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Ionization and Appearance Potentials of Selected Ions from Decaborane-16, B_5H_8I and B_5H_8Br[1]

By L. H. Hall,[2] V. V. Subbanna, and W. S. Koski

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Ionization and appearance potentials of the $^{11}B_{10}H_{16}{}^+$, $B_5H_8X^+$ (X = I, Br), and $B_5H_8{}^+$ ions from $^{11}B_{10}H_{16}$ and B_5H_8X (X = I, Br) are reported along with the monoisotopic fragmentation patterns of these compounds. The following values were determined: $I_p(^{11}B_{10}H_{16})$ = 10.1 ± 0.2, $I_p(B_5H_8I)$ = 9.2 ± 0.1, $I_p(B_5H_8Br)$ = 9.5 ± 0.1 e.v.; $A_p(^{11}B_5H_8{}^+$ from $^{11}B_{10}H_{16})$ = 11.6 ± 0.2, $A_p(B_5H_8{}^+$ from $B_5H_8I)$ = 11.1 ± 0.1, $A_p(B_5H_8{}^+$ from B_5H_8- Br) = 12.0 ± 0.2 e.v. From these and other data, values were calculated for (1) the ionization potential of the B_5H_8 radical, $I_p(^{11}B_5H_8)$ = 8.4 ± 0.2 e.v., and (2) the bond dissociation energy of the boron–boron bond which couples the two B_5H_8 units in decaborane-16, $D(B_5H_8-B_5H_8)$ = 3.2 ± 0.2 e.v. A method for the preparation of B_5H_8I and B_5H_8Br is also presented.

Introduction

One of the current interests of our program of boron hydride research is in the nature of some higher boron hydrides. We have published results on the formation of decaborane-16 by irradiation of pentaborane-9.[3–5] Lipscomb, et al., prepared decaborane-16 by an electrical discharge process and determined its structure by X-ray methods[6] and also studied some of its chemical properties.[7] The structure of decaborane-16 corresponds to the coupling of two B_5H_8 units from pentaborane-9. The two B_5H_8 units are bonded across the apical borons of the pentagonal pyramids of the pentaborane groups. We were interested in obtaining information concerning the nature of this coupling boron–boron bond, unique among boron hydrides, as well as data on the ionization potential of decaborane-16. In this paper, results are presented on some electron impact studies on decaborane-16 as well as on 1-iodo- and 1-bromopentaborane-9.

Experimental

Preparation of $^{11}B_{10}H_{16}$.—$B_{10}H_{16}$ was prepared by irradiation of B_5H_9 as previously reported.[3,4] $^{11}B_{10}H_{16}$ was prepared from $^{11}B_5H_9$ which had been synthesized from $^{11}B_2H_6$ by controlled pyrolysis as previously described.[8] Separation and purification of the $^{11}B_{10}$-H_{16} was effected by low temperature distillation followed by vacuum sublimation. The course of the purification was followed mass spectroscopically. The purification was considered complete when m/e = 64 disappeared into the background. It was believed that the major impurity, B_5H_9, was then present only in negligible quantities.

Preparation of B_5H_8Br and B_5H_8I.—The one method reported in the literature for the preparation of monohalogen pentaboranes is that of Shapiro[9] which uses CS_2 as solvent and $AlCl_3$ as cat-

alyst. We found that yields in excess of 95% (based on B_5H_9 consumed) were easily obtained without solvent or catalyst by the direct combination of B_5H_9 with I_2 or Br_2 when B_5H_9 is in slight excess. This method has the obvious advantage of easy purification. The optimum conditions for these preparations are as follows: for B_5H_8I complete reaction occurs in about 14 days at 75° with a 25% molar excess of B_5H_9; for B_5H_8Br complete reaction occurs in 6–8 hr. at room temperature with a 10% molar excess of B_5H_9. The reactions were carried out in sealed glass bulbs equipped with breakseals. The reactions usually involved 0.01-mole quantities. In a typical preparation, 2.5 g. of I_2 and 0.8 g. of B_5H_9 yielded 1.8 g. of B_5H_8I. In both cases a small amount of dark-colored, nonvolatile, intractable material is formed. When the B_5H_9–I_2 reaction is carried out at temperatures above 90°, the major product is an amber-colored, nonvolatile, glassy material. When an excess of halogen is present, polyhaloboranes are usually formed. In the B_5H_9–Br_2 system when Br_2 is in excess, BBr_3 is formed.

