Matrix Isolation Study of the Reaction of B_2H_6 with H_2S : Spectroscopic Characterization of Mercaptoborane, H_2BSH

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Merged jet copyrolysis of mixtures of Ar/B_2H_6 and Ar/H_2S followed by trapping in a cryogenic matrix has led to the formation, isolation, and characterization of mercaptoborane, H_2BSH . Eight of the nine fundamentals of this molecule were observed, including the boron-sulfur stretching mode at 804 cm⁻¹ (¹¹B). Local density functional and normal-coordinate calculations were carried out to assist in assigning the observed fundamentals. The position of B-S stretching mode, compared to a range of known compounds, suggests single bond character for the B-S bond. Additional products were observed, including HBS, and suggests further reaction of H_2BSH at high temperatures. A mechanism for the reaction is proposed.

Introduction

Diborane, B_2H_6 , is the smallest of the stable electron-deficient boron hydrides and has been of interest to chemists since its discovery shortly after the turn of the century.¹⁻³ B_2H_6 reacts readily with a range of Lewis bases, both in solution and the gas phase. Recent merged jet copyrolysis experiments⁴ involving diborane and methanol led to the formation of methoxyborane, H_2B —OCH₃, in high yield; similar experiments⁵ with NH₃ led to the isolation and characterization of aminoborane, H_2B —NH₂. Experimental data from both infrared and microwave studies suggested that these molecules contain significant double bond character. The reaction of B_2H_6 with second-row (n = 3) bases might lead to related intermediate species.

Mercaptoborane, H₂BSH, has been the subject of a number of theoretical calculations⁶⁻¹⁰ but has not been experimentally observed. All of the ab initio studies are in agreement that H₂BSH should be a stable molecule and have focused their calculations on the nature of the B-S bond and the barrier to rotation about this bond. Many of these studies conclude that there should be some π bonding and double bond character; Bernardi et al. concluded⁸ that the π bonding would be less in H₂BSH than in H₂BOH, a molecule known to have a high barrier to rotation. Experimental evidence that might help resolve this issue would include the B-S stretching frequency and the force constant of the B-S bond.

The matrix isolation technique¹¹⁻¹³ was developed for the isolation and spectroscopic characterization of reactive intermediates. This technique, combined with the newly developed merged jet pyrolysis approach, permitted the spectroscopic characterization of H_2B —NH₂, H_2B —OCH₃, and related species. Matrix isolation provides perhaps the best opportunity to form and characterize mercaptoborane. Consequently, this study was undertaken to identify the pyrolysis reaction products of B_2H_6 and H_2S .

Experimental Section

All of the experiments in the present study were carried out on conventional equipment that has been described.^{5,14} The merged jet copyrolysis apparatus has also been previously outlined. H_2S (Fisher) was introduced into the vacuum line from a lecture bottle, and purified by freeze/thaw cycles at 77 K. B_2H_6 (Matheson) was introduced into the vacuum line as a 1% mixture in argon and used without further purification. D₂S was synthesized by the reaction of CaS(s) with DCl(aq); product gases were trapped at 77 K and purified initially by freeze/thaw cycles. Additional purification was achieved by fractional distillation at 179 K using a hexane/LN₂ slush bath, and trapping the evolved gas at 77 K. Ar/B_2H_6 and Ar/H_2S (or D_2S) samples were diluted to the desired ratios in separate vacuum manifolds. Each sample was then deposited via the merged jet copyrolysis technique on a 14 K cold window for 5-12 h before final scans were recorded on a Nicolet IR 42 FTIR at 1 cm⁻¹ resolution. Pyrolysis temperatures as high as 400 °C were employed.

TABLE I: Band Positions and Assignment for Argon Matrix Isolated H_2BSH

band position (cm ⁻¹)				
H ₂ BSH			H,BSD	
obs	calc	DMOL	obs	assignment
2630	2652		2630	ν_1 , BH ₂ antisym str (¹⁰ B)
2614	2636	2652	2614	ν_1 , BH ₂ antisym str (¹¹ B)
2574	2569	2549		ν_2 , S-H stretch ^a
2549	2525			ν_3 , BH ₂ sym str (¹⁰ B)
2539	2519	2534	2535	ν_3 , BH ₂ sym str (¹¹ B)
1200	1210		1202	v_4 , BH ₂ sym bend (¹⁰ B)
1191	1191	1177	1193	ν_4 , BH ₂ sym bend (¹¹ B)
	944	947		ν_5 , BSH bend ^b
951	951			ν_6 , BH ₂ wag (¹⁰ B)
940	939	899	937	ν_6 , BH ₂ wag (¹¹ B)
824	820		818	ν_{7} , B-S str (¹⁰ B)
804	806	850	798	ν_7 , B-S str (¹¹ B)
674	672	667	676	ν_8 , BH ₂ rock
635	641	658		ν_9 , torsion ^a

^aTentative assignment, see text. ^bNot observed; calculated values only.

