TABLE VII: TABLE OF DIRECTION COSINES OF PRINCIPAL AXES FOR ANISOTROPIC THERMAL ELLIPSOIDS OF EACH ATOM

Atom	Principal axis	cos α	cos β	cos γ	Length, Å	Atom	Principal axis	cos α	cos β	cos γ	Length, Å
Cl₁	1	−0.369	0.153	−0.940	0.171	C₆	3	.419	.889	0.183	0.247
	2	− .902	.192	.386	.253	C₇	1	− .885	.452	− .111	.180
	3	.236	.969	.069	.268		2	.139	.030	− .990	.216
Cl₂	1	− .230	.051	.959	.181		3	.444	.891	.090	.235
	2	.013	.999	− .049	.293	C₈	1	.024	.003	−1.000	.163
	3	.960	.001	.280	.302		2	− .812	.583	− .017	.195
O₁	1	.986	.082	− .143	.174		3	.582	.813	.016	.259
	2	.148	.059	− .987	.231	C₉	1	− .006	.655	− .756	.173
	3	− .072	.995	− .071	.315		2	− .956	.219	.197	.197
O₂	1	− .940	.124	.317	.195		3	.294	.723	.625	.232
	2	− .313	.054	− .948	.203	C₁₀	1	− .553	.320	− .769	.203
	3	.135	.991	.012	.323		2	− .155	.868	.472	.236
C₁	1	− .013	.274	− .962	.183		3	.818	.381	− .431	.259
	2	− .843	.515	.158	.215	C₁₁	1	− .145	.267	.953	.181
	3	.538	.812	.224	.268		2	− .589	.750	− .300	.212
C₂	1	− .242	.744	− .623	.168		3	.795	.605	− .048	.287
	2	− .287	.558	.779	.197	C₁₂	1	− .777	.359	.518	.203
	3	− .927	.367	− .079	.273		2	− .504	.139	− .852	.223
C₃	1	− .601	.748	− .280	.175		3	.378	.923	− .073	.237
	2	− .085	.275	.956	.207	C₁₃	1	− .560	.524	− .642	.173
	3	.792	.604	− .089	.237		2	− .479	.427	.767	.189
C₄	1	− .739	.054	− .672	.200		3	.676	.737	.012	.245
	2	− .647	.220	.730	.210	C₁₄	1	− .142	.124	− .982	.174
	3	.188	.974	− .128	.247		2	− .604	.775	.185	.207
C₅	1	− .104	.059	− .993	.200		3	.784	.620	− .035	.283
	2	− .917	.382	.119	.238	C₁₅	1	.111	.175	− .978	.167
	3	.386	.922	.015	.257		2	− .173	.973	.154	.233
C₆	1	− .439	.022	.898	.183		3	.979	.152	.138	.281
	2	− .795	.457	− .399	.223						

of each oxygen atom parallel to the C–O bond would be increased by a distribution between longer and shorter C–O bonds of the asymmetric molecule.

The asymmetric environment of the oxygen atoms, as seen from Fig. 4, would lead one to expect asymmetry of the two carbonyl groups. But the symmetry of the two halves of the molecule in both positional and thermal parameters is quite good. Since this symmetry persists even though the two halves of the molecule do not have a symmetry environment, this is good evidence that the molecular symmetry is real, and that the hydrogen bond is symmetric although probably not linear. Of course, this structure does not preclude the possibility that the hydrogen distribution is split into two in a symmetrical double well.

A comparison was made between the packing efficiencies of the nonisostructural compounds bis-(m-chlorobenzoyl)-methane and bis-(m-bromobenzoyl)-methane. The packing coefficient of Kitaigorodskii[9]

was calculated for each of the compounds. This packing coefficient represents the ratio of the volume of the unit cell occupied by the molecules in the unit cell to the volume of the unit cell. The coefficient of the bromo derivative was 0.686 and that of the chloro derivative was 0.691. If the chloro derivative were assumed to be isostructural with the bromo derivative, the packing coefficient would be 0.648. The unit cell volume of the bromo compound is 87 Å.³ larger than the chloro compound while only 53 Å.³ would be required for bromine instead of chlorine atoms. Evidently the chloro derivative packs more efficiently than the bromo derivative. The bromine atoms in bis-(m-bromobenzoyl)-methane tend to pack in sheets while the chlorine atoms in bis-(m-chlorobenzoyl)-methane tend to pack in zig-zag chains. The large congregation of bromine atoms may in some way compensate for the loss in packing efficiency.

(9) A. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1955.

The Fragmentation of Some Boron Hydrides by Electron Impact[1]

BY T. P. FEHLNER AND W. S. KOSKI

The fragmentation of isotopically labeled volatile boron hydrides by electron impact has been studied. Monoisotopic spectra, appearance potentials of selected fragments, and metastable transitions are reported both for protonated and deuterated compounds. Ionization potentials are given for diborane, tetraborane, pentaborane-9 and -11, and hexaborane. Heats of formation are calculated for the various fragment ions produced and are used in determining the decomposition paths for the parent ions. Structures of several fragment ions are postulated from data on isotopically labeled hydrides; ionization potentials are calculated from the corresponding appearance potentials.

