High Molecular Weight Boron Sulfides. V. Vaporization Behavior of the Boron–Sulfur System[1]

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Abstract: The vaporization behavior of the boron–sulfur system has been studied mass spectrometrically with a glassy, sulfur-rich B_2S_3 sample, a stoichiometric B_2S_3 sample, a stoichiometric B_2S_3-Zn mixture, and a FeS–B–Zn mixture. Glassy B_2S_3 gave the most intense and most complicated spectra; the stoichiometric B_2S_3 sample, the stoichiometric B_2S_3–Zn mixture, and the early stages of the FeS–B–Zn mixture gave, in the temperature range 400–650°, indistinguishable spectra that were intermediate in intensity and complexity; and the ZnS–B system, to which the FeS–B–Zn mixture converted in later stages, gave the simplest spectra with the lowest intensities. Ion intensities, appearance potentials, metastable transitions, fragmentation patterns, and temperature dependences are used to show that the parent ions from stoichiometric B_2S_3 were polymers of $B_2S_3(g)$ and that $B_2S_3(s)$ vaporizes congruently. Sulfur-rich samples vaporize incongruently to give polymers of both $BS_2(g)$ and $B_2S_3(g)$. Sulfur-deficient systems also give $B_2S_2(g)$. Polysulfide bonds are suggested as the cause of the higher volatility and lower melting points of the sulfur-rich samples.

The discovery of the gaseous ions of polymeric compounds between boron and sulfur by Greene and Gilles,[2] with the help of a mass spectrometer, has led to an extensive study of the boron–sulfur binary and hydrogen–boron–sulfur ternary systems. Their viscous liquid samples of B_2S_3 were obtained by the decomposition of $(HBS_2)_3$ and were reported to contain 0.5–1.0% excess sulfur, about 1% silicon, and about 1% excess oxygen. The intensities of the high molecular weight ions depended on the activity of sulfur, indicating that these species were the products of a reaction between B_2S_3 and the excess sulfur in the sample.[3] Accordingly, they suggested that polymers of the type $(BS_2)_n$ were the neutral molecules responsible for the major part of the spectra even though they did not observe parent ions of such molecules.

Edwards, Wiedemeier, and Gilles[4,5] then investigated the decomposition of the starting material, trimeric thiometaboric acid, $(HBS_2)_3(s)$. They found that after substantial decomposition had occurred, $B_8S_{15}^+$ was the most intense high molecular weight boron–sulfur ion at 300–600°, and they did find the $(BS_2)_n^+$ polymeric ions. In all these studies B_2S_3 samples were obtained from the decomposition of $(HBS_2)_3$ which was prepared from the reaction of H_2S and boron and were, to various extents, contaminated with excess sulfur.

As opposed to these studies of sulfur-rich samples, the vaporization of B–S samples of low sulfur activity has also been studied. From a ZnS–B sample Sommer, Walsh, and White[6,7] found no ion heavier than $B_2S_3^+$ and concluded that the only B–S binary parent ions were BS_2^+, $B_2S_2^+$, and $B_2S_3^+$. A Cr_2S_3–B sample, probably of higher sulfur activity, has been studied by Margrave, Ficalora, Uy, and Muenow,[8] and the ions BS^+ and B_2S^+ were also suggested to be parent ions.

The ion intensities in both the sulfur-rich and sulfur-poor studies described above were all time dependent; congruent vaporization was not studied. The purpose of the present work was to study the B–S system under conditions of moderate sulfur activity and to compare the behavior of the congruently vaporizing sample to the properties of the nonstoichiometric systems. Toward this end, vaporization of sulfur-rich glassy B_2S_3, stoichiometric B_2S_3, stoichiometric B_2S_3–Zn mixture, and a FeS–B–Zn mixture was studied mass spectrometrically.

The results show that stoichiometric B_2S_3 vaporizes congruently into $(B_2S_3)_n(g)$ only, with n taking the values from 1 to 5 or even larger. The spectra for the sulfur-rich and sulfur-poor samples agreed with spectra by previous workers. The effects of excess sulfur on the vaporization behavior, the volatility, and the melting point are believed to be associated with the formation of polysulfide bonds in the condensed phase.

