

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

The Condensation of Borazine to Polycyclic Boron-Nitrogen Frameworks by Pyrolytic Dehydrogenation¹

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When $B_3N_3H_6$ vapor is heated at temperatures between 340 and 440° in all-glass cells it decomposes to give hydrogen, a tan colored, nonvolatile solid of composition approximately $BNH_{0.8}$ and traces of volatile materials. The pyrolysis is kinetically first order with respect to borazine. The $BNH_{0.8}$ slowly loses more hydrogen at 475°, eventually forming a white nonvolatile solid of composition approaching $BNH_{0.3}$. Batch pyrolysis of larger quantities of borazine vapor in a hot-cold apparatus, followed by separation of the products by distillation and sublimation in a vacuum system, has yielded hydrogen and a number of boron-nitrogen containing materials. Chemical analysis, mass spectra, infrared spectra and X-ray powder patterns establish that two of the volatile products are $B_5N_5H_8$ (m.p. 27–30°) and $B_6N_6H_{10}$ (m.p. 59–60°), the boron-nitrogen analogs, respectively, of naphthalene and diphenyl. Another volatile fraction, on the basis of its mass spectrum, infrared spectrum and its chemical behavior, appears to be largely $B_3N_3H_8$, 2,4-diaminoborazine. Products nonvolatile at room temperature have been separated by sublimation at 90° and their behavior has been characterized. The structural pattern followed by boron and nitrogen in building up extended frameworks is discussed. The mechanism by which borazine decomposes thermally is considered and compared with the pyrolytic behavior of benzene.

Introduction

Borazine,³ $B_3N_3H_6$, is a very interesting compound because it is both isoelectronic and isosteric with benzene. Stock⁴ first prepared it by heating the ammonia addition product $B_3H_6 \cdot 2NH_3$ at 200° for several hours. He reported that when borazine was heated to 500° it decomposed into hydrogen, a nonvolatile solid of empirical composition BNH , and traces of more volatile materials. The nonvolatile solid was insoluble in all common solvents and evidently was highly condensed. On heating at 900° it lost additional hydrogen. E. Wiberg⁵ suggested that BNH is a polymer having a boron-nitrogen framework and that boron nitride and hydrogen are formed on heating it to 900°.

The dehydrogenation of borazine to form boron nitride must proceed by a complicated series of reactions involving many intermediates. Because borazine is isoelectronic with benzene and boron nitride is isoelectronic with graphite, intermediate compounds should be isoelectronic with the corresponding polycyclic aromatic carbon compounds and therefore of great interest. Stock's pyrolysis experiment was done with such a small sample of borazine (1.53 ml. gas at STP) that he could not obtain any information about possible intermediates. The recent simple synthesis of 2,4,6-trichloroborazine⁶ and its reduction to borazine by $LiBH_4$ in ether⁷ or by $NaBH_4$ in polyethylene glycol ethers⁸ make borazine available in larger quantities, and therefore a more detailed study of the pyrolysis of borazine has been possible.

Experimental

Materials.—Borazine was prepared by the reduction of 2,4,6-trichloroborazine with sodium borohydride using the dimethyl ether of tetraethylene glycol as a solvent.⁸ The product was purified by distillation in a vacuum system. Gas chromatographs, vapor pressure measurements and melting points showed that the borazine prepared by this method was very pure.

Analytical Methods and Apparatus.—Standard methods of analysis for boron and nitrogen were employed. Active hydrogen analyses were carried out in a vacuum system by distilling 5 N HCl onto the sample, allowing the mixture to warm to room temperature and collecting and measuring the hydrogen evolved. Only the hydrogen atoms bonded to boron in the borazine materials are liberated to form molecular hydrogen by this treatment.

Mass spectra were obtained with a 12 inch, 60 degree, direction-focusing type instrument,⁹ fitted with an auxiliary vacuum system. A leak device was used to introduce gas from the vacuum system into the ionization chamber. Mass determination was made by comparison with peaks of known m/e or by calibration with a rotating coil gausmeter.¹⁰ In several cases the values of m/e obtained by this method were confirmed by the introduction of a calibrating substance. To obtain X-ray diffraction patterns, samples were loaded into thin-walled Pyrex glass tubes and exposed to $Cu K\alpha$ X-radiation in a 11.46 cm. camera. Infrared analyses were performed on a Perkin-Elmer Model 21 Infrared Spectrometer.

Studies of Hydrogen Formation by Pyrolysis of Gaseous Samples in Static Systems.—Preliminary experiments were done in all-glass cells of the type described by Laubengayer and Schirmer,¹¹ "sickle" gauges being used to measure the pressure developed inside the reaction vessel. The reaction vessel was completely enclosed in an air bath furnace capable of maintaining the temperature constant to within $\pm 0.3^\circ$. Weighed quantities of borazine of such a size that all of the borazine was in the gas phase at room temperature were introduced into the reaction vessel in sealed glass bulbs which were broken with a magnetic hammer.

