

models I, II, and III. Again the calculations for model I gave results which were consistently close to those of corresponding calculations for the hydrocarbons, model II gave results which were quite unreasonable, and model III gave reasonably good results but did not seem as preferable as model I.

### Conclusion

LACO-MO-SCF calculations for borazine have been performed for three different theoretical models for borazine. The results of the calculations for model I when compared with experimental and theoretical criteria indicate that this model is a promising one for future calculations on B-N pairs in  $\pi$ -systems of the borazine type. The results of the calculations for model II, B-N<sup>+</sup>, are always less reasonable for borazines when judged by the same criteria. Model III gives calculational results which are not too unreasonable for the borazine family; however, this model seems less preferable than model I.

Calculational results for energy levels, total energies (Table V), and coefficients of atomic orbitals in all molecular orbitals for borazine by the Hückel (Table VI) and Pople-SCF (Tables II-IV) methods are listed. The calculational results by the Pariser-Parr method, which are very similar to those by the Pople-SCF method as well as the analogous results for the naphthalene and diphenyl analogs of borazine are available upon request (to J. J. K.).

*Acknowledgment.* This research was supported in part by the Chemistry Branch, Office of Naval Research, by the Air Force Office of Scientific Research of the Office of Aerospace Research, under Contract No. AF49(638)-1220, and by the Ordnance Materials Research Office. J. J. K. wishes to thank the Soroptimist Federation of the Americas for a study grant. We also wish to thank Mr. Sol James, Chief of Auto-

Table V. Orbital and Total Energies of Borazine

MO	Hückel (in $\beta$ )	Pople-SCF (in e.v.)		
		Model I	Model II	Model III
$\phi_1$	2.0069	-14.3780	-20.9492	-17.0457
$\phi_2$	1.3255	-11.8405	-20.1712	-14.6312
$\phi_3$	1.3255	-11.8405	-20.1712	-14.6312
$\phi_4$	-1.3255	0.2704	8.0253	-1.4457
$\phi_5$	-1.3255	0.2704	8.0253	-1.4457
$\phi_6$	-2.0069	2.8603	8.8267	1.0689
$E_{total}$	9.3157	-86.0552	-148.9653	-131.4841

Table VI. Borazine. Models I, II, and III (Hückel)

MO	AO Symmetry			
	$a_2''$ $\phi_1$	$e''$ $\phi_2$	$e''$ $\phi_3$	$e''$ $\phi_4$
$\chi_1$	0.2891701	0.2194785	-0.1835251	-0.2260988
$\chi_2$	0.4997138	0.7181638	0.2627832	0.2789853
$\chi_3$	0.2891701	0.0491981	0.2818365	-0.5196197
$\chi_4$	0.4997139	-0.5866588	0.4905565	-0.0845872
$\chi_5$	0.2891701	-0.2686767	-0.0983114	0.7457185
$\chi_6$	0.4997139	-0.1315050	-0.7533397	-0.1943981
	$e''$ $\phi_5$	$a_2''$ $\phi_6$		
$\chi_1$	-0.7305434	-0.4997139		
$\chi_2$	0.0633994	0.2891701		
$\chi_3$	0.5610790	-0.4997138		
$\chi_4$	-0.2733081	0.2891701		
$\chi_5$	0.1694644	-0.4997138		
$\chi_6$	0.2099087	0.2891701		

matic Computations, Martin Company Computing Center, for arranging to have some of the calculations run at the Martin Company Computing Center; and Mr. Jon Hamann of RIAS for assistance with some of the calculations of model III.

## Rare Gas Ion Reactions with Pentaborane-9<sup>1</sup>

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The reactions between He<sup>+</sup>, Ne<sup>+</sup>, Ar<sup>+</sup>, Kr<sup>+</sup>, and Xe<sup>+</sup> ions and pentaborane-9 have been studied using a two-stage mass spectrometer in which the ionic products of collisions between positive ions with kinetic energies ranging from 2 to 200 e.v. and neutral molecules can be detected. The fragmentation of the pentaborane varied markedly as a function of the recombination energy of the rare gas ion. With xenon ions, only B<sub>5</sub>H<sub>7</sub><sup>+</sup> and B<sub>5</sub>H<sub>8</sub><sup>+</sup> were produced in significant amounts, while helium ion bombardment resulted in a variety of B<sub>3</sub>H<sub>n</sub><sup>+</sup>, B<sub>4</sub>H<sub>n</sub><sup>+</sup>, and B<sub>3</sub>H<sub>n</sub><sup>+</sup> ions. The kinetic energy of the bombarding ion in many cases had a significant effect on the relative abundances of the products. By plotting

