High Molecular Weight Boron Sulfides. III. A Mass Spectrometric Study of the Vaporization and Decomposition of Metathioboric Acid

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Abstract: Metathioboric acid, HBS_2, enriched in ^{10}B, has been vaporized in a mass spectrometer. The ions produced by electron impact have been identified, and their relative intensities, appearance potentials, and shutter effects have been measured. Six metastable decomposition reactions have been found. The results indicate that the acid HBS_2 vaporizes at temperatures below 100° in an incongruent fashion, giving primarily $H_2S(g)$ and $(HBS_2)_3(g)$ with some $H_3BS_3(g)$ and $H_2B_2S_5(g)$. These gases give parent ions and many fragment ions on electron bombardment. Two of the fragmentation reactions, that of the loss of neutral HBS_2 by $(HBS_2)_3^+$ to form $(HBS_2)_2^+$ and that of the loss of neutral BS_2 by $(HBS_2)_2^+$ to form $H_2BS_2^+$, have been established through metastable decompositions.

In his work on the spectra and thermodynamics of some boron sulfides and oxides, Greene[1] prepared $HBS_2(s)$ and $B_2S_3(gl)$ and studied the infrared spectra obtained from $HBS_2(s)$ and from the gaseous products of the reactions between $H_2S(g)$ and $B_2S_3(gl)$. He attributed some of the bands to $(HBS_2)_2(g)$ and some to a HBS_2–$(HBS_2)_3$ mixture. By studying the temperature coefficient of the infrared intensities, he also deduced some thermodynamic properties.

Greene and Gilles[2] have discovered high molecular weight boron sulfides in the vapor over slightly sulfur-rich, glassy B_2S_3 which had been prepared from solid metathioboric acid, HBS_2, by decomposition *in vacuo* at temperatures below 300°. The processes by which HBS_2 decomposes and by which the polymeric gaseous species are subsequently formed have not been well understood.

The purposes of the present mass spectrometric investigation were to clarify some features of the decomposition of solid HBS_2 and to study the gaseous species produced. Several goals were set: (1) to identify the neutral parent molecules in the gas; (2) to identify the fragmentation reactions in the electron bombardment source; (3) to establish the mode of vaporization and decomposition of HBS_2; and (4) to observe changes as the temperature was increased.

This paper gives the results of studies at temperatures below 100° on the identification, relative intensities, and appearance potentials of the observed ions; the extent to which their intensities are altered by a neutral-beam shutter; and the properties of some of their metastable decomposition reactions. Higher temperature changes in the mass spectrum are described.

Experimental Section

The preparation of ^{10}B-enriched HBS_2 followed the procedure described by Greene and Gilles.[2] The elemental boron used was an amorphous sample obtained from the Oak Ridge National Laboratory; its isotopic composition was 93% ^{10}B and 7% ^{11}B. The HBS_2 was obtained in the form of white needle crystals and was stored in a closed bottle in a desiccator.

For most of the mass spectrometric measurements, about 0.5 g of HBS_2 was used in a graphite Knudsen crucible which had been outgassed *in vacuo* at 1500°. The crucible contained an effusion orifice which was 0.4 mm in diameter and 6.3 mm long. Such an orifice restricts effusion and allows heating of the sample for a comparatively long time without significant decomposition and also directs a maximum fraction of the effusing material into the ionization chamber of the mass spectrometer. The crucible was heated by radiation from two tungsten filaments surrounding the crucible, and temperatures were measured with a Pt—Pt–10% Rh thermocouple, the hot junction of which was inserted into a well in the bottom of the crucible. The mass spectrometer was the same instrument described previously.

The intensity at each mass position was obtained by taking the difference between the signals with the shutter open and closed, thus eliminating the contribution from background gases. This intensity was apportioned among the contributing ions according to the computed isotopic distributions and the observed intensities at the lower mass positions in the usual stripping fashion. The reported intensity for each ion is the total intensity of all its isotopic ions.

The identifications of the ions were accomplished by mass number and isotopic intensity measurements as described in the earlier work.

The fractional intensity decrease, called the shutter effect, caused by closing the movable shutter was measured for each ion and its two most intense isotopic ions. The latter were measured to establish the extent to which permanent background gases contributed to the intensity.