Experimental Section

Samples. Crystalline B_2S_3 was chosen for the investigation of stoichiometric B_2S_3. It can be prepared according to Chopin and Hagenmuller[9] from the low-temperature decomposition of thiometaboric acid, but this procedure introduces complications because of the residual sulfur. Accordingly, the crystalline B_2S_3 used in this study was prepared from a mixture of FeS and B without the use of H_2S gas.

Iron sulfide was prepared from the elements according to the method described by Roberts.[10] About equal numbers of moles of 99.9% iron wire, Baker's Analyzed Reagent Grade, and 99.999% high-purity sulfur from Gallard-Schlesinger Chemical Manufacturing Co. were sealed under vacuum in a Pyrex tube and heated at 500° for 1 week. The FeS powder of 200 mesh was then obtained from the reaction product. The amorphous boron of 325 mesh was from Cooper Metallurgical Associates and had better than 99.5% purity.

Crystalline B_2S_3 was obtained by vacuum preparation from the reaction of the iron sulfide with the boron heated inductively to

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[1] Abstracted in part from the Ph.D. thesis of H. Y. Chen, submitted to the University of Kansas, 1969.

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[4] J. G. Edwards, H. Wiedemeier, and P. W. Gilles, *ibid.*, **88**, 2935 (1966).

[5] J. G. Edwards and P. W. Gilles in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series No. 72, American Chemical Society, Washington, D. C., 1968, pp 211–230.

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[8] J. L. Margrave, P. J. Ficalora, M. Uy, and D. Muenow, Sixteenth Annual Conference on Mass Spectrometry and Allied Topics, ASTM E-14, 1968, pp 388–390; and private communication.

[9] F. Chopin and P. Hagenmuller, *C. R. Acad. Sci., Paris*, **255**, 2259 (1962).

[10] H. S. Roberts, *J. Amer. Chem. Soc.*, **57**, 1034 (1935).

about 650° in a tall crucible of spectroscopic graphite. The crucible was so positioned that its upper half stayed above the work coil. The sample condensed on the cool lid and was later removed in a drybox for chemical analysis, X-ray examination, and vaporization.

Glassy B_2S_3, prepared by thermal decomposition of $(HBS_2)_3(s)$, was obtained from Werner.[11]

Twenty-mesh granular zinc metal, which was used as the medium for pressure calibration, was certified reagent grade from Fisher Scientific Co. Its purity was also determined by chemical analysis.

Analysis. Chemical analysis for both boron and sulfur in the sample was carried out by dissolving about 50 mg of the sample into concentrated ammonia solution in a closed flask. Both the H_2S and the H_3BO_3 produced were absorbed in the solution. The former, as well as the free sulfur, if any, was converted into sulfate by oxidation with hydrogen peroxide and was determined for the total sulfur content by precipitation of $BaSO_4$.

The boric acid was determined from the filtrate solution by titration with a 0.05 *N* NaOH solution using mannitol as a complexing agent. Zinc analysis was carried out by a standard method, and the purity of zinc was calculated from the amount of zinc recovered in $Zn_2P_2O_7$.[12] Iron sulfide was not analyzed, and its composition was assumed to be that of the mixture of iron and sulfur initially, *i.e.*, very close to FeS.

Procedure. The vaporization behaviors of the B–S samples were studied mass spectrometrically between 400 and 650°. The single-focusing, 12-in. section mass spectrometer, the device for temperature control and measurement, the design of the graphite crucible, and the procedures were essentially those used by Edwards, *et al.*[4,5] The spectra were obtained with 70-eV electrons by magnetic scanning downward in the range of m/e from 640 to 10. The ion species in this range were identified from their masses and their isotopic intensity distributions. The ion species arising from the sample in the crucible were distinguished from those of the background by their shutter effects. Intensity data are the shutterable portions. Ionization efficiency curves were obtained for most ions with adequate intensities. The appearance potentials were then obtained from these curves either by the extrapolated potential difference method or by the vanishing current technique. In both cases the appearance potential of Hg^+ at 10.4 eV was taken as the reference.

