responds to β_{101} and the slope of 576 corresponds to β_{201}. Thus

$$\beta_{101} = [C(NH_2)_3P_4O_{13}{}^{5-}] \div$$
$$[C(NH_2)_3{}^+][P_4O_{13}{}^{6-}] = 10^{1.84} \pm 10^{0.10} \quad (12)$$

$$\beta_{201} = [(C(NH_2)_3)_2P_4O_{13}{}^{4-}] \div$$
$$[C(NH_2)_3{}^+]^2[P_4O_{13}{}^{6-}] = 10^{2.76} \pm 10^{0.10} \quad (13)$$

Models can be constructed in which the guanidinium ion is located in a plane above or below that of the phosphorus atoms in a coiled structure. This structure appears feasible because it can account for the ease of bonding two guanidinium ions. In an alternate structure the tetraphosphate is coiled around the guanidinium ion in a plane perpendicular to that of the tetraphosphate ion. It is possible that the latter structure is predominant in the 1:1 complex and the former in the 1:2 complex. Either conventional linear hydrogen bonds or less localized bonds between nitrogen atoms and one or more oxygen atoms are possible. Related studies of various amine–polyphosphate systems are in progress.

High Molecular Weight Boron Sulfides. II. Identification, Relative Intensities, Appearance Potentials, and Origins of the Ions

BY FRANK T. GREENE AND PAUL W. GILLES

The new boron sulfides having molecular weights extending to above 850 have been further investigated by mass spectrometric techniques. Slightly sulfur-rich B_2S_3 samples were prepared from natural and B^{10}-enriched boron, were chemically analyzed, and were vaporized in a mass spectrometer at temperatures between 300 and 600°. Ions were formed by electron impact and were identified by mass number, isotopic intensity distribution, and isotopic shift. The ions are in three series. Series I consists of 37 ions containing boron and sulfur alone; series II, 20 ions containing also a third element, tentatively identified as silicon; and series III, 15 ions containing a different third element, probably oxygen. Time, temperature, and electron energy dependences indicated that several neutral molecules vaporized from the sample and that on electron impact each produced an ion which decomposed predominantly without boron loss to produce the observed ions. It is suggested that the BS_2 polymers B_8S_{16}, B_7S_{14}, $B_{10}S_{20}$, B_9S_{18}, and B_6S_{12} are the neutral parent molecules and that they are obtained in equilibrium with the viscous B_2S_3 liquid containing 0.5 to 1.0% excess sulfur, about 1% silicon, and about 1% excess oxygen. Approximate values for the appearance potentials for many of the ions were obtained. The heat of vaporization of B_2S_3 was measured as 36 ± 5 kcal./mole. The partial molal heats of vaporization of the higher molecular weight neutral parents from the sample are about 55 ± 10 kcal./mole, appreciably higher than the heat of vaporization of B_2S_3.

Introduction

The authors have recently reported the discovery of two new classes of boron sulfides with molecular weights up to 850 mass units.[1] Further mass spectrometric investigations using both normal and B^{10}-enriched boron have supported the original conclusions as to the existence of polymeric boron sulfides and have provided information on the appearance potentials of the ions, and on the identity and heats of vaporization of the neutral substances arising in the vaporization reaction. A third class of boron sulfide ions has also been detected. It is the purpose of this paper to present the new information for these complex systems.

Experimental

The condensed boron sulfide samples were prepared in silica tubing by the reaction between boron and dry, flowing H_2S at about 700° to form HBS_2, which was then thermally decomposed to B_2S_3 and H_2S. The latter reaction was performed in silica or graphite containers under vacuum at a maximum temperature of 300°. The resulting sample was a glass and contained an excess of sulfur compared to stoichiometric B_2S_3. In a few cases a part of this excess sulfur was removed by reaction with H_2 followed by a thorough flushing with purified He. The normal boron was from a high purity crystalline sample furnished by the U. S. Borax Company; the 93% B^{10}-enriched boron was an amorphous sample obtained from the Oak Ridge National Laboratory.

The boron sulfide samples were analyzed by allowing them to react with a large excess of water to form H_2S, S, and H_3BO_3. The H_2S was flushed from the solution with nitrogen and trapped in a train containing 4% ammoniacal hydrogen peroxide. The resultant solution was heated to destroy the peroxide and to complete the conversion of sulfide to sulfate, which was precipitated as $BaSO_4$.

