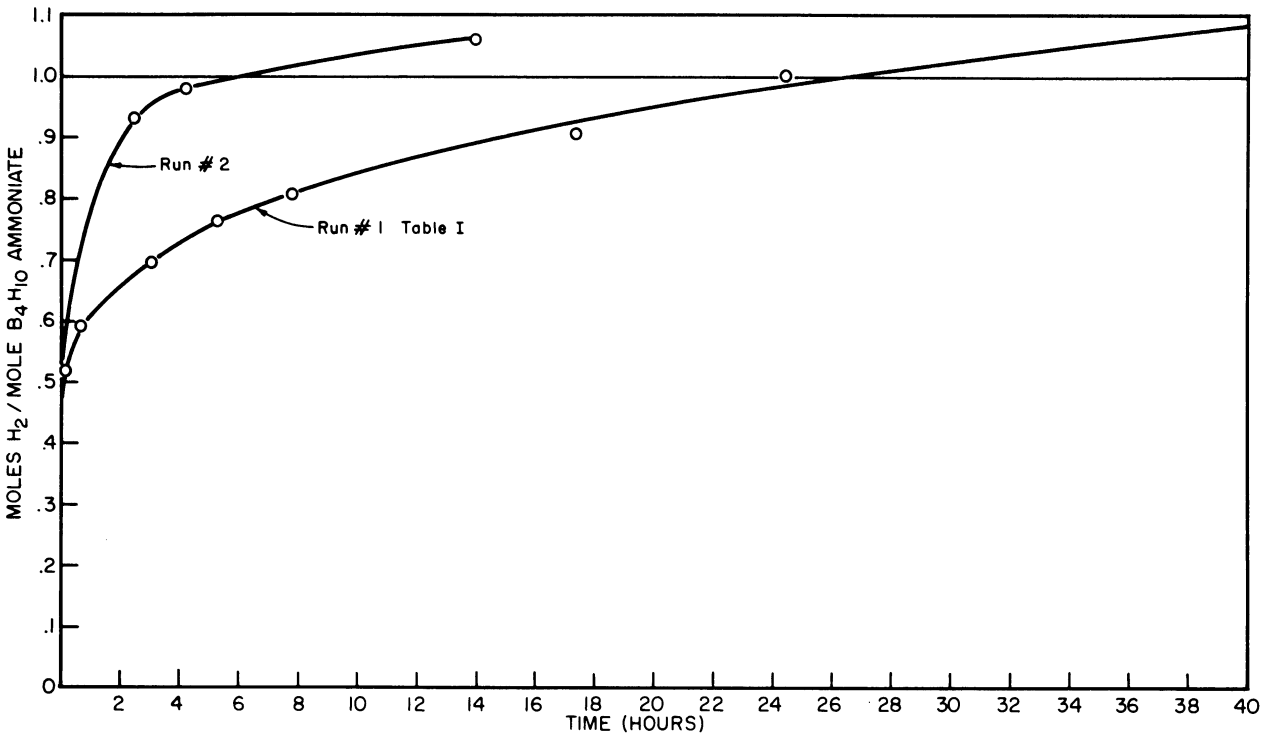
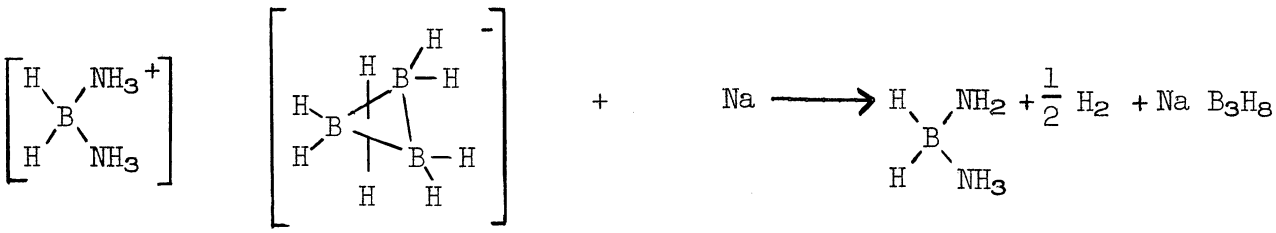


Fig. 2. Evolution of H_2 from reaction of Na with liquid-ammonia solution B_4H_{10}. (See Table A for preparative data on B_4H_{10} ammoniate.)



The compound NaB_3H_8 has been isolated and identified through an independent set of reactions by Callery Chemical Co.* and is a known species. It is ether soluble.

Accordingly, 1.859 mm of B_4H_{10} was condensed in a reaction tube and about 3 ml of ammonia was condensed above it. The system was allowed to warm slowly to dry-ice temperature, then held at -78°C overnight. The system was frozen with liquid nitrogen, sodium was added, then the temperature was raised rapidly to -78°C. After one-half hour ammonia and evolved hydrogen were removed; 1.17 equivalent of H_2 per mole of B_4H_{10} was found. Traces of ammonia were pumped off at room temperature; then the solid product was leached with dry ether in the vacuum line extraction system. Crystals were isolated by evaporation of the ether from the filtrate. If great care was taken to avoid exposure of these crystals to water, their x-ray powder pattern was identical to the pattern for NaB_3H_8. The pattern for NaB_3H_8 was generously supplied by Callery Chemical Co. and was checked by an independent preparation of NaB_3H_8 in this laboratory.