Results

Ionic Species. Data were recorded over a several-month interval at temperatures up to 100°, during which period about 19.7% of the sample vaporized. If H_2S were the only volatile substance, the mass loss on converting HBS_2 to B_2S_3 would be 22.8%; because other gases were observed, the extent of conversion was less than 86%.

In the positive ion mass spectrum, recorded with the neutral beam ionized by 70-v electrons, 29 ions with formulas $H_iB_jS_k^+$, where i and $j \leq 3$ and $k \leq 6$, were observed and identified from their masses and isotopic distributions.

The results shown in Table I were obtained at a temperature of 60° when a few per cent of the sample had vaporized and less than 25% of the H_2S had been lost. The masses of the observed ions are listed in the first column; their formulas are listed in the next three columns; their intensities relative to the intensity

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[1] F. T. Greene, Ph.D. Thesis, University of Wisconsin, 1961; University Microfilm No. 61-5933, Ann Arbor, Mich.

[2] F. T. Greene and P. W. Gilles, *J. Am. Chem. Soc.*, **86**, 3964 (1964).

Table I. Ions Observed at 60° during Vaporization of $H^{10}BS_2$

Mass of prominent peak	No. of atoms/ molecule H	B	S	Rel intensity at 70 ev	AP, ev ± 0.3	Shutter effect, %
32	0	0	1	8.4	15.3	11
33	1	0	1	8.4	15.9	11
34	2	0	1	20.	10.2	10
64	0	0	2	8.0	19.	58
10	0	1	0	2.2	23.1	76
42	0	1	1	1.3	25.8	65
43	1	1	1	0.41	24.3	47
74	0	1	2	18.	16.4	76
75	1	1	2	16.	12.4	62
76	2	1	2	20.	11.8	67
106	0	1	3	2.5	16.1	74
107	1	1	3	3.0	11.6	65
108	2	1	3	1.7	14.0	77
109	3	1	3	1.3	9.9	21
84	0	2	2	2.4	22.1	87
85	1	2	2	6.1	16.6	84
116	0	2	3	9.4	13.1	89
117	1	2	3	17.	13.1	89
148	0	2	4	3.1	13.0	92
149	1	2	4	13.	11.4	94
150	2	2	4	98.	10.5	92
182	2	2	5	0.68	8.9	50
126	0	3	3	1.0	13.0	93
158	0	3	4	0.70	15.0	92
190	0	3	5	0.34	15.2	93
191	1	3	5	3.3	11.2	93
192	2	3	5	3.3	11.5	93
193	3	3	5	0.10		91
224	2	3	6	1.8	12.3	98
225	3	3	6	100.	9.3	95

of $(HBS_2)_3^+$ are listed in the fifth column. No ion containing only hydrogen and boron was observed, and no ion containing silicon was found. Several ions, not listed in Table I, which contained one oxygen atom in place of a sulfur atom also were observed, but their relative intensities were very low.

A negative ion spectrum taken with 100-v ionizing electrons revealed several negative ions, but their intensities were very low and their identification was made difficult by the lack of a background spectrum.

Appearance Potentials. Appearance potentials, AP, were measured for the ions by using the vanishing current method. In these measurements the energy scale was calibrated from Hg^+. In the sixth column of Table I are given the appearance potentials as measured at a crucible temperature below 100°. Some of the values were measured several times to establish the reproducibility. As a result of these measurements, it was concluded that the uncertainty in the measured appearance potentials was within ±0.3 ev.

Shutter Effect. Immediately after the sample had been introduced into the mass spectrometer, the shutter effect of most ions was effectively complete. After several days, however, the shutter effects of many ions were substantially smaller. This change occurred because of sublimation of matter from the crucible region into the ionization region where it was only partially condensable. These shutter effects were measured in order of decreasing mass over a period of 2 days at the same time as the relative intensities were measured and are given in the last column of Table I.

The shutter effect results on the peaks at masses 42 and 43 corresponding to BS^+ and HBS^+ were not reliable because the backgrounds at these masses were large. Measurements of isotope peaks were not possible because of CO_2^+.

According to their shutter effects, the ions appear to be in three groups: some, including $(HBS_2)_3^+$, with values of 85–95%; some, including H_2S^+, $H_3BS_3^+$, and $H_2B_2S_5^+$, with values of 10–50%; and the others with intermediate values.

