related series of phosphonates. The experimental ${}^1J_{CP}$ correlates linearly with the C–P s-bond order, $P^2{}_{s_C s_P}$, although the bond orders vary over about half the percentage range that is evidenced by either the experimental or theoretical couplings.

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Infrared Spectra of the Pyrolysis Products of Borane Carbonyl in an Argon Matrix

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Abstract: Infrared spectra of the pyrolysis products of BH_3CO trapped in low-temperature matrices have been obtained. Bands observed at 2808, 1604, and 1125 cm^{-1} cannot be attributed to B_2H_6, BH_3CO, CO, or any known molecule containing boron and oxygen. Based on the ${}^{10}B$ isotope shifts and the special conditions required for isolation, these unidentified bands are assigned to the simple borane, BH_3. Under certain pyrolysis conditions bands at 1403, 1378, and 910 cm^{-1} are also observed. The molecule associated with these bands is identified as boroxine ($H_3B_3O_3$) from the observation of dilute-matrix spectra of that compound. Another molecule, $H_2B_2O_3$, may be found in the pyrolysis reaction if traces of O_2 are present in the gas mixture.

Borane has long been postulated as a kinetic intermediate in the reaction of boron hydrides, but it has never been isolated.[1,2] Attempts to isolate BH_3 and identify it by optical spectroscopy have proved to be inconclusive.[3–6] Mass spectrometric techniques for the study of the pyrolytic decomposition of B_2H_6 and BH_3CO only recently have become refined sufficiently for the direct identification of BH_3 in small concentration.[7–12] Of the possible experimental methods for spectroscopic study of BH_3, low-temperature matrix isolation appeared to be the most promising.[13]

Pyrolysis experiments have shown that under certain experimental conditions BH_3 is produced in good yield by the thermal dissociation of BH_3CO. In their studies Mappes and Fehlner[14] have proposed the reaction sequence

$$BH_3CO \longrightarrow BH_3 + CO \tag{1}$$

$$BH_3 + BH_3 \longrightarrow B_2H_6 \tag{2}$$

$$BH_3 + \text{wall} \longrightarrow B + {}^3/_2H_2 + \text{wall} \tag{3}$$

To maximize the BH_3 yield and reduce the extent of reactions 2 and 3, the residence time of BH_3 was reduced as low as 10^{-4} sec and the BH_3CO reactant was diluted with helium and pyrolyzed at high pressures (5 mm) and high flow rates. At 700°K a borane yield of 50% (based on borane carbonyl decomposed) was claimed. In this work we are reporting on the results of experiments in which the fast-flow pyrolysis technique used by Mappes and Fehlner was combined with the matrix-isolation technique in an attempt to obtain the infrared spectrum of BH_3.

Experimental Section

A. **Cryostat.** A helium dewar with a rotatable tail was used in these experiments The target and external windows were CsI. A third window was available for the observation of the film growth. A target window was placed in the copper block at the tail of the dewar against an indium O-ring made of 0.030 wire and the assembly was jammed tight with a screwcap. A small hole was drilled into the CsI window to its center and an Au–2.1%Co *vs.* Cu thermocouple was imbedded by packing it into the hole with indium wire. Apiezon-L was used to enhance thermal contact. The temperature, measured for the bulk CsI crystal, was monitored during all experiments. The pump-out arm of the dewar tail served as the vacuum jacket for the various pyrolysis sources. All the sources were built of quartz onto a 55/50 female ground joint. The hot zone was 30 cm from the ground joint, the tip of the pyrolysis tube 2 cm from