Experiments MS-5, -4, -8, and -7 were performed, respectively, with sulfur-rich glassy B_2S_3; crystalline B_2S_3; crystalline B_2S_3 and zinc; and FeS, boron, and zinc. In experiments MS-7 and MS-8, a few milligrams of zinc metal was used for the purpose of pressure calibration. The result of the calibration in MS-8, in which the zinc vaporized before the B_2S_3, will be reported elsewhere.[13] In MS-7, the attempt at pressure calibration did not succeed because the small amount of zinc reacted with FeS to form ZnS; after subsequent vaporization of B_2S_3, the system converted to ZnS and boron.

Results

Analytical. (a) Crystalline B_2S_3. The chemical analysis of the sample, slightly contaminated with graphite, gave the following results: 18.12 ± 0.06 and 80.89 ± 0.24% for boron and sulfur, respectively, corresponding to the atomic ratio of $S/B = 1.506 \pm 0.006$. The Debye–Scherrer powder pattern was identical with that reported for B_2S_3 by Chopin and Hagenmuller.[9]

(b) Glassy B_2S_3. The sample was found to have 17.40 ± 0.05 and 80.50 ± 0.24% for boron and sulfur, respectively; and the atomic ratio, $S/B = 1.554 \pm 0.006$, indicated that it was slightly richer in sulfur than was B_2S_3.

(c) Zinc. The purity of the zinc metal was determined to be 99.81 ± 0.02%.

Properties of the Ions. (a) General Characteristics of the Mass Spectra. All ions responded normally to the variation of the current and the voltage of the ionizing electrons and had normal shutter profiles. The spectra are grouped A, B, C, and D. The spectra in group A were from the glassy B_2S_3 in experiment MS-5 and were essentially the same as those obtained by the previous workers,[2,3,5] except that the intensities were generally weaker, particularly for the high molecular weight species. The working temperature was in the range of 450–590°, compared to 360–440° for Greene and Gilles.[3] This difference cannot be explained by the changes in the instrumental conditions but probably arises because of the smaller excess sulfur content in the present experiments.

The group B spectra were from the crystalline B_2S_3 in MS-4 and MS-8 and were also qualitatively similar to those in group A for the ions lighter than $B_4S_6^+$, but significant differences appeared in the higher mass region. A smaller number of ions appeared, their relative importance was altered, and ions containing silicon were not observed.

The spectra in group C, from the early stages of experiment MS-7 with the mixture of FeS, B, and Zn, were indistinguishable from the group B spectra, and were regarded as originating from the vaporization of the stoichiometric B_2S_3.

Group D spectra came from the last stages of experiment MS-7. The intensities for all the ions were smaller, and the spectra obtained at higher temperatures, 750–900°, were very much different from any of the previous ones. In these spectra no ion heavier than $B_2S_3^+$ was observed; the $B_2S_3^+$, $B_2S_2^+$, and BS_2^+ ions were all of comparable intensities; and, most important of all, ions such as B_2^+ and $B_2S_2^{2+}$ appeared. In many ways the spectra in group D were comparable to those reported by Sommer for the ZnS–B system[6,7] and by Margrave, *et al.*, for the Cr_2S_3–B system.[8] The change from group C to D arose because the B_2S_3 in the condensed phase was exhausted and the system was converted into a ZnS–B one.

(b) Ion Species and Intensities. The ions commonly observed in groups A, B, and C spectra were, in order of increasing m/e values, B^+, S^+, BS^+, $B_2S_3^{2+}$, S_2^+, BS_2^+, $B_2S_2^+$, $B_2S_2O^+$, BS_3^+, $B_2S_3^+$, $B_3S_3^+$, $B_2S_4^+$, $B_3S_4^+$, $B_4S_5O^+$, $B_4S_6^+$, and the heavier ions listed in Table I. In the table, the samples are briefly described at the top, and the runs, types of spectra, and temperatures are next indicated. The first columns identify the ion and the mass at which its most intense isotopic peak occurs. The intensities are the total values for all isotopic peaks.

In group D spectra only the light ions B^+, B_2^+, S^+, BS^+, $B_2S_2^{2+}$, $B_2S_3^{2+}$, S_2^+, BS_2^+, $B_2S_2^+$, and $B_2S_3^+$ appeared.