In both cases B_5H_9 is easily separated from the product by vacuum distillation at 0°. The product can be purified by vacuum sublimation following the removal of B_5H_9. B_5H_8I can be handled readily in a drybox which is dried moderately with dry N_2 and desiccants. However, B_5H_8Br requires vacuum transfer or a drybox in which the atmosphere is thoroughly dry. B_5H_8Br is spontaneously flammable when exposed to the atmosphere, whereas B_5H_8I is only slowly attacked by atmospheric oxygen and water, yielding a fuming mist of HI.

At −78°, B_5H_8I forms very long, thin needles which slowly change to a shapeless crystalline mass at room temperature. B_5H_8Br forms refractive square plates at 0°, and the plates tend to persist at room temperature.

Mass Spectral Data.—The mass spectral work was performed on a CEC Model 21-103C mass spectrometer modified in the low voltage section to allow appearance potential measurements. In order to determine the appearance potentials of the ions involved in this study, the intensity of the ion beam of interest was measured in arbitrary units of peak height on the CEC photographic chart paper as a function of the (uncorrected) ionizing voltage, yielding the ionization efficiency curve of that ion in the range 0–2 e.v. above the threshold value. The ionization efficiency curve of a rare gas ion (xenon or krypton in this study) was measured simultaneously with that of the ion of interest and was used as an internal standard to determine the correction on the ionizing voltage. The extrapolated differences method of Warren[10] was used to determine the appearance potentials of the $^{11}B_{10}H_{16}{}^+$, $B_5H_8I^+$, $B_5H_8Br^+$, and $B_5H_8{}^+$ ions. The vanishing current method[11] was used for the $^{11}B_5H_8{}^+$ (from $^{11}B_{10}H_{16}$ and B_5H_8Br)

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

(2) At present a Postdoctoral Fellow at the National Bureau of Standards, Washington 25, D. C.

(3) L. H. Hall and W. S. Koski, J. Am. Chem. Soc., **84**, 4205 (1962).

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

(5) V. V. Subbanna, L. H. Hall, and W. S. Koski, J. Am. Chem. Soc., **86**, 1304 (1964).

(6) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, Proc. Natl. Acad. Sci., U. S., **47**, 996 (1961).

(7) R. Grimes and W. N. Lipscomb, ibid., **48**, 496 (1962).

(8) W. S. Koski, P. C. Maybury, and J. J. Kaufman, Anal. Chem., **26**, 1922 (1954).

(9) I. Shapiro and H. Landesman, J. Chem. Phys., **33**, 1590 (1960).

(10) J. W. Warren, Nature, **165**, 810 (1950).