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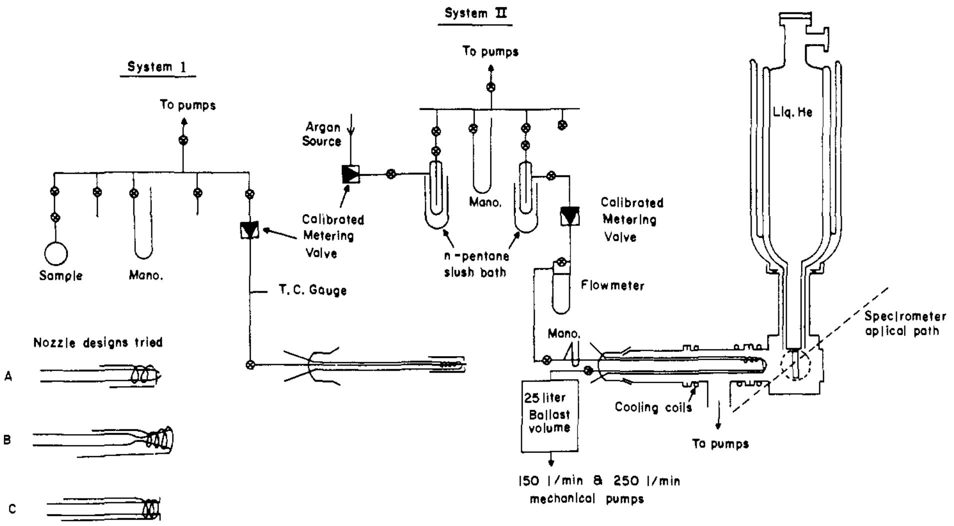

Figure 1. Matrix-isolation flow systems I and II.

the target window. Two types of pyrolysis systems were used; the first involved direct deposition with the target serving as the fast cryopump of all of the reaction products and the other was differentially pumped; both are shown in Figure 1.

B. **System I.** In Figure 1 various nozzle designs are illustrated. Designs A and B yielded only B_2H_6, CO, and BH_3CO as products. Design C, which was the most successful, will be discussed in more detail. It consisted of a straight quartz tube, 5-mm i.d., with five coils of No. 20 Kanthal wire wound in a 1-cm distance as close as possible to the tip. The temperature was measured with a Chromel–Alumel thermocouple inserted into a slit cut into the tip of the pyrolysis tube. The assembly was covered with a heat shield made of gold-plated quartz tube to protect the target window from radiation. The deposition rate in this system varied from 38 to 75 mmol/hr. The deposition time was 15–30 min. The matrix gas, argon or nitrogen, was premixed with borane carbonyl and metered into the pyrolysis zone. The background dewar vacuum was 4×10^{-8} Torr. The pressure rose to $4\text{–}6 \times 10^{-4}$ Torr during deposition. The residence time of the gases in the pyrolysis tube could be varied from as low as 2×10^{-4} sec to as high as 10^{-2} sec, although the reproducibility of this parameter was not very good. For the studies in System I, the borane carbonyl was prepared[15] in small batches before each experiment by treating boroxine[16] with CO.

C. **System II.** The differential pumping system was designed to fit both the matrix-isolation system and an AERO-VAC Model 610-611 mass spectrometer. In this manner conditions found favorable for BH_3 production in the mass spectrometer could be simulated in the matrix-isolation system. The flow system was constructed of a piece of 5-mm i.d. quartz tubing; No. 20 Kanthal wire filament was used to heat the 1.5-cm pyrolysis zone. A pinhole was produced by sand blasting the tip of the flow tube before the bend to the pump-out line. For mass spectrometric experiments 0.05-mm and for matrix isolation 0.1- and 0.8-mm hole sizes were used. The thermocouple was inserted into the pyrolysis zone at the center of the flow tube and the temperature of the gas was directly measured. The pressure in the pyrolysis tube, but ahead of the hot zone, was measured with a mercury manometer. Residence time in these experiments was $10\text{–}12 \times 10^{-4}$ sec. The deposition rates in the matrix isolation experiments ranged from 1 to 5 mmol/hr. The pressure in the dewar was maintained at 4×10^{-8} Torr before and after deposition and 2×10^{-5} Torr during deposition.