Introduction

In a previous paper the fragmentation of tetraborane was studied utilizing measured appearance potentials and the observed metastable transitions in the spectra

of monoisotopic and isotopically labeled tetraboranes.[2] Since then, this approach has been extended to the rest

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

(2) T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc., 85, 1905 (1963).

of the known volatile boron hydrides and the results are reported in this work.

Metastable ion peaks arise from ionic decompositions outside the ionization region, after acceleration but before collection. According to the "Statistical Theory of Mass Spectra"[3,4] the observation of these small diffuse peaks at nonintegral mass numbers indicates an energetically favored path of decomposition and thus provides a means of examining the formation of the fragment ions from the parent ion.

Appearance potential measurements provide access to information on the energetics of ion formation and their reactions.[5] For instance, ionization potentials, bond energies and ionic heats of formation may be obtained provided suitable thermodynamic data are available. The accuracy of the values obtained for these parameters is qualified, however, by the assumption that the excess energy of the fragments is small.

The mass spectra of these compounds containing the normal B^{10} abundance have been published and monoisotopic spectra calculated.[6,7] Besides the authors' previous paper,[2] appearance potential studies of isotopically substituted diborane, pentaborane-9, and decaborane-14 have been made.[8-10]

As it is reasonably certain that ionic species take part in the formation of products from the irradiation of the boron hydrides,[11] understanding of the processes involved requires knowledge of the properties of the ions that may be involved. With this aim in mind, the following more general study of the volatile boron hydrides was undertaken.

Experimental

A standard Consolidated 21-103C mass spectrometer was used to obtain the data presented. The mass spectra were run at slow scan, 30-mil collecting slit, ionizing voltage of 70 v., and an ionizing current of 10 μamp. An exception to this was B_5H_{11} for which a fast scan was used because of its instability.

For examination of metastable transitions the slowest scan, a high accelerating voltage, the 7-mil slit, and an ionizing current of 75 to 100 μamp. were used to obtain the best resolution and intensity. The metastable transitions were identified as described in the previous publication.[2] The fragments involved in a metastable transition were determined from the equation $m^* = m_2^2/m_1$ and it was found m^* (experimental) $= m^*$ (calculated) ± 0.05.[7]

In the appearance potential work a slow scan, 30-mil collecting slit, an ionizing current of 10 μamp., and a repeller voltage of less than 3 v. were generally used. An ionizing current of 15 μamp. was used for weak peaks. In this research, values for the appearance potentials were determined in the same manner as stated previously.[2]

In order to assign peaks unambiguously in a mass spectrum it was necessary to use compounds containing as high a B^{11} content as possible. The protonated and deuterated B^{11} compounds were prepared by pyrolysis of the suitably labeled diboranes previously prepared in this laboratory.[9] As only small amounts were needed at one time, a convenient method for the preparation of the tetraborane, pentaborane-9, and hexaborane was to subject diborane to a shock wave with subsequent separation of the products using fractionation–codistillation in a gas chromatography apparatus.[12] The pentaborane-11 was prepared as adequately described by Burg and Stone.[13]

Results

The monoisotopic spectra for protonated pentaborane-11 and hexaborane-10 and deuterated pentaborane-11 are given in Table I. The monoisotopic spectra were obtained from the raw data by removing the contribution of 1.34% B^{10} from the protonated spectra and the contribution of 1.34% B^{10} and 1.88% H from the deuterated spectra using procedures described previously.[14] The percentage B^{10} was determined from the m/e 10 to m/e 11 ratio. The percentage H used was the maximum value that could be used without obtaining negative residues. The spectra for diborane and pentaborane-9 are not given as they were found to be essentially the same as those published elsewhere.[8,9]

TABLE I

MONOISOTOPIC SPECTRA OF PENTABORANE-11, DEUTERIOPENTABORANE-11, AND HEXABORANE-10

Ion	Intensity $B_5H^1{}_{11}$	Ionizing voltage = 70 v. $B_5H^2{}_{11}$	$B_6H^1{}_{10}$
$B_6H_{10}{}^+$			41.0
$B_6H_9{}^+$			0.6
$B_6H_8{}^+$			47.1
$B_6H_7{}^+$			2.1
$B_6H_6{}^+$			100.0
$B_6H_5{}^+$			7.7
$B_6H_4{}^+$			34.8
$B_6H_3{}^+$			17.7
$B_6H_2{}^+$			14.7
B_6H^+			25.6
$B_6{}^+$			4.7
$B_5H_{11}{}^+$	0.2	0.6	
$B_5H_{10}{}^+$	0.6	0.8	
$B_5H_9{}^+$	27.8	35.8	1.8
$B_5H_8{}^+$	7.7	7.3	0.0
$B_5H_7{}^+$	100.0	100.0	3.8
$B_5H_6{}^+$	8.2	6.7	1.3
$B_5H_5{}^+$	70.0	59.7	18.5
$B_5H_4{}^+$	13.5	9.2	17.3
$B_5H_3{}^+$	13.9	8.7	11.5
$B_5H_2{}^+$	16.7	12.4	18.1
B_5H^+	11.8	10.4	15.4
$B_5{}^+$	14.8	~16	11.4
$B_4H_8{}^+$	2.9		
$B_4H_7{}^+$	5.4		
$B_4H_6{}^+$	14.8		0.6
$B_4H_5{}^+$	12.8		2.0