(6) C. A. Brown and A. W. Laubengayer, *THIS JOURNAL*, **77**, 3699 (1955).

(7) R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. E. Schlesinger, *ibid.*, **76**, 3303 (1954).

(8) L. F. Hohnstedt and D. T. Haworth, *ibid.*, **82**, 89 (1960).

(9) R. F. Porter and R. C. Schoonmaker, *J. Phys. Chem.*, **62**, 234 (1958).

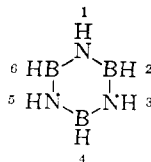
(10) Manufactured by Rawson Electrical Instrument Company of Cambridge, Massachusetts.

(11) A. W. Laubengayer and G. B. Schirmer, Jr., *THIS JOURNAL*, **62**, 1578 (1940).

(1) Presented before the Division of Inorganic Chemistry, American Chemical Society meeting, September 18, 1959, and abstracted from a thesis submitted to the Graduate School of Cornell University by P. C. Moews, Jr., June, 1960.

(2) Allied Chemical and Dye Fellow 1958–1959. The financial support of the American Cyanamid Corporation, Standard Oil Company of Ohio and the National Science Foundation is acknowledged with gratitude.

(3) In line with the recommendations of the Committee on the Nomenclature of Boron Compounds, the term borazine and the numbering sequence shown are used in this paper for this aromatic, heterocyclic, six-membered ring compound, rather than the older term borazole.

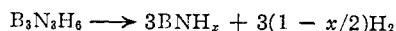


G. W. Schaeffer, Abstracts of Papers presented at the April meeting of the American Chemical Society, p. 21 (1958).

(4) A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926).

(5) E. Wiberg, *Naturwissenschaften*, **35**, 182, 212 (1948).

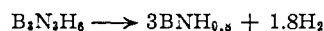
The first experiments were designed to establish the stoichiometry of the reaction



and to determine whether or not volatile compounds, other than hydrogen and borazine, were among the reaction products. Cells containing samples of gaseous borazine were heated for short periods of time. At the end of each period the pressure inside the cell was determined at the temperature of the furnace (340, 381 and 440° in different experiments) and the cell quickly cooled to room temperature. The pressure within the cell was then measured at 20, -78 and in some cases at -196°. Using the pressure, temperature and the volume of the cell the number of moles of gas present at each temperature was calculated.

nearly identical within experimental error. This indicated that no considerable quantity of material, volatile at the temperature of the air bath but not volatile at room temperature, was formed and persisted. At -78° the only gas present was hydrogen. This was confirmed by pressure measurements at liquid nitrogen temperatures. The number of moles of borazine present in the apparatus was therefore assumed to be equal to the difference in the number of moles of gas present at room temperature and at -78°. The pyrolysis later of large quantities of borazine and the separation of the volatile products in a vacuum system showed that this assumption was approximately correct. Even under the most favorable conditions used, only 5% of the borazine formed volatile decomposition products.

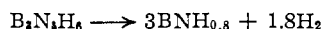
In the experiments at 340 and 381°, 1.8 moles of hydrogen were formed per mole of borazine decomposed. The composition of the residual nonvolatile material which formed must be $\text{BNH}_{0.8}$ and the net thermal decomposition of borazine at 340 and 381° can be represented by the equation



The solid residue with the over-all composition $\text{BNH}_{0.8}$ was light tan in color and nonvolatile. It was evidently a mixture of high polymers. In the experiment at 440° 1.9 moles of hydrogen was obtained per mole of borazine decomposed and the residue had the over-all composition $\text{BNH}_{0.7}$.

In the experiment run at 340° an attempt was made to decompose the nonvolatile tan colored material which remained. The cell was replaced in the furnace and heated at 475°, whereupon the material slowly lost additional hydrogen. Heating was continued until hydrogen evolution became inappreciable (48 hr.). A total of two and a half moles of hydrogen were now present in the cell per mole of original borazine. The solid residue had changed from light tan to white in color. By difference, the composition of the white nonvolatile polymer which formed must be $\text{BNH}_{0.3}$. Borazine was not decomposed to boron nitride and hydrogen by pyrolysis at 475°.

Two kinetic runs were made to determine the order with respect to borazine of the reaction



and to obtain some approximate values of the rate constants. Cells containing weighed samples of borazine vapor were held at 337 and at 371°, and the pressure inside the cells was determined periodically. In both experiments plots of $\log(P_\infty - P)$ vs. T gave straight lines. P_∞ was calculated assuming that 1.8 moles of hydrogen are formed when a mole of borazine decomposes thermally, and P was the pressure observed at time T . The reaction is first order with respect to the concentration of borazine. At 337° the specific rate constant is approximately $1 \times 10^{-5} \text{ sec.}^{-1}$ and at 371° it is $1 \times 10^{-4} \text{ sec.}^{-1}$.