The original solution could have been divided for the free sulfur, boric acid, and impurity analyses, but in actual practice fresh samples were used for the three analyses. The free sulfur was in colloidal form; it could be readily oxidized to sulfate with heated ammoniacal peroxide after which it was also determined as $BaSO_4$. Treatment of the $BaSO_4$ with HF followed by igniting and weighing showed that the precipitate did not carry SiO_2. The boric acid was analyzed by titration with 0.1 N NaOH using mannitol as a complexing agent. Silicon was determined as SiO_2 by the standard method involving heating to dryness twice with HCl, filtering, igniting, weighing, heating to dryness with HF, igniting, and weighing.

For the mass spectrometric measurements, the boron sulfide samples were placed in previously outgassed graphite Knudsen cells having 1.0-mm. orifices and heated by radiation from a W filament to between 300 and 600°. Temperatures were measured by a Pt–Pt, Rh thermocouple. At the lower end of this temperature range the sample is a glass and at the higher end, a viscous liquid. The effusing molecules were ionized by electron impact and analyzed with a Nuclide Analysis Associates HT series, 12 in., 60°, single focusing mass spectrometer having a resolution of about 1000. An electron multiplier was used as the detector. Most of the spectra were obtained with 50–70-v. electrons, and all were obtained with moderately rapid magnetic scans. The crucible region and ion source were operated at pressures of less than 5×10^{-6} and 1×10^{-6} torr, respectively, and were separated by a movable slit or shutter which could be used to stop the beam or to scan it. Shutter profiles and spectra taken with different ion source potentials revealed that the observed ions were produced from neutral molecules which had been vaporized from the sample in the crucible.

(1) F. T. Greene and P. W. Gilles, *J. Am. Chem. Soc.*, **84**, 3598 (1962).

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES FOR IDENTIFICATION OF $B_8S_{14}^+$

Mass no.	Observed	$B_2S_{16}^-$	$B_5S_{15}^+$	$B_8S_{14}^+$	$B_{11}S_{13}^+$	$B_{14}S_{12}^+$	$B_{17}S_{11}^+$	Observed	Calculated for $B_8S_{14}^+$
				Natural boron — Calculated for				93% enriched boron-10	
528	1.8							100.0	100.0
529	2.6							73.3	71.4
530	4.0			0.2	0.3	0.4	0.4	90.2	85.4
531	5.3		1.0	1.5	1.8	1.8	1.7	52.6	48.4
532	13.1	4.8	8.3	8.4	7.8	7.0	6.2	34.4	32.6
533	34.3	42.8	37.1	29.9	24.7	20.7	17.6	16.1	15.2
534	70.8	100.0	86.4	69.0	56.2	46.7	39.4	7.6	7.5
535	100.0	42.4	100.0	100.0	90.2	79.5	69.5	3.1	3.0
536	84.3	70.2	63.8	90.1	100.0	100.0	95.3	1.4	1.2
537	59.3	18.1	57.9	60.7	78.3	92.4	100.0	0.6	0.4
538	40.7	23.4	22.2	42.0	50.4	65.1	80.5		
539	17.9	4.6	17.1	18.4	29.8	39.0	51.6		
540	10.0	4.8	4.7	10.7	13.2	20.6	28.5		
541	3.6	0.8	3.1	3.4	6.5	8.9	13.8		
542	2.1	0.7	0.6	0.4	2.2	3.9	5.6		
543					1.0	1.2	2.3		

Calculations of intensities needed for the identification were performed on an IBM 1620 computer. Isotopic abundances used were: B^{10} 0.188, B^{11} 0.812 for the natural samples; B^{10} 0.93, B^{11} 0.07 for the enriched sample; and S^{32} 0.9502, S^{33} 0.0076, S^{34} 0.0422.

Results

Analytical.—Several different samples have been prepared and numerous spectra have been obtained. The analysis of a typical sample showed it to be 77.9 ± 0.5% sulfide, 0.7 ± 0.1% sulfur, 17.3 ± 0.1% boron, and 1.3 ± 0.2% silicon. The remaining 2.8% was probably oxygen introduced during the preparation of the sample. A wet qualitative analysis showed none of the other common metals. The theoretical composition of B_2S_3 is 18.36% B and 81.64% S. Thus the sample can be regarded as about 95% B_2S_3, 0.7% excess sulfur, 2.7% SiO_2, and 1.4% excess oxygen.