To provide theoretical support for the experimental spectra, vibrational spectra were calculated using local density functional (LDF) methods. The program DMOL (Biosym Technologies) was employed on a Silicon Graphics Personal Iris workstation and led to both an optimized geometry and (unscaled) vibrational frequencies. Normal-coordinate calculations were also carried out, using a program from the NRC (Canada).

Results

Before any copyrolysis experiments were conducted, blank experiments employing samples of Ar/H_2S were carried out. These were done with deposition line (pyrolysis) temperatures between 25 and 340 °C. Spectra obtained in this manner were found to be in good agreement with literature spectra.^{15,16} Initial spectra of D₂S samples showed SO₂ and CO₂ impurity; SO₂ was removed by fractional distillation. While some CO₂ remained, it was unreactive toward B₂H₆ or D₂S in these experiments and did not interfere with the subsequent copyrolysis experiments.

When B_2H_6 and H_2S were deposited through the merged jet apparatus at a concentration of 1000/1/4 in argon without pyrolysis, no new spectral features were observed. When the pyrolysis zone was heated to 260 °C, weak new features were noted and are listed in Table I. Additionally, bands at 911, 1209, 1380, 1405, and 2608 cm⁻¹ were seen along with strong bands due to both parent species. When the pyrolysis temperature was increased to 300 °C, all of these absorptions were noted with slightly greater intensity, along with a band at 1103 cm⁻¹ and a weak broad feature centered at 1142 cm⁻¹. Parent absorptions of B_2H_6 were significantly decreased while H_2S absorptions remained intense. Several experiments were conducted at this temperature and



Figure 1. Infrared spectrum, over the region $800-1250 \text{ cm}^{-1}$, of the products of the merged jet copyrolysis of a sample of $Ar/B_2H_6/H_2S$ followed by deposition at 14 K.



Figure 2. Infrared spectrum in the BH₂ stretching region of the products of the merged jet copyrolysis of a sample of $Ar/B_2H_6/H_2S$ followed by deposition at 14 K. Bands marked with an asterisk are due to unreacted parent H_2S .



Figure 3. Infrared spectrum, from 750 to 850 cm⁻¹, of the products of the merged jet copyrolysis of a sample of $Ar/B_2H_6/H_2S$ followed by deposition at 14 K.

concentration ratio to ensure reproducibility. When the pyrolysis temperature was increased to 350 °C, new weak product absorptions were noted at 1167, 2574, and 2724 cm⁻¹. Parent absorptions to B_2H_6 had disappeared (as seen in previous studies involving the pyrolysis of B_2H_6) while residual H_2S absorptions persisted. In an attempt to increase product yield, the sample concentration was increase to $Ar/B_2H_6/H_2S = 500/1/2$. More intense bands were observed; the most intense absorption, at 1191 cm⁻¹, had an optical density of about 0.1 absorbance units. In addition, new weak bands were observed at 1159 and 2739 cm⁻¹. One final experiment was conducted with a pyrolysis temperature of 400 °C, but further enhancement in product yield was not obtained. Figures 1–3 show spectra of the reaction products, over different spectral regions.

The merged jet copyrolysis of samples of Ar/B_2H_6 with samples of Ar/D_2S led to a number of new product bands, including those listed in Table I. In addition, absorptions were seen at 911, 1089, 1167, 1209, 1380, 1405, 2608, 2724, and 2739 cm⁻¹, matching exactly bands detected in the H_2S experiments. All of the band intensities were low, but the peaks were well-defined and reproducible over a set of experiments.

TABLE II: Geometry of Mercaptoborane Determined by Local Density Functional Calculations

R _{SH}	1.37 Å	H-S-B	99.6°
R _{BS}	1. 76 Å	H-B-H	123.9°
$R_{\rm BH}^{a}$	1.20 Å	S-B-H ₁	121.4°
R _{BH} ^b	1.20 Å	S-B-H ₂	114.6°
		$H-S-B-H_1$	1. 2°

^a Hydrogen on boron cis to S-H bond (H₁). ^b Hydrogen on boron trans to S-H bond (H₂).