The foregoing experiment was confirmed in a second run using an almost identical procedure. Only one significant change in method should be recorded. In the second run ammonia was removed from the solid and B_4H_{10} ammoniate was isolated; then ammonia was added again to the system, followed by sodium addition. Again NaB_3H_8 was the product when hydrogen evolution was stopped after loss of one-half H_2 per B_4H_{10}. Yields of NaB_3H_8 were estimated at 60 to 80%. This was <u>not</u> a trace quantity of material.

The foregoing observations support a symmetrical cleavage of the double-bridge bond and are consistent with earlier observations made on the system sodium-diammoniate of diborane.

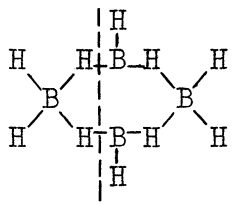
The source of the second equivalent of hydrogen which results from the sodium reaction is less certain. It was found that the solid product remaining after loss of one mole of H_2 per B_4H_{10} did not contain NaB_3H_8. Pro-

*Hough, Edwards, and McElroy, J. Am. Chem. Soc., 78, 689 (1956).

longed ether extraction provided just a trace of material which gave the x-ray pattern for $NaBH_4$. Then 1.04 millimoles of B_4H_{10} was condensed with a large excess of ammonia. The tube was held at -78°C overnight, then an excess of sodium was added and H_2 was evolved. After 48 hours, 2.45 equivalents of H_2 per mole of B_4H_{10} had been produced. The ammonia was removed from the system and the solid residue was leached with diethyl ether in the vacuum system. Only a trace of solid was extractable with ether. It should be noted that more $NaBH_4$ could have been present in the solid residue but was not removed by ether extraction. The point was not checked because excess sodium in the solid residue made residue handling difficult.

A reaction between Na and NaB_3H_8 in NH_3 to give H_2 and some $NaBH_4$ was considered as a possible explanation for the foregoing observations. A direct experimental test of the hypothesis was tried. NaB_3H_8 was prepared from B_4H_{10} and NaH in ether. Sodium and 3 cc of liquid ammonia were added. No H_2 was evolved at -78°C over a period of 15 hours. The system was raised to -45°C and held for 44 hours. Still no hydrogen was evolved.

3. Precipitation Reactions in Liquid Ammonia for the NH_3-B_4H_{10} Addition Product.—Addition of magnesium salts [$Mg(AsF_6)_2$ and $Mg(SCN)_2$] to a liquid-ammonia solution of B_4H_{10} ammoniates did not produce a precipitate of $[Mg(NH_3)_6][BH_4]_2$. Apparently an unsymmetrical cleavage which produces borohydride

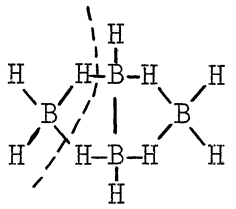


is not favored as a primary process in liquid ammonia.

A trace of still unidentified precipitate was found when $Mg(AsF_6)_2$ and $KAsF_6$ were added to liquid-ammonia solutions of B_4H_{10} at -78°C. It was thought that this might be $[H_2B(NH_3)_2][AsF_6]$; however, its x-ray pattern was not the same as that of the product, presumably $[H_2B(NH_3)_2][AsF_6]$, resulting from the reaction between $[H_2B(NH_3)_2][BH_4]$ and NH_4AsF_6. The solid is still being studied.

4. Raman Studies on B_4H_{10} Ammoniates in Liquid Ammonia.—These studies are only in a preliminary stage and conclusions are not warranted.

5. The Reaction Between Ammonia and B_4H_{10} in Diethyl Ether.—It is known that ether favors symmetrical cleavage of a double-bridge bond. Accordingly, one might expect the following reaction between ammonia and B_4H_{10} in ether:



$$+ \; 2NH_3 \longrightarrow H_3BNH_3 + H_3NB_3H_7 \; .$$

A solution of B_4H_{10} in ether absorbs NH_3 readily. The equilibrium pressure (ammonia + ether) above the solution was measured as the ammonia content of the system increased. Results are summarized in Fig. 3. Although a choice between a compound $B_4H_{10}\cdot 2NH_3$ and $B_4H_{10}\cdot 2\text{-}1/2\ NH_3$ is somewhat arbitrary, the former formula was accepted. It is significant that the ammonia addition product prepared in this manner is completely ether soluble, a fact consistent with the existence of the compounds H_3NBH_3 and $H_3NB_3H_8$; the product prepared by the reaction of NH_3 and B_4H_{10} in the absence of ether is not ether soluble, a fact consistent with nonsymmetrical cleavage of the double-bridge bond.

