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Negative Ions Mass Spectra of Some Boron Hydrides

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The negative ion mass spectra of decaborane-14, pentaborane-9 and diborane-6 was observed under a variety of conditions. The spectra vary greatly with source conditions. The parent molecules undergo several resonance electron captures at different electron energies, and then decompose to simpler species.

Introduction

In the past a considerable amount of work has been reported on the positive ion mass spectra of the boron hydrides, but very little on the negative ion spectra. Since studies of discharge tube phenomena and electron impact processes require some knowledge of negative ions, it seemed worthwhile to attempt to study them. In addition, the electron deficiency of the boron hydrides might lead one to expect that negative ions would be readily formed. This would be in contrast to hydrocarbons which yield very low ion currents. The only previous work[1] listed four appearance potentials for pentaborane-9 but no spectra were given. In addition, it was reported that negative ions for decaborane-14 and diborane-6 could not be observed. It is the purpose of this work to report some observations on the negative ion mass spectrum of these compounds.

Experimental Section

Decaborane-14, pentaborane-9 and diborane-6 where all obtained from commercial sources. The decaborane was recrystallized from hexane. The pentaborane and diborane were purified by conventional high vacuum techniques.

Spectra were obtained on a Hitachi RMU-6E mass spectrometer. The fragmentation patterns and the data for the clastograms were obtained under source conditions which gave best sensitivity at an ionizing voltage of 70 volts. (Except where specifically indicated the voltages given are the readings of the mass spectrometer meters.) Under these conditions the repellers were approximately 2 volts. The spectrum of diborane was obtained at 20 volts ionization potential and 2 volts repeller potential. The monoisotopic spectra were calculated assuming a B^{10} to B^{11} ratio of 1 to 4. Appearance potentials were obtained with the repellers set at 7 volts, and a plot of ion current *vs.* electron energy was obtained automatically by driving the ionizing energy control potentiometer with a synchronous motor. The appearance potential was then taken as the point at which the ion current reached zero. An electron multiplier was used as a detector, but no corrections were made for discrimination effects. The pressure in the analizer tube was maintained at 1×10^{-6} Torr. In this pressure range, the pressure in the ion source is larger than the tube pressure by a factor of 8.

Results and Discussion

The relative total intensities, from a qualitative observation of the spectra, are approximately

decaborane positive ions	1
pentaborane positive ions	1
diborane positive ions	1
decaborane negative ions	10^{-2}
pentoborane negative ions	10^{-3}
diborane negative ions	10^{-6}

The conditions are essentially the same for all except diborane. The intensity of the diborane was so low that no work beyond recording the spectra was attempted. This order of intensity of negative ion spectra is the same order one would predict on the basis of electron deficiency. The criteria of electron deficiency used is the excess of atomic orbitals available for bonding over the number of electrons available one would not expect this order of magnitude of differences in relative intensities. It is unlikely that any consideration of the electronic structure of these molecules could predict such wide variation. It seems likely that size is very important for a combination of reasons. First the large size should make electron impact more likely. Second the energy of the electron can be easily distributed over the greater number of degrees of freedom in the large molecule. Of less importance, due to the low pressures, are the possibilities of collisional stabilization, ion molecule reactions, and collision induced dissociations. All of these would favor the larger molecule. The spectra are given in Table I and II and a portion of the clastograms are given in Figures 1 and 2. Several metastable transitions were observed. Due to the mixture of isotopes involved these were spread over an area of several mass numbers.

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[1] R. M. Reese, V. H. Debeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, *57*, 367 (1956).