Pyrolysis of Larger Quantities of Borazine in a Hot-Cold Apparatus.—The apparatus, diagrammed in Fig. 1, was designed to carry out the thermal decomposition of larger quantities of borazine on a batch basis, in such a manner that volatile products could diffuse easily from the hot zone and be quantitatively transferred from the apparatus. The long-necked 500 ml. flask, A, was connected to the trap, B, which was in turn connected to a large bore stopcock. This stopcock was joined to a vacuum system through the palladium diffusion tube, C, and a bypass.

In a typical experiment 5 grams of borazine was distilled into trap B. When this was kept at 0° a constant partial pressure of borazine of 85 mm. was maintained in the apparatus. The lower part of the flask was heated in an air bath furnace in which the temperature could be controlled to $\pm 1^\circ$. Borazine was decomposed in the hot part of the apparatus. As the borazine decomposed it was replaced by diffusion from the supply in the 0° trap. Volatile products diffused from the hot part of the apparatus and collected in the cooler regions, while nonvolatile products remained in the flask. The hydrogen which formed was removed by constant pumping beyond the palladium diffusion tube. Heating usually was continued for 5 days, about 3 grams of the 5 gram sample decomposing in this interval.

The temperature chosen for heating the flask was determined by several considerations. A low temperature was desirable to lessen the possibility of further decomposition

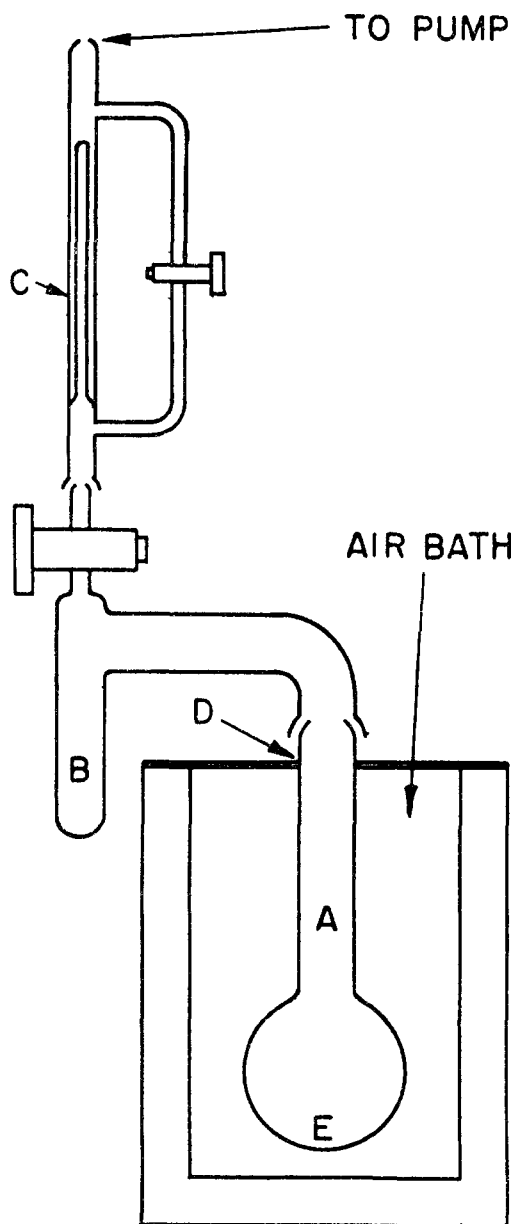


Fig. 1.—Hot-cold pyrolysis apparatus.

At the temperature of the air bath and at 20° both borazine and hydrogen would be completely in the gas phase at the pressures measured. The number of moles of gas present in the apparatus at these two temperatures was always

of volatile products. However, the temperature had to be high enough so that the decomposition of borazine took place in a reasonable period of time. Finally, the rate at which hydrogen formed had to be slow enough so that it could be removed by means of the palladium diffusion tube. The diffusion tube had a capacity for the diffusion of about a tenth of a milligram of hydrogen per minute. Some approximate calculations based on the kinetic data and a few trial experiments led to 380° as the most suitable temperature.

Separation of the Products.—At the termination of the pyrolysis the furnace was removed, and all of the material volatile at room temperature was distilled from the flask into a cold trap by pumping for several hours. The mixture of volatile compounds was then separated into several fractions by distillation, with pumping, through a series of traps held at 0, -15, -23, -45 and -196°, respectively. Besides unreacted borazine (which collected in the -196° trap) three main components, Fractions I, II and III listed in Table I, were obtained. A large amount of a white solid, nonvolatile at room temperature, remained in the reaction flask. Most of this white solid had collected in a ring just above the place where the neck of the reaction flask left the furnace (D, Fig. 1). The reaction flask was opened and the ring of white solid quickly loaded into a vacuum sublimator. On heating the sublimator to 90° small amounts of a white solid, Fraction IV, collected on the cold finger. The major portion of the material in the sublimator, Fraction V, was nonvolatile at 90°. In addition to the white, nonvolatile solid which collected above the place where the flask left the furnace, there was a small amount of a tan colored, nonvolatile solid, Fraction VI in Table I, which collected in the bottom of the flask (E, Fig. 1). Its appearance was similar to that of the $\text{BNH}_{0.3}$ polymer which had collected in the sickle cell experiments. Table I summarizes the yields of the various fractions.