Metastable Ions. Six diffuse peaks which were attributed to metastable ionic decompositions were observed. The intensities of these peaks relative to the intensity of $(HBS_2)_3^+$ taken as 100 were 0.2 or less. The reactions which produced the observed diffuse peaks were deduced by comparing each observed apparent mass m^* $(=m_2^2/m_1)$ with calculated values for all possible decompositions among the 29 ions in the mass spectrum. It was required that both the parent and fragment ions in the proposed decomposition have relatively high intensities and that the neutral products be reasonable chemical species. The decomposition reactions which were deduced are listed in Table II. The first two columns give the apparent and calculated masses. The next three sets of three columns give the identification of the reactions.

The appearance potentials of four metastable ions were measured and are listed in Table II with appearance potentials of the parent and fragment ions which are taken from Table I. For the reactions giving the transitions at 38.5 and 100.0 mass units, the metastable ion and the fragment ion have the same AP.

For the two reactions at 46.8 and 48.5 mass units, the metastable AP is lower than that for the suggested fragment, an occurrence for which no satisfactory explanation readily appears. For the other two reactions, AP measurements were not possible because the intensities were too low. These three different groups of reactions are designated in the last column of Table II.

Higher Temperature Changes. In order to follow the vaporization and the decomposition of HBS_2(s), numerous spectra at gradually increasing temperatures were taken with three different samples. The rate of increase of the temperature which was limited by the production of H_2S from the decomposition reaction was kept sufficiently slow so that the pressure was below the region of ion–molecule reaction. Between 100 and 250° numerous changes in the spectra occurred. The intensity of $(HBS_2)_3^+$ decreased until the ion was no longer observable; the intensities of $(HBS_2)_2^+$ and HBS_2^+ decreased appreciably, but did not vanish; the intensity of H_2S^+ was always largest; the intensities of $H_2B_2S_5^+$ and HBS_3^+ increased to a maximum at about 155° when they became second in importance only to H_2S^+. The high molecular weight species reported by Greene and Gilles began to appear at about 250°.

At higher temperatures, between 250 and 640°, other changes occurred. The ions $(HBS_2)_2^+$ and HBS_2^+ persisted with low intensities; the ion $B_2S_3^+$ continually increased in intensity; the high molecular weight boron sulfide ions showed maximum intensities in the range 400–600°; the ions tentatively identified by Greene and Gilles as containing silicon rose in intensity and persisted to higher temperatures than did the boron sulfides; and most of the ions tentatively identified as containing oxygen did likewise. Ultimately, in agreement with the previous work, the intensi-

Table II. Metastable Decompositions from $H^{10}BS_2$ below 100°

Mass		No. of atoms/molecule									AP, ev ± 0.3			Identification group[a]
		Parent			Fragment			Neutral						
Apparent	Calcd	H	B	S	H	B	S	H	B	S	Parent	Fragment	Metastable	
38.5 ± 0.08	38.50	2	2	4	2	1	2	0	1	2	10.5	11.8	11.8	A
46.8 ± 0.1	46.77	1	2	3	0	1	2	1	1	1	13.1	16.4	13.5	C
48.5 ± 0.08	48.49	1	2	4	1	2	2	0	0	2	11.4	16.6	14.9	C
71.3 ± 0.1	71.27	2	3	5	1	2	3	1	1	2	11.5	13.1	ND[b]	B
89.7 ± 0.2	89.66	2	2	4	0	2	3	2	0	1	10.5	13.1	ND[b]	B
100.0 ± 0.08	99.95	3	3	6	2	2	4	1	1	2	9.3	10.5	10.4	A

[a] (A) Identification established by mass, intensity, and AP; (B) identification indicated by mass and intensity; (C) identification indicated by mass and intensity, but contraindicated by AP. [b] Not detected.

ties of all high molecular weight species decreased until they became negligible in comparison with that of $B_2S_3^+$.

The course of the conversion of HBS_2 to B_2S_3 under the conditions of gradually increasing temperatures thus appears to include (1) a continual loss of H_2S(g); (2) an initial loss of $(HBS_2)_3$(g) which soon disappears from the gas; (3) later losses of $H_2B_2S_5$(g), H_3BS_3(g), and possibly $(HBS_2)_2$(g) which persist to surprisingly high temperatures; (4) the appearance of the high molecular weight ions; and (5) finally the disappearance of all gases except B_2S_3.