the relative abundances of the products as a function of the excitation energy of the rare gas ions, breakdown curves for pentaborane-9 were constructed. The mass spectrum obtained by integrating the breakdown curves is in reasonably good agreement with the 70-v. electron impact spectrum. The possible role of the pentaborane-9 fragment ions in the proposed mechanism of the rare gas sensitized radiolysis is discussed.

### Introduction

Recent studies<sup>3-5</sup> of radiolysis of the boron hydrides have reported the formation of higher hydrides as a

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) Lever Brothers Foundation Fellow.

(3) H. Schmied and W. S. Koski, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p. 38M.

result of the coupling of hydride fragments. When 2-Mev. deuterons were used to irradiate pentaborane-9 in the gas phase, the products included decaborane-16, diborane, hydrogen, and polymeric materials. Experiments in which the rare gases were used as sensitizers varied the relative yields of the products and, in the cases of helium, neon, and argon sensitization, produced small amounts of tetraborane-10 and hexaborane-10. From these studies and others, involving iodine as a scavenger and deuterium as a tracer, a mechanism was proposed in which BH, postulated as a fragmentation product, abstracts hydrogen from pentaborane, stepwise, giving  $B_5H_8$  and  $BH_3$  radicals. Decaborane-16 and diborane are believed to result from dimerization of these radicals.

The use of rare gases as sensitizers enables a controlled amount of energy to be imparted to the pentaborane molecule. The ionizing radiation excites and ionizes the rare gas atoms which subsequently transfer energy to the pentaborane molecules through charge exchange or collisions. The pentaborane molecules, thus, will be ionized and possibly fragmented, depending on the amount of energy transferred. Xenon, with a recombination energy of 12.13 e.v., should produce very little fragmentation, while helium, with a recombination energy of 24.58 e.v., should highly fragment the pentaborane molecules. The obvious effect of this on the relative yields would be a maximum yield of diborane with helium and a minimum with xenon, as was observed in the radiolysis experiment.<sup>5</sup>

A study of the ionic products of rare gas ion-pentaborane-9 reactions was undertaken in an attempt to acquire detailed information about the mechanism of rare gas sensitization.

Such studies of positive ion bombardment of polyatomic molecules are also of interest to the mass spectroscopist. Lindholm and his co-workers<sup>6-9</sup> have carried out extensive investigations of mass spectra produced by positive ion bombardment. They obtain breakdown curves, experimentally, for some polyatomic molecule (e.g., ethanol) by bombarding it with a large variety of singly and doubly charged positive ions, recording the relative abundances of the fragmented ionic products, and plotting these abundances vs. the recombination energies of the bombarding ions. Thus, they are able to make direct comparisons with the breakdown curves calculated from the quasi-equilibrium theory of mass spectra.<sup>10</sup>

Although no calculations have been attempted for the rather peculiar boron hydrides, the application of Lindholm's technique to the data yielded an interesting, although rough, estimate of the probable breakdown pattern.

## Experimental

The instrument used in this experiment has been described previously.<sup>11</sup> There have been a few minor

- (4) L. H. Hall and W. S. Koski, *J. Am. Chem. Soc.*, **84**, 4205 (1962).
- (5) V. V. Subbanna, L. H. Hall, and W. S. Koski, *ibid.*, **86**, 1304 (1964).
- (6) H. von Koch and E. Lindholm, *Arkiv Fysik*, **19**, 123 (1961).
- (7) P. Wilmenius and E. Lindholm, *ibid.*, **21**, 97 (1962).
- (8) E. Pettersson and E. Lindholm, *ibid.*, **24**, 49 (1963).
- (9) W. A. Chupka and E. Lindholm, *ibid.*, **25**, 349 (1963).
- (10) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).
- (11) E. R. Weiner, G. R. Hertel, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 788 (1964).

modifications which have improved the selection and focusing of the primary ion beam.