The sample for the flow experiments was prepared by allowing argon at a desired pressure into the sample bulb while BH_3CO was frozen at −130° (vapor pressure = 3 mm). The sample was metered into the pyrolysis zone to a predetermined pressure and the argon ratio was maintained by setting up a steady-state condition with metering valves. Borane carbonyl was prepared by the procedure of Burg and Schlesinger by treating B_2H_6 with CO at 20 atm.[17] Argon used in these experiments was obtained from the Matheson Co. and further purified by pumping on the condensed form at −195° and then expanding the amount used.

The mass spectra were obtained with both helium and argon as flow gases. In the matrix-isolation experiments with system II only argon was used as matrix material. The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer, calibrated with CO, HCl, NH_3, and CO_2.

Products of BH_3CO Pyrolysis

Since B_2H_6 and BH_3CO are present in the reaction products, we have obtained matrix spectra for each of these compounds under different matrix concentrations and deposition conditions at various intensities to use for comparison. Spectra of these compounds and of the pyrolysis products are shown in Figure 2. Spectrum B in Figure 2 was obtained using system I with the source temperature at 700°K. The composition of the starting mixture was $BH_3CO/Ar = 1/100$. The deposition lasted 15 min and the rate of deposition was 60 mmol/hr. If some BH_3 was produced, its relative concentration to the argon on the target window would be less than 1/1000. During the deposition of the sample the temperature of the target rose from 5 to 29.5°K. In this spectrum the weak band at 1604 cm^{-1} was the only band which eventually was not accounted for by B_2H_6, BH_3CO, $H_3B_3O_3$, CO, and CO_2. Spectrum C in Figure 2 shows the effect of increased dilution on the band at 1604 cm^{-1}. Other unknown weak bands, labeled R, are observed at 2808 and 1125 cm^{-1}. In this experiment the conditions were as follows: composition of starting mixture, $BH_3CO/Ar = 1/200$; deposition time, 15 min; deposition rate, 74 mmol/hr. The target temperature reached a maximum of 25°K during deposition. The residence time in each of these experiments was near 1×10^{-4} sec. The observed bands are assigned in Table I.

Table I. Assignments for BH_3 (Assume D_{3h} Symmetry)

		$^{10}BH_3$		$^{11}BD_3$	
	$^{11}BH_3$	Obsd	Calcd	Obsd	Calcd
$\nu_1(A_1')$	(2623)[a]		2623		1856
$\nu_2(A_2'')$	1125	1132	1137	845	877
$\nu_3(E')$	2808	2820	2826	2112	2118
$\nu_4(E')$	1604	1610	1610	1184	1172

[a] Calculated, infrared inactive.

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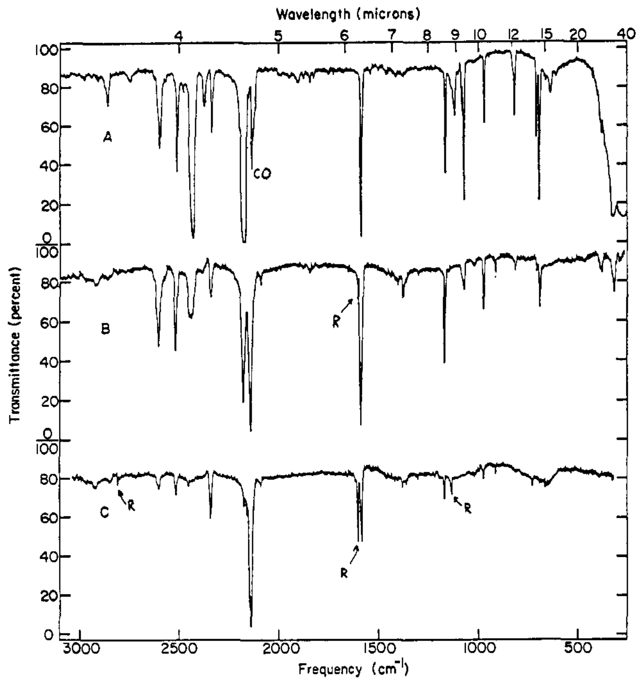

Figure 2. Infrared spectrum near 5°K of: (A) $BH_3CO/B_2H_6/Ar$ = 1/0.1/200, (B) BH_3CO/Ar = 1/100 pyrolysis products, (C) BH_3CO/Ar = 1/200 pyrolysis products.