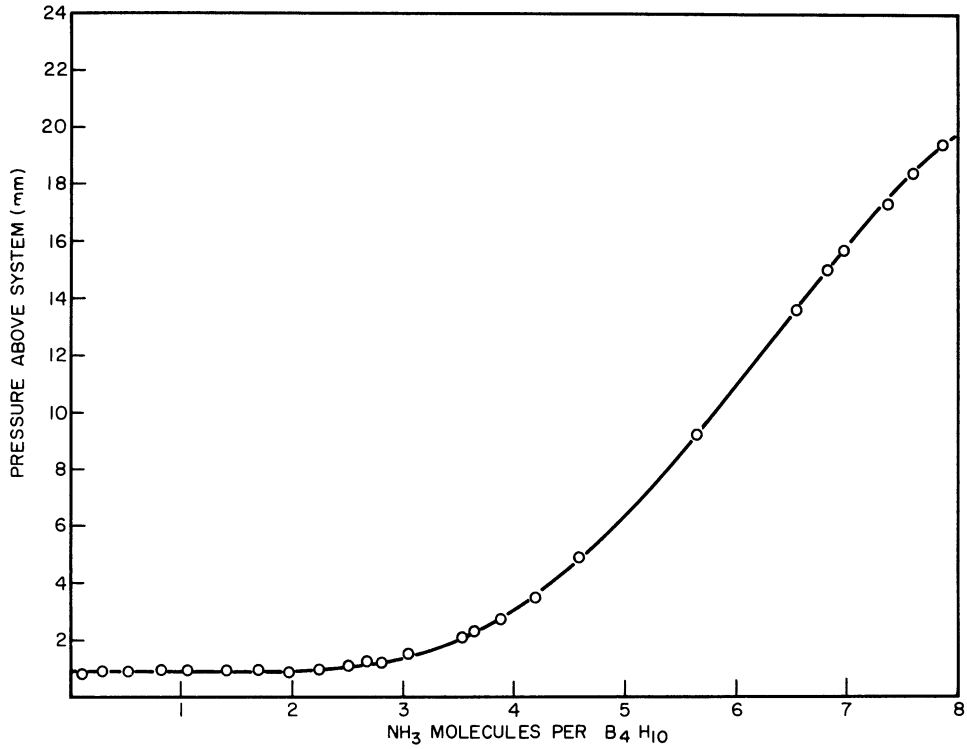


Fig. 3. The system NH_3-B_4H_{10} in diethyl ether solution.

6. The Preparation of NaB_3H_8 in Diethyl Ether from NaH and B_4H_{10}. [Method first used by Callery Chemical Co.]—Symmetrical cleavage of the double-bridge bond of B_4H_{10} would give BH_3 and B_3H_7. It is known that a sodium hydride slurry in diethyl ether will not react with B_2H_6 (BH_3 groups) to give ether insoluble $NaBH_4$. Accordingly, such cleavage should give rise to B_2H_6 from the BH_3 groups.

On the other hand, B_3H_7 should react with NaH to give ether soluble NaB_3H_8. The reaction goes as expected:

$$B_4H_{10} + NaH \xrightarrow{\text{diethyl ether}} \underset{\text{(in ether)}}{NaB_3H_8} + \frac{1}{2} B_2H_6 \quad .$$

NaB_3H_8 was isolated and identified by the powder pattern reported below. The corresponding pattern of Callery Chemical Co. is given for comparison.

Interplanar Spacings in Ångstroms

Univ. of Mich. Product	Callery NaB_3H_8	Univ. of Mich. Product	Callery NaB_3H_8
5.75 w	5.67 m	2.098 wm	--
	5.09 m	2.025 wm	2.02 w
4.66 w	4.66 m	1.871 w	1.88 w
3.95 s	3.93 s	1.783 w	1.79 vw
3.66 s	3.67 s	1.373 vw	--
3.31 vs	3.32 vs	1.675 vw	1.68 vw
? vw	3.09 vw	1.639 w	1.64 w
2.69 wm	2.71 w	1.55 vw	1.56 vw
2.47 w	2.49 vw	1.497 w	--
2.37 m	2.35 s	1.467 w	1.46 vw
2.31 w	?	1.368 vw	1.379 vw
2.18 vw	?	1.327 vw	1.318 vw
2.15 m	2.15 m		

Camera circumference = 180 mm; CaK_α radiation.
Note: w = weak; m = medium; s = strong; v = very.

An observation of great significance was made in studying this reaction. NaH of good quality, prepared by E. I. DuPont, reacted with B_4H_{10} in ether to give one H_2 per B_4H_{10}. No NaB_3H_8 was ever isolated from the system. On the other hand, NaH obtained from the Callery Chemical Co. reacted with B_4H_{10} to give some excess H_2 and high yields of NaB_3H_8. The differences in the solid NaH are still undefined, but the contrast in the reaction is striking when different samples of NaH are used.

IV. THE REACTION BETWEEN $[Al_2Cl_6]$ and PF_3

Earlier work in this laboratory suggested that PF_3 might react with dimeric Lewis acids such as B_2H_6 and Al_2Cl_6 to give a coordination compound. H_3BPF_3 has been prepared and described elsewhere.*

Under similar conditions $[AlCl_3]_2$ reacts with PF_3 to give complete halogen interchange.

$$AlCl_3 + PF_3 \longrightarrow PCl_3 + AlF_3 \quad .$$

Although there was no direct evidence for the compound Cl_3AlPF_3, it is probable that it existed as a reaction intermediate in the exchange process. Work is underway to isolate the complex Cl_3AlPF_3 if it forms.

*R. W. Parry and T. C. Bissot, J. Am. Chem. Soc., 78, 1524 (1956).

