TABLE III
RELATIVE VALUES OF TRANSITION STATE THERMODYNAMIC QUANTITIES ABOVE THE DISSOCIATION PRODUCTS
(kcal./mole, 30°)

| Substituent | $\Delta G^{*a}$ | $-\Delta H_2^{b}$ | $\Delta H^* + \Delta H_2^{b}$ | $\Delta G^{*a} + \Delta H_2^{b}$ |
|---|---|---|---|---|
| 2-Ethyl | 24.6 | 16.9 | 6.5 | 7.7 |
| 4-Methyl | 26.4 | 18.5 | 6.4 | 7.9 |
| 2-Methyl | 25.2 | 17.2 | 5.7 | 8.0 |
| 3-Methyl | 26.1 | 18.2 | 5.5 | 7.9 |
| 2,4-Dimethyl | 25.7 | 17.7[c] | 5.5 | 8.0 |
| H | 25.8 | 17.9 | 4.8 | 7.9 |
| 2,6-Dimethyl | 23.4 | 16.3 | 4.6 | 7.1 |
| 2,4,6-Trimethyl | 24.2 | 16.8[c] | ... | 7.4 |

[a] Free energy of activation. [b] Reference 10; enthalpy for the reaction $^1/_2B_2H_6$ + py → $pyBH_3$. [c] The enthalpy of reaction without steric effects is estimated by interpolation of the linear relation between enthalpy of borane adduct formation and the enthalpy of neutralization by $H^+$ (ref. 12), giving $\Delta H$(2,4-dimethyl) = −19.0 kcal./mole and $\Delta H$(2,4,6-trimethyl) = 19.5 kcal./mole. Strain energies of 1.3 kcal. for one and 2.7 kcal. for two *o*-methyl groups are added, respectively, to give the final answer (ref. 10).

with substitution. It is noteworthy that even the introduction of two *ortho* substituents does not change this result. This is indeed surprising and carries with it the strong implication that the free energy of producing the transition state from the dissociated product is also a constant, *i.e.*, the activation free energies for the reverse of dissociation are constant. This interpretation is most plausible since, by an argument similar to the one made for the enthalpies, one would expect entropy changes of transfer from one solution to another to be invariant on substitution on the pyridine. Moreover, it has been demonstrated for pyridine adducts of $B(CH_3)_3$ that the entropies for the reaction py (sol) + $B(CH_3)_3 \rightarrow pyB(CH_3)_3$ (sol) do not vary with substitution.[14] Making a similar assumption for formation of $BH_3$ adducts we arrive at the conclusion that the quantities $\Delta G^* + \Delta H_2$ differ from the free energies of the transition state by only a constant amount and that constancy of one in a series of related reactions implies constancy of the other.

Thus, in the present reaction, the boron–nitrogen bond is stretched to a constant free energy above the products. Stronger bases will necessitate longer interatomic distances to achieve this. In fact, as is evident from the enthalpy trend in Table III, the remaining B–N bond energy may actually be less for the stronger base, since the increased freedom of motion in a more highly stretched state will contribute a stabilizing and compensating increase in the entropy of the transition state.

**Acknowledgment.**—Financial support through a grant by the Research Corporation is gratefully acknowledged.

(14) H. C. Brown and D. Gintis, *J. Am. Chem. Soc.*, **78**, 5378 (1956).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# The Reactions of Borazanaphthalene and Borazine with Anhydrous Hydrogen Bromide and Hydrogen Chloride[1]

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The reactions of borazanaphthalene, $B_5N_5H_8$, and borazine, $B_3N_3H_6$,[3] with anhydrous hydrogen bromide and hydrogen chloride and the subsequent pyrolysis of the addition products have been examined. Regardless of the reactant mole ratio used, only materials of empirical compositions $B_5N_5H_8 \cdot 5HBr$, $B_5N_5H_8 \cdot 5HCl$, $B_3N_3H_6 \cdot 3HBr$, and $B_3N_3H_6 \cdot 3HCl$ are formed. The infrared spectra of these addition compounds are consistent with covalent rather than ionic behavior and with the conclusion that the hydrohalides add across the B–N bonds to form additional B–X and N–H bonds. When these adducts are heated at 100 to 130° with or without continued removal of the volatile products, the principal reaction is dissociation to barazanaphthalene or borazine and the hydrogen halide, with small and variable amounts of hydrogen and a nonvolatile residue also forming. Deuterium chloride addition compounds yield N-deuterioborazanaphthalene or -borazine and hydrogen chloride when pyrolyzed. The compounds 2,4,5,7-tetrahaloborazanaphthalene and 2,4,6-trihaloborazine were never observed as products in these experiments.