Basically, the instrument consists of two mass spectrometers in a tandem arrangement similar to that used by Lindholm.<sup>6,12</sup> The primary mass spectrometer is a 180°, 1-cm. radius of curvature commercial instrument known as a Diatron and manufactured by Consolidated Electrodynamics Corp. A specially designed permanent magnet, constructed by Indiana General Corp., produces a field strength of approximately 2500 gauss for the Diatron. This enabled selection of  $Xe^+$  at an accelerating voltage of approximately 2 v.,  $Kr^+$  at a voltage of about 3.5 v., etc. After magnetic selection, this primary beam was focused, accelerated or decelerated to the desired energy, and refocused into the reaction chamber. The ionic products were extracted from the reaction chamber at an angle of 90° to the primary beam direction, accelerated and focused by a Nier-type lens, which has been modified by the addition of z-directional focusing plates, and magnetically analyzed by an 8-in. radius of curvature, 60° sector electromagnet. The primary beam crosses the reaction chamber parallel to the z-coordinate of the system, i.e., parallel to the long dimension of the reaction chamber exit slit. Thus the z-directional deflectors in the secondary lens can be adjusted to counteract momentum imparted to product ions by the primary ions and thus detection of products of momentum-transfer reactions is possible. Detection was accomplished by an electron multiplier and suitable pulse counting equipment. Spectra were obtained by sweeping the secondary magnetic field and recording the output of a count-rate meter.

The rare gases used in these experiments were research grade from various companies: helium from Airco Co., argon from Linde Co., and neon, krypton, and xenon from The Matheson Co. The pentaborane-9, purchased from the Callery Chemical Corp., was distilled from trap to trap until no significant impurities were observed by mass spectrometric analysis.

The intensity of the primary beam passing through the reaction chamber could be measured by means of a collector connected to a Keithley electrometer. Normal operating intensities were in the range of  $10^{-12}$ – $10^{-11}$  amp. Secondary ion intensities were typically less than 100,000 c.p.m. The pressure in the vacuum manifold surrounding the source was nominally  $1-2 \times 10^{-5}$  torr during operation. The pressure in the reaction chamber is estimated to be a factor of 10 to 100 greater than the manifold pressure, or roughly  $10^{-4}$ – $10^{-3}$  torr.

Since the pentaborane-9 contained the normal isotopic distribution of  $B^{10}$  and  $B^{11}$ , the spectra had to be reduced to the corresponding monoisotopic spectra in order to determine the relative abundances of the ions produced. This was accomplished in the usual manner. The highest mass peak observed (M) was attributed to the ion containing five boron-11 atoms plus the appropriate number of hydrogens to give the observed mass. The contributions of this  $B_5H_n^+$  ion to lower mass peaks were calculated and subtracted out. The remaining intensity of the  $M - 1$  peak was then due to the boron-11 contribution of the  $B_5H_{n-1}^+$  ion. The procedure was repeated until the entire

- (12) E. Lindholm, *Z. Naturforsch.*, **9a**, 535 (1954).

spectrum had been analyzed and the resulting mono-isotopic spectrum deduced.

## Results and Discussion

Xenon bombardment produced relatively little fragmentation, as expected, since the recombination energy is relatively low and the excess energy available to the  $B_5H_9^+$  ion is less than 2 e.v. Krypton changed the distribution of ions and produced more fragmentation. With argon, the major product was  $B_4H_4^+$  and the fragmentation was quite extensive. Neon and helium continued this trend producing large amounts of highly fragmented species. Table I lists the relative

**Table I.** Relative Abundances of Pentaborane-9 Fragment Ions Produced by Rare Gas Ion Bombardment<sup>a</sup>

Ion	Xe	Kr	Ar	Ne	He
$B_5H_7$	73				
$B_5H_6$		2	1		
$B_5H_5$	20	76	18		
$B_5H_4$			8	11	7
$B_5H_3$	<1		25	8	7
$B_5H_2$				24	23
$B_5H$			3	3	8
$B_5$				6	15
$B_4H_6$	3	<1			
$B_4H_5$	<1	2	8		
$B_4H_4$	2	20	31	3	
$B_4H_3$			<1	19	11
$B_4H_2$		<1	2	11	4
$B_4H$			<1	1	13
$B_4$				1	3
$B_3H_4$			<1	2	
$B_3H_3$			2	4	4
$B_3H_2$			<1	6	3
$B_3H$					2

<sup>a</sup> Kinetic energy of rare gas ions = 10 e.v.

abundances of the major products observed to illustrate the increasing fragmentation as the bombarding ion varied from xenon to helium.

