The minor peak (4% of the total) was tentatively characterized as 1,1,2,2,3,3-hexamethyldichlorotrisilane or one of its isomers by its partial analysis. *Anal.* Calcd for $(CH_3)_6Cl_2Si_3$: C, 29.37; H, 7.39. Found: C, 30.12; H, 7.51. The mass spectrum showed peaks at *m/e* 244 (M), 229 (M − CH_3), 209 (M − Cl), 151 (M − $SiCl(CH_3)_2$).

Preparation of 1,1,1,2-Tetramethyldichlorodisilane.—A mixture of methyldichlorosilane (19 mmol) and bis(trimethylsilyl)mercury (5.13 mmol) in an evacuated sealed vessel was allowed to stand at room temperature. The solution in the reaction vessel, originally yellow, gradually bleached to a colorless solution and a precipitate of mercury during a 7-day period. The vessel then was attached to the vacuum apparatus and opened, and the materials volatile at room temperature were removed and separated by fractional condensation into a fraction retained at −79° and one retained at −196°. The −79° fraction was separated into its components by gas chromatography (on a 20 ft × $^3/_8$ in. column of QF-1 fluorosilicone, 30% on 60/80 Chromosorb P, at 151° with a flow rate of 270 cm^3/min). One component, 32% by volume, was identified as hexamethyldisilane by its 4.0-min retention time. The only other component, 68% by volume, had a retention time of 10.7 min. This was characterized as 1,1,1,2-tetramethyldichlorodisilane. *Anal.* Calcd for $(CH_3)_4Si_2Cl_2$: C, 25.9; H; 6.32; Cl, 29.8; Si, 38.0. Found: C, 25.7; H, 6.46; Cl, 30.0; Si, 37.9.

The proton nmr spectrum of a concentrated solution in tetramethylsilane consisted of two peaks at τ 9.24 and 9.76 with relative areas of 1:3 as expected. The molecular weight, by vapor density measurement, was found to be 195 (calculated 187).

Preparation of Pentamethylchlorodisilane.—A mixture of yellow crystalline bis(trimethylsilyl)mercury (7.896 mmol) and liquid dimethylchlorosilane (28.2 mmol) was irradiated for nearly 4 hr. During this time the yellow solid disappeared and mercury precipitated. At this point a clear colorless liquid was present in the reaction tube along with the mercury. This liquid was separated into its components by gas chromatography on a 30% QF-1 column at 151° with a helium flow of 270 cm^3/min. It consisted mainly of unreacted dimethylchlorosilane. Two peaks, one with a retention time of 4.2 min and one with a retention time of 8.35 min, were identified as disilanes. The former compound (retention time 4.2 min) was identified as hexamethyldisilane by comparison with an authentic sample. The latter compound (retention time 8.35 min) was identified as pentamethylchlorodisilane by analysis. *Anal.* Calcd for $(CH_3)_5ClSi_2$: C, 36.00; H, 9.06; Cl, 33.68; Si, 21.26. Found: C, 36.23; H, 8.95; Cl, 33.73; Si, 21.30.

Reaction of Bis(trichlorosilyl)mercury with Dimanganese Decarbonyl.—A mixture of bis(trichlorosilyl)mercury, 0.7426 g (1.582 mmol), and dimanganese decacarbonyl, 0.5829 g (1.496 mmol), was prepared in an inert-atmosphere box and placed in a reaction vessel without exposure to air or moisture. The reaction vessel then was evacuated, sealed off, and heated at 140° for nearly 60 hr. At the end of this treatment, as the reaction vessel cooled, a liquid present in the reaction vessel solidified. The reaction vessel was attached to the vacuum apparatus, opened, and heated to 60°. A crystalline white solid sublimed from the reaction vessel along with a trace of hexachlorodisilane and silicon tetrachloride (0.344 mmol). The white crystalline sublimate obtained in this fashion weighed 0.6746 g. This crystalline solid was characterized as trichlorosilylmanganese pentacarbonyl by the following data. *Anal.* Calcd for $Cl_3SiMn(CO)_5$: C, 18.3; Cl, 32.0; Si, 8.54; Mn, 13.7. Found: C, 17.9, Cl, 31.0; Si, 7.33; Mn, 14.8.