TABLE I

PRODUCTS OBTAINED FROM THE THERMAL DECOMPOSITION OF 3 GRAMS OF BORAZINE

Volatile at room temperature

Fraction I, 0.05 g., retained by a -45° trap but passing through a -23° trap
 Fraction II, 0.05 g., retained by a -15° trap but passing through a 0° trap
 Fraction III, 0.05 g., retained by a 0° trap but volatile at room temperature

Nonvolatile at room temperature

Fraction IV, 0.01 g., volatile in a sublimator at 90°
 Fraction V, ca. 2 g., nonvolatile at 90° in a sublimator
 Fraction VI, ca. 0.5 g., tan colored, nonvolatile solid at bottom of reaction flask

Characterization of Fraction II, $\text{B}_5\text{N}_6\text{H}_3$.—Fraction II formed colorless, needle-like crystals on the walls of the trap. The melting point of the crude material was 16–20°. After repeated trap to trap distillation in a vacuum system the melting point of the crystals was 27–30°.

Anal. Calcd. for $\text{B}_5\text{N}_6\text{H}_3$: B, 40.9; N, 53.0. Found: B, 41.2, 41.2; N, 52.2, 51.4.

The infrared spectrum of a liquid film of $\text{B}_5\text{N}_6\text{H}_3$ is given in Table II and an X-ray diffraction pattern is listed in Table III.

A complete mass spectral analysis of borazine has already been reported.¹² The strongest and most characteristic group of peaks in the mass spectrum of borazine is the series due to the parent and the parent minus one or more hydrogen atoms. For this reason the same group of peaks, those due to the parent and the parent minus one or more hydrogen atoms, was determined accurately for the materials formed by the thermal decomposition of borazine.

(12) American Petroleum Institute Research Project 44, "Mass Spectral Data," Serial No. 1346, Petroleum Research Laboratory, Pittsburgh, Pa., 1956.

TABLE II

INFRARED SPECTRA OF FRACTIONS I, II AND III

The symbols used to designate intensities are, s = strong, m = medium, w = weak, v = very, sh = shoulder, and br = broad.

Fraction I Microns	I/I^0	Fraction II, $\text{B}_5\text{N}_6\text{H}_3$ Microns	I/I^0	Fraction III, $\text{B}_5\text{N}_6\text{H}_3$ Microns	I/I^0
2.88	m	2.89	m	2.89	s
3.44	w	4.01	m	3.99	s
3.55	sh	6.95	vs(br)	6.95	vs(br)
4.01	s	7.35	sh	7.47	sh
6.42	w	8.35	w	7.81	m
6.69	vs	11.15	s	8.00	m
6.94	vs	14.20	m	11.25	vs
7.16	sh			12.95	w
7.40	m				
7.82	m				
7.95	sh				
9.65	m				
10.83	s				
10.89	sh				
10.98	s				
14.35	s				

TABLE III

X-RAY DIFFRACTION PATTERNS OF FRACTIONS II AND III

The symbols used to designate intensities are, s = strong, m = medium, w = weak, v = very and br = broad.

Fraction II, $\text{B}_5\text{N}_6\text{H}_3$ $d, \text{Å.}$	I/I^0	Fraction III, $\text{B}_5\text{N}_6\text{H}_3$ $d, \text{Å.}$	I/I^0
10.4	s	11.2	s
5.39	vs	9.60	m
5.09	w	7.69	m
4.27	w(br)	5.42	vvs
4.02	vs	4.88	s
3.75	w(br)	4.37	w
3.38	vs	3.67	vvs
3.05	m	3.48	s
2.79	w	3.20	m
2.43	m(br)	3.09	m
2.17	w(br)	2.72	m
2.01	w	2.63	w
1.94	w	2.53	w
1.87	w	2.44	w
1.71	vw	2.36	w
1.68	vw	2.19	vw
1.64	vw	2.04	vw
1.61	vw	1.92	vw
		1.80	vw
		1.54	vw

In the mass spectrum of Fraction II a strong series of peaks was observed in the m/e region of 129–133 (relative intensities: 129, 13; 130, 45; 131, 91; 132, 100; 133, 45). No peaks were observed at m/e greater than 133. The m/e of the peaks was determined unambiguously by the introduction of a small quantity of SiCl_4 into the mass spectrometer while the spectrum of $\text{B}_5\text{N}_6\text{H}_3$ was being determined.