The addition of polar molecules, such as HCl, to borazine to form adducts of the type $B_3N_3H_6 \cdot 3HCl$ has long been known.[4,5] It has been suggested that such polar molecules add across the B–N bonds, the more electronegative group bonding to boron and the less elec-

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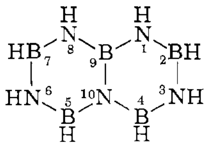
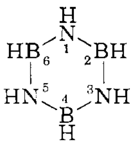
[1] Presented before the Inorganic Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 10, 1963, and abstracted from a thesis submitted to the Graduate School of Cornell University by O. T. Beachley, Jr., Sept. 1963.

[2] Gulf Research and Development Company Fellow, 1961–1962; NSF Research Fellow, 1962–1963.

(3) The following numbering systems will be used in this paper.



borazanaphthalene



borazine

tronegative group adding to nitrogen to produce cyclic borazanes such as $H_3Cl_3B_3N_3H_6$, the structural analogs of the cyclohexanes. Now that the synthesis and structure of borazanaphthalene have been established,[6,7] it is of interest to extend the study of the addition of polar molecules to this bicyclic B–N system. The pyrolysis of the adducts of borazanaphthalene with the hydrogen halides has given results which have led to further study of the pyrolytic behavior of the hydrohalide adducts of borazine.

## Experimental

**Materials.**—Borazine was prepared in the usual fashion[8] and borazanaphthalene was made from borazine by the electrical discharge method.[7] Hydrogen bromide, hydrogen chloride, and deuterium chloride (prepared by the reaction of acetyl chloride with 98% $D_2O$) were purified by fractional vacuum distillation. All solvents were dried by refluxing with sodium and then were distilled.

**Reaction of Borazanaphthalene with Excess Hydrogen Bromide and Hydrogen Chloride.**—In a typical experiment 1.53 mmoles of $B_5N_5H_8$ and 8.15 mmoles of hydrogen bromide were mixed in 15 ml. of toluene at $-78°$. The mixture was allowed to stand for several hours at 20°, and then the materials volatile at 20° were drawn off and fractionated using traps at $-46$, $-96$, and $-196°$. Only unreacted hydrogen bromide (0.55 mmole) and the toluene collected in the traps. A colorless, nonvolatile solid, which had a ratio of 4.97 moles of HBr per mole of $B_5N_5H_8$, remained. A very small amount of hydrogen, probably the result of hydrolysis since it is difficult to remove all traces of water from hydrogen halides, was also observed. Hydrogen chloride and deuterium chloride reacted in a similar manner, the HX to $B_5N_5H_8$ reacting mole ratios being 4.96 and 4.96, respectively.

Many repetitions of these reactions were run using various excesses of hydrogen halide to confirm the stoichiometry. The complete reaction and removal of the volatile materials from the reaction mixture were also accomplished at $-78°$ and at 0°. Benzene, diethyl ether, and pentane were also used as solvents for the $B_5N_5H_8$. The products were always consistent with the empirical formulations $B_5N_5H_8 \cdot 5HBr$ or $B_5N_5H_8 \cdot 5HCl$.

*Anal.* Calcd. for $B_5N_5H_8 \cdot 5HBr$: B, 10.0; N, 13.0; Br, 74.4. Found: B, 10.1; N, 13.0; Br, 74.2. Calcd. for $B_5N_5H_8 \cdot 5HCl$: B, 17.2; N, 22.3; Cl, 56.3. Found: B, 17.0; N, 22.3; Cl, 56.1.

The following equation therefore summarizes the addition reaction.

$$B_5N_5H_8 + 5HX = B_5N_5H_8 \cdot 5HX$$

When borazanaphthalene and hydrogen chloride or hydrogen bromide were allowed to react in the absence of a solvent, there was incomplete reaction.