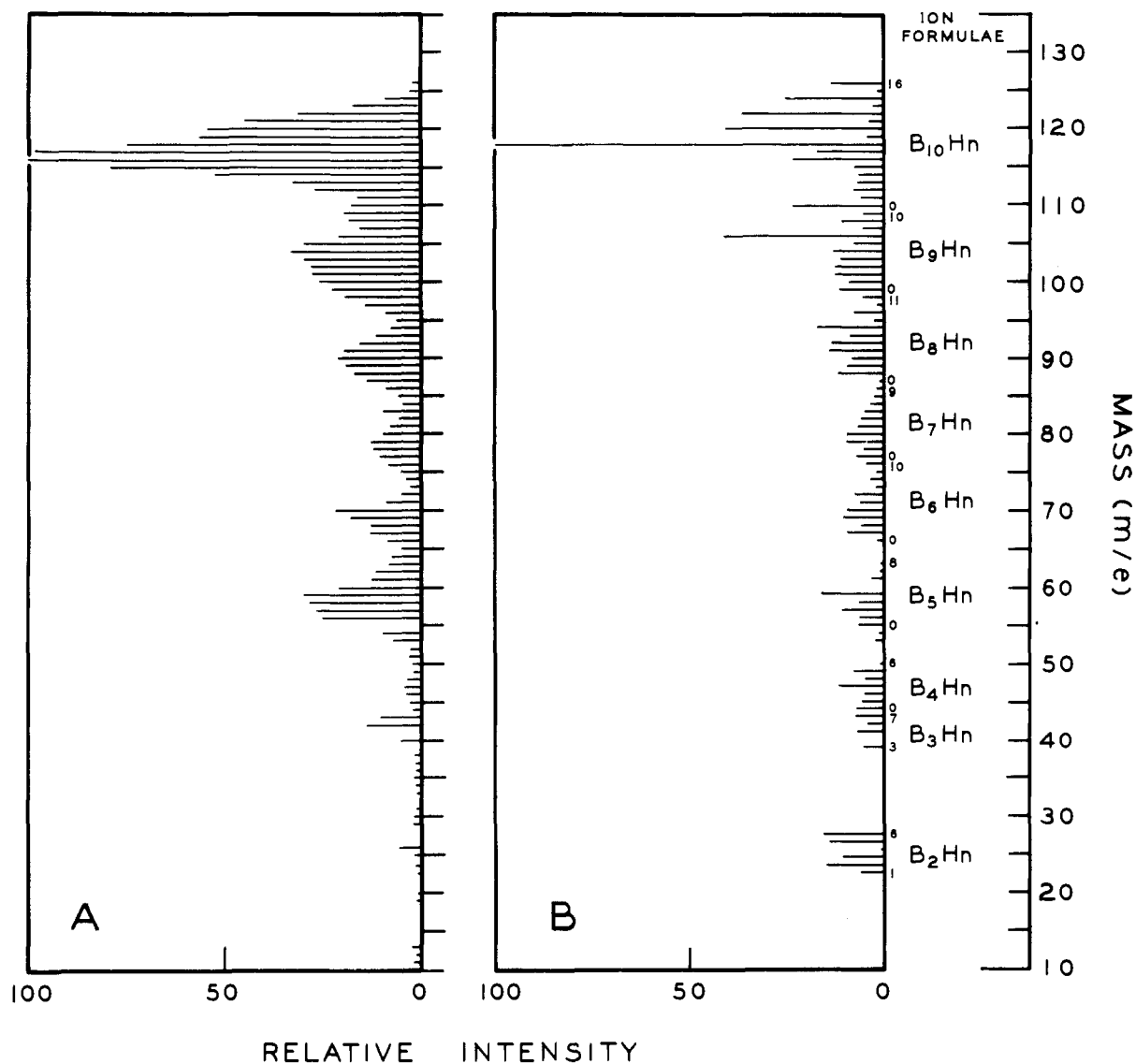(11) J. B. Farmer, F. P. Lossing, D. G. H. Marsden, and J. McDowell; J. Chem. Phys., **24**, 52 (1956).

Fig. 1.—Normal (A) and monoisotopic (B) mass spectrum of decaborane-16.

ions and as a check on the $^{11}B_{10}H_{16}^{+}$ ion appearance potential.

Results and Discussion

Molecular Ionization Potentials.—In the usual manner, the ionization potential can be associated with the mass spectroscopic appearance potential as shown in the following equations for molecule M and the ionic species M^{+}.

$$M + e^{-} \longrightarrow M^{+} + 2e^{-}$$
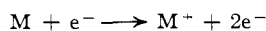
$$I_p(M) = A_p(M^{+})$$

The appearance potentials determined in this study are listed in Table I.

The ionization potential of decaborane-16 as determined by the mass spectroscopic appearance potential is then $I_p(B_{10}H_{16}) = 10.1 \pm 0.2$ e.v. This ionization potential is somewhat lower than those of decaborane-14 and pentaborane-9 as determined mass spectroscopically by Koski, et al.: $I_p(B_{10}H_{14}) = 10.3 \pm 0.2$,[12] $I_p(B_5H_9) = 10.5 \pm 0.2$ e.v.[13]

(12) J. J. Kaufman, W. S. Koski, L. J. Kuhns, and R. W. Law, J. Am. Chem. Soc., **84**, 4198 (1962).

(13) J. J. Kaufman, W. S. Koski, L. J. Kuhns, and S. Wright, ibid., **85**, 1369 (1963).