The mass spectrum just described is in good agreement with that expected for the compound $\text{B}_5\text{N}_6\text{H}_3$. The highest mass observed is 133, that due to the molecules of $\text{B}_5\text{N}_6\text{H}_3$ in which all of the boron atoms are those of B^{11} . These results, together with the chemical analyses, unambiguously establish the molecular formula of the compound. The relative intensities of the peaks are also in quantitative agree-

ment with those expected for $B_5N_5H_8$, being consistent with those expected for a compound containing 5 boron atoms. Perhaps the best way to show this is to use the data to calculate a monoisotopic spectrum for the ions of $B_5N_5H_8$ due to the parent and the parent minus hydrogen atoms as follows. Naturally occurring boron was assumed to be composed of 20% B^{10} and 80% B^{11} . The distribution of the isotopes of boron in $B_5N_5H_8$ was computed with the aid of a simple theorem of probability and the results were used, together with the intensity data, to calculate a monoisotopic spectrum of $B_5N_5H_8$ (Table IV). A self-consistent fit of the observed data was obtained.

TABLE IV

MONOISOTOPIC MASS SPECTRA OF FRACTIONS I, II AND III

(Ionizing electron energy = 100 volts)

Fraction I, $B_2N_5H_8$ Ion	I/I^0	Fraction II, $B_5N_5H_8$ Ion	I/I^0	Fraction III, $B_6N_6H_{10}$ Ion	I/I^0
$B_2N_5H_8$	100	$B_5N_5H_8$	100	$B_6N_6H_{10}$	50.5
$B_2N_5H_7$	91.7	$B_5N_5H_7$	97.2	$B_6H_6H_9$	100
$B_3N_5H_6$	1.0	$B_5N_5H_6$	18.0	$B_6N_6H_8$	4.6
		$B_5N_5H_5$	2.0	$B_6N_6H_7$	88.5

Characterization of Fraction III, $B_6N_6H_{10}$.—Fraction III deposited as colorless, needle-like crystals on the walls of the trap. The crude material melted at 54–56°. After several sublimations the material had a melting point of 59–60°.

Anal. Calcd. for $B_6N_6H_{10}$: B, 40.8; N, 52.8; active H for 4 B–H bonds per molecule, 2.53; active H for 5 B–H per molecule, 3.17; active H for 6 B–H per molecule; 3.80. Found: B, 40.3, 41.1; N, 50.9, 51.4; active H, 3.11.

The infrared spectrum of a sample of $B_6N_6H_{10}$ contained in a KBr pellet is recorded in Table II and an X-ray diffraction pattern is given in Table III.

In the mass spectrum of $B_6N_6H_{10}$ a strong series of peaks was observed in the m/e region of 154–160 (relative intensities: 154, 13; 155, 43; 156, 80; 157, 100; 158, 100; 159, 87; 160, 25). No peaks were observed at m/e greater than 160. The assignment of m/e to the peaks was confirmed by the introduction of $SiCl_4$ as a calibrating substance. The spectrum is in qualitative agreement with that expected for $B_6N_6H_{10}$. The highest mass observed is 160, that due to the molecules of $B_6N_6H_{10}$ in which all of the boron atoms are those of B^{11} . These results, together with the chemical analyses, unambiguously establish the molecular formula of the compound.

A monoisotopic spectrum (Table IV) was computed using the method described for $B_5N_5H_8$. One would expect that the relative intensity of the ions $B_6N_6H_9^+$, $B_6N_6H_8^+$ and $B_6N_6H_7^+$ should decrease in a uniform manner. The apparent relative intensity of the $B_6N_6H_7^+$ is therefore rather surprising. Two explanations are possible. One is that the $B_6N_6H_{10}$ sample contained a small amount of an impurity which increased the relative intensity of the $B_6N_6H_7^+$; the fact that spectra of $B_6N_6H_{10}$ from different preparations show good agreement makes this seem unlikely. Another possible explanation is that the $B_6N_6H_7^+$ has some unusual structural features which make it more stable than expected.

Characterization of Fraction I, Material Retained by a –45° Trap.—This material was evidently a mixture, the major component of which is thought to be $B_3N_3H_3$. Immediately after being isolated it was a colorless, mobile liquid at room temperature. An infrared absorption spectrum (Table II) of the material contained in a 10 cm. gas cell (vapor pressure 3 mm. at room temperature) was taken. On standing for a short time a white solid began to separate from the liquid. In a few weeks the material changed to a white, nonvolatile solid.

Mass spectra of several freshly prepared samples of Fraction I were obtained. A series of peaks at m/e of 107–111 (relative intensities: 107, 2; 108, 13; 109, 53; 110, 100; 111, 60) were the strongest peaks in the spectra. No peaks of m/e higher than 111 were observed. A series of very weak peaks was observed at m/e of 90–96, and the relative inten-

sities of the peaks below m/e of 80 corresponded to the relative intensities expected for borazine.