**Reaction of One Mole of Borazanaphthalene with Two Moles of Hydrogen Bromide or Hydrogen Chloride.**—This series of experiments, using limited amounts of hydrogen halide, was undertaken to determine if products other than $B_5N_5H_8 \cdot 5HBr$ and $B_5N_5H_8 \cdot 5HCl$ could be obtained. For example, if 2 moles of HX would add to only one ring a tetralin type of derivative might be formed.

In a typical experiment 0.666 mmole of $B_5N_5H_8$ was mixed with 1.33 mmoles of HBr in *n*-pentane at $-78°$. Upon fractionation of the reaction mixture 0.372 mmole of unreacted $B_5N_5H_8$ and 0.1415 g. of a colorless, nonvolatile solid were isolated. The stoichiometry, the elemental analysis, and infrared spectrum of the solid showed that $B_5N_5H_8 \cdot 5HBr$ was the only product. When hydrogen chloride was used, $B_5N_5H_8 \cdot 5HCl$ was the only product.

These results are consistent with the assumption that the initial reaction between borazanaphthalene and the hydrogen halide probably occurred at the 9–10 boron–nitrogen ring juncture bond. This would destroy the resonance stabilization of both rings and the addition of a total of 5 moles of hydrogen halide would be required to form a stable product.

**The Pyrolysis of $B_5N_5H_8 \cdot 5HBr$ and $B_5N_5H_8 \cdot 5HCl$ at 130°.**—In a typical experiment, summarized quantitatively in Table I, 0.3742 mmole of $B_5N_5H_8 \cdot 5HBr$ was pyrolyzed at 130° on the vacuum line. The volatile products of the reaction were continually drawn off through $-78$ and $-196°$ traps, and hydrogen was removed and measured by means of a Toepler pump and a gas buret and identified by its mass spectrum. After approximately 5 hr. of pyrolysis there was no further buildup of volatile products.

TABLE I

PYROLYSIS OF $B_5N_5H_8 \cdot 5HBr$ AND $B_5N_5H_8 \cdot 5HCl$ AT 130° AND IN THE THERMOGRAVIMETRIC BALANCE

| | $B_5N_5H_8 \cdot 5HBr$ | | $B_5N_5H_8 \cdot 5HCl$ | |
|---|---|---|---|---|
| | 130° | TG[a] | 130° | TG[a] |
| Mole ratio $H_2$ collected to $B_5N_5H_8 \cdot 5HX$ heated | 0.706 | 1.24 | 0.526 | 0.633 |
| Mole ratio HX collected to $B_5N_5H_8 \cdot 5HX$ heated | 3.54 | 3.32 | 3.12 | 2.82 |
| Mole ratio $B_5N_5H_8$ collected to $B_5N_5H_8 \cdot 5HX$ heated | 0.226 | 0.209 | 0.313 | 0.318 |
| % of initial sample isolated as recombined $B_5N_5H_8 \cdot 5HX$ | 20.0 | 26.7 | 30.2 | 42.5 |
| % of initial sample remaining as nonvolatile residue | 20.8 | 17.7 | 20.2 | 11.1 |

[a] Ambient temperature in thermogravimetric balance.

A white, fluffy solid residue containing boron, nitrogen, hydrogen, and bromine remained in the pyrolysis bulb. This residue was only slightly reactive to water. The $-78°$ trap when warmed to 20° contained a volatile solid and a nonvolatile solid. The volatile solid was identified by its mass spectrum as borazanaphthalene. The nonvolatile solid was shown by its elemental analysis and infrared spectrum to be $B_5N_5H_8 \cdot 5HBr$. The $-196°$ trap contained only hydrogen bromide.

These results are consistent with the assumption that the addition compound first undergoes the thermal dissociation reaction

$$B_5N_5H_8 \cdot 5HBr \xrightarrow{130°} B_5N_5H_8 + 5HBr$$

Then some of the $B_5N_5H_8$ may undergo decomposition to give hydrogen and boron–nitrogen fragments which react with HBr to form nonvolatile products. At the same time some of the adduct may be undergoing dehydrogenation to give polymeric material. In the $-78°$ trap some of the adduct is re-formed and collects along with $B_5N_5H_8$, the rest of the more volatile HBr passing on and condensing in the $-196°$ trap.