General Characteristics.—The mass spectra obtained consisted of a large number of well-resolved peaks extending to beyond 850 mass units. These peaks were grouped into bands, each of which originated from ions of a particular stoichiometry. The individual peaks arose from the one or more isotopic compositions possible for an ion with a given chemical composition. In the normal boron spectra there were prominent intervals between bands of 11, 32, 15, and 17 mass units. Two series of interleaving bands were easily distinguishable, with bands of the second system appearing 17 mass units above or 15 below the bands in the first. Within each series, the bands differed from adjacent ones by the addition or subtraction of a boron or sulfur atom. The enriched B^{10} spectra also showed bands but, as expected, with radically different envelopes from the normal boron spectra. The same two series of bands, shifted to lower mass, appeared in the B^{10} spectra, and, in addition, a third series of bands was evident. The prominent intervals between bands became 10, 32, 14, 18, 6, and 26 mass units. The system II bands lay 18 mass units above or 14 below those of the nearby system I bands. The system III bands were 6 mass units below or 26 mass units above those of system I.

Identification of the Ions.—The identity of the ions was established by their mass numbers, the intensity distribution within the bands, and the isotope shifts.

The mass numbers were unambiguously obtained by counting individual lines in many spectra. Because two B^{11} atoms and one B^{10} atom make the same contribution to the mass number as one S^{32} atom, the mass number of ions from the natural boron samples is insufficient for the identification, and the intensities were used. Table I contains a comparison of the observed relative intensities of the lines in the band centered on mass 535 in the natural boron spectrum with those calculated for $B_2S_{16}^+$, $B_5S_{15}^+$, $B_8S_{14}^+$, $B_{11}S_{13}^+$, $B_{14}S_{12}^+$, and $B_{17}S_{11}^+$, all of which would give a band in this region. The first column gives the mass; the second, the normalized observed intensity for the natural sample; the next six, the normalized calculated intensities for each of the six ions. The observed values were taken as the peak heights from moderate speed magnetic scans. The excellent agreement between the calculated and observed intensities for $B_8S_{14}^+$ identifies the ion and indicates that it is probably the only important species in the center of that mass region. The overlap of a subsequently identified weak band in system III is indicated by the too small intensity decrease at the low mass end of the band.

The identity of the system I ions, which had previously been obtained with natural boron samples in the fashion just described, has been fully confirmed through the use of B^{10}-enriched samples. For ions lighter than $B_9S_{16}^+$ or $B_{10}S_{14}^+$, the most abundant isotopic species in the enriched sample contains no B^{11}, S^{33}, or S^{34}. Hence, the mass number of the most intense line, which is also the one of lowest mass, gives immediately the ion formula. The intensity comparison for the enriched sample is also shown in Table I for $B_8S_{14}^+$.

The spectra contain several examples of obviously overlapping bands, but many appear to be free from such interference. The agreement between the observed and calculated intensities of $B_8S_{14}^+$, which is typical of many bands, limits the possible abundance of other bands to a few per cent in this case. The enriched boron spectrum allows an even more sensitive test for the purity of a band. An ion in the same mass region as another but having three more boron atoms and one fewer sulfur atom would appear two mass units lower. This mass is in a region with little overlap arising from bands 6 or 10 mass units removed.

TABLE II

IDENTIFICATION OF BORON SULFIDE IONS AND THEIR RELATIVE INTENSITIES IN FRESH SAMPLES

Series I (700°K.)