Discussion

Product Identification. The copyrolysis of samples of Ar/B_2H_6 and Ar/H_2S followed by trapping into cryogenic matrices led to the observation of a number of new infrared absorptions that could not be attributed to either parent species. Over numerous experiments at different concentrations and pyrolysis conditions, intensity variations indicated that three distinct sets of absorptions could be identified. Specifically, intensity ratios were calculated for each observed band compared to several reference bands, and the absorptions within a given set maintained constant intensity ratios over all of the experiments conducted.

The first set of bands consisted of a ¹¹B, ¹⁰B doublet at 2724, 2739 cm⁻¹, and a singlet at 1168 cm⁻¹. These bands only were seen in the higher temperature experiments, above 350 °C. When D_2S was employed, the same bands were seen, with no shift in band position. These bands are readily assigned to the HBS molecule by comparison to literature infrared spectra of this species.¹⁷⁻¹⁹ The third fundamental of this triatomic, the low-energy H–B–S bending mode, was not observed (this mode was not in the earlier gas-phase studies, presumably due to low intensity). Observation of this species is also consistent with the reaction mechanism proposed, below.

A second set of bands was observed in most experiments, with absorptions at 911, 1209, 1380, 1405, and 2608 cm⁻¹. The intensities of these bands were relatively independent of the concentration of the H₂S reactant and match closely bands that have previously been assigned²⁰ to boroxin, H₃B₃O₃. Boroxin has been reported after the reaction of B₂H₆ with smaller amounts of O₂ in argon matrices,²¹ likely through the initial formation of HBO followed by rapid trimerization to H₃B₃O₃. The observation of small amounts of boroxin here is due to reaction of B₂H₆ with trace residues of O₂ in the vacuum system. The formation of boroxin in these experiments is unrelated to the reaction of B₂H₆ with H₂S.

The third set of product bands was the most extensive and is listed in Table I. These bands maintained a constant intensity ratio with respect to one another, indicating that they may be attributed to a single infrared absorber. Several absorptions can readily be identified as ¹⁰B, ¹¹B doublets, based on splittings and relative intensities (boron occurs naturally in a 20:80 10 B:11 B ratio). This indicates the presence of boron in the product species. B-H stretching bands (assigned below) are clearly in a region attributable to a terminal BH_2 unit (above 2500 cm⁻¹) and not to a coordinated BH₃ unit (near 2300 cm⁻¹). A number of the product bands showed small to moderate shifts when D₂S was employed, indicating deuterium incorporation into the product species. These observations, coupled with previous studies of the reaction of B₂H₆ with NH₃ and CH₃OH, strongly support identification of the product species as mercaptoborane, H₂BSH. Band assignments, normal-coordinate calculations, LDF calculations, and the reaction mechanism are all consistent with this identification.

LDF and Normal-Coordinate Calculations. Local density functional calculations using DMOL were performed on H_2BSH to provide assistance in assignments of the observed infrared absorptions. The structure optimized to the geometry described in Table II. Of note is the near-planarity of the molecule, with a 1.2° HSBH torsional angle. A complete set of vibrational frequencies was calculated; these are listed in Table I for comparison to the experimental values and will be used in band assignments, below. Normal-coordinate analysis (NCA) calculations were also carried out in support of the experimental data and provided good agreement for most of the vibrational assignments. The LDF-calculated geometry was used in the NCA calculations, with a force field refined to the experimental data. Since the NCA calculations were dependent on the LDF results, for the purposes of assignment the frequencies calculated directly by LDF methods were used as the primary source of assistance in making assignments.

Band Assignments. Mercaptoborane is a five-atom molecule with nine vibrational degrees of freedom. There have been no experimental determinations of the structure of this compound. As noted above, the LDF calculations indicate a structure that is nearly planar, with a 1.2° HBSH torsional angle. For the purposes of description, vibrational modes are most readily discussed in terms of a (nearly) planar structure; this terminology will be used in the following discussion. Thus, all nine of the fundamentals are infrared active; seven are of (nearly) A' symmetry (in-plane modes) and two are of (nearly) A'' symmetry (out-of-plane modes). In a small molecule such as this, some coupling or mixing is anticipated between modes of similar frequency and the same symmetry, an expectation that is borne out by the LDF and NCA calculations.

Two ¹⁰B, ¹¹B doublets were observed in the terminal BH₂ stretching region, at 2630, 2614 and 2549, 2539 cm⁻¹. These occur very close to the antisymmetric and symmetric BH₂ stretching modes for a number of analogous compounds, ^{4,5,22,23} including H₂B=NH₂, H₂B=N(CH₃)₂, and H₂B=OCH₃ (for example, in the H₂B=NH₂, these doublets were observed at 2585, 2568 and 2520, 2499 cm⁻¹). In all cases, the antisymmetric stretch was observed at higher energies than the symmetric stretch. The antisymmetric stretch is also expected to show a larger ¹⁰B shift due to the increased boron participation in the normal vibration. All of these observations lead to assignment of the two doublets observed here to ν_3 and ν_1 , the antisymmetric and symmetric BH₂ stretches, respectively.