Results from a typical B-type spectrum, No. 7051, for crystalline B_2S_3 at 530° are shown in Figure 1. The ordinate and the abscissa in the figure are respectively the numbers of boron and sulfur atoms in each species; their intensities are shown relative to 100 for the intensity of $B_4S_6^+$. The dashed line on the graph connects locations of the ionic polymers of B_2S_3. The ion species for group B spectra were distributed along the line of $S/B = 3/2$, and the ions on the left of the line were generally rather strong. The data in Figure 1 show that the intensities of $(B_2S_3)_n^+$ ions decrease sharply from $n = 1$ to $n = 3$, then increase significantly as n becomes greater. On the other hand, the extent of fragmenta-

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Table I. Mass Spectrometric Intensities (mV) at 70 eV of High Molecular Weight Boron Sulfide Ions

				Sample	Sulfur-rich, glassy B_2S_3								B_2S_3(c)		B_2S_3(c) and Zn			FeS, B, Zn
				Run no.	MS-5 (A type)								MS-4 (B type)		MS-8 (B type)			MS-7 (C)
				Chart no.	5121	5122	5127	5128	5129	5130	5131	5132	5093	5094	7024	7043	7051	6058
				Temp, °C	453	506	544	560	574	584	562	547	563	581	495	515	530	620
B	S	O	Si	Main peak														
4	6	0	0	236	8	38	76	129	141	320	121	66	480	657	170	630	2100	180
3	6	0	1	253			5	16	25	37	17	9						3
4	7	0	0	269	3	4	6	15	18	29	12	6		31			44	5
5	7	0	0	279	1	4	5	12	18	28	9	5	48	55		115	363	14
5	8	0	0	311	2	3	5	6	7	19	6	3	13	15		~10		2
5	8	1	0	327			6	8	7	28	10	7						2
6	9	0	0	353		2	3	4	5	8	4	1	10	10	2	46	125	3
5	9	0	1	371			1	3	3	7	2	1						
7	10	0	0	396		4	4	5	6	13	5	2	21	26		89	286	5
7	10	1	0	412		~0		1	1	3	1	~0			9			
7	11	0	0	428	3	5	5	7	10	16	6	4	13	20	<2	15	46	<2
7	12	0	0	460	4	4	4	5	9	14	5	3			<5	10		
8	12	0	0	471		6	4	5	4	11	4	3	15	15	9	80	195	4
8	12	1	0	487		2	1	2	3	4	2	2				20	50	
8	13	0	0	503	5	9	6	11	11	26	8	5	15	20	<5	20	62	<2
9	13	0	0	514		6	5	5	6	14	5	4	20	26	16	115	340	5
7	13	0	1	520		18	2	2	3	6	5	2						
8	14	0	0	535	8	8	11	7	11	19	6	4	5					
9	14	0	0	546		5	5	5	6	11	5	3	2			15	50	1
10	15	0	0	589	2	7	6	5	8	14	6	4			24	220	415	5
9	15	0	1	606		2	3	2	2	5	4	2						
10	16	0	0	621	3	6	7	5	8	13	5	3				31	72	1

Table II. Appearance Potentials of Some B–S Ions from Stoichiometric B_2S_3 and Reported Values from Nonstoichiometric Systems (eV)

Ions	This study (B_2S_3) EPD (± 0.2)[a]	VC (± 0.2)[b]	Sommer[c] (S-poor)	Margrave, *et al.*[d] (± 0.3) (S-rich)	Greene, *et al.*[e] (± 0.8) (S-rich)
B^+	17.0	17.3	...	...	...
BS^+	...	17.2	18.0	...	...
$B_2S_3^{2+}$	...	24.4	...	...	...
S_2^+	10.0	...	...	...	...
BS_2^+	13.6	14.0	13.4	11.4	...
$B_2S_2^+$	12.5	12.4	11.4	11.8	...
$B_2S_3^+$	9.4	9.9	10.6	10.2	10.4
$B_3S_4^+$	...	11.0	...	...	...
$B_4S_6^+$	...	10.0	...	...	9.5

[a] Extrapolated potential difference method, MS-4. [b] Vanishing current method, MS-8. [c] By extrapolation of the linear portion: ref 7. [d] By extrapolation of the linear portion: ref 8. [e] By semilogarithm technique: ref 3.

tion with the loss of neutral BS_2 appears to increase from $n = 1$ to $n = 3$ and then to decrease again. Thus, the ion $(B_2S_3)_3^+$ has the lowest abundance of polymeric ions $(B_2S_3)_n^+$. A similar graph for the sulfur-rich sample by Edwards, *et al.*,[5] showed that most of the ions lay between the lines of S/B = 3/2 and 2/1. In agreement with the earlier results, the glassy samples leading to the group A spectra of MS-5 produced these more sulfur-rich ions.