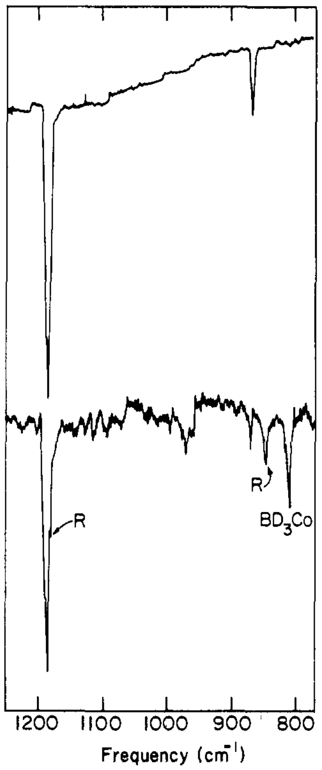

Figure 3. Infrared spectrum near 5°K of: top, B_2D_6/Ar = 1/10,000; bottom, BD_3CO/Ar = 1/200 pyrolysis products.

Spectrum C in Figure 2 had the strongest of the unknown bands that we obtained during all the experiments. We have never observed these bands in experiments where the target temperature rose above 35°K. Similar experiments were performed using $^{10}BH_3CO$ and BD_3CO. In the BD_3CO experiment a marked increase in the decomposition rate of both

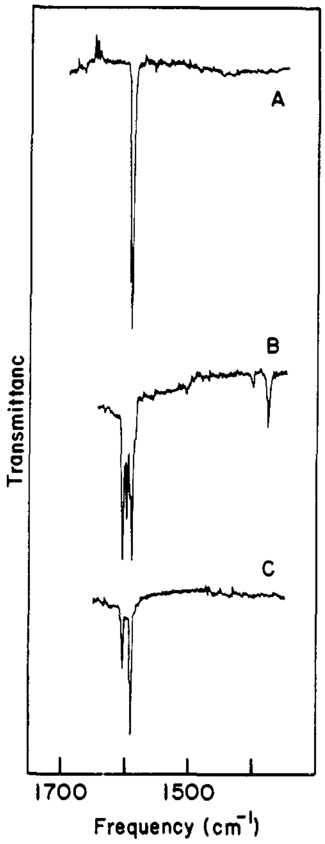

Figure 4. Infrared spectrum near 5°K of: (A) B_2H_6/Ar = 1/10,000; (B) BH_3CO/Ar = 1/200 pyrolyzed, pyrolysis zone not conditioned; (C) same as B, but pyrolysis zone conditioned with hot argon before experiment commenced.

borane carbonyl and borane was noted. Figure 3 shows a portion of the spectrum of the deuterated species.

With system II it was possible to observe the pyrolysis products with a mass spectrometer and note the extreme sensitivity of the borane yield to experimental conditions. When the temperature was maintained at 750°K and the pressure raised from 10 to 12 mm, the *m/e* 12, 13, and 14 peaks used to monitor borane nearly doubled in intensity. (Corrections on *m/e* 12 and 14 for C^+ and CO^{2+} from CO, and *m/e* 14 for N^+ were made.) When the source temperature was increased at constant pressure to 810°K the drop in the intensity of ions with *m/e* 12, 13, and 14 was evident and in line with published observations of decreased borane yield. At the same time the intensity of ions with *m/e* 17, 29, 30, 44, and 45 rose very rapidly, indicating that some other species are produced.[18]

In the matrix isolation experiments utilizing system II the strong band at 1604 cm^{-1} was again observed with the ratio of matrix gas/reactive species = 10,000. Figure 4 shows the results of these experiments. The bands at 1403, 1379, and 910 cm^{-1} shift with deuterium substitution to 1388, 1365, and 808 cm^{-1}, respectively. The compound for which these bands arise has been identified as boroxine ($H_3B_3O_3$) by comparison with a weak matrix spectrum obtained for that compound[19]

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(18) Similar data are reported in ref 12.

