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Contribution from the Department of Chemistry,
University of Toledo, Toledo, Ohio 43606

Preparation and Properties of $H_2B_2S_5$ and Its Decomposition Products[1]

ALFRED S. GATES and JIMMIE G. EDWARDS*

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The preparation of solid $H_2B_2S_5$ and its decomposition product $H_2S{\cdot}xBS_2$, $x = 4.84 \pm 1.75$, and observations of their properties by visual and chemical means and by x-ray, infrared, Raman, and mass spectrometry are reported. Metathioboric acid, $(HBS_2)_3$, was prepared by two methods and heated with sulfur in evacuated, sealed Vycor tubes to yield $H_2S{\cdot}xBS_2$. Diiodotrithiadiborolane, $I_2B_2S_3$, was prepared and treated with H_2S to obtain $H_2B_2S_5$ in benzene solution. Solid $H_2B_2S_5$ decomposed and polymerized spontaneously to yield $H_2S{\cdot}xBS_2$. X-ray, infrared, and Raman spectrometry revealed polymerization and extensive S–S bonding in the solid. Mass spectrometry of the vapor from the solid products gave predominantly $H_2B_2S_5^+$, H_2S^+, and their fragments at temperatures below 80 °C and then high molecular weight ions up to $B_8S_{16}^+$ at higher temperatures. Fragmentation of $H_2B_2S_5^+$ was shown to yield HBS_3^+ by identification of the corresponding metastable ion. A relationship of $H_2B_2S_5$ to $(BS_2)_n$ through polymerization and condensation is proposed.

Introduction

The only previously known solid thioboric acid was metathioboric acid, HBS_2. It can be prepared by reaction of H_2S with hot boron[2] or by reaction of H_2S with BBr_3 in solution.[3] The solid is trimeric, $(HBS_2)_3(s)$,[4-6] with monoclinic crystal structure in space group C_{2h}^2 or $P2_1/c$.[6] The decomposition and vapor over $(HBS_2)_3$ have been extensively studied.[4,7-13] This paper reports the preparation of $H_2B_2S_5$ and its decomposition product $H_2S{\cdot}xBS_2$, $x = 4.84 \pm 1.75$, and observations of their properties by visual and chemical means and by x-ray, infrared, Raman, and mass spectrometry.

When heated under vacuum below 100 °C $(HBS_2)_3(s)$ decomposes with loss of $H_2S(g)$ toward $B_2S_3(s)$, vaporizes and decomposes to produce $(HBS_2)_3(g)$ and $H_3BS_3(g)$, disproportionates toward a sulfur-rich solid, and produces in small amounts the sulfur-rich gas $H_2B_2S_5(g)$. At higher temperatures, $HBS_2(g)$ and $(HBS_2)_2(g)$ have been reported.[4] Mass spectrometry of the vapor over partially decomposed $(HBS_2)_3(s)$ at temperatures above 250 °C yields polymeric ions $B_nS_{2n}^+$ with n up to 12.[8,11-13] Prominent among the polymeric ions is $B_8S_{16}^+$. It has been proposed that the polymeric ions result from gaseous polymers $(BS_2)_n(g)$[8] and that condensation of $H_2B_2S_5$ with loss of H_2S could be the source of B_8S_{16}.[12]

The goal of this work was to prepare $H_2B_2S_5$ and other materials in the H_2S–BS_2 system, viz., $H_2S{\cdot}xBS_2$, and to determine their properties. Chemical decomposition with loss of H_2S was of particular interest because of the possibility that the proposed BS_2 polymers would be produced.

Experimental Section

Starting Materials. Sulfur (99.9999%) and boron (99.8%) from Electronics Space Products, Inc., 92% ^{10}B-enriched boron from Oak Ridge National Laboratory, CP grade hydrogen sulfide gas from Matheson Co., and boron triiodide and boron tribromide from K & K Laboratories were used as starting materials. The H_2S was bubbled through $Ba(OH)_2$ solution and dried before use. The method given by Perrin et al.[14] was utilized to purify reagent grade CS_2. Reagent grade benzene was treated in succession with concentrated sulfuric acid, sodium carbonate solution, and anhydrous calcium chloride and then was distilled over phosphorus pentoxide. All other solvents were reagent grade chemicals and were dried before use.