(c) Appearance Potentials. The ionization efficiency curves showed no unusual features. The appearance potentials obtained from stoichiometric B_2S_3 samples are listed in Table II. The ions are listed in the first column, and the AP data, obtained by extrapolated potential difference and vanishing current techniques, are shown in the second and third columns, respectively. In the next three are the values by Sommer[7] for the ZnS–B system, by Margrave, *et al.*,[8] for the Cr_2S_3–B system, and by Greene and Gilles[3] for sulfur-rich B_2S_3.

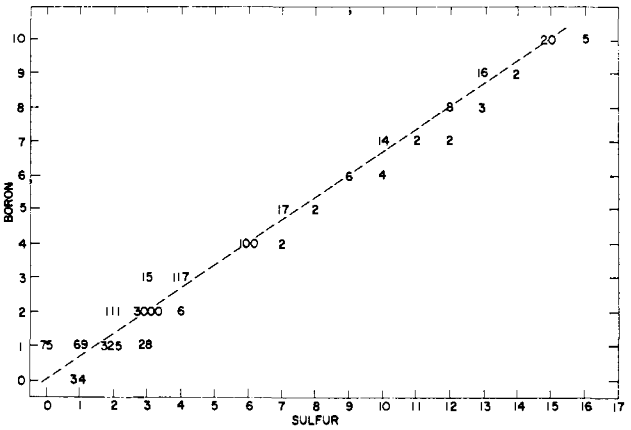

Figure 1. Relative intensities of boron sulfide ions at 530° from stoichiometric crystalline B_2S_3. The data are from MS-8, Chart No. 7051, given in the penultimate column of Table I. The numbers of boron and sulfur atoms in the ion are given as ordinate and abscissa. The intensity of $B_4S_6^+$ is taken as 100. The dashed line passes through points corresponding to the compositions of $(B_2S_3)_n$ polymers.

(d) Metastable Transitions. In slow magnetic scans five metastable transitions were observed in the group B spectra from samples of crystalline B_2S_3. They are shown in Table III, where the first two columns give the observed and calculated masses, and the next columns identify the reaction. The intensities in the last column are estimated values and are meant to show the relative importance of these transitions. The most intense ions observed in MS-8, as shown in Figure 1, are the ones in-

Table III. Metastable Decompositions of B_2S_3 Polymers in MS-8 at 530° and 70 eV

Mass		Number of atoms per molecule						Intensity (mV) ± 30%
		Parent		Fragment		Neutral		
Obsd	Calcd	B	S	B	S	B	S	
47.7	47.2	2	3	1	2	1	1	10
62.7	62.7	2	3	2	2	0	1	10
110.0	109.8	4	6	3	4	1	2	15
330	332.9	8	12	7	10	1	2	1
450	448.6	10	15	9	13	1	2	5

volved in these five processes. Except for the second case in Table III, one of the fragments of the decomposition of the $(B_2S_3)_n^+$ ion was a BS_2 group, charged in the first case and neutral in the others. The charge always stayed with the larger clusters of atoms.

(e) **Temperature Dependence.** Measurements of temperature coefficients in MS-8 with crystalline B_2S_3 reported elsewhere[13] showed that the values for $B_2S_2^+$, BS_2^+, $B_2S_3^{2+}$, BS^+, and B^+ were the same as for $B_2S_3^+$, while BS_3^+, $B_3S_3^+$, and $B_3S_4^+$ had values similar to that of $B_4S_6^+$. Values were not obtained for the heavier ions.

Vapor Species over Stoichiometric B_2S_3. The vapor species formed in the vaporization of stoichiometric B_2S_3 have been deduced from the identification of the ions, their appearance potentials, their intensities, their metastable transitions, and their temperature coefficients.

The appearance potential data for ions listed in Table II indicate that the ions $B_2S_3^+$, $B_4S_6^+$, and S_2^+ are parent ions. The high intensities for the first two substantiate this conclusion. The ions BS_3^+, $B_2S_4^+$, and $B_3S_3^+$ had such small intensities that appearance potentials could not be measured, and they were probably fragment ions.