(19) Samples of $H_2O/B_2H_6/Ar$ = 1/1/1000, $H_2B_2O_3/Ar$ = 1/1000, and $H_3B_3O_3/Ar$ = 1/1000 were prepared, and for each a series of matrix-

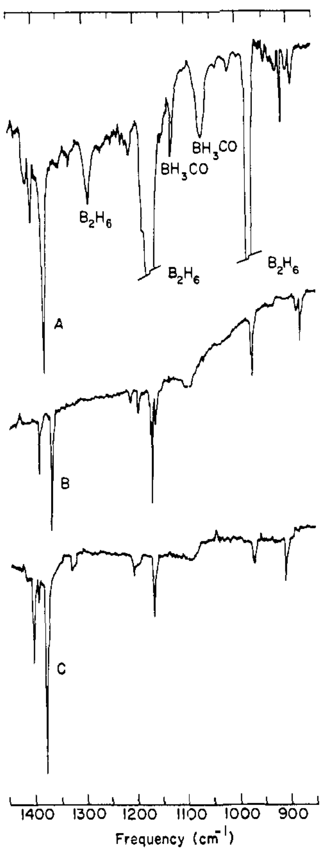

Figure 5. Infrared spectrum near 5°K of: (A) pyrolysis products of BH_3CO/Ar = 1/200 after prolonged exposure of pyrolysis zone to air, (B) $H_2B_2O_3/Ar$ = 1/1000, (C) $H_3B_3O_3/Ar$ = 1/1000.

(Figure 5C). When the pyrolysis tube was exposed to air prior to an experiment, the boroxine bands were observed along with weak bands due to $H_2B_2O_3$[19] (Figure 5). It should be noted in comparing spectra A and B in Figure 5 that the band at 910 cm^{-1} shows a weak ^{10}B isotope effect, suggesting that the molecule may contain only one boron atom. This anomalous isotope effect has already been noted in the gas-phase spectrum of $H_3B_3O_3$.[20]

To test the possible effect of the presence of a trace of O_2 in the pyrolysis zone, we obtained the matrix spectrum of the products from an initial mixture of $BH_3CO/O_2/Ar$ = 1/0.1/200 pyrolyzed at 750°K. Under these conditions $H_3B_3O_3$ and $H_2B_2O_3$ were observed as primary products. Similar experiments with H_2O instead of O_2 in an identical ratio produced $H_3B_3O_3$ as the major product. With both O_2 and H_2O other weak bands were observed which were very sensitive to pyrolysis and deposition conditions and were not very reproducible. These weak bands may be due to the presence of H_2BOH, $HB(OH)_2$, and $B(OH)_3$.

Spectrum C in Figure 4 was obtained when hot argon was passed through the pyrolysis zone to remove traces of oxygen and water from the surfaces before the experiment was started. After this treatment the band at 1599 cm^{-1} and the bands due to boroxine (Figure 4B) were not observed.

Since H_2O has a fundamental, ν_2, close to 1600 cm^{-1}, spectra of a dilute H_2O/B_2H_6 mixture in argon were obtained for comparison with the spectra given in Figure 2C.[19] The multiplet structure associated with H_2O[21] and present in the $H_2O/B_2H_6/Ar$ matrix spectrum was not observed in spectrum C, Figure 2, and the location of the strongest H_2O line did not coincide with the unknown band at 1604 cm^{-1}. (The B_2H_6 band at 1592 cm^{-1} was used for calibration.) The absorption band at 1599 cm^{-1} in spectrum B, Figure 4, is probably due to H_2O.