It is obvious that one can qualitatively reconcile the observed data with the proposed mechanism of the radiolysis.<sup>5</sup> With xenon very few ions containing four boron atoms are produced which implies that very few BH radicals are formed. Thus, production of the radicals necessary for diborane and decaborane-16 formation is severely limited. As the rare gas is varied from xenon to helium, the energy available to the pentaborane-9 increases so that one might expect the probability of BH production to increase smoothly and thus could account for the variation in the yields of the products. An examination of Table I indicates that the fragmentation does not vary smoothly but that Ne<sup>+</sup> produces more than He<sup>+</sup>, and even Ar<sup>+</sup> produces more  $B_4H_n^+$  ions than He<sup>+</sup>, although fewer  $B_3H_n^+$  ions. However, this table gives simply the relative yields, *i.e.*, the number of any specific ion produced per 100 reactions. The absolute cross sections will ultimately determine whether, *e.g.*, He<sup>+</sup> or Ar<sup>+</sup> produces more BH radicals and, since we did not measure the cross sections of these reactions, we can only suggest that this may be the explanation for the apparent smooth variation in the diborane yield in the radiolysis.<sup>5</sup>

The mechanism attributes  $B_5H_8$  formation to the abstraction of hydrogen by BH and  $BH_2$ , but only

those  $B_5H_8$  radicals which have had an apical hydrogen removed can couple to form decaborane-16. Therefore, for every decaborane-16 molecule formed, eight "useless"  $B_5H_8$  radicals (assuming equal probability for removal of any one of the five terminal hydrogens) and five  $BH_3$  radicals (or 2.5 diborane molecules) are formed. The ratio of diborane to decaborane-16 should be 2.5 then, if this mechanism is correct, and the assumption is made that every BH produced abstracts hydrogen atoms only from  $B_5H_9$  molecules. The validity of such a restrictive assumption is highly questionable in what is undoubtedly a complicated and "messy" system. The observed ratio of 2.8 in the irradiation of pure pentaborane-9<sup>5</sup> was either a fortunate coincidence or indicates that the assumption is not as questionable as it appears. In the rare gas sensitization experiments, the ratio varied from approximately 1 (for Xe) to over 10 (for He). For the cases where the ratio is greater than 2.5, it is possible to explain the increase in the diborane yield as due to more fragmentation and more BH radicals. The decrease in decaborane-16 could conceivably be due to a less quantitative production of  $B_5H_8$  from the BH abstraction mechanism. With the large amounts of hydrogen-deficient fragments produced with He, Ne, and Ar, a large amount of hydrogen must be present and readily available to the BH radicals or it is entirely possible that species such as  $BH_2$  and  $BH_3$  are produced in the initial fragmentation processes.

In the Kr and Xe reactions, where the ratio is below 2.5, one must postulate an alternate mechanism for the production of decaborane-16. There is evidence that some of the  $B_5H_n^+$  ions react rapidly to produce  $B_{10}H_m^+$  ions ( $m \leq 10$ ). A group of peaks in the  $B_{10}H_m^+$  mass range were observed in the Xe<sup>+</sup>- $B_5H_9$  reactions when the pressure in the reaction chamber was increased two to five times the normal operating pressure. Similar  $B_{10}H_m^+$  peaks and traces of  $B_9H_n^+$  peaks were observed in the Kr<sup>+</sup>- $B_5H_9$  reactions under the same conditions of higher pressure. It is not inconceivable that such  $B_{10}H_m^+$  ions would lead to decaborane-16 by hydrogen abstraction and finally neutralization. When the same "high" pressure conditions were produced in the Ar, Ne, and He reactions, no peaks corresponding to ions higher than  $B_5H_n^+$  were observed.

The bulk of the ions produced in all cases most probably end up in the polymeric solid material always found in the radiolysis. The tetraborane-10 and hexaborane-10, observed with Ar, Ne, and He sensitization, can be attributed to some reaction or chain of reactions induced by some ion or ions produced by the higher recombination energies of these rare gases, *e.g.*, possibly some  $B_3H_n^+$  ion.