The appearance potential measurements also revealed that the ionization potentials of B_5H_8I and B_5H_8Br are more than 1 e.v. lower than that of B_5H_9: $I_p(B_5H_8I) = 9.2 \pm 0.1$, $I_p(B_5H_8Br) = 9.5 \pm 0.1$ e.v.

TABLE I

APPEARANCE POTENTIALS FOR SOME IONS, FROM $B_{10}H_{16}$, B_5H_8I, AND B_5H_8Br

Compound	m/e	A_p, e.v.[a]
$^{11}B_{10}H_{16}$	126	10.1 ± 0.2^{b}
	63	11.6 ± 0.2^{b}
B_5H_8I	190	9.2 ± 0.1^{c}
	63	11.1 ± 0.1^{c}
B_5H_8Br	144	9.5 ± 0.1^{c}
	63	12.0 ± 0.2^{d}

[a] The errors listed on the appearance potentials are about twice the errors in the precision of the measurements made in this study. [b] Extrapolated differences method and vanishing point method. [c] Extrapolated differences method [d] Vanishing point method.

Ionization Potential of the B_5H_8 Radical.—One of the quantities of interest in this study is the dissociation energy of the boron–boron bond which couples the two B_5H_8 groups in decaborane-16. In order to obtain such a quantity from appearance potential data on
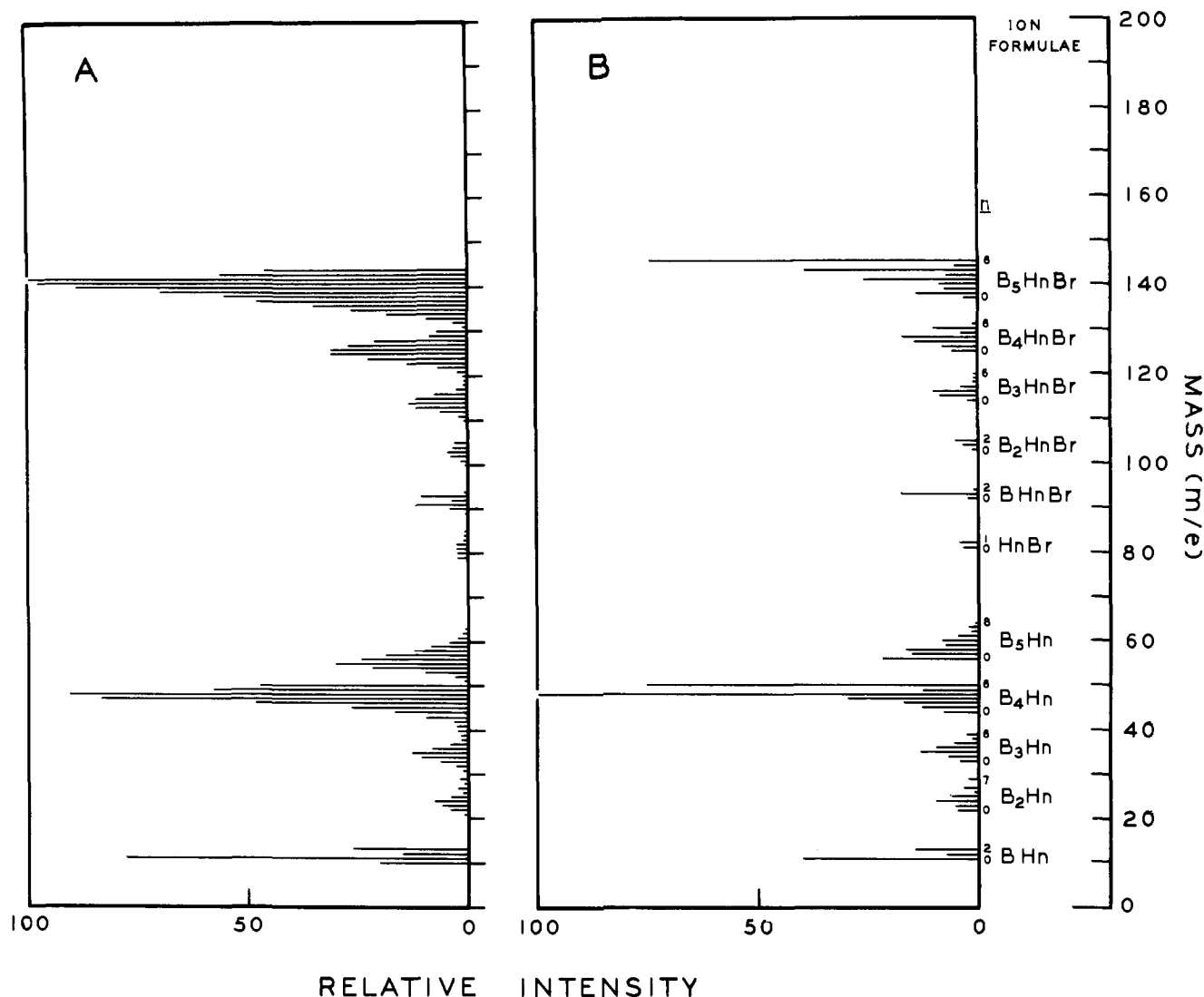
RELATIVE INTENSITY