Preparation of $H_2S{\cdot}xBS_2$. Metathioboric acid, $(HBS_2)_3$, was prepared by the method of Moissan[2]

$$6H_2S(g) + 3B(s) \xrightarrow{600-750\ ^\circ C} (HBS_2)_3(s) + {}^9/_2H_2(g) \tag{1}$$

and by the method of Stock and Poppenberg[3]

$$6H_2S(g) + 3BBr_3(soln) \xrightarrow[\text{benzene}]{\text{refluxing}} (HBS_2)_3(soln) + 9HBr(g) \tag{2}$$

In reaction 1 two volumes of $H_2(g)$ were added to each volume of $H_2S(g)$ to suppress dissociation of the latter in the hot zone. Samples isotopically enriched with 92% ^{10}B were prepared by reaction 1. Products from reactions 1 and 2 will be denoted I and II, respectively.

Stoichiometric amounts of metathioboric acid I or II and sulfur were heated in an evacuated, sealed Vycor tube in a resistance furnace between 350 and 500 °C for several days.

$$(x/3)(HBS_2)_3 + (x/16)S_8 = H_2S{\cdot}xBS_2 + [(x-2)/2]\,H_2S \tag{3}$$

Fourteen samples of 1.0–1.5 g were prepared by this method, the first 12 with natural boron, the 13th with 92% ^{10}B in $(HBS_2)_3$ from reaction 1, and the 14th with $(HBS_2)_3$ from reaction 2. In the first preparation the sealed tube was cooled to room temperature over a period of 24 h, in the fifth the tube was air quenched, and in the others the tubes were quenched in liquid nitrogen. The tubes were opened by breaking them in a dry nitrogen atmosphere in a glovebox. Samples were transferred to vials and stored in a desiccator over magnesium perchlorate.

Preparation of $H_2B_2S_5$. The method of Schmidt and Siebert[15] was used to prepare 3,5-diiodo-1,2,4,3,5-trithiadiborolane, $I_2B_2S_3$

$$2BI_3 + {}^3/_8S_8 \xrightarrow[25\ ^\circ C]{CS_2} I_2B_2S_3 + 2I_2 \tag{4}$$

The solvent was evaporated and excess I_2 was removed from the product by vacuum pumping at 50 °C; then the $I_2B_2S_3$ was vacuum distilled from the reaction flask at 95 °C. Dry hydrogen sulfide saturated with benzene vapor was passed into a refluxing solution of $I_2B_2S_3$ in benzene

$$2H_2S(g) + I_2B_2S_3(soln) \xrightarrow[\text{benzene}]{\text{refluxing}} H_2B_2S_5(soln) + 2HI(g) \tag{5}$$

The reaction was continued until HI could not be detected in the effluent gas. The benzene solvent was pumped off to yield a solid product. Solid products from reactions 3 and 5 will be denoted III and IV, respectively.

Spectra and Properties. Mass spectra were obtained with a Nuclide 12-90-G mass spectrometer. Samples were introduced into the mass spectrometer by means of a solid-sample inlet probe with a borosilicate glass sample container heated by a nichrome coil. Sample temperatures were measured with a Pt—Pt-10% Rh thermocouple. During introduction into the mass spectrometer some samples were exposed to the air for ca. 5–20 s and other samples were protected by a dry helium atmosphere. Mass spectra were observed at constant temperatures in the range from room temperature up to 400 °C. Temperatures were increased between observations such that the pressure in the ion-source region of the mass spectrometer was always below 10^{-4} Pa as measured with a Bayard-Alpert gauge. Ions were identified by counting. Perfluorokerosene was used as a counting aid for identification of ions with m/e greater than 300. Sources of metastable ions were identified with the equation

$$M^* = M^2(\text{fragment})/M(\text{parent}) \qquad (6)$$

Total intensity of a given ionic species was obtained by deconvolution to separate intensities, where ions due to different species had the same value of m/e, and then summation of intensities of all isotopic varieties of the given species. Such deconvolution was done both when natural boron was used and when 92% ^{10}B was used. The relative intensity was obtained by dividing the total intensity by the total intensity of the reference ion and then multiplying by 100.

Debye–Scherrer x-ray diffractograms of each solid product were obtained.