Mass of prominent peak		No. of atoms/molecule				
Natural B	Enriched B	B	S	Si	Ox	Intensity
43	42	1	1	0	0	6.0
75	74	1	2	0	0	38.0
107	106	1	3	0	0	4.3
86	84	2	2	0	0	7.1
118	116	2	3	0	0	100.0
150	148	2	4	0	0	11.1
182	180	2	5	0	0	1.1
129	126	3	3	0	0	6.4
161	158	3	4	0	0	9.1
193	190	3	5	0	0	2.9
225	222	3	6	0	0	1.5
236	232	4	6	0	0	4.0
268	264	4	7	0	0	3.4
300	296	4	8	0	0	1.3
246	241	5	6	0	0	0.5
279	274	5	7	0	0.	2.2
311	306	5	8	0	0	4.0
342	338	5	9	0	0	1.4
353	348	6	9	0	0	1.1
385	380	6	10	0	0	0.7
417	412	6	11	0	0	1.1
396	390	7	10	0	0	1.2
428	422	7	11	0	0	3.5
460	454	7	12	0	0	6.2
492	486	7	13	0	0	1.9
471	464	8	12	0	0	1.1
503	496	8	13	0	0	5.2
535	528	8	14	0	0	10.3
567	560	8	15	0	0	5.1
514	506	9	13	0	0	0.8
546	538	9	14	0	0	2.0
578	570	9	15	0	0	1.0
589	580	10	15	0	0	1.0
621	612	10	16	0	0	2.6
653	644	10	17	0	0	1.4
685	678	10	18	0	0	0.5
698	688	11	18	0	0	0.3

Series II (700°K.)

Mass of prominent peak		No. of atoms/molecule				
Natural B	Enriched B	B	S	Si	Ox	Intensity
135	134	1	3	1	0	0.9
210	208	2	5	1	0	1.1
242	240	2	6	1	0	0.6
253	250	3	6	1	0	3.0
285	282	3	7	1	0	0.6
296	292	4	7	1	0	0.3
328	324	4	8	1	0	1.0
360	356	4	9	1	0	0.2
371	366	5	9	1	0	0.8
403	398	5	10	1	0	1.3
446	440	6	11	1	0	0.3
488	482	7	12	1	0	0.7
520	514	7	13	1	0	2.5
552	546	7	14	1	0	1.3
595	588	8	15	1	0	1.7
627	620	8	16	1	0	1.0
606	598	9	15	1	0	0.7
638	630	9	16	1	0	0.5
681	674	10	17	1	0	0.4
713	706	10	18	1	0	0.3

Series III (861°K.)

Mass of prominent peak		No. of atoms/molecule				
Natural B	Enriched B	B	S	Si	Ox	Intensity
59	58	1	1	0	1	2.10
102	100	2	2	0	1	1.36
145	142	3	3	0	1	0.47
220	216	4	5	0	1	0.39
263	258	5	6	0	1	0.67
295	290	5	7	0	1	0.37
327	322	5	8	0	1	0.12
337	332	6	8	0	1	0.15
380	374	7	9	0	1	0.18
412	406	7	10	0	1	0.31
444	438	7	11	0	1	0.25
455	448	8	11	0	1	0.09
487	480	8	12	0	1	0.04
530	522	9	13	0	1	0.14
562	554	9	14	0	1	0.06

Thus far 37 ions of series I containing boron and sulfur have been positively identified and are listed in Table II with their total relative intensities obtained with a fresh sample at $700 \pm 5°K$. The first two columns contain the mass of the most intense line in the band for the natural and enriched samples, respectively; the next four columns contain the formula of the ion; and the last column contains the intensity of the entire band relative to that for $B_2S_3^+$. The sulfur to boron ratio for most of the ions is slightly greater than 1.5, but less than 2.0.

Ions in series II and III contain other elements, and their identification is still uncertain, although it appears that they contain silicon and oxygen, respectively. On the basis of the prominent mass intervals of 17 and 15, boron sulfur hydroxides were originally incorrectly suggested[1] as composing series II, and tentative identifications were proposed on that basis. But the isotope shift, which indicates the number of boron atoms, was one mass unit less than expected. The number of sulfur atoms cannot be fixed with the present information, and hence the mass of the unknown component is uncertain by some multiple of 32. The ion at 135 shows an isotope shift of one mass unit corresponding to the existence of one boron atom in the ion; the ion at 210 contains two boron atoms. Hence the third component has mass 28, 60, or 92 depending on whether the ion at 135 contains three, two, or one sulfur atom. The presence of silicon in the sample and rough intensity comparisons indicate that silicon is probably the third element in system II ions. On this basis 20 ions thus far identified are also listed in Table II with their relative intensities.

The ions in series III are much weaker than those in series II, and are overlapped in the natural boron spectrum by those in the first two series. Consequently, it was not possible to determine the number of boron atoms in the series III ions by the method used for series I and II, nor was it possible to determine their composition from the intensity distribution within the bands. Calculations based only on the ionic masses suggest that the unknown radical has a mass of $16 + n32$, indicating that it may be oxygen. This suggestion is consistent with the probable oxygen content of the sample. On this basis, 15 ions of series III are also listed in Table II with their tentative identification and intensity. The intensities for these ions were obtained from a different spectrum but have been corrected to the same intensity scale used for series I and II.