The major component of this mixture is evidently the material giving the series of peaks at m/e of 107–111. The series of peaks at m/e of 90–96 might be due to a small amount of an unknown impurity or they could be due to fragments of the major component. Borazine was present in small amounts in all the samples, evidently formed by the decomposition of some of the material after it was collected, since borazine easily passes through a –45° trap.

Consideration of the infrared spectrum and the relative intensities of the series of mass spectral peaks at m/e 107–111 show that the molecular formula of the major component of the mixture is probably $B_3N_3H_3$. The infrared spectrum indicated that the major component was a borazine derivative. The highest peak observed in the mass spectrum, that due to the molecule in which all of the boron atoms are B^{11} , was 111. From the infrared spectrum the molecule contains the borazine ring skeleton, in this case $B_3^{11}N_3$, accounting for 75 of the 111 mass units. Thirty-six mass units remain unaccounted for and must be made up of atoms of B^{11} , nitrogen or hydrogen. Thus compounds containing 3, 4, 5 or 6 boron atoms are all possibilities. Attempts were made to fit the intensity data for the series of peaks at m/e 107–111 by assuming that the compound contained 3, 4, 5 or 6 boron atoms. The procedure used was the calculation of monoisotopic mass spectra, using the method outlined for the calculation of the monoisotopic spectrum of $B_5N_5H_8$, and seeing if the results could be made self-consistent. Only when one assumed that the molecule contained 3 boron atoms was a satisfactory, self-consistent fit obtained. The assumption that the molecule contained 4 boron atoms gave a considerably less satisfactory fit, while the assumption that the molecule contained 5 or 6 boron atoms was obviously incorrect. The molecule with a mass number of 111 must therefore contain 3 atoms of B^{11} and the remainder of the molecule must be made up of nitrogen and hydrogen atoms. Five nitrogen atoms is the maximum number possible with the mass that remains. A molecule containing four nitrogen atoms can be eliminated by valence considerations. This reasoning leads one to $B_3N_3H_3$ as the most probable composition of the major component of the mixture. Table IV shows the computed monoisotopic spectrum of $B_3N_3H_3$.

Characterization of Fraction IV, Material Volatile at 90° in a Sublimator.—Fraction IV was a white solid, evidently a mixture. Melting points of samples from different preparations varied somewhat. Many samples showed signs of softening at 70° and melted from 90–95° with the evolution of a gas. Some samples melted more sharply from 100–103°, still with the evolution of a gas. The infrared spectrum of a sample contained in a KBr pellet and an X-ray diffraction pattern of the material were obtained.

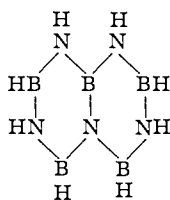
Only one preliminary mass spectral analysis of this material was carried out. Five to ten very strong peaks were observed at m/e about 173, with weaker series about m/e of 157 and 185.

Characterization of Fraction V, Material Nonvolatile at 90° in a Sublimator.—Fraction V was a white solid which did not melt at temperatures up to 250°. Analysis showed that it contained boron and nitrogen in a one to one mole ratio. The material liberated hydrogen when treated with water, demonstrating the presence of active hydrogens. An infrared spectrum of a sample of this material contained in a KBr pellet was obtained.

Discussion

The experimental data for the pyrolysis of borazine and the nature of the products clearly indicate the structural pattern characteristic of boron–nitrogen polymeric frameworks and the way such frameworks proliferate in the sequence of reactions leading from borazine to boron nitride. As in borazine itself, alternating, tricoordinated boron and nitrogen atoms build up more and more extended planar polycyclic structures which possess considerable aromatic character and probably involve π bonding.

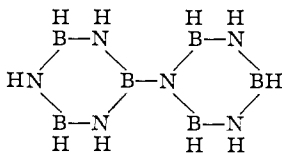
The Structure of $B_5N_5H_8$, Fraction II.—The following structure, analogous to that of naphthalene, is consistent with all of the experimental observations.



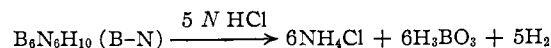
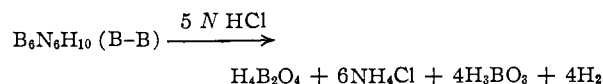
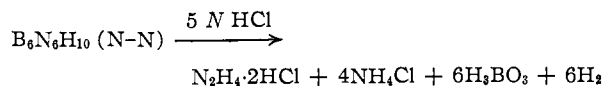
The infrared spectrum (Table II) shows frequencies which correspond to B-H (4.0μ) and N-H (2.9μ) stretching vibrations and the characteristic^{13,14} borazine ring vibration (6.9μ). The powder X-ray diffraction patterns of $B_5N_5H_8$ (Table III) and naphthalene are similar in complexity although the crystals are not obviously isomorphous. One, however, would not expect $B_5N_5H_8$ and naphthalene to be isomorphous. Naphthalene crystallizes in the space group $P2_1/a$ with two molecules per unit cell.¹⁵ This requires the naphthalene molecule to have a center of inversion. Since $B_5N_5H_8$ does not have a center of inversion, it cannot be strictly isomorphous with naphthalene. Still, one would expect its structure to be related to that of naphthalene. Lonsdale¹⁶ has shown that although 1,3,5-trichlorobenzene and 2,4,6-trichloroborazine are not isomorphous they do have related crystal structures.