Infrared spectra were observed with a Perkin-Elmer Model 621 spectrometer; the samples were Nujol mulls between sodium chloride plates or carbon disulfide solutions in a 0.75-mm path length cesium iodide cell. The infrared spectrometer was calibrated from known absorptions of polystyrene film. Raman spectra of the powdered sample sealed in a melting point capillary were observed with a previously described instrument.[16]

Melting points were obtained with a Laboratory Devices Mel-Temp apparatus. Qualitative solubilities of product III were determined in xylene, bromobenzene, pyridine, carbon tetrachloride, carbon disulfide, chloroform, and dimethyl sulfoxide and of product IV were determined in carbon tetrachloride, carbon disulfide, and benzene. The reaction of each product with water was observed.

Chemical Analyses. Analyses were performed on samples obtained by reaction 3 from the seventh and eighth preparations and on the $(HBS_2)_3$ starting material from reaction 1. Prior to analysis each sample was powdered and extracted with carbon disulfide to remove excess sulfur. Total combined sulfur content was determined by oxidation with ammoniacal hydrogen peroxide and then precipitation as barium sulfate. Basic sulfur was analyzed by dissolving the sample in dilute hydrochloric acid, carrying the resulting H_2S with helium into an ammoniacal hydrogen peroxide solution, and then precipitating as barium sulfate. Boron was analyzed as boric acid by titration in the presence of mannitol.

Results

Intermediate Products: $(HBS_2)_3$ and $I_2B_2S_3$. Metathioboric acid I was white needle crystals. Metathioboric acid II initially was a light tan solid. Upon sublimation the latter yielded white needle crystals in the cold end of the tube and a tan solid residue at the hot end. Products I and II were 50–75% soluble in CS_2 or benzene. Both melted at 139 °C with decomposition.

Two chemical analyses of I gave 77.2 ± 1.4% sulfur and 14.8 ± 0.5% boron by weight. These results are consistent with a sample composition by weight of 99.7 ± 4.7% HBS_2, −8.3 ± 4.6% B_2S_3, and 8.8 ± 2.2% HBO_2; thus the sample was slightly H_2S rich. A mass spectrum of I at 60 °C is in Table I, which is discussed subsequently. The same ions reported by EWG[10] were observed with the same relative intensities within a factor of 2 except that the relative intensity of $(HBS_2)_3^+$ was lower by a factor of 3–5. The ion $H_2B_2S_2^+$ was not observed by EWG. Mass spectrometry of II before purification by sublimation gave the same ions and, in addition, Br-containing ions with relative intensities indicating 10% of the bromine had not been replaced from the BBr_3 starting material. Intensities of oxygen-containing ions from I or II indicated less than 0.5 mol % oxygen.

IR spectra in CS_2 and in CCl_4 of I and of purified II are in Table IV and are described in the IR and Raman spectrometry section. All were the same except that a shoulder at ca. 1030–1035 cm^{-1} was not observed with product I in CCl_4 and a line near 790 cm^{-1} was observed only in CS_2 solution. These spectra were in agreement with those previously reported.[4,9,13] The IR spectrum of I in Nujol mull contained lines at 1260, 1155, and 713 cm^{-1} which were not observed in the solution spectra.

The x-ray powder diffractogram of I was interpreted on the basis of a monoclinic unit cell in space group $P2_1/c$ with cell parameters a = 13.98 Å, b = 4.13 Å, c = 17.46 Å, and β = 115° 5′.

The $I_2B_2S_3$ from reaction 4 was light purple. After purification by vacuum pumping the $I_2B_2S_5$ became off-white, but then it became light violet after storage for several hours in the dark in a desiccator over magnesium perchlorate.

Final Products: $H_2S{\cdot}xBS_2$. The sealed tube exploded in the furnace during the third preparation of III; the sample was contaminated in the fourth, sixth, and tenth preparations. The following results were obtained with samples from the other preparations.

Products III from reaction 3 had properties independent of the method of preparation of the reactant $(HBS_2)_3$. At the preparation temperature the contents of the sealed tubes were liquids. When the sealed tube was cooled slowly to room temperature, in preparation 1, three phases resulted: transparent needle crystals, a tan solid, and a white solid. The needle crystals accounted for less than 2% of the sample and the white solid accounted for less than 10% of the sample. When the sealed tube was quenched in air, in preparation 5, an off-white to pale yellow solid was produced. When the sealed tube was quenched in liquid nitrogen, in preparations 2, 7–9, and 11–14, a yellow solid and a white solid formed. When the tube was warmed to room temperature, the white solid disappeared; then when the tube was opened, it popped. Presumably the white solid was H_2S; its pressure at room temperature in the sealed tubes was estimated to be 1–3 atm.