Figure 6. High-resolution infrared spectrum near 5°K of BH_3CO/Ar = 1/200 pyrolyzed.

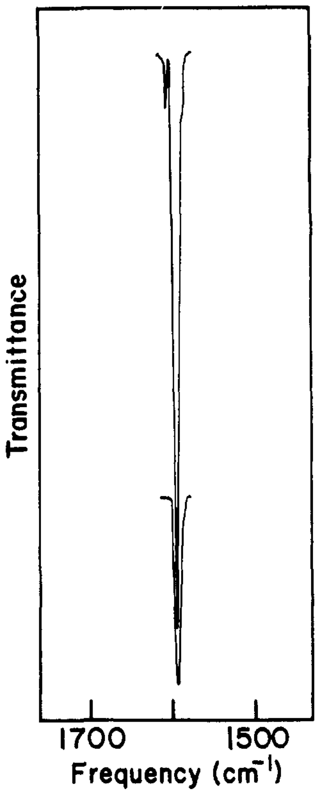

Figure 7. Diffusion experiment on BH_3CO/Ar = 1/200 pyrolysis products: top, before diffusion; bottom, after diffusion.

Under high resolution (see Figure 6), the shape of the B_2H_6 band at 1592 cm^{-1} is quite different from

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isolation spectra, ranging from very weak to strong, was obtained. $H_2B_2O_3$ was prepared by the procedure of F. A. Grimm and R. F. Porter, *ibid.*, 7, 706 (1968). The deposition rates were 1–5 mmol/hr.

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(21) E. Catalano and D. E. Milligan, *J. Chem. Phys.*, 30, 45 (1959).

that for the unknown band at 1604 cm^{-1}. The effect of diffusion on the band at 1604 cm^{-1} is shown in Figure 7. As the matrix is warmed above 35°K the band disappears and the 1592-cm^{-1} diborane band broadens.

It was observed that the unknown bands at 2808, 1604, and 1125 cm^{-1} are present only if the CO band is split into two components at 2148 and 2138 cm^{-1}. When the experiments failed to produce the unknown bands, only the 2138-cm^{-1} band was observed. The intensity of the 1604-cm^{-1} band is the strongest when the 2148-cm^{-1} band is strongest. Several workers have studied CO in an argon matrix and observed this splitting phenomenon;[22,23] Pimentel and his coworkers[24] have done a careful series of studies on CO at low temperatures and have concluded that the CO band at 2138 cm^{-1} is due to an aggregate of CO, while the band at 2148 cm^{-1} is due to CO monomer. The present results indicate matrix-induced aggregation for CO under conditions when B_2H_6 is produced, and similarly the unknown bands are observed under conditions when CO is isolated as a monomer.

The pyrolysis at 850°K of diborane at 10^{-6}-Torr partial pressure in an argon stream produced only the very weak band at 1604 cm^{-1} and none of the diborane bands. When the source temperature was lowered to 700°K, diborane passed through. Experiments were performed on mixtures of BH_2DCO and BHD_2CO, but the spectra of the $B_2D_nH_{6-n}$, $n = 1$-5, species in the pyrolysis products were so complicated that attempts at an analysis were abandoned.

Vibrational Assignment

In the spectrum of pyrolyzed BH_3CO the band at 1604 cm^{-1} and two very weak bands at 2808 and 1125 cm^{-1} cannot be assigned to any of the stable pyrolysis products such as B_2H_6, CO, or CO_2; to BH_3CO; to any species produced in the presence of O_2 or H_2O; or to BH_2,[25] which sometimes has been postulated as decomposition product. From the mass spectrometric studies it is known that BH_3 is produced in the pyrolysis zone, and the only doubt in assigning the bands to BH_3 is that in the matrix the species may be partially bonded in some aggregate form. This is particularly of concern since two of the bands lie so close to B_2H_6 bands. If the unknown bands belong to some form of B_2H_6, more than three bands should be observed. Studies on CH_3 produced in high-temperature sources and isolated in low-temperature matrices indicate a great deal of association to produce C_2H_6, but no intermediates have been reported.[26] It should further be recalled that the band at 1604 cm^{-1} does not show the contribution due to $^{11}B^{10}B$ isotopic species characteristic of molecules containing two boron atoms such as the shoulder on the diborane band at 1594 cm^{-1}.