The above observations are strong support for the naphthalene-like structure proposed for $B_5N_5H_8$.¹⁷ While one can imagine other structures having the formula $B_5N_5H_8$, they are usually eliminated by the experimental observations. In addition, it is difficult to see how these other structures could be formed by the thermal decomposition of borazine.

The Structure of $B_6N_6H_{10}$, Fraction I.—The following structure, analogous to that of diphenyl, is consistent with all of the experimental observations.



The infrared spectrum (Table II) shows frequencies which correspond to B-H and N-H stretching vibrations and a characteristic borazine ring vibration. The B-N bond is only one of three possible bonds which could connect the borazine rings in a diphenyl-like structure. B-B and N-N bonds are also possibilities. The fact that $B_6N_6H_{10}$ gives five moles of hydrogen on hydrolysis is strong support for a diphenyl-like structure with a B-N central bond. The expected reactions with 5 *N* hydrochloric acid of the three possible diphenyl-like structures of $B_6N_6H_{10}$ are



The structure containing an N-N bond is definitely eliminated since $B_6N_6H_{10}$ gives only 5 moles of hydrogen on hydrolysis. If $B_6N_6H_{10}$ contained a B-B bond one would expect it to give 4 moles of hydrogen and one mole of subboric acid on hydrolysis. Subboric acid, if further hydrolyzed, might give an additional mole of hydrogen which would make it impossible to distinguish between a B-B and a B-N central bond. Wiberg,¹⁸ however, has shown that subboric acid is comparatively stable to hydrolysis. Aqueous solutions of subboric acid persist at room temperature and are stabilized by acid. Stock¹⁹ pointed out that B_2Cl_4 dissolves in water at room temperature without the evolution of hydrogen. Therefore, for the conditions under which the hydrolysis of $B_6N_6H_{10}$ was run (acid hydrolysis at room temperature), a B-B bond would not be hydrolyzed. Since the compound evolved 5 moles of hydrogen on hydrolysis, the central bond must be a B-N bond.

The powder X-ray diffraction patterns of $B_6N_6H_{10}$ (Table III) and biphenyl are similar in complexity, but the two crystals are not obviously isomorphous. Biphenyl is believed²⁰ to belong to the space group $P2_1/a$ with two molecules per unit cell. As in the case of $B_5N_5H_8$ and naphthalene, $B_6N_6H_{10}$ cannot be strictly isomorphous with biphenyl. Again, however, one would expect its crystal structure to be related to that of biphenyl.

The above observations are strong support for the biphenyl-like molecular structure proposed for $B_6N_6H_{10}$, and the name diborazinyl is therefore appropriate. One can imagine still other structures having the formula $B_6N_6H_{10}$ but they are eliminated by the experimental observations. In addition, it is obvious that the biphenyl-like material could be formed in the thermal decomposition of borazine simply by intermolecular condensation with the elimination of H_2 and the formation of a B-N bond.

The Structure of the Material Retained by a -45° Trap, Fraction I.—On the basis of a mass spectral study, the major component of Fraction I is probably $B_3N_3H_6$. An infrared spectrum of the material (Table II) shows B-H and N-H stretching frequencies and characteristic borazine ring vibrations. This seems to indicate that the major component is a borazine ring derivative. Assuming that the borazine ring is retained, two extra NH groups remain to be accounted for. It seems most likely that these go to form two amino groups attached to the borazine ring. The major component of this mixture might well be 2,4-diaminoborazine.

(13) W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950).

(14) J. J. Becher and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958).

(15) S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.*, **2**, 233, 238 (1949).

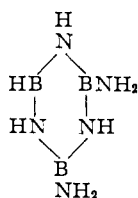
(16) K. Lonsdale, *Nature*, **184**, 1060 (1959).

(17) N.m.r. examination of $B_5N_5H_8$ now under way has given preliminary results which support this structure.

(18) E. Wiberg and W. Ruschmann, *Ber.*, **70**, 1393 (1937).

(19) A. Stock, A. Brandt and H. Fischer, *ibid.*, **58**, 643 (1925).

(20) J. Dhar, *Proc. Natl. Inst. Sci. India*, **15**, 11 (1949).