In other experiments when the hydrogen was removed more slowly, a higher ratio of hydrogen to initial sample was observed and less $B_5N_5H_8$ was isolated. The diffusion of borazanaphthalene out of the hot zone was probably hindered by the higher partial pressure of hydrogen and the $B_5N_5H_8$ decomposed to form more hydrogen and nonvolatile products.

When $B_5N_5H_8 \cdot 5HCl$ was pyrolyzed at 130° the same type of products, $H_2$, HCl, $B_5N_5H_8$, and re-formed $B_5N_5H_8 \cdot 5HCl$ were observed (see Table I). There was always a fluffy, white, nonvolatile residue containing boron, nitrogen, hydrogen, and chlo-

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(4) A. Stock, E. Wiberg, and H. Martini, *Ber.*, **63**, 2927 (1930).

(5) E. Wiberg and A. Boltz, *ibid.*, **73**, 209 (1940).

(6) A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *J. Am. Chem. Soc.*, **83**, 1337 (1961).

(7) A. W. Laubengayer and O. T. Beachley, Jr., Advances in Chemistry, No. 42, American Chemical Society, Washington, D. C., 1963, p. 281.

(8) L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).

rine remaining in the pyrolysis bulb. None of the products had properties indicative of a chloroborazanaphthalene molecule.

**Pyrolysis of $B_5N_5H_8 \cdot 5HBr$ and $B_5N_5H_8 \cdot 5HCl$ in the Thermogravimetric Balance.**—The thermogravimetric balance (American Instrument Co.) was programmed for a 3°/min. rise in temperature in the range of 25 to 950°. A portable vacuum system, which permitted the volatile products to be withdrawn continually, separated, and measured in the manner previously described, was attached to the outlet of the furnace tube.

Loss in weight by $B_5N_5H_8 \cdot 5HBr$ started at about 50° and proceeded in one step rapidly through the range 100 to 200°, tailing off to constant weight at about 600°. Decomposition of $B_5N_5H_8 \cdot 5HCl$ started at about 75° and proceeded in one step rapidly through the range 100 to 180°, tailing off to constant weight at about 500°.

The products of the pyrolysis, hydrogen, the hydrogen halide, $B_5N_5H_8$, re-formed addition compound, and a nonvolatile residue, were identical with those observed at 130°. The amounts of the various products are summarized in Table I.

**Pyrolysis of $B_5N_5H_8 \cdot 5HBr$ and $B_5N_5H_8 \cdot 5DCl$ in the Mass Spectrometer.**—The sample was contained in a small tube connected directly to the variable leak device of the mass spectrometer[6] so that the volatile products of the reaction were observed directly. The relative percentages of these volatile products are given in Table II. Hydrogen and hydrogen bromide were the only products observed during the pyrolysis of $B_5N_5H_8 \cdot 5HBr$ at 90°, a nonvolatile residue remaining in the tube. At 110° $B_5N_5H_8 \cdot 5DCl$ was observed to decompose principally to borazanaphthalene and hydrogen chloride. However, other products such as small quantities of monochloroborazine and dichloroborazine indicated secondary reactions. Volatile chloroborazanaphthalenes were not detected. The very small amount of borazanaphthalene observed by the mass spectrometer probably was due to decomposition in the hot zone.

**Reactions of Borazine with Anhydrous Hydrogen Bromide and Hydrogen Chloride.**—Failure to get appreciable yields of haloborazanaphthalenes by pyrolysis of the $B_5N_5H_8 \cdot 5HX$ adducts suggested that the report[5] that on pyrolysis $B_3N_3H_6 \cdot 3HX$ adducts undergo dehydrogenation to yield haloborazines needed further study. Accordingly, borazine was allowed to react with hydrogen bromide and hydrogen chloride. Even with excess borazine, 3 moles of HX always combined with 1 mole of $B_3N_3H_6$.

*Anal.* Calcd. for $B_3N_3H_6 \cdot 3HBr$: B, 10.0; N, 13.0; Br, 74.2. Found: B, 10.2; N, 13.1; Br, 73.8. Calcd. for $B_3N_3H_6 \cdot 3HCl$: B, 17.1; N, 22.1; Cl, 56.0. Found: B, 17.5; N, 21.9; Cl, 55.7.