Product IV from reaction 5 was a soft, tan, claylike material after the benzene solvent was pumped off; then after a few hours it became hard. When IV was treated with CS_2, it became white and the CS_2 became pink.

Product III was insoluble in xylene, bromobenzene, pyridine, carbon tetrachloride, carbon disulfide, chloroform, and dimethyl sulfoxide though some reacted with the ethanol preservative in chloroform. Product IV was prepared in benzene solution; 1 day after the solvent was removed, IV would not redissolve in benzene and was insoluble in carbon tetrachloride and only slightly soluble in carbon disulfide.

The melting point of III was 405 ± 5 °C and of IV was 376 ± 10 °C. After cooling, III remelted at 402 ± 5 °C. Melting either III or IV produced a color change from white to yellow. Increasing the temperature of either melt caused the color to intensify, at ca. 460 °C to become red-brown and at ca. 500 °C to become amber.

Both III and IV reacted with water to produce H_2S, H_3BO_3, and sulfur. Three analyses of III from preparations 7 and 8 gave 14.5 ± 0.1% B, 65.4 ± 0.3% basic S, and 82.1 ± 0.5% total S by weight. These results are consistent with a sample composition of 85% $H_2S{\cdot}xBS_2$, x = 4.84 ± 1.75, 10.5 ± 1.1% B_2S_3, and 4.4 ± 0.8% B_2O_3.

The x-ray diffractograms of III and IV contained only diffuse lines varying in width from 0.3 to 0.7° in θ. Those lines with estimated relative intensity greater than 1 on a scale of 1–10 are given here with d spacings in Å corresponding to the

Table I. Mass Spectrometry of Vapors from Heated Samples of $(HBS_2)_3$ or $H_2S{\cdot}xBS_2$

	Relative intensities[a]			
Ion	Product I, 60 °C, 50 V	Product III, natural boron, 70 °C, 35 V	Product III, ^{10}B enriched, 80 °C, 50 V	Product IV, 80 °C, 40 V
S^+	64	74	210	96
HS^+	53	41	180	69
H_2S^+	115	110	350	130
S_2^+	48	44	120	63
BS_2^+	74 ± 10	24	82	65
HBS_2^+	61 ± 12	22	87	46
$H_2BS_2^+$	65 ± 12	8	12	5 ± 3
$B_2S_2^+$	17	5 ± 1		10 ± 6
$H_2B_2S_2^+$	56			
BS_3^+	9	12	23	27
HBS_3^+	15	100	100	100
$H_2BS_3^+$	7	1 ± 0.6	8	2 ± 0.4
$H_3BS_3^+$	3	2 ± 0.6	2	6
$B_2S_3^+$	30	4 ± 0.8	12	15
$HB_2S_3^+$	50	15	28	19
$B_2S_4^+$	8 ± 2	3 ± 0.7		5 ± 0.6
$HB_2S_4^+$	30		5 ± 2	2 ± 0.6
$H_2B_2S_4^+$	182	9 ± 1	7 ± 2	2 ± 0.6
$HB_2S_5^+$		6 ± 1	6 ± 3	
$H_2B_2S_5^+$	5	34	56	50
$B_3S_5^+$	2 ± 0.6			
$HB_3S_5^+$	4 ± 0.6			
$H_2B_3S_5^+$	6			
$HB_3S_6^+$	10			
$H_2B_3S_6^+$	2 ± 0.3			
$H_3B_3S_6^+$	100			

[a] Deconvoluted and corrected for isotopic abundances. Standard deviations greater than 10% are given.

centers of the lines (*d* spacing, relative intensity): for product III, 6.03, 3; 5.25, 5; 3.88, 5; 3.50, 10; 3.06, 2; 2.96, 2; 2.91, 4; 2.62, 4; 2.46, 5; 2.30, 1.5; for product IV, 6.02, 2.5; 5.40, 2.5; 3.88, 5; 3.51, 10; 3.07, 2.5; 2.92, 2.5; 2.57, 2.