The molecular weight in benzene was found to be 342 (calculated 330). The infrared spectrum (CsBr, matched cell, cyclohexane solution) showed the absorptions (cm^{-1}): 2128 (s), 2037 (vs), 2005 (m), 660 (s), 650 (s), 555 (w), 533 (w), 503 (s), 467 (w).

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Mass Spectrometric Observations of Gaseous Boron Selenides

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The vapor species evaporating from a sample prepared to be B_2Se_3 were identified with a time-of-flight mass spectrometer. The sample was heated to progressively higher temperatures over the range from *ca.* 100 to *ca.* 700°. The sample was contained in a tungsten Knudsen cell. Parent gaseous species believed to be present were BSe_2(g) and B_2Se_3(g). In addition there were products from the hydrolysis reaction with the condensed B_2Se_3 phase. These results are compared with those for the B–S system by Gilles, *et al.* The B–S and B–Se systems show similar vaporization behavior; the principal difference observed was the absence of gaseous polymers of BSe_2 and B_2Se_3.

Introduction

Previous investigations of the B–Se system have been restricted to the condensed state. In two recent studies by Hutchinson and Eick[1] and Cueilleron and Hillel,[2] B_2Se_3(s) was prepared. Hutchinson and Eick[1] reported transformations at several temperatures, infrared spectra of B_2Se_3(s), and values of X-ray diffraction interplanar spacings. Cueilleron and Hillel[2] reported different infrared and X-ray diffraction data; in addition they noted the reaction of B_2Se_3 and silica. The latter

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[1] W. E. Hutchinson and H. A. Eick, *Inorg. Chem.*, **1**, 434 (1962).

[2] J. Cueilleron and R. Hillel, *Bull. Soc. Chim. France*, **8**, 2973 (1967).

authors recommended a preparation procedure to avoid the reaction of B_2Se_3 and silica.

Recently Boryakova, *et al.*,[3] reported a phase diagram study of the B–Se system with compositions principally from B_2Se_3 to Se. They reported that there is no compound formation between B_2Se_3 and Se; BSe_2(s) was not found. The only compound that they found was B_2Se_3(s) which melted at 480°. On both sides of B_2Se_3, they reported that the compositions have liquidus temperatures below 480°.

Gaseous boron sulfides have been reported by Gilles, *et al.*[4–8] Mass spectrometric investigations of gaseous products from the vaporization of B_2S_3(s) (of variable composition) and the thermal decomposition of HBS_2(s) revealed polymeric species of boron and sulfur with masses extending beyond 850. Because of the chemical similarities between sulfur and selenium, the boron–selenium system seemed likely to produce interesting gaseous species.

Experimental Section

Samples.—All samples of B_2Se_3 prepared for this study of the B–Se system were prepared from the elements. Boron of 99.15% purity was obtained from Matheson Coleman and Bell Co. Selenium had a stated purity of 99.999+% with impurities being Te, Cu, As, and Si, each less than 0.0001%; the selenium was obtained from the American Smelting and Refining Co., South Plainfield, N. J.

Chemical reaction of the elements was accomplished by heating weighed portions of them in an evacuated ampoule. In initial preparations (method 1), the sample was heated at 490° for 24 hr in a quartz or Pyrex ampoule. In later preparations (method 2), a method suggested by Cueilleron and Hillel[2] was followed. The quartz ampoule was initially washed with 25% HF solution; the interior surface was then carbonized. In this method, the sample was heated at 750° for 4 hr. The carbonized interior surface prevented the attack of the sample on the quartz at elevated temperatures. In both methods, there is no reason to believe that the reaction was incomplete. No chemical analyses of samples were performed.