APPENDIX

THE RAMAN SPECTRUM, VIBRATIONAL ASSIGNMENTS, AND FORCE CONSTANTS FOR BH_3CO AND BD_3CO

Robert C. Taylor

INTRODUCTION

Despite the rather active chemical interest in boron hydrides and their derivatives, the amount of spectroscopic work which has been carried out on these compounds has been disproportionately small. This disparity is particularly marked if one compares the data available on vibrational frequencies, assignments, force constants, molecular parameters, and so on for the derivatives of simple hydrocarbons with the corresponding data for the various boron hydride derivatives. Experimental difficulties caused by the high reactivities of the boron compounds are responsible to a large degree for this situation; however, if one is willing to work in condensed phases and at low temperatures, a great deal of spectroscopic information can be obtained which can yield significant values for molecular constants and also provide a basis for comparisons of chemical properties.

The class of compounds containing the BH_3 group is of particular interest here, from the spectroscopic point of view, as yielding information about the hypothetical simple boron hydride BH_3, and from the chemical point of view as an example of complex formation through a Lewis acid-base interaction. In the present work, the Raman spectrum of a simple member of this class, BH_3CO, has been obtained, a complete assignment of fundamental frequencies has been made, and a set of valence force constants determined which agrees with the experimental data for four isotopic combinations. It is hoped these data will serve as a basis for comparison with other molecules containing the borane group.

Only one previous spectroscopic paper on BH_3CO has appeared, a paper by Cowan[1] reporting the infrared spectrum of the vapor. Five fundamentals reported by him agree with the values found in the present work, two he did not observe, and his assignment of the last appears incorrect. No data for the BD_3CO molecule have been found.

EXPERIMENTAL

Both BH_3CO and BD_3CO were prepared by reaction of B_2H_6 or B_2D_6, respectively, with CO in a sealed tube at several atmospheres pressure. After several days, the tubes were opened and the contents carefully fractionated at low temperatures on the vacuum line. After fractionation, the sample was distilled into the Raman cell which was then sealed off. To reduce thermal decomposition, the vapors were never allowed to come in contact with surfaces warmer than about -50°C during all transfer operations. The spectra obtained showed no bands attributable to diborane or CO which would be produced as decomposition products. The sample of BH_3CO examined was about 1 ml in volume while the BD_3CO was about 0.2 ml. During the exposures, the samples were maintained at approximately -80°C, at which temperature the decomposition occurring in the liquid is negligible. A general description of the apparatus and spectrograph has been given previously.[2] Exposure times varied from ten minutes to three hours, using Eastman 103a-J plates. Measurements were made with a comparator directly on the plates and also on enlarged tracings made with a Leeds and Northrup microphotometer. The estimated probable error for most lines reported is approximately 1 cm^{-1}.

EXPERIMENTAL RESULTS

The experimentally observed frequencies for BH_3CO are listed in Table I, while those for BD_3CO are listed in Table II. Tracings of spectra of the two substances selected to show the fundamentals most clearly are shown in Figs. A-1 and A-2. The agreement between the frequencies here reported and those found previously in the infrared of the vapor is very satisfactory, the differences at most amounting to a few cm^{-1} and being well within the normal shift in frequency observed in the transition from vapor to liquid. Several overtones and combinations were observed on some of the longer exposures on BH_3CO which are not shown in the figure. No bands attributable to diborane or CO were observed in any of the spectra, indicating a fairly high purity for the compounds. However, a weak band was observed at 2411 cm^{-1} in the spectrum of the deuterated compound, which indicates a small amount of hydrogen to be present.

ASSIGNMENTS

The BH_3CO molecule has C_{3v} symmetry which predicts eight fundamentals, all active in the Raman effect, which are either totally symmetric (A_1) or doubly degenerate (E). Previous work on boron compounds has shown that B-H stretching frequencies fall in the range between 2000 and 2600 cm^{-1}. Three frequencies appear in this range in the BH_3CO spectrum. Deuterium substitution affects only two, however, and on the basis of their polarization characteristics the band at 2380 cm^{-1} is assigned as ν_1 and the band at 2434 cm^{-1} as ν_5.

TABLE I. OBSERVED RAMAN FREQUENCIES OF LIQUID BH_3CO AT -80°C

Band Position (in cm^{-1})	Intensity	Assignment
317	m	ν_8 - e fundamental
632	vvw	$2\nu_8$
692	w (pol.)	ν_4 - a_1 fundamental
705 ± 2	vw	ν_4' - B^{10} isotopic species
816	w	ν_7 - e fundamental
1073	s (pol. ?)	ν_3 - a_1 fundamental
1101	m	ν_6 - e fundamental
1133	w	$\nu_7 + \nu_8$
1626	vvw	$2\nu_7$
1761	vvw	$\nu_3 + \nu_4$
1887	vvw	$\nu_6 + \nu_7$
2129	vw	$2\nu_3$
2169	s (pol.)	ν_2 - a_1 fundamental
2380	s (pol.)	ν_1 - a_1 fundamental
2434	s	ν_5 - e fundamental
2703	vvw	$\nu_1 + \nu_8$

TABLE II. OBSERVED RAMAN FREQUENCIES OF LIQUID BD_3CO AT -80°C

Band Position (in cm^{-1})	Intensity	Assignment
264	w	ν_8 - e fundamental
619	m	ν_4 - a_1 fundamental
706	w	ν_7 - e fundamental
808	m	ν_6 - e fundamental
860	m	ν_3 - a_1 fundamental
881	w	ν_3' - B^{10} isotopic species
991	w	?
1678	s	ν_1 - a_1 fundamental
1749	s	$2\nu_3$
1777	w	$2\nu_3'$ - B^{10} isotopic species
1825	s	ν_5 - e fundamental
2169	s	ν_2 - a_1 fundamental
2411	w	B-H stretch