Fig. 2.—Normal (A) and monoisotopic (B) mass spectrum of B_5H_8Br.

this molecule, the ionization potential of the B_5H_8 radical must be obtained independently. $I_p(B_5H_8)$ cannot be obtained from electron impact studies on pentaborane-9 because $B_5H_8{}^+$ ions do not appear in its mass spectrum.[13] For this reason, the appearance potentials of the $m/e = 63$ peaks ($^{11}B_5H_8{}^+$ ions) from B_5H_8I and B_5H_8Br, as well as from $^{11}B_{10}H_{16}$, were determined. These appearance potentials are listed in Table I.

In this study it is assumed that the excitation energy or excess kinetic energy of ions or neutral fragments is negligible. In his study of hydrocarbons, Stevenson[14] found that ion $B_1{}^+$ from the electron impact induced dissociation of molecule B_1–B_2 will involve negligible excitation energy when the following inequality is satisfied

$$B_1{-}B_2 + e^- \longrightarrow B_1{}^+ + B_2 + 2e^-$$
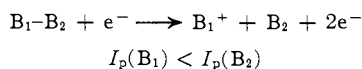
$$I_p(B_1) < I_p(B_2)$$

Further, the appearance potential is given by the equation

$$A_p(B_1{}^+) = I_p(B_1) + D(B_1{-}B_2) \qquad (1)$$

where $A_p(B_1)$ is the mass spectroscopic appearance potential of ion fragment B_1, $I_p(B_1)$ is the ionization

(14) D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc., **64**, 1588 (1942).

potential of the neutral B_1 species, and $D(B_1{-}B_2)$ is the dissociation energy of the bond joining B_1 and B_2. Since this principle, often expressed as a rule by some, has been used in the successful interpretation of appearance potential data in the study of other boron hydrides such as B_2H_6,[15] B_4H_{10},[16] B_5H_9,[13] and $B_{10}H_{14}$[12] and the boron trihalides BI_3, BBr_3, and BCl_3,[17] it is also used as a guideline in this study.

There are two possible simple processes which could produce the $B_5H_8{}^+$ ions upon electron impact of B_5-H_8X (X = I, Br). The rupture of the boron–halogen bond may lead to the formation of $B_5H_8{}^+$ ions[18] and neutral halogen atoms

$$B_5H_8X + e^- \longrightarrow B_5H_8{}^+ + X + 2e^- \qquad (2)$$
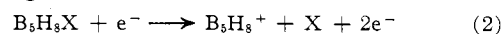
Thus, the appearance potential as expressed by eq. 1 is

$$A_p(B_5H_8{}^+) = I_p(B_5H_8) + D(B_5H_8{-}X) \qquad (3)$$

However, whenever halogen atoms are present, one must admit the possibility that the negative halogen

(15) W. S. Koski, J. J. Kaufman, C. F. Pachucki, and F. J. Shipko, ibid., **80**, 3202 (1958).

(16) T. P. Fehlner and W. S. Koski, ibid., **85**, 1905 (1963).

(17) W. S. Koski, J. J. Kaufman, and C. F. Pachucki, ibid., **81**, 1326 (1959).