A particularly important vibrational mode for mercaptoborane is the B-S stretching mode, a mode that should provide insights into the structure and bonding of H₂BSH. A ¹⁰B, ¹¹B doublet was observed at 804, 824 cm⁻¹, as shown in Figure 3, with each component having a deuterium shift of 6 cm^{-1} to lower energy. The boron isotopic shift of this vibration is quite large, indicative of the vibration of a boron atom against a quite heavy atom; the deuterium shift indicates some coupling to the hydrogen/deuterium on the sulfur. Given the composition of H_2BSH , assignment to the B-S stretching mode is strongly suggested. For a B-S diatomic with the ¹¹B frequency at 800 cm⁻¹, a ¹⁰B shift of 29 cm⁻¹ is predicted. Coupling to the S-H bond (giving rise to a 6-cm⁻¹ deuterium shift) should reduce this slightly, toward the observed value of 20 cm⁻¹. No other vibration in H₂BSH should have a relative ¹⁰B, ¹¹B shift of this magnitude (the ${}^{10}B/{}^{11}B$ ratio is 1.006 for the antisymmetric stretch and 1.0117 for the out-of-plane wag, compared to 1.025 for this mode). LDF calculations place this mode at 850 cm⁻¹, in reasonable agreement with the observed value. Consequently, assignment of the 824, 804 cm⁻¹ doublet to a vibrational mode dominated by B-S stretching character (ν_7) is made.

A ¹⁰B, ¹¹B doublet was observed at 1200, 1191 cm⁻¹, in a region where the BH₂ symmetric bend has previously been observed.^{4,5} The 9-cm^{-1 10}B shift is consistent with a motion of the BH₂ group in the molecule. Normal-coordinate calculations place the symmetric bend at 1191 cm⁻¹, with a ¹⁰B shift comparable to that observed experimentally. These calculations also indicate that this mode is slightly coupled to the B-S stretching mode and predict a small blue shift upon deuteration at the sulfur (i.e., with H₂BSD) as a result of decreased coupling. This is precisely the observed result. LDF calculations place this mode at 1177 cm⁻¹, in quite acceptable agreement with the observed value. These arguments all point to the assignment of the 1200, 1191 cm⁻¹ doublet to v_4 , the symmetric BH₂ bend.

A doublet at 951, 940 cm⁻¹ has characteristics of a ¹⁰B, ¹¹B pair and lies in a region associated with the A" BH₂ out-of-plane (wagging) motion. For comparison, the ¹¹B counterpart of this mode was observed at 1002 cm⁻¹ in H₂B=NH₂ and at 895 cm⁻¹ for H₂B=OCH₃. To conserve center of mass, this mode would be expected to involve slight participation of the S-H moiety as well, and a 3-cm⁻¹ deuterium shift was noted. Normal-coordinate calculations place this mode at 939 cm⁻¹, with appropriate ¹⁰B and deuterium shifts. Consequently, assignments of the 951, 940 cm⁻¹ doublet to ν_6 , the BH₂ out-of-plane mode, is made.

Two bands were observed between 600 and 700 cm⁻¹, at 635 and 674 cm⁻¹. No ¹⁰B counterparts were observed for either band, although intensities were quite low in this region, and a band only 20% as intense as the observed bands might well not have been detectable. Upon deuteration, the 674-cm⁻¹ band showed a 2-cm⁻¹ blue shift, while no deuterium counterpart could be detected for the 635-cm⁻¹ band (presumably due to low frequency and/or low intensity). Candidate vibrational modes include the BH₂ rocking mode, the B-S-H bending mode, and the torsional mode (although normal-coordinate calculations indicate that these three modes are substantially mixed). The latter two should have distinct deuterium shifts to lower energy, while the first should not. The lack of a red shift upon deuteration, and the fact that the BH₂ rocking mode has been observed in this region for comparable species, suggest that the 674-cm⁻¹ band be assigned to ¹¹B counterpart of v_8 , the BH₂ rock, with the ¹⁰B band too weak to be seen. LDF calculations predict that this mode should be observed at 667 cm⁻¹, in very good agreement with the observed value.