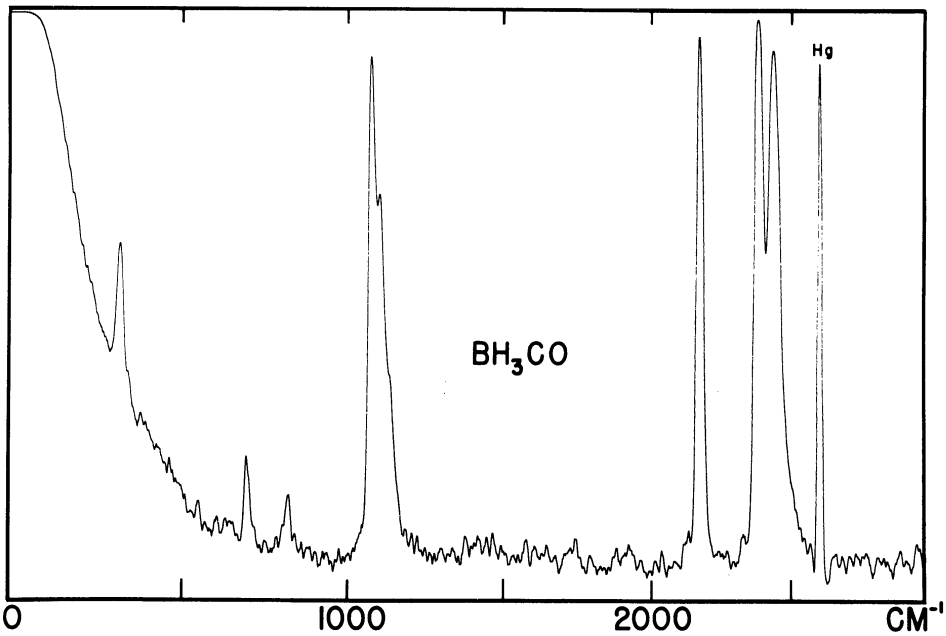


Fig. A-1. The Raman spectrum of liquid BH_3CO at -80°C (1-ml sample).

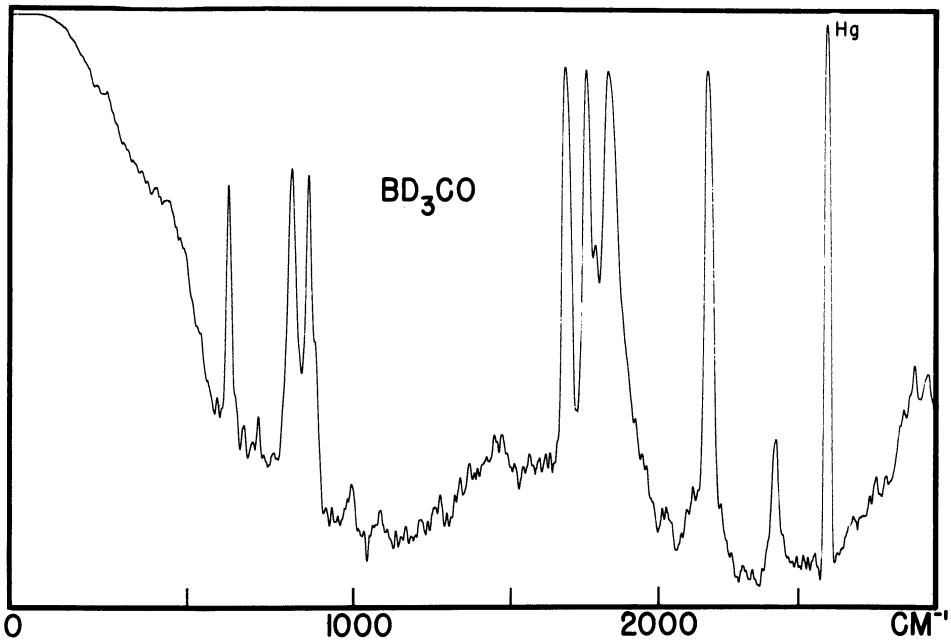


Fig. A-2. The Raman spectrum of liquid BD_3CO at -80°C (0.2-ml sample).

In the BD_3CO spectrum, the asymmetric frequency ν_5 occurs at 1825 cm^{-1}, but the position of ν_1 cannot be determined exactly because of Fermi resonance with the overtone of the fundamental at 860 cm^{-1}. The two members of the Fermi doublet occur at 1678 and 1749 cm^{-1}. The latter is assigned as the overtone and the former to the fundamental on the basis of the B^{10} satellite appearing on the high-frequency side of 1749 at 1777 cm^{-1}. Comparison of the intensities of the two bands indicates that the coincidence between the overtone and

the fundamental is very close and consequently the unperturbed value of ν_1 probably is not far from 1700 cm^{-1} on the high-frequency side. The frequency ν_1 was not observed in the infrared spectrum of the hydrogen compound[1] but its predicted value agrees with that given above. The third band in the 2000-cm^{-1} region is immediately identified as the C-O stretch both from its nearness to the carbon monoxide frequency at 2143 cm^{-1} and from the fact that deuterium substitution does not shift its position. The assignment of the band is further confirmed by its polarization characteristics.