Mass Spectrometry. Numerous mass spectra of the vapor from heated samples of III and IV were produced. In Table I are represented typical mass spectra of these products along with a mass spectrum of product I. The first column identifies the ion. The second column gives intensities of ions relative to the intensity of $(HBS_2)_3^+$ from the vapor of product I heated at 60 °C and ionized by 50-V electrons. The third and fourth columns give intensities of ions relative to the intensity of HBS_3^+ from the vapor of product III made with natural boron and with ^{10}B-enriched boron, respectively. The intensities in the third column were obtained with a sample temperature of 70 °C and 35-V ionizing electrons and those in the fourth column with a sample temperature of 80 °C and 50-V ionizing electrons. The fifth column gives intensities of ions relative to the intensity of HBS_3^+ obtained with 40-V ionizing electrons from the vapor of product IV heated at 80 °C. The mass spectra reported here were obtained with samples protected by dry helium during transfer. Ions containing one oxygen atom in place of a sulfur atom were observed, but their relative intensities were less than 0.5. When the sample was exposed to air during transfer, more intense oxygen-containing ions were observed as well as S_n^+ with n up to 8 and $H_2S_n^+$ with n up to 3.

When samples of products III and IV were vaporized above 150 °C in the mass spectrometer, more ions appeared and high molecular weight ions were observed. Table II gives a mass spectrum of a sample of products III which had been heated and decomposed in the mass spectrometer until the temperature of the sample was 195 °C, at which temperature the mass spectrum was observed, with 50-V ionizing electrons. Alternate columns give first the ion and then the intensity relative to that of HBS_3^+, deconvoluted and corrected for isotopic distribution as described previously. In cases where deconvolution gave standard deviations greater than 10%, such are reported. Some oxygen-containing ions were observed, the most intense being $B_8S_{15}O^+$ with relative intensity of 0.56 ± 0.05. Doubly charged ions $B_8S_{16}^{2+}$, $B_8S_{14}^{2+}$, and $B_2S_5^{2+}$ were observed with relative intensities of 3.1 ± 0.3, 3.9 ± 0.3, and 0.41 ± 0.3, respectively.

Metastable ions observed in mass spectra of samples of products III and IV are shown in Table III. Columns 1 and 2 give the observed and calculated m/e, respectively. The next three columns give the ionic precursor, the ionic fragment, and the neutral fragment, respectively.

IR and Raman Spectrometry. Infrared spectra of products I and II in carbon tetrachloride and carbon disulfide and of product I in Nujol mull are listed in Table IV. Units are cm^{-1}; relative intensities are given in parentheses by the symbols w for weak, m for moderate, and s for strong and the modifiers v for very, b for broad, and sh for shoulder. The first three columns give spectra of carbon disulfide solutions, the first column of product I made with natural boron, the second

Table II. Mass Spectrometry, with 50-V Ionizing Electrons, of Vapors from $H_2S{\cdot}xBS_2$ Heated at 195 °C[a]