Table I. Polyisotopic Spectra

Decaborane-14 m/e	Relative Intensity	Pentaborane-9 m/e	Relative Intensity
124	10.5	64	15.4
123	35.4	63	86.9
122	70.3	62	100.0
121	94.8	61	55.2
120	100.0	60	14.5
119	99.4	59	3.31
118	95.9	58	2.41
117	79.2	57	1.45
116	51.2	56	1.03
115	23.1	55	0.48
114	7.73		
113	2.21	50	10.9
112	0.70	49	15.7
		48	6.28
110	1.80	47	35.8
109	5.06	46	30.6
108	12.4	45	11.4
107	22.8	44	2.76
106	25.3	43	0.43
105	18.8		
104	10.0	38	4.69
103	4.42	37	22.4
102	1.40	36	17.2
101	0.41	35	5.38
		34	1.10
96	14.5	33	0.23
95	30.2		
94	27.9	27	1.30
93	15.3	26	1.24
92	5.35	25	2.26
91	1.74	24	1.79
90	0.58	23	.48
89			
84	0.35	Diborane-6	
83	0.76	m/e	Relative Intensity
82	0.76	26	3
81	0.58	25	100
80	0.35	24	62
		25	11
72	<0.1		
71	<0.1	15	20
70	<0.1	14	8
69	<0.1	13	8
68	<0.1	12	2

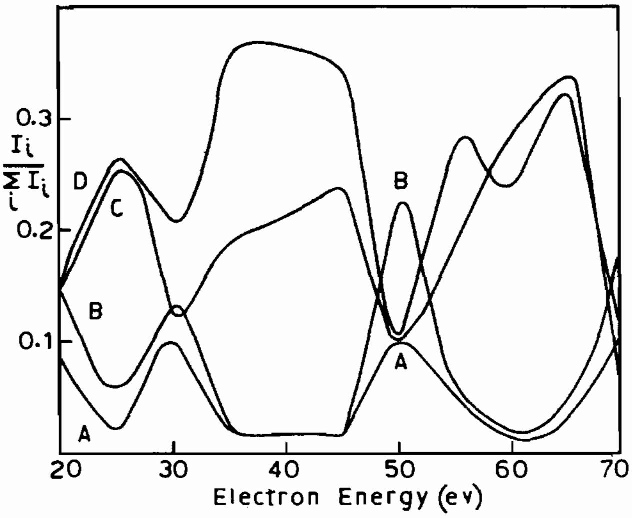

Figure 1. Portion of Clastogram for Decaborane. A, $B_{10}H_{14}^-$; B, $B_{10}H_{12}^-$; C, $B_8H_8^-$; D, $B_{10}H_9^-$.

Table II. Monoisotopic Spectra

	Decaborane-14		
$B_{10}H_{14}$	58.5	B_8H_8	80.5
$B_{10}H_{13}$	50.2	B_8H_7	6.78
$B_{10}H_{12}$	100.0	B_8H_6	.73
$B_{10}H_{11}$	24.5	B_8H_5	1.57
$B_{10}H_{10}$	69.6		
$B_{10}H_9$	65.0	B_7H_7	1.91
$B_{10}H_8$	28.9	B_7H_6	.81
$B_{10}H_7$	4.4	B_7H_5	.24
		B_7H_4	.68
B_9H_{11}	10.0		
B_9H_{10}	5.52		
B_9H_9	33.8		
B_9H_8	25.2		
	Pentaborane-9		
B_5H_9	22.8	B_3H_5	6.94
B_5H_8	100.0	B_3H_4	27.9
B_5H_7	8.58	B_3H_3	3.19
B_5H_6	4.83	B_3H_2	.22
		B_3H_1	.43
B_4H_6	16.2		
B_4H_5	7.10	B_2H_5	1.93
B_4H_3	49.2	B_2H_4	.87
		B_2H_3	2.78
		B_2H_2	1.20
	Diborane-6		
B_2H_4	3	BH_4	14
B_2H_3	100	BH_3	3
B_2H_2	14	BH_2	8