Choosing between assignment of the 635-cm⁻¹ band to the torsion or the B–S–H bend is less apparent, particularly without observed ¹⁰B or deuterium shift. Given the close match to experiment for the above bands, the LDF calculations provide the most effective basis for assignment. These calculations place the in-plane BSH bend near 950 cm⁻¹ and the torsion at 658 cm⁻¹. Calculations using DMOL have been shown to predict frequencies within 5% of experiment; the agreement for the above bands is better than this. Given the close proximity of the 635-cm⁻¹ band to the predicted torsional mode, and the large disparity with the predicted BSH bending mode, assignment to the torsion is favored. Also, the BSH bending mode is likely to be very weak, by analogy to the HBS molecule, and may well escape detection. Consequently, the 635-cm⁻¹ band is tentatively assigned to ν_9 , the torsional mode.

Assignment of the S-H stretching mode remains. In a variety of related compounds (including H₂S) the S-H stretching mode was very weak. A weak band was observed in a number of experiments at 2574 cm⁻¹ and was partially obscured by absorptions of parent H₂S. LDF calculations place the S-H stretching mode within 25 cm⁻¹ of this position, supporting its assignment to this mode. The deuterium shift should be very large, to near 1850 cm⁻¹. This region contains strong absorptions of parent D_2S , along with residual bands of atmospheric H_2O . Consequently, a deuterium counterpart was not observed. In fact, the 2574-cm⁻¹ band was observed in the D₂S experiments, but since the D_2S was not 100% isotopically enriched, this is not unexpected. Consequently, assignment of the 2574-cm⁻¹ band to the S-H stretch is made, but must be viewed as tentative in light of the low intensity of the band and structural congestion in the 2500cm⁻¹ region.

Bonding in Mercaptoborane. The central question concerning bonding in H_2BSH deals with the bond order of the boron-sulfur bond. For the analogous first-row compounds aminoborane and methoxyborane, a number of pieces of information supported substantial double bond character in the boron-nitrogen bond and the boron-oxygen bond. Since the experimental B-S bond length is not known, and the barrier to rotation about the B-S bond has not been determined, the primary data relevant to the B-S bond resides with the B-S stretching frequency and force constant. Normal-coordinate calculations place the B-S stretching frequency at 794 cm⁻¹, with a force constant of 4.09 mdyn/Å. This force constant is slightly over one-half the force constant determined²⁴ for the B-S stretching mode of HBS, 7.4 mdyn/Å, where multiple bond character is expected. The force constant of 4.09 mdyn/Å is a bit over one-half of the value of 7.04 mdyn/Å determined for the B=O stretching mode in methoxyborane⁴ (which appears to have significant boron-oxygen double bond character). The

observation of a low frequency and a force constant around 50% of these related species argues for primarily single bond character for the B-S bond in H₂BSH. This conclusion is in agreement with Vahrenkamp²⁵ who examined the B-S stretching frequencies of a variety of boron-sulfur compounds. He reported frequencies in this spectral region and concluded that the compounds contained a B-S single bond.

Few examples exist of multiple bonding involving sulfur, particularly with boron-sulfur bonds. As a result, a comparison of bond lengths provides only an approximate picture of the bonding in H₂BSH. Nonetheless, LDF calculations predict a B-S bond length of 1.76 Å; DMOL calculations are generally within 0.01-0.02 Å of the experimental value (when known). The B-S bond length in HBS has been measured²⁶ by microwave spectroscopy to be 1.5994 Å. Multiple bonding is anticipated in HBS based both on valence bond considerations and the observed linearity of the molecule. For comparison, the C=S bond lengths in carbonyl sulfide and ethylene thiourea are 1.56 and 1.71 Å, respectively.²⁷ Clearly, the calculated B-S bond length in H₂BSH is substantially longer than the experimental B-S bond length in HBS, which argues for lower bond order. Also, typical B-S single bonds are known²⁸ to be in the range 1.75-1.80 Å. These points all support the above conclusion that the B-S bond in H₂BSH has largely single bond character.

Reaction Mechanism. Previous studies of the reaction of B_2H_6 with NH₃ and related bases^{4,5,22} concluded that the reaction proceed via formation of an adduct of the type H₃B·NH₃, followed by rapid H_2 elimination to form the primary product. In the present study, no evidence of the H₃B·SH₂ adduct was obtained, but it is a likely intermediate before H_2 elimination occurs to form the observed H₂BSH. The observation of HBS at high pyrolysis temperatures along with reduced intensity of the H₂BSH bands is parallel to the observed decomposition of H_2BOCH_3 to CH_4 and HBO. This, then, further supports identification of the primary product in this study as H₂BSH.

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