Discussion

The identification, intensities, appearance potentials, and shutter effects of the ions and the metastable reactions indicate the constituents of the vapor from HBS_2 and some of the ionic fragmentation processes. As Table I shows, the most intense ions originating from the crucible region below 100° are $(HBS_2)_2^+$; $(HBS_2)_3^+$; H_2S^+ and its fragments; the group $H_2BS_2^+$, HBS_2^+, and BS_2^+; and the pair $HB_2S_3^+$ and $B_2S_3^+$. The ions with the lowest appearance potentials are $H_2B_2S_5^+$, $(HBS_2)_3$, $H_3BS_3^+$, H_2S^+, and $(HBS_2)_2^+$.

The agreement of the measured appearance potential of H_2S^+ with its known value and the known decomposition of HBS_2 to B_2S_3 show that H_2S is a neutral molecule. The low appearance potential and high intensity of $(HBS_2)_3^+$, the absence of any higher molecular weight hydrogen species, and the fact that the trimer has the same composition as the solid sample show that it also is a neutral molecule. The low AP and the low shutter effect of $H_3BS_3^+$, the fact that H_3BS_3, orthothioboric acid, lies on the join containing H_2S, HBS_2, and B_2S_3 of the ternary H–B–S system, and the known volatility of its oxygen analog all indicate that H_3BS_3 is a neutral molecule of importance in this system.

Consider next $H_2B_2S_5^+$. This ion has the lowest AP, indicating that it is also a parent ion. The only higher molecular weight ions, and therefore those to which it might be related by a fragmentation process involving negative ion formation, all have much larger shutter effects, thus substantiating the conclusion that it is a parent ion.

The low AP, high intensity, and composition of $(HBS_2)_2^+$ suggest that it also is a parent ion. On the other hand, the observation of the metastable decomposition from the trimer to the dimer at 100 mass units, the agreement of the AP's for the metastable and the dimer ions, and the same shutter effect for the dimer and trimer all suggest that $(HBS_2)_2^+$ is a fragment. It is probable that the dimer molecule is not important at the temperatures below 100°.

The other ions of mass greater than 110 show appearance potentials greater than 11 ev and large shutter effects, and they most likely arise from fragmentation of $(HBS_2)_3^+$. The ions with masses between 50 and 108 also have AP's greater than 11 ev and intermediate shutter effects, and they probably arise from two or more processes from parent ions with different shutter effects, *e.g.*, $(HBS_2)_3^+$, $H_3BS_3^+$, and $H_2B_2S_5^+$. Consider for example the ion $H_2BS_2^+$. The metastable decomposition at 38.5 mass units is one source of the product at electron energies above 11.8 ev. The ionization efficiency curve for $H_2BS_2^+$ contains a slight break which may represent the onset of its formation from another parent ion.

The AP reported here for $B_2S_3^+$ is 13.1 ± 0.3 ev, and that given previously was 10.4 ± 0.8 ev. The difference arises from the fact that in the present studies the ion is a fragment from one of the acid species, and in the earlier, higher temperature studies on B_2S_3 the ion is a parent.

Inasmuch as both the initial reactant HBS_2 and the principal ultimate product B_2S_3 lie on the H_2S–B_2S_3 join, the *a priori* hypothesis is that the principal gaseous product of the decomposition will be H_2S. The results show indeed that H_2S(g) is the major product except for HBS_2(g) and its polymers, thus demonstrating the incongruent vaporization of HBS_2(s). Of the ions believed to be parents, only $H_2B_2S_5^+$ does not lie on this join, and its intensity is very small below 100°.

Work on the H–B–O system can be divided into two categories, one containing the several papers by Porter[3] and his co-workers on boroxine $H_3B_3O_3$(g) and its derivatives, and the other including work on the spectra and thermodynamic properties of HBO_2(g), $(HBO_2)_3$(g), H_3BO_3(g), B_2O_3(s), and B_2O_3(g) by Greene,[1] by Meschi, Chupka, and Berkowitz,[4] by Randall and Margrave,[5] and by White, Mann, Walsh, and Sommer.[6]

The present work appears to bear little relationship to that on boroxine and its derivatives. The principal species in the present study lie on the H_2S–B_2S_3 join or slightly to the sulfur-rich side, but the boroxine compounds are on the oxygen-deficient side of the corresponding join and could be obtained only in more reducing systems than those used here.