Time Effects and the Identification of Neutral Species.—Prolonged vaporization of the samples produced a decrease in the intensities of all the higher

molecular weight species in series I and II relative to $B_2S_3^+$, and an ultimate disappearance of all the higher ions. Because both the sample and most of the high molecular weight ions were rich in sulfur relative to $B_2S_3^+$, it seemed that the decrease of their intensities with time might be understandable in terms of a progressive decrease of the sulfur activity. To investigate this possibility, two experiments were made at the same temperature of 754°K. with a sample before and after extensive vaporization. The ratios of the intensities I^{15}/I^{11} in the two different experiments are listed in the fourth column of Table III for series I and II ions identified in the first three columns.

TABLE III
PROPERTIES OF BORON SULFIDE IONS

B	S	Si	$I^{15}/I^{11\ a}$ ($\pm 10\%$)	Appearance potential[b] (e.v. $\pm$ 0.8)
2	3	0		10.4
3	6	0		12.4
4	6	0	0.067	9.5
4	7	0	0.049	10.0
4	8	0	0.055	
5	7	0	0.050	
5	8	0	0.048	10.7
6	9	0	0.053	
6	10	0	0.048	
7	10	0	0.040	
7	11	0	0.031	9.1
7	12	0	0.031	9.1
8	12	0	0.026	
8	13	0	0.018	8.3
8	14	0	0.016	8.3
8	15	0	0.017	8.3
9	13	0	0.013	8.8
9	14	0	0.011	8.8
10	15	0	0.0096	
10	16	0	0.0093	8.2
2	5	1	0.071	9.7
2	6	1	0.054	
3	6	1	0.082	10.1
3	7	1	0.046	
4	8	1	0.058	8.5
4	9	1	0.044	
5	9	1	0.068	10.0
5	10	1	0.048	
7	12	1	0.030	9.3
7	13	1	0.019	9.1
7	14	1	0.022	9.1
8	15	1	0.019	7.9
8	16	1	0.015	7.9
9	15	1	0.013	8.3
9	16	1		8.3

[a] The temperature was 754°K. for the I^{15}/I^{11} measurement.
[b] The temperature was 676°K. for the appearance potential measurement.

The fact that these ratios are the same for large ions in series I containing the same number of boron atoms indicates that they are produced primarily by the fragmentation of a common parent molecule, and that the parent is different for ions of different numbers of boron atoms. It is not certain whether the parent has the same number of boron atoms as the fragment.

The nature of the parent for each set of ions cannot be definitely established from the present information, but two kinds of evidence suggest that the parents are polymers of BS_2. No ion of the type $B_xS_{2x}^+$ nor any with a higher S:B ratio appears with great intensity;

and the most intense ions for the series $B_xS_y^+$ with x = 7 and 8 are $B_xS_{2x-2}^+$ containing one S_2 group fewer than in $(BS_2)_x$.

On the basis that the parent molecules are BS_2 polymers and that equilibrium exists in the liquid state and also between the liquid and vapor according to the reaction

$$\frac{x}{2}\ B_2S_3(\text{solution}) + \frac{x}{2}\ S(\text{solution}) = B_xS_{2x}(g) \qquad (1)$$
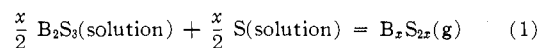
the equilibrium constant for a given x is given by the expression

$$K = p_{B_xS_{2x}}/a_{B_2S_3}^{x/2}a_S^{x/2} \qquad (2)$$

For the two previously mentioned experiments conducted before and after the extensive vaporization, the equilibrium constant is the same for a given species because the temperature is the same.