It appears, however, that little can be said quantitatively about the detailed mechanisms of the reactions which give rise to the observed products. It seems likely that the radical mechanism, proposed by Subbanna, *et al.*,<sup>5</sup> is a possible, even probable, path which leads to the products. It also seems likely that ion-molecule reactions may contribute significantly to the observed yields.

When one is faced with the fragmentation of a complex, polyatomic molecule such as pentaborane-9, one is tempted to search for an approach which will

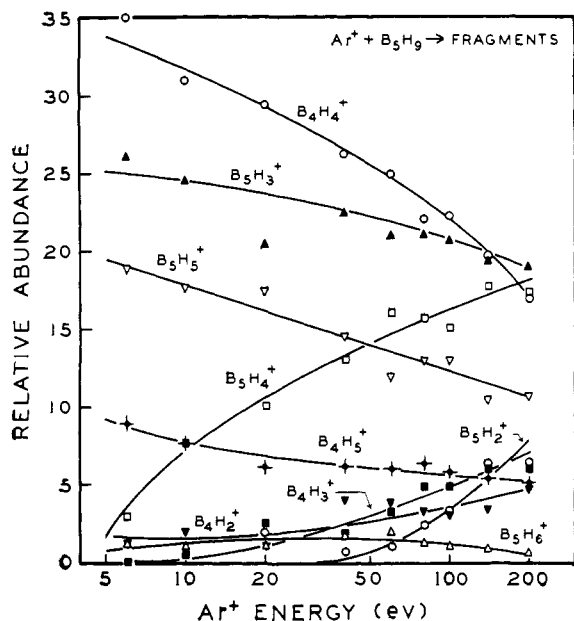


Figure 1. Relative abundances of major products of  $\text{Ar}^+\text{-B}_5\text{H}_9$  reactions as a function of the  $\text{Ar}^+$  kinetic energy.

add meaning to the observations made and perhaps indicate a logical pattern of decomposition. The procedure used by Lindholm, as outlined above, was applied to the rare gas ion-pentaborane-9 data. Although only five points were available for the breakdown curves, it had been observed that the relative abundances of the ions varied slowly with the kinetic energy of the primary ion beam, indicating that some reactions were being observed in which the relative kinetic energy of the colliding ion and molecule was contributing to the excitation energy imparted to the pentaborane. An example of this is shown in Figure 1 where the relative abundances of secondary ions produced in the  $\text{Ar}^+\text{-B}_5\text{H}_9$  reactions are plotted as a function of the bombarding energy of the argon ions.

Lambert<sup>13</sup> has reported a simple empirical relationship between the frequency of the lowest fundamental mode and the average number of collisions required to produce a vibrational-translational transition in polyatomic gases. The experimental data indicate that the probability of a transition is determined mainly by the size of the vibrational quantum and the kinetic energy of the collision. Assuming that the implications of this relationship hold for the interaction of low velocity ions and molecules, a similar relationship was found for the energy transferred ( $E_{tr}$ ) which varied logarithmically with the relative kinetic energy of the colliding species.

$$E_{tr} \sim \log C \frac{h\nu}{E_{rel}}$$

A value of  $10^{14}$  was assumed for  $\nu$ .  $C$  is a constant based on the assumption that our instrument is capable of detecting only those secondary ions having momentum vectors within an angle of  $70\text{--}110^\circ$  from the primary beam direction. Admittedly, this is an empirical formula whose merit is that it fits the experimental data quite well. It appears to be based upon

(13) J. D. Lambert, "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 789.