The situation with regard to the B-H bending modes is somewhat more complicated. In the hydrogen compound, a triplet is observed in the 1100-cm^{-1} region with maxima at 1073, 1101, and 1133 cm^{-1}, the first being the most intense and probably polarized. In the BD_3CO spectrum, two bands of approximately equal intensity appear at 808 and 860 cm^{-1}, the latter having a weak satallite on its high-frequency side at 881 cm^{-1}. Since polarization measurements were not made on the deuterated spectrum, the product rule plus the results of the normal coordinate treatment were necessary to arrive at a satisfactory assignment. Fortunately, the dimensions and moments of inertia of the four possible isotopic molecules of C_{3v} symmetry, $B^{11}H_3CO$, $B^{11}D_3CO$, $B^{10}H_3CO$, $B^{10}D_3CO$, have been determined from microwave results[3] so that the theoretical product ratios can be calculated with no assumptions. The closest agreement with the theoretical values is obtained by assigning ν_3 to the 1073-cm^{-1} and ν_6 to the 1101-cm^{-1} band in the hydrogen compounds and ν_3 to the 860-cm^{-1} and ν_6 to the 808-cm^{-1} band of the deuterium species. Confirmation for the interchange in the relative positions of the two bands in the deuterium case is found in the normal coordinate treatment. This predicts that the A_1 frequency of the isotopic B^{10} molecule is 22 cm^{-1} higher than the A_1 frequency of the molecule containing the more abundant B^{11} isotope. In the case of the E frequencies, however, the difference amounts to only 5 cm^{-1}, a separation that would not be resolved under the present circumstances. The presence of a weak satellite 21 cm^{-1} higher than 860 cm^{-1} is therefore accepted as evidence that the latter band is actually the A_1 band, the satellite being assigned as ν_3 of the B^{10} isotopic species. In the hydrogen compound, the B^{10} isotope shifts are calculated to be +12 and +4 cm^{-1}, respectively, for ν_3 and ν_6. Since the observed spacings between the members of the triplet are 28 and 32 cm^{-1}, it appears that neither can be easily assigned to the B^{10} species. However, the combination of the two E modes at 816 and 317 cm^{-1} has a calculated value of 1133 cm^{-1} and the correct symmetry to resonate with the E fundamental and borrow sufficient intensity to appear as a weak band. The band at 1101 cm^{-1} accordingly is assigned as ν_6.

In the infrared work,[1] ν_6 was assigned to a band at 1392 cm^{-1}. No band at this position was observed in the Raman spectrum and it appears that the infrared band most likely is $\nu_3 + \nu_8$ which, from the Raman data, is calculated at 1390 cm^{-1}. The infrared band at 1105 cm^{-1} was assumed to be ν_3. The error in the infrared assignments thus appears to arise from the failure to resolve the three bands observed in the Raman spectrum in this region. The remaining fundamentals may all be classed as skeletal modes. The only polarized,

fairly intense band left occurs at 692 cm^{-1} in the BH_3CO spectrum and shifts to 619 cm^{-1} upon deuteration. This is assigned to ν_4 in agreement with the infrared results. A satellite was observed at 705 cm^{-1} in the more intense exposures on the hydrogen compound and on the basis of a calculated shift of +16 cm^{-1} from the force-constant treatment is assigned to ν_4 of $B^{10}H_3CO$. The corresponding shift in the deuterated molecule is calculated to be only 5 cm^{-1} and accounts for the failure to observe a satellite to the 619-cm^{-1} band.

The two fundamentals ν_7 and ν_8 can be considered as bending motions of the axial chain of atoms. The second, ν_8, the B-C-O deformation, is to be expected at a rather low frequency in view of the masses of the atoms involved. It consequently is assigned to the moderately intense depolarized band at 317 cm^{-1} in the BH_3CO spectrum. This fundamental was not observed in the infrared work but its position was predicted quite accurately. In the deuterated spectrum it appears at 264 cm^{-1}.

The last fundamental, ν_7, which is most simply described as a BH_3 rock, is assigned to 816 cm^{-1} partly by a process of elimination and partly from the infrared evidence. The corresponding band at 706 cm^{-1} in the deuterated compound is rather weak but the correctness of the assignment is substantiated by the product-rule calculations.

NORMAL-COORDINATE TREATMENT

Cowan[1] carried out a normal-coordinate treatment of the BH_3CO molecule based on the results of his infrared study and obtained a set of force constants which produced reasonably satisfactory agreement with his assignments. However, in view of the incorrect assignment for ν_6 and the fact that data on the deuterated molecule were not available, it would appear that a better approximation can now be obtained. Since his equations did not include interaction force constants, the molecule was reanalyzed using the FG method of Wilson and the following symmetry coordinates:

A_1 species: $S_1 = \Delta T$

$S_2 = \Delta R$

$S_3 = 1/\sqrt{3}\,(\Delta r_1 + \Delta r_2 + \Delta r_3)$

$S_4 = 1/\sqrt{6}\,(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$

E species: $S_5 = 1/\sqrt{2}\,(\Delta r_2 - \Delta r_3)$

$S_6 = 1/\sqrt{2}\,(\Delta\beta_2 - \Delta\beta_3)$

$S_7 = 1/\sqrt{2}\,(\Delta\alpha_{31} - \Delta\alpha_{12})$

$S_8 = \Delta\delta_x$

In terms of the molecule parameters, T refers to the C-O bond, R to the B-C bond, r_i to the ith B-H bond, α_{ij} to the H-B-H angle between r_i and r_j, β_i to the ith H-B-C angle, and δ_x to the B-C-O angle. The equilibrium values for these parameters taken from the microwave work[3] are as follows: T = 1.131 Å, R = 1.540 Å, r = 1.194 Å, α = 113°52', β = 104°37', and δ = 180°.