(18) N.m.r. data of R. Schaeffer, et al., ibid., **80**, 2670 (1958), indicate that the halogen atom in B_5H_8X is located on the apical boron of the B_5H_8X pentagonal pyramid. Thus, the B_5H_8 radical corresponds to B_5H_9 with the removal of the apical proton.
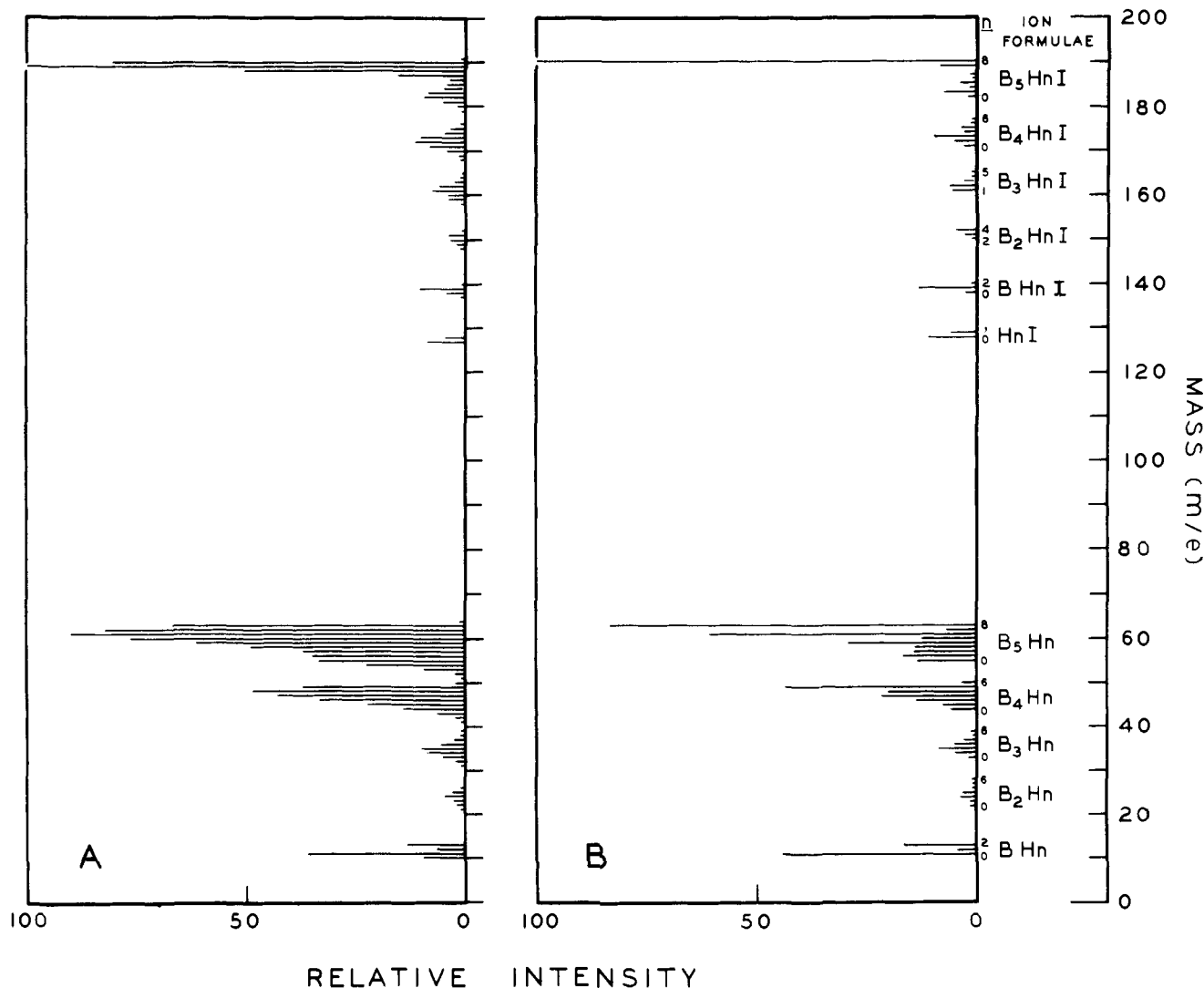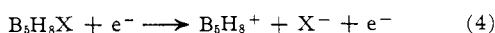
Fig. 3.—Normal (A) and monoisotopic (B) mass spectrum of B_5H_8I.