Ion	Intensity $B_6H^1{}_{11}$	Ionizing voltage = 70 v. $B_6H^1{}_{10}$
$B_4H_4{}^+$	39.8	4.8
$B_4H_3{}^+$	21.4	5.7
$B_4H_2{}^+$	15.8	4.1
B_4H^+	9.1	2.8
$B_4{}^+$	4.5	3.8
$B_3H_5{}^+$		2.0
$B_3H_4{}^+$		1.4
$B_3H_3{}^+$		1.3
$B_3H_2{}^+$		2.0
B_3H^+		0.8
$B_3{}^+$		.2
$B_2H_4{}^+$		.9
$B_2H_3{}^+$		.6
$B_2H_2{}^+$		.9
B_2H^+		.2
$B_2{}^+$		.2
$BH_3{}^+$		.2
$BH_2{}^+$		9.3
BH^+		1.0
B^+		10.4
m/e	$\frac{1}{2}$ — mass peaks	
36.5		0.2
35.5		.05
34.5		.05
33.5		.03

A difficulty was encountered with pentaborane-11 in that it tended to decompose after being in the spectrometer for a short while. This meant that large samples had to be used and that work had to be done quickly. Consequently the values obtained in this research for this molecule are not as reliable as the data for the more stable molecules.

It is noted that no peak corresponding to the parent ion of relative intensity greater than 0.6% was observed in pentaborane-11. Small peaks were observed in the protonated and deuterated compounds, and it is believed that these peaks do correspond to the parent ions although they cannot be definitely assigned as such. A similar situation is found with tetraborane.[2]

Appearance potentials of selected fragments were determined for protonated diborane, pentaborane-9, pentaborane-11, and hexaborane and deuterated diborane, pentaborane-9, and pentaborane-11. These are given in Table II.

The agreement between the listed values of appearance potentials for diborane and pentaborane-9 and those that were measured previously[8,9] is reasonable.

In Table III are presented the metastable transitions involving the loss of H_2 (or D_2) for the same molecules

(3) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhafig. and H. Eyring, *Proc. Natl. Acad. Sci. U.S.*, **38**, 667 (1952).

(4) H. M. Rosenstock, A. L. Wahrhaftig, and H. Eyring, *J. Chem. Phys.*, **23**, 2200 (1955).

(5) W. J. Dunning, *Quart. Rev.* (London), **9**, 23 (1955).

(6) B. Keilin, *Nucl. Sci. Abstr.*, **10**, 908 (1956).

(7) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p. 423.

(8) W. S. Koski, J. J. Kaufman, C. F. Pachucki, and F. J. Shipko, *J. Am. Chem. Soc.*, **80**, 3202 (1958).

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

(10) J. J. Kaufman, W. S. Koski, L. J. Kuhns, and R. W. Law, *ibid.*, **84**, 4198 (1962).

(11) L. H. Hall and W. S. Koski, *ibid.*, **84**, 4205 (1962).

(12) T. P. Fehlner and W. S. Koski, *ibid.*, in press.

(13) A. B. Burg and F. G. Stone, *ibid.*, **75**, 228 (1953).

(14) W. S. Koski, J. J. Kaufman, L. Friedman, and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

TABLE II

APPEARANCE POTENTIALS OF SELECTED FRAGMENTS OF SOME BORON HYDRIDES

Ions: $B_nH_x^+$

x	H	D
(a) Diborane, $n = 2$		
5	12.0 ± 0.1	12.0 ± 0.1
4	12.3 .2	12.3 .2
3	14.3 .2	14.5 .2
2	14.1 .2	
(b) Tetraborane $n = 4$ See ref. 2		
(c) Pentaborane-9 $n = 5$		
9	10.5 ± 0.1	10.0 ± 0.1
7	11.6 0.2	11.2 .2
6		12.4 .2
5	12.8 0.2	12.4 .4
		14.3 .4
$n = 4$		
6		12.4 ± 0.2
4		13.7 0.2
(d) Pentaborane-11 $n = 5$		
10	11.8 ± 0.4	11.3 ± 0.4
9	10.3 .2	10.4 .2
8	12.0 .3	11.4 .3
7	11.5 .2	11.1 .2
6	12.6 .3	12.2 .3
5	12.7 .2	12.3 .2
4	14.2 .4	
$n = 4$		
6		11.4 ± 0.5
4		12.4 0.5
(e) Hexaborane $n = 6$		
10	9.3 ± 0.1	9.7 ± 0.2
9	11.1 .4	
8	11.2 .1	
7	11.5 .3	
6	11.9 .1	
5	12.0 .3	
4	13.4 .3	
$n = 5$		
7	12.0 ± 0.2	
5	13.6 0.2	

TABLE III

METASTABLE TRANSITIONS OBSERVED IN DIBORANE, PENTABORANE-9, PENTABORANE-11, AND HEXABORANE-10

(a) $B_nH_x^+ \rightarrow B_nH_{x-2}^+ + H_2$

x	2		5^9		5^{11}		6	
	m^*	I	m^*	I	m^*	I	m^*	I
10							72.2	2.6
9			60.2	2.0	60.2	2.2		
8					59.1	~0.8	70.2	3.2
7			58.2	4.4	58.1	2.7	69.2	~0.5
6			57.2	0.7	57.1	0.4	68.2	1.0
5	24.4	0.07	56.2	.9	56.1	.5	67.2	0.4
4	23.3	0.06	55.2	.6	55.1	.3	66.2	.6
3			54.2	.6	54.1	.3	65.2	.6
2			53.2	.4	53.1	.2	64.2	.1