The elements of the inverse kinetic-energy (G) matrix were evaluated from the tables of Decius[4] and the note by Ferigle and Meister.[5] As a check on the correctness of the equations, the force constants of Cowan were substituted into the secular equation and the roots were found to agree with his calculated values with an average deviation of about 0.5 cm^{-1}, an amount consistent with accumulated rounding-off errors. It was found possible to match the frequencies of the hydrogen compound to within 0.5% by modifying Cowan's force constants somewhat and introducing two interaction constants, k_{rr} and $k_{\alpha\alpha}$. However, this set of constants reproduced the frequencies of the deuterium compound very poorly and was discarded. The final set obtained reproduces the sixteen frequencies of the $B^{11}H_3CO$ and $B^{11}D_3CO$ molecules with a standard deviation of 0.3% from the observed values. The calculations actually were carried out in terms of the symmetry force constants, F_i, of which ten were required to produce the above fit according to the following potential function:

$$2V = F_1S_1^2 + F_2S_2^2 + F_3S_3^2 + r^2F_4S_4^2 + F_5S_5^2 + r^2F_6S_6^2 + r^2F_7S_7^2 + RT\,F_8S_8^2$$
$$+ R\,F_{24}S_2S_4 + R^2F_{68}S_6S_8 \quad .$$

Since there are four product-rule relations, twelve of the frequencies are independent, making the problem slightly overdetermined. The potential energy may also be expressed in terms of the valence force potential constants which are related to the preceding symmetry force constants.

$$2V = k_T\Delta T^2 + k_R\Delta R^2 + k_r \sum \Delta r_i^2 + k_{rr} \sum \Delta r_i\Delta r_j + r^2k_\alpha \sum \Delta\alpha_{ij}^2$$
$$+ r^2k_{\alpha\alpha} \sum \Delta\alpha_{ij}\Delta\alpha_{jk} + r^2k_\beta \sum \Delta\beta_i^2 + r^2k_{\beta\beta} \sum \Delta\beta_i\Delta\beta_j + RT\,k_\delta\Delta\delta_x^2$$
$$+ R\,k_{R\beta} \sum \Delta R\Delta\beta_i + R^2k_\beta \sum \Delta\beta_i\Delta\delta_x \quad .$$

To calculate the eleven constants in the latter equation from the ten in the preceding, one assumption is necessary. The most convenient one is to equate $k_{\alpha\alpha}$ to $k_{\beta\beta}$. Both sets of constants are given in Table III. The observed values of the fundamentals are compared with the calculated values in Table IV. Since two frequencies attributed to B^{10} molecules were observed, the calculations were extended to include the two boron isotopic species, the calculated

TABLE III. FORCE CONSTANTS FOR THE BH_3CO MOLECULE

Symmetry Force Constant	Value (Millidynes/Å)	Valence Force Constant	Value (Millidynes/Å)
F_1	17.9800	k_T	17.9800
F_2	2.7875	k_R	2.7875
F_3	3.2980	k_r	3.1607
F_4	0.7057	k_α	0.4013
F_5	3.0920	k_β	0.3782
F_6	0.2203	k	0.2744
F_7	0.2434	k_{rr}	0.0687
F_8	0.2744	$k_{\alpha\alpha} = k_{\beta\beta}$	0.1579
F_{24}	-0.1778	$k_{R\beta}$	0.1451
F_{68}	0.0793	k_β	0.1121

values also being listed in Table IV as the shift in frequency from the calculated value of the respective B^{11} frequencies. As an additional check on the calculations, the B^{10} product-rule ratios were calculated from the experimentally observed B^{11} frequencies and B^{10} frequencies obtained by adding the calculated shifts to the B^{11} values. The agreement as shown by the numerical values in Table V is quite satisfactory.

DISCUSSION

Valence force potential constants can be used in a number of ways to obtain information about the electronic structure of molecules. In general, however, some caution must be used in making comparisons between different molecules since the validity of such comparisons may be affected by a number of factors. For example, the type of potential function employed affects the magnitude of the calculated force constant, as does also the number of assumptions made regarding interaction constants. Other sources of disagreement may arise from anharmonicity effects, the inadequacy of the potential function used, and the closeness of fit obtained, assuming, of course, that the correct assignments have been made initially. Obviously, the most meaningful comparisons are those made within a group of fairly closely related molecules of the same symmetry type for which the data have all been analyzed in the same way. Conclusions arrived at under other circumstances may still be of considerable value but should be considered qualitative, or at best semi-quantitative, and subject to possible revision.