ion is produced in ion-pair formation

$$B_5H_8X + e^- \longrightarrow B_5H_8^+ + X^- + e^- \qquad (4)$$

Thus, since the electron affinity of the halogen must be taken into account

$$A_p(B_5H_8^+) = I_p(B_5H_8) + D(B_5H_8-X) - E_a(X) \qquad (5)$$

where the electron affinities are given as $E_a(I) = 3.06$, $E_a(Br) = 3.6$ e.v.[19]

The values of $D(B_5H_8-X)$ for B_5H_8I and B_5H_8Br are not known, and in this paper it has been assumed that they are approximately the same as in the corresponding trihalides. This assumption should be taken with some reservation; however, it is interesting to note that the quadrupole coupling data indicate considerable similarity between the halogen bonds in these two classes of compounds.

The dissociation energies of the boron trihalides as determined from electron impact studies have been reported by Koski, et al.[17]: $D(B_5H_8-X) \approx D(B-X)$ in BX_3 (X = I, Br); $D(B-I) = 2.7 \pm 0.1$, $D(B-Br) = 3.7 \pm 0.1$ e.v.

When the case of negative halogen ion formation is considered, the following results are obtained from eq. 5: $I_p(B_5H_8^+) = 11.5 \pm 0.2$ (from B_5H_8I) and 11.9 ± 0.2

e.v. (from B_5H_8Br). The calculation based on B_5H_8I data clearly does not satisfy the inequality relation

$$I_p(B_5H_8^+)_{calcd} = 11.5 > 10.4 = I_p(I)[20]$$

The second result, from B_5H_8Br data, is also questionable in this respect because $I_p(Br) = 11.9$ e.v.[20]

Further, these calculated ionization potentials are more than 2 e.v. higher than those of the parent compounds as shown in Table I. It has been observed in every case in which the ionization potential of a free radical has been measured that it is lower than that of the parent molecule because a lower binding energy is associated with an unpaired electron. Hence, the dissociation process involving negative halogen ion formation, eq. 4, must be discarded in favor of the one in which neutral halogen atoms are produced as shown in eq. 2.

When the process of eq. 2 is considered, calculations according to eq. 3 yield the same result for data from both B_5H_8I and B_5H_8Br (in contrast to results based on eq. 4).

$$I_p(B_5H_8)_{calcd} = 8.4 \pm 0.2 \text{ e.v.} \qquad (6)$$

This is a reasonable result since the electronic structure of the B_5H_8 group is not expected to differ significantly

(19) R. S. Berry and C. W. Reiman, J. Chem. Phys., 38, 1540 (1963).

(20) C. E. Moore, "Atomic Energy Levels," Vol. 1, National Bureau of Standards, Washington, D. C.

between the two compounds. In addition, this calculated value satisfies the inequality relation $I_p(B_5H_8)_{calcd}$ = $8.4 < I_p(I)$, $I_p(Br)$, and is lower in magnitude than those of the parent compounds $I_p(B_5H_8)_{calcd}$ = $8.4 < I_p(B_5H_8I)$ and $I_p(B_5H_8Br)$.

The ionization efficiency curves of the I^+ and Br^+ ions from B_5H_8I and B_5H_8Br, respectively, exhibit much complex structure with $A_p(X^+) > 20$ e.v. (X = I, Br). These results are in agreement with the Stevenson principle since the X^+ ions possess ionization potentials higher than that of the B_5H_8 radical and, thus, are expected to be formed only with energies in excess of the sum of the bond dissociation energy and the ionization potential of the ions.

Dissociation Energy of the Coupling Boron–Boron Bond.—In the fragmentation of decaborane-16 by electron impact, a process similar to that of eq. 2 is proposed as the one which leads to $B_5H_8^+$ ion formation

$$B_5H_8\text{--}B_5H_8 + e^- \longrightarrow B_5H_8^+ + B_5H_8 + 2e^-$$
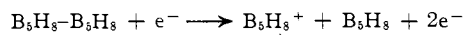
Thus

$$D(B_5H_8\text{--}B_5H_8) = A_p(B_5H_8^+) - I_p(B_5H_8)$$

Using the value of $I_p(B_5H_8)$ from eq. 6 along with the experimentally determined value of $A_p(B_5H_8)$ from Table I, we find $D(B_5H_8\text{---}B_5H_8) = 3.2 \pm 0.2$ e.v.