(b) $B_nD_x^+ \rightarrow B_nD_{x-2}^+ + D_2$

x	2		5^9		5^{11}		6	
11					69.2 ?	0.05 ?		
10					67.3	0.1		
9			65.3	1.6	65.3	1.7		
8					63.3	0.1		
7			61.3	3.9	61.4	2.3		
6			59.3	0.3	59.3	0.05		
5	24.5	0.07	57.3	.5	57.3	.2		
4	22.6	0.1	55.3	.3	55.3	.3		
3			53.3	.3	53.2	.2		
2			51.3	.2	51.4	.3		

decompose into two singly charged fragments. However, the fragments would undoubtedly possess considerable excess kinetic energy, and thus would not be observed, as the normal spectrometer discriminates strongly against ions formed with high kinetic energy.

TABLE IV

TRANSITIONS BETWEEN DOUBLY CHARGED IONS INVOLVING BH_x FRAGMENTS

Transition	m^*	I	Compound obsd. in
$52^{++} \rightarrow 39^{++} + 13$	14.5	0.0004	B_4D_{10}
$54^{++} \rightarrow 37^{++} + 17$	12.5	.0002	B_4D_{10}
$50^{++} \rightarrow 38^{++} + 12$	14.5	.003	B_4H_{10}
$60^{++} \rightarrow 46^{++} + 14$	17.6	.006	B_5H_9

Finally, Table V lists the doubly charged ions observed in these compounds. The relative intensities are generally less than 0.1% and consequently there is some doubt involved in the assignment of these peaks.

TABLE V

DOUBLY CHARGED IONS OBSERVED IN THE MASS SPECTRA OF THE BORON HYDRIDES

Diborane		Tetraborane		Pentaborane-9		Hexaborane	
Ion	I	Ion	I	Ion	I	Ion	I
B_2DH^{++}	0.03	$B_4D_4H^{++}$	0.0005	$B_5D_8^{++}$	0.02		
$B_2D_2H^{++}$	0.008	$B_4D_3H^{++}$	.003	$B_5D_6^{++}$	.02		
		$B_4D_2H^{++}$	.001	$B_5D_5^{++}$	.01		
		B_4DH^{++}	.001	$B_5D_4^{++}$	.02		
		$B_4D_4^{++}$	.0002	$B_5D_3^{++}$	.07		
		$B_4D_3^{++}$	.002	$B_5D_2^{++}$	.01		
		$B_4D_2^{++}$	.002				
		$B_4H_7^{++}$	.006	$B_5H_8^{++}$	.008	$B_5H_7^{++}$	0.2
		$B_4H_5^{++}$	.03	$B_5H_6^{++}$	.01	$B_5H_5^{++}$	.05
		$B_4H_3^{++}$	.08	$B_5H_4^{++}$	.1	$B_5H_3^{++}$	.05
		B_4H^{++}	.003	$B_5H_2^{++}$	.05	B_6H^{++}	.03
		$B_5H_2^{++}$	.006				

For instance, in the case of hexaborane the 36.5 peaks could be due to $B_6{}^{11}H_7{}^{++}$ or $B_5{}^{11}B^{10} H_8{}^{++}$ (1.3% B^{10} present). In this case one would tend to favor $B_6{}^{11}$-$H_7{}^{++}$ as the intensity is relatively high; however, in the other cases, it is not so certain.

for which appearance potentials were measured. Only transitions occurring on fragments containing the highest number of borons for a certain molecule are given. In general, it was found for the lower fragments that transitions would be observed if both the parent ion and the fragment ion had relative intensities greater than 3%.

A peak having a relative intensity of 1 to 2 was observed in B_5D_{11} at m/e 65.6 and is believed to correspond to the transition $77^+ \rightarrow 71^+ + 6$. The transition $13^+ \rightarrow 11^+ + 2$ was found in B_2D_6 and B_5D_9 with relative intensities 0.02 and 0.004, respectively. These transitions, involving an odd number of deuteriums, are similar to those found in tetraborane.[2]

Only two transitions involving the loss of a boron atom were observed in these compounds and these were found in deuterated diborane. They were $28^+ \rightarrow 17^+ + 11$ at m/e 10.3 and $26^+ \rightarrow 15^+ + 11$ at m/e 8.7. Both had weak relative intensities of 0.003 and 0.002, respectively.

Table IV lists transitions involving the decomposition of doubly charged ions. These were observed quite recently (in hydrocarbons) by Meyerson and Van der Haar.[15] Presumably these doubly charged ions also

(15) S. Meyerson and R. W. Van der Haar, *J. Chem. Phys.*, **37**, 2458 (1962).