Ion	Rel intens	Ion	Rel intens	Ion	Rel intens
S^+	220 ± 50	$B_3S_3^+$	9.7	$HB_4S_8^+$	0.86 ± 0.17
HS^+	94	$B_2S_4^+$	23	$B_5S_8^+$	6.5
H_2S^+	330	$HB_2S_4^+$	3.3 ± 0.6	$H_2B_4S_9^+$	2.1
BS^+	7.4 ± 3.1	$H_2B_2S_4^+$	5.6 ± 0.6	$B_5S_9^+$	4.5
HBS^+	9.7 ± 3.1	$B_3S_4^+$	15	$B_6S_9^+$	1.8
S_2^+	68 ± 13	$B_2S_5^+$	6.5	$B_5S_{10}^+$	0.30 ± 0.08
HS_2^+	7.6	$HB_2S_5^+$	1.7 ± 0.5	$B_6S_{10}^+$	1.4 ± 0.18
$H_2S_2^+$	12	$H_2B_2S_5^+$	76	$B_7S_{10}^+$	1.0
BS_2^+	60	$B_3S_5^+$	8.3	$B_6S_{11}^+$	1.5
HBS_2^+	61	$HB_3S_5^+$	0.59 ± 0.21	$B_7S_{11}^+$	1.5 ± 0.2
$H_2BS_2^+$	5.0	$B_4S_5^+$	2.0	$B_6S_{12}^+$	0.38 ± 0.08
$B_2S_2^+$	4.4 ± 0.8	$B_3S_5O^+$	0.66 ± 0.17	$B_7S_{12}^+$	11
$HB_2S_2^+$	4.1 ± 0.9	$B_5S_5^+$	0.41 ± 0.17	$B_8S_{12}^+$	1.0 ± 0.2
S_3^+	2.8	$B_3S_6^+$	46	$B_7S_{13}^+$	1.4 ± 0.2
HS_3^+	0.86	$HB_3S_6^+$	2.8 ± 1.1	$B_8S_{13}^+$	0.54
$H_2S_3^+$	0.20	$B_4S_6^+$	1.8	$B_8S_{13}O^+$	0.41 ± 0.08
BS_3^+	22	$B_5S_6^+$	0.97	$B_7S_{14}^+$	0.54
HBS_3^+	100	$B_3S_7^+$	1.7	$B_8S_{14}^+$	17
$H_2BS_3^+$	3.3	$HB_3S_7^+$	1.4 ± 0.2	$B_8S_{15}^+$	1.4
$H_3BS_3^+$	8.3	$B_4S_7^+$	7.3	$B_8S_{15}O^+$	0.56
$B_2S_3^+$	17	$B_5S_7^+$	3.5	$B_8S_{16}^+$	30
$HB_2S_3^+$	16	$B_4S_8^+$	4.8		

[a] Relative intensities are deconvoluted and corrected for isotopic abundances. Standard deviations greater than 10% are given.

Table III. Metastable Ions in Mass Spectra of $H_2S \cdot xBS_2$[a]

m/e				
Obsd	Calcd	Parent	Fragment	Neutral species
27.3	27.3	$B_2S_4^+$	S_2^+	B_2S_2
62.6	62.6	$H_2{}^{10}B^{11}BS_5^+$	$H^{10}BS_3^+$	$H^{11}BS_2$
63.4	63.4	$H_2B_2S_5^+$	HBS_3^+	HBS_2
478	477.8	$^{10}B^{11}B_7S_{16}^+$	$^{10}B^{11}B_7S_{14}^+$	S_2

[a] Calculations based on ^{11}B and ^{32}S except where otherwise noted.

Table IV. Infrared Spectra (cm^{-1}) of Products I and II[a]

CS_2 soln			CCl_4 soln		Nujol mull
I	I, ^{10}B enriched	II	I	II	I
2552 vw	2555 w	2553 w	2562 w	2566 w	2522 w
		1259 vw			1260 b, w
					1155 b, w
1050 sh	1055 vs	1055 sh	1052 sh	1057 sh	1050 sh
1041 m		1046 m	1045 m	1049 m	1041 s
1031 sh	1034 sh	1034 sh		1035 sh	
1018 s		1022 s	1019 s	1022 s	1017 vs
	954 vw				
938 w	942 w	942 w	940 w	943 vw	932 w
915 sh		923 sh		922 sh	916 sh
895 w	903 vs	898 w	900 w	901 w	902 sh
879 m	875 m	884 s	883 s	885 s	878 s
863 vs	855 m	867 vs	868 vs	869 vs	863 vs
	801 w				
787 m	784 w	793 m			783 m
					713 m
				333 vw	
257 w	259 w	256 vw		270 vvw	

[a] Key: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

column of product I made with 92% ^{10}B-enriched boron, and the third column of product II. The next two columns give spectra of carbon tetrachloride solutions, the fourth column of product I with natural boron and the fifth column of product II. The sixth column gives a spectrum of a Nujol mull of product I with natural boron.

Table V gives infrared spectra of product IV in carbon disulfide solution in column 1 and of Nujol mulls of product III with natural boron in column 2, of product III with ^{10}B-enriched boron in column 3, and of product IV in column 4. The units and codes are the same as in Table IV.

Table VI gives the Raman spectrum of product III from the 12th preparation with natural boron. The Raman frequencies are given first and then the corresponding relative intensities in the units and codes of Table IV.

Discussion

Chemical analysis, IR and mass spectrometry, and the x-ray structure show that the intermediate products I and II in this work were $(HBS_2)_3$ and were the same as that prepared by others. Less was learned about the intermediate product $I_2B_2S_3$, because it was unstable, apparently decomposing with loss of I_2.