The appearance potentials for $B_2S_2^+$ and $B_3S_4^+$ suggest the possibility that they could be parent ions, but the first three metastable decompositions indicate that these two and BS_2^+ are fragment ions. This conclusion is supported by temperature coefficients. Additional confirmation regarding this conclusion about $B_2S_2^+$ arises from experiments giving D-type spectra in which it was a parent ion; B_2^+ and $B_2S_2^{2+}$ were observed but were not observed over stoichiometric B_2S_3.

Intensities in Figure 1 and metastable transitions in Table III can be used to identify the predominant vapor species of high molecular weight. Six reasonably intense ions, $B_5S_7^+$, $B_6S_9^+$, $B_7S_{10}^+$, $B_8S_{12}^+$, $B_9S_{13}^+$, and $B_{10}S_{15}^+$, were found. The last four are related in pairs as fragment and parent ions in metastable decompositions listed in Table III. Similarly, $B_5S_7^+$ is probably a fragment of the parent ion $B_6S_9^+$ with the corresponding metastable transition too weak to be observed.

Thus, all the parent ions over stoichiometric B_2S_3 can be expressed as $(B_2S_3)_n^+$ with $n = 1, 2, 3, 4$, and 5.

Vapor Species over the ZnS–B System. In this chemically reducing system, as was mentioned earlier, the ions BS_2^+, $B_2S_2^+$, and $B_2S_3^+$ were of comparable intensity, and no heavier ion appeared. Above 850°, $B_2S_2^+$ became the most intense ion, and it and $B_2S_3^+$ were parent ions. The ions B_2^+ and $B_2S_2^{2+}$ were observed as fragments of B_2S_2.

Discussion

The fact that crystalline B_2S_3 vaporizes into $B_2S_3(g)$ and its polymers only proves the congruency of the vaporization of B_2S_3 suggested by Greene and Gilles[3] and also forms a bridge between the S-rich and S-poor studies of previous workers.[2-8] The vaporization behavior of the B–S system can be very concisely summarized.

(1) A B–S system richer in sulfur than B_2S_3 vaporizes incongruently into $(BS_2)_n(g)$ as well as $(B_2S_3)_n(g)$. The $(BS_2)_n(g)$ can be regarded as the product of the reaction between $B_2S_3(l)$ and the excess sulfur, as was suggested by Greene and Gilles.[3] Such a system will lose sulfur preferentially until its composition reaches B_2S_3. The intensities of the ions are, therefore, time dependent. (2) Stoichiometric B_2S_3 vaporizes congruently to give $B_2S_3(g)$ and its polymers. (3) A B–S system of low sulfur activity, which can be maintained by the presence of boron or of some metal which forms a moderately stable sulfide, gives the reduced vapor species B_2S_2 also.

Not only do the proportions of the vapor species vary with the sulfur activity, but some of the properties of the condensed phase also do. The sulfur-rich glassy sample is much more volatile than stoichiometric B_2S_3. The melting point of stoichiometric B_2S_3 is reported by Chen and Gilles[13] to be 563 ± 5°, much higher than the 310° determined for the glass by Moissan.[14] These facts suggest that excess sulfur in B_2S_3 diminishes the strength of binding. The low density of B_2S_3 samples, 1.55–1.70 g/cm³ as compared to 2.44 g/cm³ for B_2O_3 reported by Berger,[15] indicates the presence of large spaces in the condensed phase in which excess sulfur could form polysulfide bonds. The presence of S–S bonds could account for the increase in the volatility and the lowering of the melting point.

Both $BS_2(g)$ and $B_2S_3(g)$ exhibit a strong tendency to polymerize. The polymerization of $BS_2(g)$ to form $(BS_2)_n(g)$ can probably be accomplished with ease by the formation of polysulfide bonding. For $(B_2S_3)_n$ a different bonding scheme is needed if both the boron and the sulfur atoms are to remain in their ordinary valence states. The two sets of polymers have similar variations in intensity and in fragmentation patterns, and the ions with six borons have low abundances relative to heavier and lighter ones. Possibly a common steric effect militates against the molecules with six boron atoms.

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