Although the error associated with this bond energy is subject to some uncertainty in view of the numerous assumptions that are involved in the determination of appearance potentials of large molecules,[21] the value obtained for the B–B bond energy[22] in decaborane-16 is approximately what one would expect if the bond was mainly of single bond character, i.e., a normal two-center electron pair bond. The B_5H_8 group simply replaces the apical hydrogen atom of B_5H_9 to give decaborane-16 $(B_5H_8\text{--}B_5H_8)$.

It is interesting to note here the results of an LCAO–MO calculation on decaborane-16 by Moore.[23] From

(21) H. M. Rosenstock and M. Krauss, "Advances in Mass Spectrometry," Vol. 2, Pergamon Press, New York, N. Y., 1963.

(22) Other values given for $D(B\text{--}B)$ are 3.6 e.v. by S. Gunn and L. Green, *J. Phys. Chem.*, **65**, 2173 (1961), and 3.58 e.v. by E. Prosen in a private communication quoted in ref. 12. These values, however, are for boron–boron bonds of the three-center type.

(23) E. B. Moore, *J. Am. Chem. Soc.*, **85**, 676 (1963).

an inspection of the population matrix for the decaborane-16 molecule, Moore concluded that the coupling boron–boron bond is not a multiple bond. His calculations also yielded a value of 10.2 e.v. for the ionization potential of decaborane-16.

Monoisotopic Fragmentation Patterns.—The monoisotopic mass spectrum or electron impact fragmentation pattern of decaborane-16 was calculated from the spectrum of the compound containing 1.23% ^{10}B by subtraction of the contributions of all the ions containing ^{10}B to the spectrum. The mass spectrum of $^{11}B_{10}$-H_{16} is presented in Fig. 1 along with the spectrum of the compound of natural isotopic content. The alternation of intensities of the peaks in the parent peak region ($^{11}B_{10}H_n^+$) is characteristic of the monoisotopic spectrum of the boron hydrides. This alternation arises from the fact that hydrogen is presumably lost from the hydride upon electron impact predominantly as molecular hydrogen and, consequently, ions corresponding to the loss of an odd number of hydrogen atoms are not abundant. Also, it is to be noted that no peak in the $B_5H_n^+$ ion region occurs with $n > 8$. Thus, as expected, there are probably no $B_5H_n^+$ rearrangement ions resulting from hydrogen migration from one B_5H_8 unit to the other.

The monoisotopic spectra of 1-iodo- and 1-bromopentaborane-9 were calculated from the spectra of the compounds of natural boron isotopic content on the basis of 18.83% ^{10}B and in the B_5H_8Br case, 50.57% ^{79}Br. These calculated spectra are shown in Fig. 2 and 3 along with the observed spectra of the compounds of natural isotopic content. The monoisotopic $^{11}B_5$-H_8I spectrum is quite similar to that given by Shapiro[9] but the $^{11}B_5H_8^{79}Br$ spectrum differs in several respects. Perhaps this may be due to impurities introduced by the use of CS_2 and $AlCl_3$ which are not completely removed by the purification methods used.

Chemistry of Boranes. XIX.[1] Derivative Chemistry of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

BY W. H. KNOTH, J. C. SAUER, D. C. ENGLAND, W. R. HERTLER, AND E. L. MUETTERTIES

$B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ react under acidic conditions with a number of oxygen- and sulfur-containing species and with olefins to form substitution derivatives. The substituents observed have included acyl, hydroxy, alkoxy, alkyl, mercapto, and alkylthio groups. The chemical properties of these species resemble those of organic compounds. Some of the substitution reactions are by definition electrophilic, but the majority are characterized as acid-catalyzed nucleophilic substitutions.

Introduction

This is the third of several papers[2,3] detailing the chemistry of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions[4-6] that

(1) Paper XVIII: B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964).

(2) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *ibid.*, **3**, 444 (1964).

(3) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *ibid.*, **3**, 159 (1964).

was previously outlined in a communication.[7] The previous two papers[2,3] discussed the extreme oxidative

(4) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(5) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **82**, 3228 (1960).

(6) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

(7) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *ibid.*, **84**, 1056 (1962).