Discussion

The ionization potentials of molecules are of significant value both as orbital parameters and in corre-

lation of molecular properties. They may generally be obtained from appearance potential measurements as the appearance potential of the molecular ion is associated with the vertical ionization potential of the molecule. Unfortunately the intensity of the parent ion of tetraborane and pentaborane-11 precluded an appearance potential measurement. However, it was possible to obtain an estimate of their values using the statistical theory in a qualitative manner.

This was done in the following manner. The rate constant for the parent ion decay is given by

$$k(E) = z(1 - E_0/E)^N$$

where z is a frequency factor generally greater than 10^8 sec.$^{-1}$; E is the excitation energy of the ion; E_0 is the activation energy for the decomposition, generally taken to be the difference between the appearance potentials of the parent and daughter ions; and N is the number of oscillators, generally greater than one.[3] It may be observed that when the parent ion intensities are practically zero, nearly all the ions must decay in the ion transit time of the spectrometer. This time is about 10^{-5} to 10^{-6} sec., which requires $k(E)$ to be greater than 10^6 sec.$^{-1}$ for nearly all E. This occurs when E_0 is small and thus, to a good approximation, $A(B_5H_{11}^+) = 10.3$ e.v. and $A(B_4H_{10}^+) = 10.4$ e.v.[2] according to the proposed reaction scheme. (It might be argued that E_0 could be negative; that is, that the ions are formed in a repulsive state. Krauss, *et al.*,[16] believe that in molecules of this size, it is not very probable that ions are formed in repulsive states and that this probability decreases as the molecular complexity increases. Also it is believed that the small peaks observed corresponding to these ions are real. If E_0 were less than zero, $k(E)$ would always be greater than 10^6 sec.$^{-1}$ and consequently no peak would be observed for the parent ion.) This assumption is supported somewhat by the case of diborane. Here the parent peak is quite small and the difference in its appearance potential and that of the major primary ion is only 0.1 e.v. (ref. 8). The measured values for the ionization potentials are given in Table VI.

TABLE VI

IONIZATION POTENTIALS OF SOME BORON HYDRIDES

|	I, e.v.	
Molecule	X = H	X = D
B_2X_6	12.0 ± 0.1^a	12.0 ± 0.1^a
B_4X_{10}	$10.4 \pm .1^a$	$9.9 \pm .1^a$
B_5X_9	$10.5 \pm .1$	$10.0 \pm .1$
B_5X_{11}	$10.3 \pm .2^a$	$10.4 \pm .2^a$
B_6X_{10}	$9.3 \pm .1$	$9.7 \pm .2$

^{a} Estimated as described in the text.

It will be noted from comparison of the protonated and deuterated spectra (see ref. 2 and 9 also) that there is an isotope effect occurring in the decomposition of the parent ion. It is seen that the substitution of deuterium for protium causes an increase in the loss of boron-containing fragments and a decrease in the fragments produced by hydrogen loss only. In the reaction schemes it will be noted that BX_3 loss (X = H, D) competes with X_2 loss. The substitution of deuterium in the molecule would not be expected to change the B–B bond strength much and consequently the frequency factor for BD_3 loss would nearly equal that for BH_3 loss. However, one would expect the frequency factor for the loss of deuterium molecules to be less than that for protium molecules. This would allow BD_3 loss to compete more effectively with D_2 loss and would re-

(16) M. Krauss, A. L. Wahrhaftig, and H. Eyring, *Ann. Rev. Nucl. Sci.*, 5, 241 (1955).

duce D_2 loss with respect to H_2 loss, thereby accounting for the observed effects.

It would also be valuable to know the low energy reaction paths for these molecules. This can be done by consideration of observed metastable transitions and by energetic considerations. As mentioned above, metastable transitions correspond to low energy paths and automatically give the favored reaction path. Unfortunately, no strong transitions involving BH_x fragments are observed and consequently the path for the loss of BH_x cannot be determined in this manner.

If the heats of formation of the various ions were available, one could calculate the heats of reaction for various possible reaction paths. Unfortunately, they are not available at the present, but there is a way to get around this difficulty. This is done as follows:

If an ion is formed according to the reaction

$$AB + e \longrightarrow A^+ + B + 2e$$
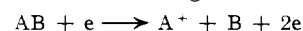
then one can write

$$\Delta H_f(AB) = \Delta H_f(A^+) + \Delta H_f(B) + \Delta H_R$$

where ΔH_f is the heat of formation and ΔH_R is the heat of reaction as determined from the appearance potential.[17] The heats of formation of the various boron hydrides have been determined recently[18] and compare favorably with those previously determined.[19] Therefore the heat of formation for a certain ion A^+ from AB can be determined. If the same ion A^+ is now produced by a different process, say

$$AC + e \longrightarrow A^+ + C + 2e$$

the heat of formation of A^+ can again be calculated. As only the low energy processes will be considered, the two values for the heat of formation of A^+ should be equal. If for the second process there is more than one route for the formation of A^+, then the correct route is given by the one that gives a heat of formation of A^+ equal to that of the first process.

Consider the following example.