A portion of a sample prepared by method 2 was examined by X-ray powder diffraction. The absence of diffracted lines indicated that the sample was amorphous.

The samples of B_2Se_3 prepared in this study were very reactive with H_2O, either in liquid form, as moisture present in the atmosphere, or at low pressures in a drybox filled with argon, prepurified grade, 99.998% minimum purity, obtained from the Matheson Co. One of the products of the reaction between B_2Se_3(s) and H_2O is H_2Se(g); H_2Se(g) can be prepared in large quantities by this reaction. Samples were placed in Knudsen cells in the drybox. Transfer of Knudsen cells to the mass spectrometer was done as quickly as possible so as to minimize contact with the atmosphere.

Mass Spectrometry.—The mass spectrometer used in this study was a time-of-flight mass spectrometer, Bendix Model 12-107. The circuits of Model 12-107 were modified following a suggestion by Studier;[9] the resolution was improved so that it was at least 350 with a maximum detectable mass of *ca.* 5000 and with a sensitivity such that pressures as low as 10^{-9} atm in the Knudsen cell could be measured. The inlet system to the mass spectrometer was a high-temperature Knudsen cell source following a design similar to that of Chupka and Inghram.[10]

The Knudsen cell in this study was fabricated from swaged tungsten rod. It was heated by radiation from a hot tungsten filament. Samples were heated in successive steps to higher temperatures with mass spectra taken at each step.

Temperatures of the Knudsen cell were ascertained by a calibration chart prepared by comparing power settings and chromel–alumel thermocouple readings. It is estimated that the uncertainties in temperature are within ±10°.

Ionization of gaseous species in the mass spectrometer was accomplished by electron bombardment usually at 50 eV.

Mass scans were recorded with a strip chart recorder. Values of the mass:charge ratio for ions observed in a mass spectrum were determined by counting peaks (including background) from easily recognized species or by construction of a calibration chart of mass:charge *vs.* (chart position)^2. Isotopic distributions of species also proved valuable for identification of sets of peaks in the spectra.

Results

When the samples of B_2Se_3, prepared by either of the two methods, were heated, gaseous atomic and molecular products were observed in the mass spectrometer. Identification of these species revealed two types of molecules (series 1 and 2). Series 1 has as its members species with B and Se: B^+, selenium and its polymers—Se^+, Se_2^+, Se_3^+, Se_4^+, Se_5^+, Se_6^+, Se_7^+—BSe_2^+, $B_2Se_3^+$, and usually in small quantities BSe^+, $B_2Se_2^+$, and BSe_3^+; there is weak evidence for $B_3Se_3^+$ and $B_2Se_4^+$. Series 2 has as its members species with B, Se, and H: H_2Se^+, $H_2Se_2^+$, $H_2BSe_2^+$, and perhaps $H_2B_2Se_3^+$.

Species designated by X^+ and H_2X^+ will have the same intensity *vs.* mass distribution caused by the isotopic distributions of elements constituting X and the nearly monoisotopic nature of H; the intensity *vs.* mass distribution for H_2X^+ will be shifted 2 mass units higher than for X^+. Through intensity *vs.* mass distributions, the presence of series 2 species was detected.

In addition to the above two series of species, the following peaks were observed: a set centering on mass 71, a set at 108 (Se isotopic distribution), and a set at 136 (Se isotopic distribution plus H_2Se). It is believed that these peaks are associated with species containing oxygen such as $HB_2O_3^+$ (71), $HBOSe^+$ (108), and $H_2B_2O_2Se^+$ (136). Oxygen was probably introduced into the samples by the hydrolysis reaction previously mentioned.

In Table I may be found data giving intensities of different species for a sequence of heatings on a single sample (prepared by method 1). During initial heating of a sample (not indicated in Table I), the principal gaseous species were Se and its polymers. At temperatures of *ca.* 300°, BSe_2(g) was observed; see scans 2–4. Gaseous B_2Se_3 was observed only when the samples were heated to temperatures of *ca.* 500°; see scans 12, 15, 16, and 19.