**Pyrolysis of $B_3N_3H_6 \cdot 3HBr$ and $B_3N_3H_6 \cdot 3HCl$ at 130° and in the Thermogravimetric Balance.**—The experimental methods were identical with those used for the borazanaphthalene compounds, except that a −96° trap was substituted for the −78° trap. The results obtained when the volatile products were continually removed are summarized in Table III. The products of the pyrolysis, hydrogen, the hydrogen halide, borazine, re-formed adduct, and a nonvolatile residue, and the thermogravimetric plots were analogous to those obtained for the pyrolysis of $B_5N_5H_8 \cdot 5HBr$ and $B_5N_5H_8 \cdot 5HCl$. There was no evidence for the formation of 2,4,6-trihaloborazines in these experiments where the volatile products were withdrawn continually from the hot zone. It was suggested that, if the volatile products were kept in the hot zone by carrying out the pyrolysis in a sealed tube, trihaloborazines might be formed, as previously reported to take place at 100°.[5]

**Sealed Tube Pyrolysis of $B_3N_3H_6 \cdot 3HCl$ and $B_3N_3H_6 \cdot 3HBr$.**—When $B_3N_3H_6 \cdot 3HCl$ was held at 130° for 8 hr. in a sealed tube and then cooled to 20°, the only volatile product was a small amount of hydrogen (0.17 mole per mole of adduct used). The bulk of the product was nonvolatile and amorphous and was identified by its infrared spectrum as $B_3N_3H_6 \cdot 3HCl$. No formation of 2,4,6-trichloroborazine could be detected. It seems likely that the hydrogen was a product of thermal decomposition of a small amount of the borazine presumably formed by dissociation in the hot sealed tube, the rest of this borazine recombining with hydrogen chloride to re-form the adduct when the tube was cooled. Similar results were obtained when $B_3N_3H_6 \cdot 3HBr$ was heated in a sealed tube at 130° for 8 hr.

TABLE II

THE RELATIVE PERCENTAGES OF THE VOLATILE SPECIES OBSERVED BY THE MASS SPECTROMETER

Pyrolysis of $B_5H_5N_8 \cdot 5HBr$ at 90° (75 volts—electron energy)

| Species | *m/e* | Percentage of volatile products |
|---|---|---|
| $H_2$ | 2 | 8.3 |
| HBr | 79–82 | 91.7 |

Pyrolysis of $B_5N_5H_8 \cdot 5DCl$ at 110° (20 volts—electron energy)

| Species | *m/e* | Percentage of volatile products |
|---|---|---|
| $H_2$ | 2 | 3.5 |
| HD | 3 | 14.5 |
| $D_2$ | 4 | 1.0 |
| HCl | 36,38 | 60.0 |
| DCl | 37,39 | 17.0 |
| $B_3N_3ClH_5$[a] | 110–120 | 1.5 |
| $B_5N_5H_8$[a] | 129–133 | 0.5 |
| $B_3N_3Cl_2H_4$[a] | 145–152 | 2.0 |

[a] The number of deuterium atoms in these species could not be determined quantitatively. Therefore, the molecules are represented as the hydrogen compound for simplicity.

It is possible now to reconcile our results with the earlier report of Wiberg and Boltz.[5] They gave experimental details for only the sealed tube pyrolysis of $B_3N_3H_6 \cdot 3HBr$ when this was heated at 100° for 3–4 hr. The hydrogen formed was not measured. A solid which collected on the cool portion of the pyrolysis vessel had an atomic bromine:nitrogen ratio of 1:1. These observations led them to the conclusion that tribromoborazine had formed. However, in the light of our data, it seems probable that in their experiment initial dissociation of the adduct occurred in the hot zone, with some limited dehydrogenation to give polymeric nonvolatile material, but with the bulk of the borazine recombining with HBr when cooled to give $B_3N_3H_6 \cdot 3HBr$, which would also analyze to a 1:1 bromine:nitrogen ratio.

It is noteworthy that Wagner and Bradford[9] have found that when the hydrogen chloride adduct of N-trimethyl-B-dimethylborazine is pyrolyzed at 130° the main reaction is dehydrogenation to give the N-trimethyl-B-dimethylchloroborazine.