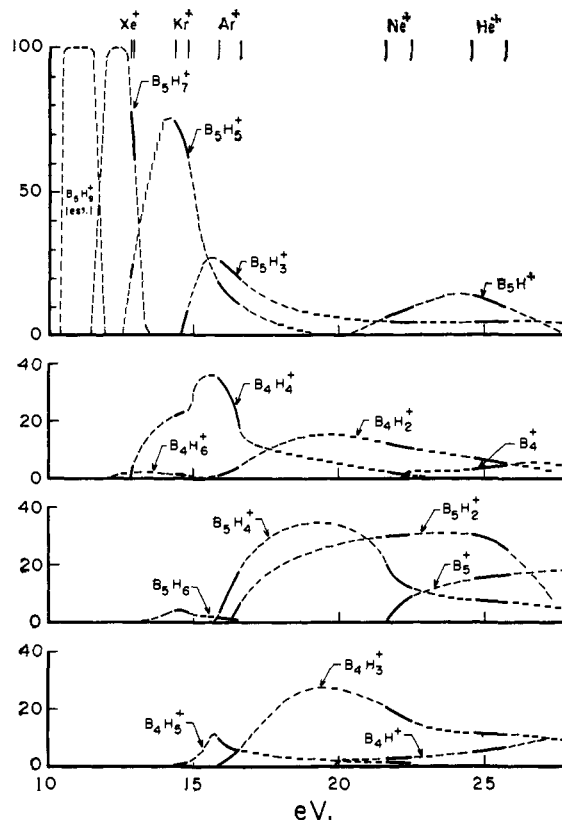


Figure 2. Breakdown curves of  $\text{B}_5\text{H}_9$  as a function of the excitation energy; solid line segments represent the experimentally determined points.

vibrational excitation only, overlooking any possibility of rotational excitation—a possibility which should probably not be ignored.

By taking into account the possibility of additional excitation energy as the relative kinetic energy increased, it was possible to construct breakdown curves for pentaborane-9 as shown in Figure 2. The solid line segments are the experimentally determined abundances plotted as a function of the excitation energy.

Imagination was a great assist in filling in the dotted portions of the curves, but there were other factors available to guide the construction work. For example, the appearance potentials for several of these ions have been reported in the literature.<sup>14</sup> Also, one of the initially surprising observations—that no detectable parent ion was seen even with  $\text{Xe}^+$  bombardment at low energies—must mean that the probability of producing  $\text{B}_5\text{H}_9^+$  ions has decayed to essentially zero when the excitation energy is less than 2 e.v. above the ionization potential of 10.4 e.v. Thus, it is possible to estimate the parent ion curve. Beginning at 10.4 e.v., the parent ion is the only ion produced. At the appearance potential of  $\text{B}_5\text{H}_7^+$  (11.4), the probability of producing the parent ion must drop rapidly as the  $\text{B}_5\text{H}_7^+$  abundance rises. At the excitation energy supplied by  $\text{Xe}^+$  ions, small amounts of  $\text{B}_4\text{H}_6^+$  and  $\text{B}_4\text{H}_4^+$  are present, the  $\text{B}_5\text{H}_7^+$  abundance is already decreasing rapidly, and the  $\text{B}_5\text{H}_5^+$  intensity is increasing. At an energy corresponding to krypton excitation, the probability of producing  $\text{B}_5\text{H}_7^+$  has vanished, the  $\text{B}_5\text{H}_5^+$  is decreasing, and the intensities

(14) J. J. Kaufman, W. S. Koski, L. J. Kuhns, and S. S. Wright, *J. Am. Chem. Soc.*, **85**, 1369 (1963).

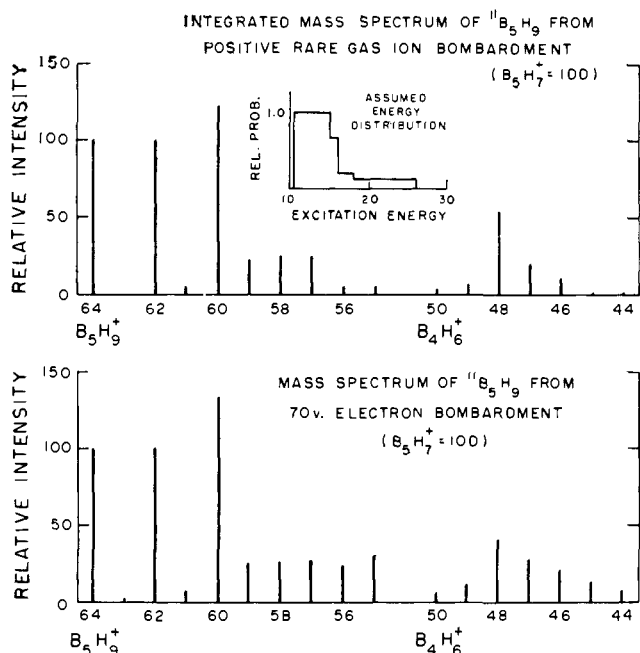


Figure 3. Upper: Mass spectra from integration of breakdown curves (Figure 2); assumed energy distribution shown in insert. Lower: Mass spectra from 70-v. electron impact data (ref. 11).

of other ions are gaining significance. Thus, it is possible to logically follow the growth and decay of the various ions as a function of the excitation energy imparted to the pentaborane molecule and construct reasonable breakdown curves.