From the observed metastable transitions it is known that $B_4H_6^+$ is formed by the process

$$B_4H_{10} + e \longrightarrow B_4H_6^+ + 2H_2 + 2e \qquad (1)$$
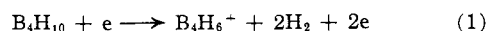
this gives

$$\Delta H_f(B_4H_{10}) = \Delta H_f(B_4H_6^+) + 2\Delta H_f(H_2) - \Delta H_R$$

or $\Delta H_f(B_4H_6^+) = 11.8$ e.v. as $\Delta H_R = A(A^+)$ obtained from ref. 2. From pentaborane-9 $B_4H_6^+$ may be formed by the processes

$B_5H_9 + e \longrightarrow B_4H_6^+ + 2e + BH_3$	(2)(a)
$+ BH_2 + H$	(b)
$+ BH + H_2$	(c)
$+ B + H_2 + H$	(d)
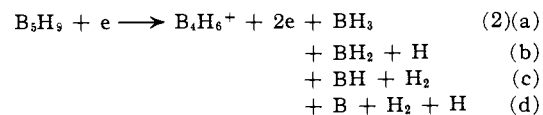
which gives

$\Delta H_f(B_4H_6^+) = 12.1$ e.v.	(a)
$= 8.7^a$	(b)
$= 9.8$	(c)
$= 6.5$	(d)

^{a} Choosing a reasonable value of 40 kcal./mole for BH_2.

It can be seen then that process 2(a) has a heat of formation equal to that for (1). Therefore 2(a) is the correct process for the formation of $B_4H_6^+$ from pentaborane-9. The results of similar calculations on ions from different compounds are given in Table VII. The results are remarkably good and definitely show the favored process.

(17) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

(18) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

(19) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties, Part I," National Bureau of Standards Circular 500, 1961.

TABLE VII

HEATS OF FORMATION FOR SELECTED FRAGMENT IONS FROM SOME BORON HYDRIDES

Ion	Process	ΔH_f°, e.v.
$B_6H_{10}^+$	$B_6H_{10} + e \rightarrow B_6H_{10}^+ + 2e$	10.2 ± 0.1
$B_6H_8^+$	$B_6H_{10} + e \rightarrow B_6H_8^+ + H_2 + 2e$	$12.0 \pm .1$
$B_6H_6^+$	$B_6H_{10} + e \rightarrow B_6H_6^+ + 2H_2 + 2e$	$12.8 \pm .1$
$B_5H_9^+$	$B_5H_9 + e \rightarrow B_5H_9^+ + 2e$	$11.2 \pm .1$
	$B_5H_{11} + e \rightarrow B_5H_9^+ + H_2 + 2e$	$11.4 \pm .2$
$B_5H_7^+$	$B_5H_9 + e \rightarrow B_5H_7^+ + H_2 + 2e$	$12.2 \pm .1$
	$B_5H_{11} + e \rightarrow B_5H_7^+ + 2H_2 + 2e$	$12.5 \pm .2$
	$B_6H_{10} + e \rightarrow B_5H_7^+ + BH_3 + 2e$	$12.1 \pm .2$
$B_5H_5^+$	$B_5H_9 + e \rightarrow B_5H_5^+ + 2H_2 + 2e$	$13.4 \pm .1$
	$B_5H_{11} + e \rightarrow B_5H_5^+ + 3H_2 + 2e$	$13.7 \pm .2$
	$B_6H_{10} + e \rightarrow B_5H_5^+ + BH_3 + H_2 + 2e$	$13.7 \pm .2$
$B_4H_8^+$	$B_4H_{10} + e \rightarrow B_4H_8^+ + H_2 + 2e$	$11.0 \pm .1$
$B_4H_6^+$	$B_4H_{10} + e \rightarrow B_4H_6^+ + 2H_2 + 2e$	$11.8 \pm .1$
	$B_5H_9 + e \rightarrow B_4H_6^+ + BH_3 + 2e$	$12.1 \pm .2$
	$B_5H_{11} + e \rightarrow B_4H_6^+ + BH_3 + H_2 + 2e$	$11.6 \pm .5^a$
$B_4H_4^+$	$B_4H_{10} + e \rightarrow B_4H_4^+ + 3H_2 + 2e$	$13.2 \pm .2$
	$B_5H_9 + e \rightarrow B_4H_4^+ + BH_3 + H_2 + 2e$	$13.9 \pm .1$
	$B_5H_{11} + e \rightarrow B_4H_4^+ + BH_3 + 2H_2 + 2e$	$12.6 \pm .5^a$
$B_3H_5^+$	$B_4H_{10} + e \rightarrow B_3H_5^+ + BH_3 + H_2 + 2e$	$11.9 \pm .2$
$B_3H_3^+$	$B_4H_{10} + e \rightarrow B_3H_3^+ + BH_3 + 2H_2 + 2e$	$14.0 \pm .3$

^{a} Values for the deuterated compound used.

Given below are the various decomposition paths (determined as explained above) for the compounds studied.