Using valence-bond theory Jordan and Longuet-Higgins have predicted borane to be planar D_{3h} in its ground state, similar to CH_3 and BF_3.[27] There are three infrared-active fundamentals expected for such a molecule, two of species E′ and one of species A$_2$″. The band at 1604 cm^{-1} observed in the pyrolysis of $^{11}BH_3CO$ shifts to 1610 cm^{-1} with ^{10}B substitution. This band is assigned to ν_4 of species E′ which corresponds to the in-plane bend. Estimates of this frequency listed in Table II range from 1134 to 1765 cm^{-1}. The weak band at 2808 cm^{-1} which shifts to 2820 cm^{-1} with ^{10}B substitution can only be assigned to ν_3, the other E′ frequency corresponding to the B–H stretch. The remaining band at 1125 cm^{-1}, which moves to 1132 cm^{-1} upon ^{10}B substitution, is tentatively assigned to ν_2, the out-of-plane bend of species A$_2$″. Estimates of this frequency (Table II) have been as low as 590 cm^{-1}. The product rule fit, shown in Table III, for the above assignments is quite good for the E′ species, but poor for the A$_2$″.

Table II. Observed Borane Frequencies Compared to Those in the Literature[a]

ν_1 (A$_1$′)	ν_2 (A$_2$″)	ν_3 (E′)	ν_4(E′)
(2623)	1125	2808	1604
2384[b]	802	2976	1765
c	590		1388
2400[d]	1163	2665	1171
2310[e]	1527	2470	1190
2400 ± 300[f]	1560 ± 50	2560 ± 100	1190 ± 10
g			1134

[a] Assumed D_{3h} symmetry. [b] A. Shepp and S. H. Bauer, *J. Amer. Chem. Soc.*, **76**, 265 (1954). [c] L. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **47**, 3637 (1967). [d] Reference 4. [e] J. S. Rigden and W. S. Koski, *J. Amer. Chem. Soc.*, **83**, 3037 (1961). [f] Reference 3. [g] Reference 6.

Table III. Product Rule Calculations

	Exptl	Theor
$\frac{(\nu_3\nu_4)_H}{(\nu_3\nu_4)_D}$ =	1.80	1.79
$\frac{(\nu_2)_H}{(\nu_2)_D}$ =	1.33	1.28
$\frac{(\nu_3\nu_4)_{^{10}B}}{(\nu_3\nu_4)_{^{11}B}}$ =	1.008	1.011
$\frac{(\nu_2)_{^{10}B}}{(\nu_2)_{^{11}B}}$ =	1.006	1.011

Spectra obtained from the pyrolysis of BD_3CO were unfortunately very weak. The only band of unknown origin and clearly resolved was that at 845 cm^{-1}. This band was assigned to ν_2 of BD_3. Using valence force constants calculated from the frequencies assigned to the hydrogenated species, the expected frequencies of BD_3 were generated.[28] The ν_2 calculated this way was expected at 877 cm^{-1}. Similarly, ν_3 and ν_4 were predicted at 2118 and 1172 cm^{-1}, respectively. These two bands could not be observed with certainty. It is possible that the band at 1604 cm^{-1} in the hydrogenated spectrum may have shifted into the region masked by the strong band in B_2D_6 at 1190 cm^{-1}. (Note shoulder at 1184 cm^{-1} in Figure 3.) Failure

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to observe with certainty a counterpart of the 1604-cm^{-1} band in the deuterated spectra may reflect the extreme sensitivity of these studies to changes in experimental conditions. Mass spectrometric data for the pyrolysis of BD_3CO have not been reported. It is possible that the pyrolysis conditions for the isolation of BD_3 are even more restrictive than for BH_3.