Product III had a stoichiometry from chemical analysis corresponding to a formula in the range $H_2B_3S_7$–$H_2B_7S_{15}$. The stable composition in the H_2S–BS_2 system at room temperature and H_2S pressures of 1–3 atm is in this range, since these were the conditions in the sealed tubes. The white solid observed when the sealed preparation tubes were quenched with liquid nitrogen was taken to be H_2S. Its presence as a result of reaction 3 accounts for the excess pressure which caused the tubes to pop when they were opened. Product IV was probably $H_2B_2S_5$ in the benzene solution in which it was prepared by reaction 5. When the solvent was removed, the solid lost H_2S to produce an insoluble, high-melting solid with a composition near that of product III. The x-ray diffractograms indicate that solid IV was very similar to solid III.

Table V. Infrared Spectra (cm^{-1}) of Products III and IV

CS_2 soln	Nujol mull		
IV	III	III, ^{10}B enriched	IV
2552 vw			2543 w
	1523 s	1524 m	1524 w
	1517 sh	1519 sh	
	1290 vb, s	1306 b, m	
1259 vw			
	1153 b, vw		
	1080 b, w		
		1036 vs	
1008 m	1018 sh		1011 vs
1003 sh	1009 m		1002 vs
988 sh	992 m		
981 sh		983 w	
970 w		961 m	967 w
	941 w		955 vw
931 m	927 w		934 m
915 sh			
909 vs	905 sh	901 vs	902 vs
899 vs	891 sh		891 vs
882 sh	869 s		873 vs
860 sh	856 s	865 vs	860 vs
851 s			850 b, sh
	836 s	839 w	
773 w			
			764 w
726 w	717 m	718 m	720 w
660 vvw			
646 w			

Table VI. Raman Spectrum of III

Freq, cm^{-1}	Intens	Freq, cm^{-1}	Intens
2553	vw	841	w
2529	vw	807	vvw
2456	vw	770	vvw
2427	vw	660	vvw
2366	vw	522	w
2119	vw	517	w
2076	vw	489	w
2007	vw	440	vs
1870	vw	412	vvw
1653	vw	395	vw
1637	vw	373	vw
1571	vw	345	w
1012	vvw	329	w
962	vw	300	vw
915	vw	170	w
904	vw	162	w
897	vw	135	w
889	vvw	105	m
879	vw	76	s
874	vw	64	m

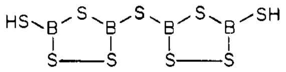
The mass spectrum of $(HBS_2)_3$ in Table I is in agreement with that published by EWG.[10] The mass spectra of $H_2S \cdot xBS_2$ contain no $(HBS_2)_3^+$, insignificant amounts of $(HBS_2)_2^+$, and relatively more $H_2B_2S_5^+$. The most massive ion in the mass spectra of $H_2S \cdot xBS_2$ was $H_2B_2S_5^+$; in the mass spectrum of $(HBS_2)_3$ the most massive ion is $(HBS_2)_3^+$. The $(HBS_2)_2^+$ ion is the most intense one in the mass spectrum of $(HBS_2)_3$ but is one of the least intense in the mass spectrum of $H_2S \cdot xBS_2$. The absence of $B_2S_2^+$ and $B_2S_4^+$ in the low-temperature mass spectrum of $H_2S \cdot xBS_2$ with 92% ^{10}B possibly means that both are artifacts of the deconvolution process with natural boron.

Differences in the molecular compositions of $H_2S \cdot xBS_2$ and $(HBS_2)_3$ are revealed by the mass spectral differences. Molecules of $H_2B_2S_5$ are important in the vapor of $H_2S \cdot xBS_2$, whereas they are of minor importance in the vapor of $(HBS_2)_3$. The predominant boron-containing molecule in the vapor over

$(HBS_2)_3(s)$ is $(HBS_2)_3(g)$, whereas the latter is not present in the vapor of $H_2S{\cdot}xBS_2$. Appearance of high molecular weight ions at temperatures above 150 °C indicates that the activity of H_2S has decreased due to loss of $H_2S(g)$ and $H_2B_2S_5(g)$ and that $H_2B_4S_9$ and $(BS_2)_n$ have become the important vapor species. The fact that $B_nS_{2n}^+$ high molecular weight ions were observed in this work from samples with compositions close to $BS_2(s)$ supports the proposal that the ions result from molecules of $(BS_2)_n(g)$.