**Pyrolysis of $B_3N_3H_6 \cdot 3HBr$ and $B_3N_3H_6 \cdot 3DCl$ in the Mass Spectrometer.**—The borazine addition compounds were pyrolyzed in the mass spectrometer in a manner identical with that described for the borazanaphthalene adducts. A sample of $B_3N_3H_6 \cdot 3HBr$ was heated at 110° and only $H_2$, HBr, and $B_3N_3H_6$ were observed, the relative percentage of these volatile products being given in Table IV. There was no evidence for any 2,4,6-tribromoborazine.

The pyrolysis of $B_3N_3H_6 \cdot 3DCl$ at 140° gave hydrogen chloride and borazine as the major products but there were also small amounts of hydrogen, deuterium chloride, and monochloroborazine as given in Table V. Initially in the experiment, there had been a trace of dichloroborazine. However, as the sample was heated longer, the dichloroborazine completely disappeared and the intensity of the monochloroborazine decreased.

The mass spectrum of the observed borazine showed the presence of a maximum of three deuterium atoms, the highest *m/e* being 84. The ratio of the various deuterated borazine species could not be determined because of the complications arising from the various ratios of boron and chlorine isotopes and the combination of a loss of a hydrogen or deuterium.

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(9) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, 1, 93 (1962).

TABLE III

PYROLYSIS OF $B_3N_3H_6\cdot 3HBr$ AND $B_3N_3H_6\cdot 3HCl$ AT 130° AND IN THE THERMOGRAVIMETRIC BALANCE

| | $B_3N_3H_6\cdot 3HBr$ | | $B_3N_3H_6\cdot 3HCl$ | |
|---|---|---|---|---|
| | 130° | TG[a] | 130° | TG[a] |
| Mole ratio $H_2$ collected to $B_3N_3H_6\cdot 3HX$ heated | 1.20 | 1.56 | 0.338 | 0.712 |
| Mole ratio HX collected to $B_3N_3H_6\cdot 3HX$ heated | 1.41 | 1.40 | 0.843 | 1.34 |
| Mole ratio $B_3N_3H_6$ collected to $B_3N_3H_6\cdot 3HX$ heated | 0.083 | 0.089 | 0.035 | 0.053 |
| % of initial sample isolated as recombined $B_3N_3H_6\cdot 3HX$ | 43.0 | 47.5 | 59.3 | 58.4 |
| % of initial sample remaining as nonvolatile residue | 18.8 | 14.3 | 22.8 | 12.9 |

[a] Ambient temperature in thermogravimetric balance.

TABLE IV

THE RELATIVE PERCENTAGES OF THE VOLATILE SPECIES OBSERVED BY THE MASS SPECTROMETER

Pyrolysis of $B_3N_3H_6\cdot 3HBr$ at 110° (75 volts—electron energy)

| Species | m/e | Percentage of volatile products |
|---|---|---|
| $H_2$ | 2 | 29.0 |
| HBr | 79–82 | 24.0 |
| $B_3N_3H_6$ | 76–81 | 47.0 |

Pyrolysis of $B_3N_3H_6\cdot 3DCl$ at 140° (22 volts—electron energy)

| Species | m/e | Percentage of volatile products |
|---|---|---|
| $H_2$ | 2 | ... |
| HD | 3 | 0.01 |
| HCl | 36–38 | 9.8 |
| DCl | 37,39 | 0.5 |
| $B_3N_3H_6$[a] | 76–84 | 86.2 |
| $B_3N_3ClH_5$[a] | 110–120 | 3.5 |

[a] The deuterium atoms in these species could not be determined quantitatively. Therefore, the molecules are represented as the hydrogen compound for simplicity.

TABLE V

INFRARED SPECTRA (CM.$^{-1}$)[a]