The B_2S_3 can be regarded as the solvent in which a small quantity of sulfur is dissolved. If the activity of B_2S_3 does not change greatly, the pressures of the gaseous polymers will vary with the $x/2$ power of the sulfur activity. Hence, a plot of the logarithm of the intensity ratio for the ions before and after the vaporization against $x/2$ will be straight line and the slope is the logarithm of the ratio of the activity of sulfur before and after the vaporization. The intercept is the logarithm of the ratio of the sensitivities of the instrument in the two experiments. If eq. 1 is rewritten in terms of S_2, the stoichiometric coefficient is $x/4$ instead of $x/2$. The plot would be made against $x/4$, and a straight line will also result. Actually a linear plot shows only that c in the formula $B_xS_{2x\ +\ c}$ is constant; as indicated previously, we believe it to be zero. The quantity x, which is characteristic of the parent molecule, is related to the boron number of the ions through the primary fragmentation process. Inasmuch as this process is not known, we assume in the following that x is also the boron number of the ions. If boron-containing neutral groups are produced in the primary fragmentation process, the straight line will only be shifted horizontally.

The intensity ratio data for ions with the same number of boron atoms were averaged and plotted against $x/2$. The points for x = 6, 7, 8, 9, and 10 fell reasonably well on a straight line whose slope indicated that during the experiments the activity of monatomic sulfur had decreased to about 0.4 of its value before the experiments, corresponding to a diatomic sulfur activity decrease to about 0.16 of the initial value. The results of this equilibrium treatment strongly suggest that equilibrium exists within the condensed state and also between it and the gaseous parent molecules.

The data for ions containing three, four, or five boron atoms do not lie on the extension of the straight line, but rather are nearly the same as for the B_6 ions. It appears as if these are principally fragments, possibly arising predominantly from $(BS_2)_6$ or from a combination of B_3, B_4, and B_5 parents and fragments from higher species.

The series II ions exhibit approximately the same kind of behavior as series I. Usually the intensity ratios of series II ions are nearly the same as those of series I ions containing the same number of boron atoms. Thus it appears as if the number of sulfur

atoms reacting according to eq. 1 or its equivalent for series II ions is the same for members of both series with the same number of boron atoms, possibly because the series II ions contain an added SiS_2 or SiS group.

Appearance Potentials.—Appearance potentials for $B_2S_3^+$ and $B_8S_{15}^+$ were obtained by the method of Lossing, Tickner, and Bryce.[2] Background mercury was used as a calibrating gas. Plots were made of about a dozen values of log I_V/I_{56} against the electron energy where I_V is the ion intensity at each electron energy V, and I_{56} is the ion intensity at 56 v. At energies near the appearance potentials the curves were straight, and from the voltage differences, the appearance potential for $B_2S_3^+$ was obtained as 10.4 ± 0.2 and for $B_8S_{15}^+$ 8.3 ± 0.5 e.v.

Additional approximate appearance potentials for some of the large ions of series I and II were obtained by the same method from magnetic scans at 767°K. at 56, 14, 12.5, and 12 e.v. in which the calibrating ion was $B_8S_{15}^+$ rather than mercury. The values are probably accurate to about ± 0.8 e.v., but the difference between any pair is probably reliable to about 0.4 e.v. The results are given in the fifth column of Table III.

The appearance potential values do not in themselves reveal the identity of the neutral parent molecules. The appearance potential values for the large ions are sufficiently small so that they could be parent ions. Yet the values for ions containing the same number of boron atoms are very nearly the same, probably because each arises from the unimolecular decomposition of a common parent ion that is formed in the primary ionization process.

Temperature Coefficients and Heats of Vaporization.—In a separate series of experiments extending from 633 to 722°K., an approximate value for the heat of vaporization of B_2S_3 was obtained as 36 ± 5 kcal./mole. This result is in agreement with the value of 36 ± 3 obtained by Greene.[3]

Spectra were taken at several different temperatures between 731 and 809°K. in order to obtain approximate temperature coefficient measurements for the other species. Interpretation of the results was complicated by the changing composition of the sample, and heats of vaporization could not be obtained directly. The partial molal heats of vaporization of the series I and series II boron sulfides from the sample are of the order of 55 ± 10 kcal./mole and thus are appreciably larger than the heat of vaporization of B_2S_3. Also, the temperature coefficients of the intensities for those ions previously assigned to a common parent are the same within experimental error.

Discussion

The present mass spectrometric studies indicate the existence of many high molecular weight ions and at least several different neutral molecules containing boron and sulfur; boron, sulfur, and silicon; and boron, sulfur, and oxygen. They have been obtained from the vaporization of a viscous B_2S_3 liquid containing 0.5 to 1.0% excess sulfur, about 1% silicon, and about 1% excess oxygen.