The metastable decomposition of $H_2B_2S_5^+$ into HBS_3^+ relates the intense 108 and 107 peaks in the mass spectrum of $H_2B_2S_5$ to fragmentation of $H_2B_2S_5^+$. A relationship between $H_2B_2S_5^+$ and HBS_3^+ at 155 °C was reported by EWG,[10] and an unsuccessful special search for the metastable decomposition of $H_2B_2S_5^+$ into HBS_3^+ was reported.[11] Edwards et al.[12] previously reported the metastable decomposition of $B_8S_{16}^+$ into $B_8S_{14}^+$.

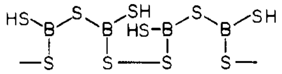
The high melting point, the insoluble nature, and the diffuse lines of the x-ray powder pattern indicate that $H_2S{\cdot}xBS_2$ is polymeric in the solid state. If it were a molecular solid with molecules, e.g., of $H_2B_4S_9$ with a structure based on that of $I_2B_2S_3$[15,17]



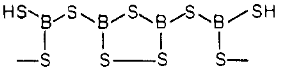
then its melting point should be lower than 400 °C; metathioboric acid, which has been shown to be a molecular solid, melts incongruently at 139 °C.[13] Melting samples III or IV and heating them above their melting points produce the same color changes one observes as sulfur is melted and heated to its boiling point; this property indicates that polymeric sulfur–sulfur bonds are present in the melt. Finally, polymerization is indicated by the fact that $H_2B_2S_5$, soluble in the benzene in which it is prepared, becomes insoluble after removal of the solvent.

The Raman emission at 440 cm^{-1} in Table VI was assigned to the S–S stretch by comparison with the S–S stretching frequencies assigned by others.[18-20] The fact that it was a very strong peak indicates that S–S bonds are important in solid $H_2S{\cdot}xBS_2$. The infrared absorptions in the region from 850 to 1055 cm^{-1} were assigned to B–S stretches by comparing spectra of I with natural boron and with 92% ^{10}B. The infrared absorptions of product IV in Table V at 2542 cm^{-1} for the Nujol mull and at 2552 cm^{-1} for the CS_2 solution and the Raman emission of product III in Table VI at 2553 cm^{-1} were assigned to the S–H stretch. Nujol mulls of product III did not show an absorption between 2500 and 2600 cm^{-1}. These observations support the conclusion that product IV contained relatively more H_2S than did product III and thus was nearer in composition to $H_2B_2S_5$. Probably the CS_2 solution contained $H_2B_2S_5$ molecules.

Two interactions between molecules of $H_2B_2S_5$ could cause them to polymerize and to lose H_2S to approach the composition $(BS_2)_n$: (1) a tendency to form intermolecular S–S bonds



and (2) loss of H_2S because of steric interaction of SH groups



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Registry No. I/II, 13703-97-4; III, 63148-36-7; IV, 61349-21-1; $I_2B_2S_3$, 13845-20-0.

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Contribution from the Division de Chimie, Département de Génie Isotopique,
Centre d'Etudes Nucléaires de Saclay, B.P. n° 2, 91190 Gif-sur-Yvette, France

Synthesis and Characterization of the Difluorotris(fluorosulfate) of Uranium(V): $UF_2(SO_3F)_3$[1]

W. W. WILSON, C. NAULIN, and R. BOUGON*

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A new U(V) compound, $UF_2(SO_3F)_3$, has been synthesized by the reaction of UF_6 and SO_3 in both the gaseous phase and $CFCl_3$ solution. This leads to a blue-green solid, the x-ray powder diffraction pattern of which has been recorded. Its oxidation state has been deduced from chemical analysis, the electronic absorption spectrum, and magnetic measurements. The environment around uranium is discussed from Raman and infrared spectra recorded at ambient and liquid nitrogen temperatures.

Introduction

As part of a continuing investigation of uranium fluorides in the highest oxidation state, the possibility of obtaining new derivatives was examined in which one or several fluorine atoms would be replaced by another univalent ligand. In this connection, the well-known ability of the fluorosulfate ion, SO_3F^-, to take the place of a fluoride ion[2,3] in many compounds prompted the search for the existence of any uranium fluo-