| Frequency | $I/I^0$ | Frequency | $I/I^0$ | Frequency | $I/I^0$ |
|---|---|---|---|---|---|
| $B_5N_5H_8\cdot 5HBr$ | | $B_5N_5H_8\cdot 5HCl$ | | $B_5N_5H_8\cdot 5DCl$ | |
| 3242 | sh | 3280 | sh | | |
| 3205 | m | 3222 | m | 3205 | m |
| 3155 | sh | 3122 | sh | | |
| 2522 | m | 2500 | m | 2510 | m |
| | | | | 2359 | m |
| | | | | 2278 | sh |
| 1570 | sh | 1568 | sh | 1588 | m |
| 1553 | m | 1548 | m | 1540 | m |
| 1500 | sh | | | | |
| 1250 | vs | 1258 | vs | 1240 | vs |
| 1213 | sh | 1218 | sh | 1218 | sh |
| 1145 | m | 1148 | m | 1142 | m |
| 1100 | w | 1101 | w | 1093 | s |
| 1073 | sh | 1081 | sh | 1078 | sh |
| 1062 | m | 1063 | m | 1065 | sh |
| 1021 | sh | 1037–1010 | br | 1023 | m |
| 1003 | m | | | 1010 | m |
| 944–930 | br | 942–924 | br | | |
| 903 | w | | | | |
| 855 | w | 873 | w | | |
| 818 | w | 810 | w | | |
| 730 | m | 730 | w | 728 | m |
| 694 | m | 694 | m | 693 | w |
| $B_3N_3H_6\cdot 3HBr$ | | $B_3N_3H_6\cdot 3HCl$ | | $B_3N_3H_6\cdot 3DCl$ | |
| 3242 | sh | 3265 | sh | | |
| 3184 | m | 3222 | m | 3223 | m |
| 2520 | m | 2520 | m | 2500 | m |
| | | | | 2400 | m |
| 1587 | m | 1550 | m | 1558 | m |
| 1562 | m | | | | |
| 1249 | vs | 1280 | vs | 1259 | vs |
| 1219 | sh | 1228 | sh | | |
| 1138 | s | 1146 | s | 1142 | s |
| 1088 | m | 1105 | m | 1099 | s |
| 1000 | s | 1032 | s | 1038 | m |
| 932 | m | 930 | w | 926–913 | m |
| 926 | m | 858 | vw | | |
| 819 | w | 834–823 | w | 833–826 | w |
| 739–732 | w | 730 | w | 727 | m |

[a] w, weak; m, medium; s, strong; vs, very strong; br, broad; sh, shoulder.

**Infrared Spectra.**—The infrared spectra of the addition compounds of borazanaphthalene and borazine with the hydrogen halides as mulls in Nujol and halocarbon oil, series 11–14, were recorded with a Perkin-Elmer Model 21 spectrometer and are tabulated in Table V. Table VI gives the spectra of the nonvolatile residues from pyrolysis. The hydrogen halide addition compounds of borazanaphthalene have three resolved N–H stretching frequencies in the 3200 cm.$^{-1}$ region, a sharp B–H singlet in the 2500 cm.$^{-1}$ region, and a poorly resolved doublet for B–Cl or B–Br in the 1000 cm.$^{-1}$ region. The replacement of DCl for HCl gives one N–H stretching frequency at 3205 cm.$^{-1}$ and two N–D frequencies at 2359 and 2378 cm.$^{-1}$, while the remaining frequencies are essentially unchanged. In a similar manner, the hydrogen halide addition compounds of borazine also have an N–H doublet around the 3200 cm.$^{-1}$ region, a B–H singlet in the 2500 cm.$^{-1}$ region, and a B–Cl or B–Br singlet at 1032 and 1000 cm.$^{-1}$, respectively. The compound $B_3N_3H_6\cdot 3DCl$ has an N–H singlet at 3223 cm.$^{-1}$ and an N–D doublet at 2400 cm.$^{-1}$. These addition compounds do not have an intense absorption in the 1450 cm.$^{-1}$ region which is characteristic of the planar boron–nitrogen ring system in borazanaphthalene[3] and borazine.[10] The assignments of the various stretching frequencies were made by comparison with the assigned spectra of known compounds.[11-13]

**X-Ray Powder Patterns.**—An exposure time of 3 hr. showed all samples of $B_5N_5H_8\cdot 5HBr$, $B_5N_5H_8\cdot 5HCl$, $B_3N_3H_6\cdot 3HBr$, and $B_3N_3H_6\cdot 3HCl$ to be amorphous to Cu K$\alpha$ radiation. However, when the samples were exposed for 6 hr., very faint patterns were observed. These patterns were shown to be due to ammonium chloride, ammonium bromide, or boric acid by comparison to the patterns of known samples. Apparently a very small amount of slow hydrolysis had occurred to produce trace amounts of these compounds.