TABLE IV. COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE FUNDAMENTAL FREQUENCIES FOR THE VARIOUS ISOTOPIC SPECIES OF THE BH_3CO MOLECULE

Fundamental		$B^{11}H_3CO$				$B^{11}D_3CO$				$B^{10}H_3CO$		$B^{10}D_3CO$	
		Obs.	Calc.	Diff.	%	Obs.	Calc.	Diff.	%	Calc. Shift	Obs.	Calc. Shift	Obs.
A_1	ν_1	2380	2380	0	0	(1700)	1703	-	-	+2.5	-	+4.3	-
	ν_2	2169	2169	0	0	2169	2169	0	0	0.4	-	0.4	-
	ν_3	1073	1070	-3	0.3	860	863	+3	0.3	12.1	-	22.5	21 ± 2
	ν_4	692	692	-1	.1	619	621	+2	.3	16.0	13 ± 2	4.8	-
E	ν_5	2434	2431	-3	.1	1825	1827	+2	.1	15.0	-	21.3	-
	ν_6	(1101)	1101	-	-	808	805	-3	.4	3.6	-	5.4	-
	ν_7	816	816	0	0	706	704	-2	.3	6.3	-	3.2	-
	ν_8	317	315	-2	.6	264	265	+1	.4	.0	-	.1	-

Note: Standard deviation for 14 frequencies = 0.3%.

The data enclosed in parentheses are for fundamentals disturbed by Fermi resonances and are estimated values.

TABLE V. COMPARISON OF PRODUCT-RULE RATIOS FOR VARIOUS ISOTOPIC COMBINATIONS OF THE BH_3CO MOLECULE

Isotope Held Constant	Isotopes Interchanged	Symmetry Class	Frequency Product Ratio		
			Theoret.*	Calc.**	Dev.
B^{11}	H/D	A_1	1.931	1.953	1.1%
B^{11}	H/D	E	2.513	2.522	.4
B^{10}	H/D	A_1	1.929	1.951	1.1
B^{10}	H/D	E	2.498	2.507	.4
H	B^{11}/B^{10}	A_1	1.036	1.036	.0
H	B^{11}/B^{10}	E	1.017	1.017	.0
D	B^{11}/B^{10}	A_1	1.037	1.037	.0
D	B^{11}/B^{10}	E	1.024	1.023	-.1

*Calculated from moments of inertia of Ref. 3 and the masses involved.

**The frequencies for the B^{11} molecules were those observed; the frequencies for the B^{10} molecules were obtained by adding the shifts determined in the force-constant treatment to the experimental values of the B^{11} frequencies.

Of the various types of potential constants employed in the valency force field, the bond-stretching force constants are the least affected by the factors mentioned above and can be interpreted in much the same way as bond energies and bond lengths as giving an indication of the electron density concentrated in a given bond. In the carbon-monoxide—borane molecule, one of the interesting observations is the small effect which the presence of the borane group has on the C-O bond. The force constant of the C-O bond in carbon monoxide gas calculated from the observed infrared frequency of 2143 cm^{-1} is 18.5 md/Å. This is decreased only to 17.98 md/Å in BH_3CO, whereas in nickel carbonyl the C-O force constant is 15.9 md/Å[6] and in carbon dioxide it is 15.5 md/Å. The B-C bond, however, appears about normal, the value of 2.79 md/Å being only slightly less than the value 2.9 md/Å given by Badger's rule, and the bond length is in good agreement with the sum of Pauling's covalent-bond radii. The force constant for the B-H bond of 3.16 md/Å is slightly less than the value 3.42 md/Å given for the B-H bond in diborane.[7] These comparisons, if significant, lead to some very interesting speculations regarding the electronic structure of the BH_3CO molecule and to some unexpected conclusions about the BH_3CO group. Since there is some uncertainty involved, a more detailed discussion will be postponed until the analyses of two or three other molecules containing the BH_3 group have been completed.

The rest of the force constants calculated for the BH_3CO molecule either involve the bending of bond angles or are interaction constants. The bending constants are quite reasonable in magnitude, although the H-B-H constant of 0.401 md/Å is nearly twice as great as the corresponding value of 0.243 md/Å reported for diborane.[7] It was found that the calculated frequencies were rather insensitive to most of the possible interaction force constants but quite sensitive to others. In the final set listed in Table III, none of the insensitive constants appear. If the symmetry force constants are examined instead of the valence force constants, it will be seen that the F matrices are nearly diagonal, only one off-diagonal element appearing in each case. In the A_1 matrix, the off-diagonal element is F_{24}, linking the symmetrical bending coordinate and the B-C stretching coordinate, while in the E matrix it is F_{68}, connecting the BH_3 rocking coordinate with the B-C-O deformation. In both cases, the two lowest frequencies in the respective symmetry classes are involved.

In conclusion, it may be pointed out that the experimental product-rule ratios for the hydrogen-deuterium substitution listed in Table V are greater than the theoretical values, even though the differences are not large. Exact agreement, of course, is not to be expected since the observed rather than harmonic values have been used in calculating the ratios. However, the normal effect of anharmonicity is to cause the experimental ratios calculated in this way to be less than the theoretical.[8] In view of the weight of other evidence, plus the fact that all experimental ratios are greater than the theoretical, it does not seem probable that there is an error in the assignments. The difference, therefore, may also reflect the specific electronic structure of the molecule or the BH_3 group and if so, should be found in other molecules containing the borane group.

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