Niedenzen and Dawson²¹ have pointed out that 2,4,6-triaminoborazine is quite unstable. They could not isolate 2,4,6-triaminoborazine as a pure compound. The instability of Fraction I is thus consistent with the supposition that it is an amino-substituted borazine, 2,4-diaminoborazine. Niedenzen and Dawson prepared several aminoborazines in which the amine nitrogen was substituted. In all of these compounds a very strong peak at 6.7 μ and another at 7.4 μ was noted in the infrared spectra. The infrared spectrum of Fraction I shows a strong band at 6.7 μ and a weaker one at 7.4 μ , again consistent with the supposition that the major component is 2,4-diaminoborazine.

The Structure of the Material Volatile at 90° in a Sublimator, Fraction IV.—Melting points and a preliminary mass spectral analysis suggest that Fraction IV is a mixture. It seems logical to assume that higher molecular weight products would be of the same type as those already described for $B_5N_5H_8$, $B_6N_6H_{10}$ and $B_3N_3H_6$. The mass spectrum shows a strong series of peaks about m/e of 185. These might be due to an anthracene-like $B_7N_7H_{10}$ (mol. wt. 184) or to a diamino-substituted analog of biphenyl, $B_6N_8H_{12}$ (mol. wt. 189). The series of peaks about m/e of 173 might be due to a monoamino-substituted analog of biphenyl, $B_6N_7H_{11}$ (mol. wt. 174), or to the fused tricyclic molecule $B_6N_7H_9$ (mol. wt. 172). The infrared spectrum is consistent with the above supposition. It shows B-H and N-H stretching vibrations and the characteristic borazine ring vibration.

The Structure of the Material Nonvolatile at 90° in a Sublimator, Fraction V.—All of the observations made on this material are consistent with the

(21) K. Niedenzen and J. W. Dawson, *THIS JOURNAL*, **81**, 3561 (1959).

assumption that it is a highly condensed boron-nitrogen framework approaching that of boron nitride but still containing B-H and N-H bonds. The infrared spectrum of Fraction V shows some similarity to that of boron nitride but also shows that B-H and N-H bonds are present.

Comparison of the Pyrolysis of Borazine and Benzene.—The experimental data available do not allow one to write a detailed mechanism for the thermal decomposition of borazine. However, the observation of first order kinetics does suggest that a free radical mechanism is involved. The intermediate compounds obtained indicate that on pyrolysis borazine must first form dicyclic boron-nitrogen compounds by loss of hydrogen. These compounds in turn lose hydrogen to form an extended boron-nitrogen framework like that of boron nitride. The compounds which were isolated imply that at least two types of reaction are taking place. The existence of $B_5N_5H_8$ and $B_3N_3H_6$ indicate that there is some breakdown of the borazine ring. The production of $B_6N_6H_{10}$ does not require the breaking of the borazine ring but only intermolecular dehydrogenation.

The thermal decomposition of borazine is not completely analogous to the thermal decomposition of benzene. Intermediates in the thermal decomposition of benzene are biphenyl, terphenyls and triphenylene.²² No modern worker has been able to isolate any naphthalene from the thermal decomposition products of benzene. Intermolecular dehydrogenation without the breaking of benzene rings, therefore, is the important mechanism in the thermal decomposition of benzene. This process of intermolecular dehydrogenation is also important in the thermal decomposition of borazine. However, the presence of $B_5N_5H_8$ and $B_3N_3H_6$ in the decomposition products of borazine require that ring cleavage must be another important mechanism in its thermal decomposition. Thus the thermal decomposition of borazine proceeds in a more complicated manner than does the thermal decomposition of benzene.

(22) C. R. Kinney and E. DelBel, *Ind. Eng. Chem.*, **46**, 548 (1954).

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Preparation and Properties of Tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes

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The cohydrolysis of trimethylchlorosilane with a dialkyltin dichloride has been studied as a means of preparing compounds containing the Si-O-Sn linkage. Crystalline tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes, $Me_3SiO(SnR_2O)_2SiMe_3$, are obtained by hydrolyzing a mixture of Me_3SiCl and R_2SnCl_2 ($R = Me, Et, n-Pr, n-Bu$) in benzene with excess aqueous ammonia in petroleum ether. Bis-(trimethylsiloxy)-dialkyltin compounds, $Me_3SiOSnR_2OSiMe_3$, are formed when an equivalent amount of aqueous ammonia is used, but these compounds are unstable and cannot be isolated in a pure state. Tetraalkyl-1,3-bis-(trimethylsiloxy)-distannoxanes also are produced by the cohydrolysis of Me_3SiCl with a tetraalkyl-1,3-dichlorodistannoxane. Some chemical and physical properties of these compounds have been investigated, and characteristic infrared absorption frequencies are given.

The search for polymers with greater stability at high temperatures has brought about a recent

(1) National Science Foundation Fellow at Osaka University, 1960.

interest in the preparation of modified organosiloxanes, in which some of the silicon atoms in the siloxane chain are replaced by various metallic