Fraction

$B_5H_9^+ \longrightarrow B_5H_7^+ \longrightarrow B_5H_5^+$ 0.98
$ \longrightarrow B_4H_6^+ \longrightarrow B_4H_4^+$

$B_6H_{10}^+ \longrightarrow B_6H_8^+ \longrightarrow B_6H_6^+ \longrightarrow B_6H_4^+$ 0.94
$\phantom{B_6H_{10}^+} \longrightarrow B_5H_7^+ \longrightarrow B_5H_5^+$

$B_5H_{10}^+ \longrightarrow B_5H_8^+ \longrightarrow B_5H_6^+$

$B_5H_{11}^+ \longrightarrow B_5H_9^+ \longrightarrow B_5H_7^+ \longrightarrow B_5H_5^+$ 0.99

$ B_4H_6^+ \longrightarrow B_4H_4^+$
$B_4H_9^+ \longrightarrow B_4H_7^+ \longrightarrow B_4H_5^+$

$B_4H_{10}^+ \longrightarrow B_4H_8^+ \longrightarrow B_4H_6^+ \longrightarrow B_4H_4^+$ 0.98

$ B_3H_5^+ \longrightarrow B_3H_3^+$

The fraction of the total ion yield accounted for by the ions shown for each path at about 5.5 e.v. above the ionization potential is also given.

This type of energetic consideration cannot be applied to tetraborane as the molecule triborane has not been studied. Consequently, it was necessary to postulate that the same type of process would be energetically favorable in this compound too. The reaction path for tetraborane then is as given above.

Primary information has been obtained on the state of the neutral fragments involved in the unimolecular reactions of some hydrocarbons by Beck and Niehaus.[20] They exc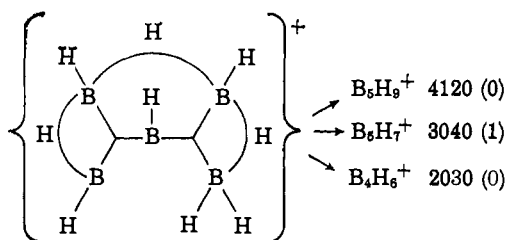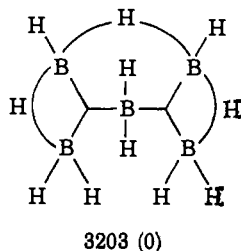ited molecules by electron impact and approximately 10^{-5} sec. after excitation ionized and analyzed the fragments in a mass spectrometer. Their results tend to confirm decomposition schemes based on considerations similar to those used above.

Some calculations using the "Statistical Theory of Mass Spectra" mentioned above were made. Using frequency factors reasonable in light of the work of Friedman, et al.,[21] and a number of oscillators consistent with the work of Chupka, et al.,[22] the spectra were calculated at an ionization energy of 5.5 e.v. The results were qualitatively in agreement with observed spectra at this energy and thus tend to indicate that the mechanism proposed is correct.

(20) D. Beck and A. Niehaus, J. Chem. Phys., 37, 2705 (1962).
(21) L. Friedman, F. A. Long, and M. Wolfsberg, ibid., 27, 613 (1957).
(22) W. A. Chupka and J. Berkowitz, ibid., 32, 1546 (1960).

Having determined the reaction path, it would be of interest to obtain some information on the structures of the various ions. This may be most conveniently done by studying molecules labeled in various specific positions. One is limited, however, in the preparation of specifically labeled compounds as the boron hydrides are not amenable to the techniques available to carbon compounds. However, it was possible to obtain some information on two labeled hydrides as is described below.

The mass spectrum of 1,3-dideuteriotetraborane was previously published[2] and it was found by comparison of this spectrum with that of normal tetraborane that the initial loss of H_2 did not involve the positions labeled with deuterium. As it has been suggested that the formation of a "normal" two-center B–B bond is a part of the process of losing $2H$,[9] the following structure is thought to be the stable form of $B_4X_8^+$ (X = H, D)

$$\begin{array}{c} D \quad H \\ B \diagdown \ H \\ HB \quad B \\ B \diagup \ H \\ H \quad H \\ D \end{array}$$

Although it was not noted in the previous paper,[2] the loss of BH_3 also does not involve the deuterated positions. This may be seen as follows. Since $B_3H_5^+$ appears in the spectrum of B_4H_{10} and is about five times larger than $B_3H_6^+$, it is fairly certain that the m/e 40 peak in the dideuterio compound is due to $B_3H_3D_2^+$. This means that the reaction

$$B_4H_6D_2^+ \longrightarrow B_3H_3D_2^+ + BH_3$$

takes place, and the BH_3 lost contains one BH_2 group. The structure of $B_3H_3D_2$ is then

$$\begin{array}{c} D \\ | \\ H-B-B-H \\ H \diagdown B \\ | \\ D \end{array}$$

The spectrum of this labeled compound also indicates that rearrangement is not taking place as fast as the primary decompositions. If it were, one would not be able to make the above deductions (i.e., m/e 53 would not be zero if rearrangements occurred, etc.). This is in distinct contrast to the situation for hydrocarbons.[23] In the previous paper[2] it was postulated that the same type of losses were the most probable and the structures of the lower fragments deduced. However, the more fragmentation that occurs, the more likely rearrangement becomes.

It was also possible to gain some information on the fragmentation of labeled pentaborane-9. In some previous work[14] it was found that the terminal positions of pentaborane-9 exchange preferentially. The partial spectrum of pentaborane-9 that had undergone exchange was published. This consisted in part of pentaborane-9 that had been synthesized from the deuterated diborane. Consequently the spectrum in Table IV of ref. 14 was analyzed in the following manner. A spectrum of pentaborane-9 containing 85% of D randomly distributed throughout the molecule was subtracted from the raw data. This left the spectrum of pentaborane-9 with 75% D in the terminal positions (the values of the % D are unpublished data). Finally the B^{10} content is stripped from this spectrum giving the results contained in Table VIII. Although the error must be considerable, it is very interesting to note that it appears as if a mass loss of 3 from the parent ion is

(23) W. H. McFadden and A. L. Wahrhaftig, J. Am. Chem. Soc., 78, 1572 (1956).

very favorable. This means that a terminal deuterium and a bridge proton are probably involved in the initial hydrogen loss.