The in-plane-bending force constant of borane was found to be 0.46 mdyn/Å, the stretching force constant 4.08 mdyn/Å. Other molecules where three coordinated boron atoms are bound to terminal hydrogen are borazine and boroxine. The B–H stretching force constants in these molecules are 3.35 and 3.68 mdyn/Å, and the in-plane-bending force constants are 0.55 and 0.65 mdyn/Å, respectively.[29,30]

Borane is most analogous to the CH_3 radical. In CH_3 the in-plane bend was observed at 1396 cm^{-1} and the force constant was found to be 0.32 mdyn/Å.[26] From the above it appears that the E′ assignments for BH_3 are reasonable. The out-of-plane-bending force constant for borane was found to be 0.59 mdyn/Å compared with 0.52 mdyn/Å for borazine,[29] but for the methyl radical a much lower value of 0.18 mdyn/Å was found.[26]

Conclusion

In these experiments weak spectra attributed to BH_3 were obtained from the pyrolysis of borane carbonyl. In order to maximize the BH_3 yield the matrix gas was used as the diluent in the pyrolysis zone. This resulted in a severe thermal load on the window, and particularly on the growing film (5 mW). A great deal of association of borane was expected and observed. As the argon film grew, its thermal conductivity dropped to such a point that association at the surface became complete. Hence there was a maximum tolerable film thickness and also a maximum amount of borane that could be isolated. In order to observe BH_3 the following conditions appear to be necessary. (a) The argon film has to be maintained below 35°K. (b) The matrix gas to borane ratio has to be greater than 1000. (c) Traces of O_2 and H_2O cannot be present. (d) The quartz surface has to be conditioned until an elemental boron surface is formed. (e) The temperature in the pyrolysis zone cannot exceed 850°K or be lower than 700°K. (f) Residence time in the pyrolysis zone has to be less than, or equal to 10^{-3} sec.

If the source and the capacity of the target to bear a larger thermal load can be improved, the amount of borane isolated might be substantially increased. Once this is accomplished, the many short-lived intermediates that make borane's chemistry exciting can be studied by producing them either (a) in the pyrolysis zone and trapping them on the target window, or (b) by codepositing borane and the second reactant in the matrix and allowing diffusion to lead to subsequent reaction.

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Temperature Dependence of the Proton Nuclear Magnetic Resonance Spectra of Copper(I) Borane Complexes, $B_3H_8^-$ Salts, and Icosahedral Carboranes. Quadrupole-Induced Spin Decoupling. Fluxional Behavior

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Abstract: Variable-temperature proton magnetic resonance spectroscopy has revealed efficient boron–hydrogen spin decoupling due to quadrupole-induced ^{10}B and ^{11}B spin relaxation in TlB_3H_8, $(CH_3)_4NB_3H_8$, $[(C_6H_5)_3P]_2CuBH_4$, $[(C_6H_5)_3P]_2CuB_3H_8$, *o*-carborane, and *m*-carborane. An additional temperature dependence of the proton nmr spectrum of $[(C_6H_5)_3P]_2CuB_3H_8$ provides unequivocal evidence for slowed intramolecular exchange in a $B_3H_8^-$ adduct. A total nmr line-shape analysis of the spectral behavior for $[(C_6H_5)_3P]_2CuB_3H_8$ allows calculation of the rate of pseudorotation as a function of temperature.

In a host of boron hydrides and related compounds, particularly metal derivatives of borane anions, there exists an apparent discrepancy between the crystal structure and the solution structure as studied by nuclear magnetic resonance (nmr) spectroscopy.[1] For ex-

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