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(3) L. Barton, S. K. Wason, and R. F. Porter, *J. Phys. Chem.*, **69**, 3160 (1965), and earlier papers.

(4) D. J. Meschi, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **33**, 530 (1960).

(5) S. P. Randall and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **16**, 29 (1960).

(6) D. White, D. E. Mann, P. N. Walsh, and A. Sommer, *J. Chem. Phys.*, **32**, 488 (1960).

The most pronounced difference between the studies on the acids and on the thioacids lies in the temperature range. The present experiments were performed with $HBS_2(s)$ mostly at temperatures below 100°, where the principal species are $(HBS_2)_3(g)$ and $H_2S(g)$, but the experiments on the oxygen acids employed the reaction between water and boric oxide above 800°, where the principal species is $HBO_2(g)$. The great difference in the volatilities of the acids and thioacids arises presumably because of hydrogen bonding in the former.

The second difference is that the species found mass spectrometrically in the sulfur system are more numerous and more complicated than in the oxygen system.[4] The third difference is that metastable decompositions have not been reported for the oxygen acids. Finally, the extensive studies on the spectra and thermodynamic properties of oxygen species[4-6] have not yet been accomplished for the sulfur analogs.

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Bond Energies and the Interactions between Next-Nearest Neighbors. III. Gaseous and Liquid Alkanes, Cyclohexane, Alkylcyclohexanes, and Decalins[1]

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Abstract: The heats of formation of alkanes, cyclohexane, alkylcyclohexanes, and decalins are expressed as a linear function of seven structural parameters for both the gaseous and liquid states. Root-mean-square differences between calculated and experimental values are ±0.0185 kcal mole^{-1} bond^{-1} for 56 gases and ±0.0214 kcal mole^{-1} bond^{-1} for 63 liquids. In branched hydrocarbons the energy contributions by *gauche-n*-butane and *gauche–gauche* prime *n*-pentane structures are similar to those in the rotational isomers of normal paraffins. In some molecules the effect of a *gauche-n*-butane structure is accentuated by locking, where the H···H distance cannot be increased by internal rotation about any carbon–carbon bond without simultaneously decreasing the H···H distance in another interaction. The energetic effects of H···H interactions in ordinary and locked *gauche-n*-butane have been calculated independently by energy minimization.

In the first paper[3] of this series it was shown that inclusion of a single parameter, the next-nearest-neighbor interaction energy, removed practically all of the deviation from constancy in bond-energy calculations. Two other parameters, a trigonal interaction and a steric interaction between fifth-neighbor hydrogen atoms of the *gauche-n*-butane type, gave additional small but significant improvements. Molecules which were treated included the C_1 through C_7 alkanes, some cyclanes, diamond, the sulfanes, S_8, and some alkyl mercaptans, sulfides, and disulfides. This approach has been applied to many other molecules by McCullough and Good,[4] and by Skinner and co-workers,[5-10] and the theoretical basis of the method has been explored.[11,12]

The present study was undertaken to obtain more accurate equations for the heats of formation of saturated hydrocarbons and to obtain further information about steric interactions in these molecules. We were also interested in applying the method to liquids as well as gases.

Treatment of Data

Our general approach was to adjust the coefficients in linear equations for heats of formation (similar to eq 33 and 35 of ref 3) so as to give optimum correlation with the experimental data. The equations were of the form

$$-\Delta H_f{}^\circ = A_K K + A_n n + A_X X + A_T T + A_S S + A_Z Z + A_L L \quad (1)$$

The *A*'s are the coefficients to be determined, and *K*, *n*, etc., are the structural parameters. *K* reflects differences between the numbers of C–H and C–C bonds; it is 1 for acyclic, 0 for unicyclic, and −1 for bicyclic compounds. *n* is the number of carbon atoms; *X* is the number of pairs of next-nearest-neighbor carbon atoms. For the alkanes beyond methane it is conveniently calculated by eq 8 of ref 3. *T* is the number of trigonal

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[1] Abstracted in part from the Ph.D. dissertation of A. J. Kalb, University of California, Davis, Calif., 1963.

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