In the case of B_5H_{11} it is thought that the $B_5H_9{}^+$ formed decomposes to $B_5H_7{}^+$ before it rearranges to normal $B_5H_9{}^+$. Structurally this would be

3203 (0)

$$B_5H_9{}^+ \quad 4120 \ (0)$$
$$B_5H_7{}^+ \quad 3040 \ (1)$$
$$B_4H_6{}^+ \quad 2030 \ (0)$$

For convenience, Lipscomb's nomenclature is used to denote the structures.[24] In his topological theory the structural notation (styx) denotes a boron hydride with s hydrogen bridge bonds (B–H–B), t 3-center boron–boron bonds (B–B–B), y 2-center boron–boron bonds (B–B), and x BH_2 groups. In addition each boron atom has at least one BH terminal bond. The additional number in parentheses used here gives the number of borons without hydrogens.

Finally it is quite likely that hexaborane behaves in an analogous manner to pentaborane-9.

Using previously measured bond energies[18] one can now calculate ionization potentials for some of the frag-

(24) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 118 (1959).

TABLE VIII

THE FRAGMENTATION PATTERN OF 1,2,3,4,5-PENTADEUTERIO-PENTABORANE

	Relative intensity		
m/e	$B_5{}^{11}H_9$	$B_5{}^{11}H_4D_5$ (75% D)	Possible ions
	20% B^{10}	0% B^{10}	
69		8.9	8.9	$B_5H_4D_5{}^+$
68		25.1	−0.9	$B_5H_3D_5{}^+$
67		34.3	0.6	$B_5H_2D_5{}^+$ $B_5H_4D_4{}^+$
66		37.3	11.0	$B_5HD_5{}^+$ $B_5H_3D_4{}^+$
65		40.0		
64	75	40.1		
63	1			
62	75			
61	5			
60	100			

ment ions in the same manner as was done previously.[2] Ionization potentials along with the structure of the ion are given in Table IX. In general the agreement between ionization potentials of fragments from different molecules is good, lending consistency to the structures derived.

TABLE IX

IONIZATION POTENTIALS IN E.V. OF SELECTED FRAGMENT IONS

		From			
Ion	Structure	B_6H_{10}	B_5H_{11}	B_5H_9	B_4H_{10}
$B_5H_8{}^+$	3050 (1)	9.6			
$B_5H_9{}^+$	4120 (0)		10.6	10.5	
$B_5H_7{}^+$	3040 (1)	10.3	10.7	10.3	
$B_4H_6{}^+$	2030 (0)			10.3	10.0
$B_3H_5{}^+$	1021 (0)				10.1

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

Olefin Exchange Reactions in Platinum(II) Complexes Containing Pyridine N-Oxides

BY SAUL I. SHUPACK AND MILTON ORCHIN

Some 66 new 1-(4-substituted pyridine N-oxide)-3-olefin-2,3-dichloroplatinum(II) complexes were prepared where the olefin is one of a series of 3- and 4-substituted styrenes. The styrene complexes were equilibrated with 1-dodecene and the equilibrium constants of the competitions for a site on the platinum were determined spectrophotometrically. The equilibrium is affected by the substituents on the styrene and to an even greater extent by the substituents on the pyridine N-oxide. The ratio of the two extreme equilibrium constants thus far determined is about 100,000.

Introduction

Previous work in this Laboratory has shown that pyridine N-oxide (PyO) can readily displace the *trans* chloride in Zeise's salt,[1] and a series of 4-substituted PyO moieties coordinated to Pt(II) were prepared[2] to study the substituent effect. The ethylene in these PyO complexes can be displaced by other olefins and the complexes containing styrene and various 4-substituted PyO moieties have been described.[2,3] The present paper reports the preparation of a series of complexes of general structure I, in which both the styrene and the pyridine N-oxide are substituted by a
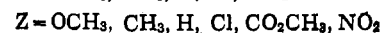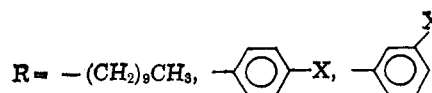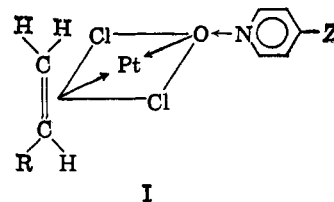
(1) L. Garcia and M. Orchin, *J. Chem. Soc.*, 2254 (1961).
(2) L. Garcia, S. I. Shupack, and M. Orchin, *Inorg. Chem.*, **1**, 863 (1962).
(3) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1962).

I

$R = -(CH_2)_9CH_3,$

$X = OCH_3, CH_3, H, Cl, NO_2$

$Z = OCH_3, CH_3, H, Cl, CO_2CH_3, NO_2$