**Solubility.**—The adducts $B_5N_5H_8\cdot 5HBr$ and $B_3N_3H_6\cdot 3HBr$ are insoluble in benzene, toluene, chlorobenzene, *n*-pentane, cyclohexane, decalin, *n*-heptane, diethyl ether, diglyme, tetrahydrofuran, acetone, chloroform, carbon tetrachloride, and acetonitrile. $B_5N_5H_8\cdot 5HCl$ and $B_3N_3H_6\cdot 3HCl$ were soluble in only diglyme, tetrahydrofuran, and acetone. The infrared spectra of $B_5N_5H_8\cdot 5HCl$ and $B_3N_3H_6\cdot 3HCl$ before, when put in solution,

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TABLE VI

INFRARED SPECTRUM OF THE NONVOLATILE RESIDUE FROM $B_3N_3H_6\cdot 3HBr$, $B_5N_5H_8\cdot 5HBr$, $B_3N_3H_6\cdot 3HCl$, AND $B_5N_5H_8\cdot 5HCl$[a]

| Frequency, cm.$^{-1}$ | $I/I^0$ |
|---|---|
| 3484 | s |
| 3258–3138 | sh |
| 2500 | w |
| 1489–1368 | vs |
| 1262 | sh |
| 1158–1019 | s |
| 919–906 | m |
| 773–750 | m |

[a] The spectra of all of the samples of the various pyrolysis residues were identical.

and after recovery from solution were identical. All of the addition compounds reacted with water.

## Discussion

Anhydrous hydrogen chloride and hydrogen bromide react with borazine and with borazanaphthalene to form compounds of empirical composition $B_3N_3H_6\cdot 3HX$ and $B_5N_5H_8\cdot 5HX$, respectively. This type of derivative was considered by Stock[14] and by Wiberg[5] to be a molecular rather than an ionic material. The stoichiometry and the infrared spectra of the adducts which we have observed provide evidence for their covalent nature. The infrared spectra of the adducts formed by isotopic substitution using deuterium chloride further confirm that the hydrogen halide adds across the boron–nitrogen bonds, forming new boron–halogen and nitrogen–hydrogen bonds. Thus, each boron and nitrogen atom of the adducts is tetracoordinated.

The amorphous character and the insolubility in organic solvents of the adducts suggest that they may be higher polymers rather than simple ring systems, although the latter structures cannot be eliminated on the basis of available evidence. Polymers composed of rings of varying sizes have been suggested for other tetracoordinated group III–V amorphous compounds.[15]

The formation of borazine or borazanaphthalene by pyrolysis at 100–130° from the suggested polymeric adducts may be a consequence of the thermodynamic stability of these unique six-membered ring systems, the larger unsaturated rings being much less favorable. However, a residue of unknown composition, probably having a high degree of association, always remains after the pyrolysis.

The monochloroborazine observed in the mass spectrometer when $B_3N_3H_6\cdot 3DCl$ was pyrolyzed could be a product of the reaction of borazine with the ammonium chloride[16] detected by powder X-ray diffraction. The dichloroborazine observed could then be a disproportionation product, although formation in small amounts of this and the monochloroborazine by direct dehydrogenation of $B_3N_3H_6\cdot 3DCl$ cannot be eliminated.

A remaining feature of this series of addition and elimination reactions involving hydrogen halides is the stereospecificity. In the borazine–deuterium chloride system, deuterium chloride is added across the B–N bond but pyrolysis eliminates predominantly hydrogen chloride. The hydrogen originally bound to the nitrogen is exchanged for deuterium. Thus there is a required orientation for the two atoms being eliminated during pyrolysis. The most favorable positions would be *cis* if the reaction proceeds by the usual pyrolytic route, a concerted unimolecular mechanism. The observed ratio of HCl to DCl was approximately 20 : 1, but for ideal results no deuterium chloride should have been eliminated. Therefore, either the reaction is not proceeding by one single mechanism or, more probably, there is twisting of the B–N bond during the proposed polymer formation of the adduct and also during reformation of the six-membered borazine ring to place the deuterium in the preferred orientation. If the pyrolytic reaction proceeded by a *cis* elimination, steric considerations based upon the course of the two reactions, addition and elimination, would require the addition reaction to have been *trans*. A *trans* product represents the usual orientation for polar addition of hydrogen halides.

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