These new high molecular weight boron sulfides are important species; the total intensity of the larger ions

is about one-half that of B_2S_3. If the total ionization cross sections are approximately proportional to the number of atoms, the total pressure of the high molecular weight molecules is approximately 10% of the B_2S_3 pressure. Based on the assumption that boron atoms are not lost in the primary electron impact process, the data indicate that the principal boron sulfide species are B_2S_3, B_8S_{16}, B_7S_{14}, $B_{10}S_{20}$, B_9S_{18}, and B_6S_{12} in order of abundance.

Sommer, Walsh, and White[4] have previously examined the mass spectrum of the gases arising from a system containing boron and ZnS. They observed B^+, BS^+, BS_2^+, $B_2S_2^+$, and $B_2S_3^+$, but did not report any high molecular weight ions. Our studies revealed that the high molecular weight ions disappear as the sulfur activity decreases; they failed to observe them, probably because their system did not have a sufficiently high sulfur activity.

A consistent, though incomplete, picture of the vaporization and electron impact phenomena can be obtained by a consideration of the time dependences, the appearance potentials, and the temperature coefficients together. The first and third experiments indicate that ions with the same number of boron atoms originate predominantly from a single neutral parent which is different from the parent for other isoboron sets of ions. The appearance potentials indicate that ions with the same number of boron atoms arise primarily from the decomposition of a single parent ion. The neutral parent species have not been firmly identified, but that they are BS_2 polymers is likely. Similarly, whether the electron impact on a neutral parent causes only simple ionization or loss of sulfur, boron, or both has not been established; but probably only one of these ionization modes is important, and subsequently decomposition occurs without loss of boron.

The relative intensity of the ions in both series I and series II containing six boron atoms is much less than the intensity of ions containing seven or eight boron atoms. The intensities of the B_3, B_4, and B_5 ions indicate that they may be formed predominantly from ions containing six boron atoms. Thus, the parent of the B_6 ions may undergo fragmentation considerably more readily than other parents.

The fragmentation patterns, insofar as they are indicated by the present information, do not show an alternation from even to odd in the number of sulfur atoms removed. This behavior is different from that for the hydrocarbons and boron hydrides.

A comparison of the intensities of the series II and series III ions with those of series I does not firmly reveal the relationship among the series. They suggest, however, that the series II ions are related to those of series I by the addition of an SiS or SiS_2 group, a possibility which is supported by the time dependences. The series III ion intensities indicate that they are probably related to those of series I by the substitution of an oxygen atom for a sulfur atom.

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Ionization and Appearance Potentials of Selected Ions from Decaborane-16, B_5H_8I and B_5H_8Br[1]

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Ionization and appearance potentials of the $^{11}B_{10}H_{16}{}^+$, $B_5H_8X^+$ (X = I, Br), and $B_5H_8{}^+$ ions from $^{11}B_{10}H_{16}$ and B_5H_8X (X = I, Br) are reported along with the monoisotopic fragmentation patterns of these compounds. The following values were determined: $I_p(^{11}B_{10}H_{16})$ = 10.1 ± 0.2, $I_p(B_5H_8I)$ = 9.2 ± 0.1, $I_p(B_5H_8Br)$ = 9.5 ± 0.1 e.v.; $A_p(^{11}B_5H_8{}^+$ from $^{11}B_{10}H_{16})$ = 11.6 ± 0.2, $A_p(B_5H_8{}^+$ from $B_5H_8I)$ = 11.1 ± 0.1, $A_p(B_5H_8{}^+$ from $B_5H_8-Br)$ = 12.0 ± 0.2 e.v. From these and other data, values were calculated for (1) the ionization potential of the B_5H_8 radical, $I_p(^{11}B_5H_8)$ = 8.4 ± 0.2 e.v., and (2) the bond dissociation energy of the boron–boron bond which couples the two B_5H_8 units in decaborane-16, $D(B_5H_8-B_5H_8)$ = 3.2 ± 0.2 e.v. A method for the preparation of B_5H_8I and B_5H_8Br is also presented.