Table II contains data for heatings in which only series 1 species were observed; Table III is a similar

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(3) V. A. Boryakova, Ya' Kh. Grinberg, E. G. Zhukov, V. A. Koryazhkin, and Z. S. Medvedeva, *Izv. Akad. Nauk SSSR, Neorgan. Materialy*, **5**, 477 (1969); see *Chem. Abstr.*, **70**, 100169 (1969).

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

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

(7) J. G. Edwards and P. W. Gilles in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, No. **72**, J. L. Margrave, Ed., American Chemical Society, Washington, D. C., 1968, p 211.

(8) H.-Y. Chen and P. W. Gilles, *J. Am. Chem. Soc.*, **92**, 2309 (1970).

(9) M. H. Studier, *Rev. Sci. Instr.*, **34**, 1367 (1963).

(10) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955)

TABLE I

INTENSITIES OF SPECIES IN A SEQUENTIAL VAPORIZATION[a]

Scan	Temp, °C	$^{11}\mathrm{B}$	$^{80}\mathrm{Se}$	$^{91}\mathrm{BSe}$	$^{160}\mathrm{Se}_2$	$^{171}\mathrm{BSe}_2$	$^{240}\mathrm{Se}_3$	$^{251}\mathrm{BSe}_3$	$^{262}\mathrm{B}_2\mathrm{S}_3$	$^{320}\mathrm{Se}_4$	Se	Se_6
2	285	u	$>100_\mathrm{H}$		3_H	4_H						
3	323	u	$>100_\mathrm{H}$		2_H	16_H						
4	362	u	95_H		9	54_H						
5	393	u	>100		37_H	5_H	4			4	1	9
7	425	u	55_H		84	2	1			2		
12	567	u	>100		4	10_H			3			
15[b]	645	u	>100			31			17			
16	672	u	69_H			24_H			6			
19	. . .	u	>100		2_H	20_H			8			

[a] Definitions: u, mass not scanned; H, both column species and column species + H_n present; no entry, intensity too small to observe. All data are from set II. [b] Probably no hydrogen.

TABLE II

SERIES 1 SPECIES AND THEIR INTENSITIES[a]

Set	Scan	Temp, °C	$^{11}\mathrm{B}$	$^{80}\mathrm{Se}$	$^{91}\mathrm{BSe}$	$^{160}\mathrm{Se}_2$	$^{171}\mathrm{BSe}_2$	$^{182}\mathrm{B}_2\mathrm{Se}_2$	$^{240}\mathrm{Se}_3$	$^{251}\mathrm{BSe}_3$	$^{262}\mathrm{B}_2\mathrm{Se}_3$	Se_4	Se_5	Se_6
II	7	425	u	55_H		84	2		1			2		
II	15	645	u	>100			31				17			
I	1	. . .		>100		57	12		1		3	1		4
I	2	480	9	$\gg 100$		43	4		4		1	5		8
IV	3[b]	592	2	$\gg 100$	21	>100	68	10		2	37			
IV	4	645	u	~ 100	75_H	83	>100	23			74			

[a] See footnote *a* of Table I for meanings of symbols. [b] High-mass species appeared.

TABLE III

SERIES 2 SPECIES AND THEIR INTENSITIES[a]

Set	Scan	Temp, °C	$^{11}\mathrm{B}$	$^{80}\mathrm{Se}$	$^{91}\mathrm{BSe}$	$^{160}\mathrm{Se}_2$	$^{171}\mathrm{BSe}_2$	$^{182}\mathrm{B}_2\mathrm{Se}_2$	$^{240}\mathrm{Se}_3$	$^{251}\mathrm{BSe}_3$	$^{262}\mathrm{B}_2\mathrm{Se}_3$	Se_4	Se_5	Se_6
II	2	285	u	$>100_\mathrm{H}$		3_H	4_H							
II	3	323	u	$>100_\mathrm{H}$		2_H	16_H							
II	5	393	u	$>100_\mathrm{H}$		37_H	5_H		4			4	1	9
II	7[b]	425	u	55_H		84	2		1			2		
II	12	567	u	$>100_\mathrm{H}$		4	10_H				3			
II	16	672	u	69_H			24_H				6			
II	19	707	u	$>100_\mathrm{H}$		2_H	20_H				8			
III	3	663	u	u	u	5	15_H				6			
III	5	693	u	>100		15	24_H				9_H	5		7