In most cases where the appearance potentials (AP) were known, it was possible to use these values as the starting points of the curves. Exceptions were  $B_4H_4^+$  (reported AP is 14.0 e.v.),  $B_4H_2^+$  (AP = 17.9 e.v.), and  $B_5H_4^+$  (AP = 13.0 e.v.). The  $B_5H_4^+$  curve does not seem to appear until well above 15 e.v.; however, there may be an undetected low energy tail which actually extends down to the appearance potential. In the other two cases, the ions appeared with significant intensity at energies well below the reported appearance potentials. It seems probable that the excitation process which produces these ions differs depending upon the nature of the bombarding species. It appears production from electron impact must involve excited states of these ions to account for the higher appearance potentials. Any variations between positive ion and electron bombardment must be minor since only two or three ions seem to show anomalous behavior.

A complication in applying this method is the existence in many cases of more than one important recombination energy for an ion. This is true for all rare gases except helium. The recombination energies are given in Table II. The two values arise from ions in the  $^2P_{1/2}$  and  $^2P_{3/2}$  states. For the purpose of constructing the breakdown curves, the two values for each ion were averaged. The only case in which the difference is sizable enough to create a problem is xenon. The resulting curves do not reflect any anomalies due to the averaging procedure although it is recognized that an accurate representation would require more rigorous consideration of the specific contributions of the individual recombination energies.

Table II. Important Recombination Energies of Singly Charged Rare Gas Ions

	Energy, e.v.
He	24.58
Ne	21.56 and 21.66
Ar	15.76 and 15.94
Kr	14.00 and 14.67
Xe	12.13 and 13.44

It might be worthwhile to point out that one could decrease the disparity between the reported AP and the observation that  $Xe^+$  bombardment produces  $B_4H_4^+$  by assuming that the  $B_4H_4^+$  arises due to excitation from the higher recombination energy of xenon.

A comparison may be made between the mass spectrum obtained from electron impact studies and the curves in Figure 2 by integrating the breakdown curves, assuming a proper energy distribution function. Chupka and Kaminsky<sup>15</sup> have determined, experimentally, ionization efficiency curves for electron impact work on propane and *n*-butane and compared them with the assumed energy distributions which have been used in mass spectral calculations for these molecules. Using their curves as a guide, an energy distribution was assumed and an integrated mass spectrum was calculated from our data. The results are shown, along with the 70-v. electron impact spectrum<sup>14</sup> in Figure 3. The agreement is generally satisfactory. The poor agreement at masses 55 and 56 (corresponding to  $B_5^+$  and  $B_5H^+$ ) is attributed to the upper limit of our data. Above 26 e.v., extrapolation of the breakdown curves became very hazardous. Therefore, 26 e.v. was taken as the upper limit of our integrations. As a result, ions requiring large amounts of energy are poorly represented. Also, the anomalous behavior of the  $B_4H_4^+$  curve again is evident. The intensity of the integrated peak is 35% greater than the electron impact peak.

## Conclusions

The mass spectrometer studies reported here indicate that the proposed radiolysis mechanism is qualitatively correct, but that fragmentation is greater than predicted. Initial loss of a hydrogen molecule, followed by loss of a second hydrogen molecule, appears to be the most probable decomposition path of pentaborane-9 after which loss of BH, H, or  $H_2$  seem almost equally likely.

Of perhaps greater interest is the fact that reasonable breakdown curves can be constructed from charge-exchange data. A desired extension of this work would be further experimentation using a variety of bombarding ions, as Lindholm has done, to gain a better, more complete picture of the experimental curves. Ultimately, it would be of interest to compare the experimentally determined breakdown curves with those calculated from the statistical theory of mass spectra.

*Acknowledgment.* The authors wish to express their appreciation to Marsha S. Hertel who undertook the tedious task of reducing the original data to the mono-isotopic spectra.

(15) W. A. Chupka and M. Kaminsky, *J. Chem. Phys.*, **35**, 1991 (1961).