Introduction

One of the current interests of our program of boron hydride research is in the nature of some higher boron hydrides. We have published results on the formation of decaborane-16 by irradiation of pentaborane-9.[3-5] Lipscomb, et al., prepared decaborane-16 by an electrical discharge process and determined its structure by X-ray methods[6] and also studied some of its chemical properties.[7] The structure of decaborane-16 corresponds to the coupling of two B_5H_8 units from pentaborane-9. The two B_5H_8 units are bonded across the apical borons of the pentagonal pyramids of the pentaborane groups. We were interested in obtaining information concerning the nature of this coupling boron-boron bond, unique among boron hydrides, as well as data on the ionization potential of decaborane-16. In this paper, results are presented on some electron impact studies on decaborane-16 as well as on 1-iodo- and 1-bromopentaborane-9.

Experimental

Preparation of $^{11}B_{10}H_{16}$.—$B_{10}H_{16}$ was prepared by irradiation of B_5H_9 as previously reported.[3,4] $^{11}B_{10}H_{16}$ was prepared from $^{11}B_5H_9$ which had been synthesized from $^{11}B_2H_6$ by controlled pyrolysis as previously described.[8] Separation and purification of the $^{11}B_{10}$-H_{16} was effected by low temperature distillation followed by vacuum sublimation. The course of the purification was followed mass spectroscopically. The purification was considered complete when m/e = 64 disappeared into the background. It was believed that the major impurity, B_5H_9, was then present only in negligible quantities.

Preparation of B_5H_8Br and B_5H_8I.—The one method reported in the literature for the preparation of monohalogen pentaboranes is that of Shapiro[9] which uses CS_2 as solvent and $AlCl_3$ as cat-

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alyst. We found that yields in excess of 95% (based on B_5H_9 consumed) were easily obtained without solvent or catalyst by the direct combination of B_5H_9 with I_2 or Br_2 when B_5H_9 is in slight excess. This method has the obvious advantage of easy purification. The optimum conditions for these preparations are as follows: for B_5H_8I complete reaction occurs in about 14 days at 75° with a 25% molar excess of B_5H_9; for B_5H_8Br complete reaction occurs in 6–8 hr. at room temperature with a 10% molar excess of B_5H_9. The reactions were carried out in sealed glass bulbs equipped with breakseals. The reactions usually involved 0.01-mole quantities. In a typical preparation, 2.5 g. of I_2 and 0.8 g. of B_5H_9 yielded 1.8 g. of B_5H_8I. In both cases a small amount of dark-colored, nonvolatile, intractable material is formed. When the B_5H_9–I_2 reaction is carried out at temperatures above 90°, the major product is an amber-colored, nonvolatile, glassy material. When an excess of halogen is present, polyhaloboranes are usually formed. In the B_5H_9–Br_2 system when Br_2 is in excess, BBr_3 is formed.

In both cases B_5H_9 is easily separated from the product by vacuum distillation at 0°. The product can be purified by vacuum sublimation following the removal of B_5H_9. B_5H_8I can be handled readily in a drybox which is dried moderately with dry N_2 and desiccants. However, B_5H_8Br requires vacuum transfer or a drybox in which the atmosphere is thoroughly dry. B_5H_8Br is spontaneously flammable when exposed to the atmosphere, whereas B_5H_8I is only slowly attacked by atmospheric oxygen and water, yielding a fuming mist of HI.

At −78°, B_5H_8I forms very long, thin needles which slowly change to a shapeless crystalline mass at room temperature. B_5H_8Br forms refractive square plates at 0°, and the plates tend to persist at room temperature.

Mass Spectral Data.—The mass spectral work was performed on a CEC Model 21-103C mass spectrometer modified in the low voltage section to allow appearance potential measurements. In order to determine the appearance potentials of the ions involved in this study, the intensity of the ion beam of interest was measured in arbitrary units of peak height on the CEC photographic chart paper as a function of the (uncorrected) ionizing voltage, yielding the ionization efficiency curve of that ion in the range 0–2 e.v. above the threshold value. The ionization efficiency curve of a rare gas ion (xenon or krypton in this study) was measured simultaneously with that of the ion of interest and was used as an internal standard to determine the correction on the ionizing voltage. The extrapolated differences method of Warren[10] was used to determine the appearance potentials of the $^{11}B_{10}H_{16}{}^+$, $B_5H_8I^+$, $B_5H_8Br^+$, and $B_5H_8{}^+$ ions. The vanishing current method[11] was used for the $^{11}B_5H_8{}^+$ (from $^{11}B_{10}H_{16}$ and B_5H_8Br)

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