[a] See footnote *a* of Table I for meanings of symbols. [b] Mostly nonhydrogen.

table for series 2. From these tables it can be noted that there were some cases in which series 2 species appeared and others in which they did not appear. The series 2 species which first appeared was $\mathrm{H_2Se^+}$; see Table II, set II, scan 7 in which it is the only series 2 species. Presumably the appearance of series 2 species depended upon the extent of the hydrolysis reaction discussed previously. The same trends with temperature as indicated for Table I may also be observed in these data although different series of heatings are combined.

Discussion

In the initial vaporization of samples of boron selenides, large ion intensities from selenium vapor and $\mathrm{H_2Se(g)}$ were observed. After Se had vaporized from the sample, B–Se ion species, series 1, and B–Se–H ion species, series 2, appeared in the mass spectrum.

Fragmentation of ions can occur in the electron bombardment ion source of a mass spectrometer. It is highly probable that the following ions occurred by loss of Se: $\mathrm{BSe^+}$, $\mathrm{B_2Se_2^+}$. The ion $\mathrm{BSe_3^+}$ (rarely observed) could occur by the loss of B from $\mathrm{B_2Se_3}$. The ion $\mathrm{B^+}$ was observed a few times; since B(g) could not occur under equilibrium conditions at these temperatures, it must have arisen from fragmentation. All of these suspected fragments were present in small quantities compared to their suspected parents.

The ions $\mathrm{BSe_2^+}$ and $\mathrm{B_2Se_3^+}$ are concluded to originate from the parent gaseous molecules $\mathrm{BSe_2}$ and $\mathrm{B_2Se_3}$. In early low-temperature heatings, $\mathrm{BSe_2^+}$ occurred either in the absence of $\mathrm{B_2Se_3^+}$ or when the intensity of $\mathrm{B_2Se_3^+}$ was much lower than the intensity of $\mathrm{BSe_2^+}$; *i.e.*, the intensities of $\mathrm{BSe_2^+}$ and $\mathrm{B_2Se_3^+}$ are not related and in some mass spectra $\mathrm{BSe_2^+}$ was the highest mass species. Thus, $\mathrm{BSe_2^+}$ could be a fragment produced from $\mathrm{B_2Se_3}$ but must be a parent species in some cases. The ion $\mathrm{B_2Se_3^+}$ has been observed frequently as the highest mass species. Since the pressure in the entire mass spectrometer was low ($\sim 5 \times 10^{-7}$ mm) and the ion intensities of B–Se species were not appreciably higher than the background peak at mass 44 during the observation of $\mathrm{BSe_2^+}$ and $\mathrm{B_2Se_3^+}$, the origin of these species is not likely to be ion–molecule reactions.

The presence of species with masses greater than $\mathrm{B_2Se_3}$ cannot be excluded. Indeed, data presented in Table II indicate that $\mathrm{B_3Se_3^+}$ and $\mathrm{B_2Se_4^+}$ may have been present. It is possible that higher molecular weight species might have been present if higher temperatures had been achieved earlier in the vaporizations.

The presence of series 2 species probably arises from the reactivity of B_2Se_3 with $H_2O(g)$ even at low H_2O pressures. This hydrolysis reaction would be expected to introduce an oxygen contaminant also into the sample. The presence of oxygen in some species was deduced for sets of ions at masses 71, 108, and 136 as discussed previously. The presence of series 2 species $H_2BSe_2^+$ and $H_2B_2Se_3^+$ is assumed to be caused by parent species also bearing H atoms, probably $H_2BSe_2(g)$ and $H_2B_2Se_3(g)$.

The data reported in Tables I–III indicate that the gaseous molecules BSe_2 and B_2Se_3 are thermally stable to 700°.

The results of this study of the boron selenides show some similarities to the studies of the vaporization of B_2S_3;[4,5,8] the gaseous species observed were BS_2, B_2S_3, and their polymers. In the earlier studies,[4,5] as the vaporization proceeded by heating to progressively higher temperatures, the higher molecular weight species decreased in importance leaving only $B_2S_3(g)$. In the study by Chen and Gilles,[8] the gas composition was studied as a function of the composition of the condensed B–S phase. Congruent vaporization of B_2S_3 was found to produce only $B_2S_3(g)$ and its polymers. If the sample was S rich in comparison to B_2S_3, $BS_2(g)$ and its polymers were found also. If the sample was S poor, then $B_2S_2(g)$ was detected in addition to BS_2^+ and $B_2S_3^+$. In the study of the thermal decomposition of HBS_2,[6,7] it was concluded that HBS_2 initially lost large amounts of $H_2S(g)$, samples then lost gaseous polymers of HBX_2, and finally the mass spectra of boron sulfides similar to those of the earlier studies were observed.

The appearance in this study of the vaporization of $B_2Se_3(s)$ of series 1 gaseous species may be compared with what occurred with the similar vaporization of $B_2S_3(s)$ by Gilles, *et al.*[4,5,8] The initial appearance of selenium and its polymers suggests that these B_2Se_3 samples were of high selenium activity. In later stages of the vaporization of these samples, the species $BSe_2(g)$ and $B_2Se_3(g)$ were observed. Gilles, *et al.*, in addition to $BS_2(g)$ and $B_2S_3(g)$, found gaseous polymers of BS_2 and B_2S_3. If polymers of BSe_2 or B_2Se_3 were present, their importance was significantly less than in the case of the boron sulfides. The fact that vaporizations terminating at high temperatures led to B_2S_3 and BSe_2 (BSe_2^+ may be a fragmentation product at the end of the vaporization) and B_2Se_3 as the important gaseous molecular species shows the similarities in sulfur and selenium chemistry.

In the case of the boron selenides, the hygroscopic nature of the sample introduced H (and O) into the condensed phase. Initial stages of the vaporization showed large amounts of $H_2Se(g)$. In addition, $H_2BSe_2(g)$ was observed. These results show similarities to the thermal decomposition of $HBS_2(s)$ studied by Gilles, *et al.*;[6,7] in the case of HBS_2, $H_2S(g)$ and $HBS_2(g)$ were observed. Further heating of the HBS_2 sample gave gaseous products as found in the vaporization of $B_2S_3(s)$. In this study of the B–Se system, further heating of samples showing H species, see Table III, gave rise to $B_2Se_3(g)$ just as vaporization of a sample showing only series 1 species.

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The Formation of Silene and Germene from the Pyrolyses of Disilane and Digermane and the Relative Insertions of Silene into Silanes

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The products from the pyrolysis of disilane-d_6 and methylsilane were silane-d_4 and $CH_3SiH_2SiD_2H$. These results demonstrate that the pyrolysis of disilane yields silene (probably singlet) and silane. The rate of insertion of silene into silicon–hydrogen bonds appears to increase greatly with an increase in the hydridic character. The pyrolysis of digermane was found similar to that of disilane.

Introduction

We have proposed that the pyrolysis of disilane occurs *via* the formation of silene and silane.[1] This proposed mechanism (eq 1 and 2) was based on the fact

$$Si_2H_6 \longrightarrow SiH_2 + SiH_4 \quad (1)$$

$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \quad (2)$$

that the pyrolysis of disilane with low-temperature trapping yielded only silane and trisilane (eq 3).

$$2Si_2H_6 \longrightarrow SiH_4 + Si_3H_8 \quad (3)$$

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[1] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).