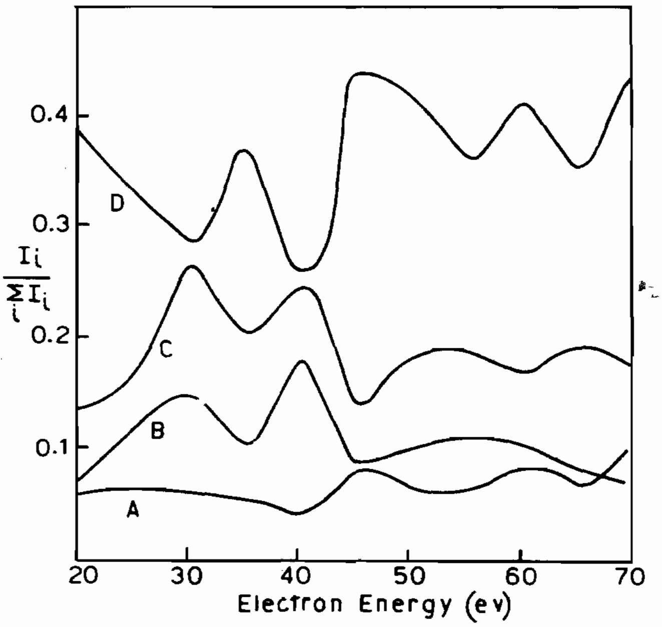

Figure 2. Portion of Clastogram for Pentaborane. A, $B_5H_9^-$; B, $B_3H_4^-$; C, $B_4H_3^-$; D, $B_5H_8^-$.

In most cases the metastables appeared in portions of the spectrum which contained other ions. They were best assigned as the loss of H_2 from the heaviest ion in each group, for example:

$$B_9H_{11}^- \longrightarrow B_9H_9^- + H_2$$

The assignment was not entirely unambiguous due to the overlap of peaks. The only case in which a clear assignment could be made was for the transition

$$B_{10}H_{14}^- \longrightarrow B_9H_{11}^- + BH_3$$

It is apparent from the clastograms that the spectra are very sensitive to the ionizing voltage. At low ionizing voltages they are also very sensitive to repeller voltage. The most reasonable interpretation of these spectra is that the parent molecule, decaborane or pentaborane, undergo a series of resonance electron captures to form negative ions of different energies. Each of these ions can then decompose by a relatively limited number of pathways. From the appearance of the clastograms[2] and the metastable transitions it seems that a large portion of the voltage range the following types of reactions take place.

$$B_xH_y^- \longrightarrow B_xH_{y-2}^- + H_2$$

$$B_xH_y^- \longrightarrow B_{x-1}H_{y-3}^- + BH_3$$

In order to rationalize the appearance of the spectra one is forced to assume that there is a special stability associated with certain of the observed ions. A high relative intensity for an observed ion cannot be attributed to the stability of the unobserved fragments, since the ionization efficiency curves indicate that this fragment can be lost in several degrees of dissociation. It can be an instructive exercise to attempt to predict, by Lipscomb «rules»[3] for instance, if an ion such as $B_3H_4^-$ should be stable. The difficulty comes in that one cannot easily explain why $B_4H_3^-$ should be more stable than $B_4H_6^-$. Fortunately the most probable ion in each spectrum, $B_{10}H_9^-$, $B_5H_8^-$ and BH_4^- is closely related to a known species. For $B_{10}H_9^-$ a likely structure is that of $B_{10}H_{10}^{=}$ with a hydride ion removed. This would leave the very stable B_{10} cage undisturbed giving a relatively stable ion. The $B_5H_8^-$ ion is electronically identical with B_5H_9 and the BH_4^- ion is known species, therefore one should not be too surprised to find them present in high relative intensity.

The ionization efficiency curves for these ions were very complex at low repeller voltages. Decaborane showed ten easily identifiable resonance capture peaks and indications of several others. Unfortunately these peaks were relatively broad and overlapped in varying degrees. Increasing the repeller voltage decreased the number of ions produced and by setting the repeller voltage at 7 volts most of the peaks disappeared into the background but left sufficient sensitivity to determine the appearance potentials. Appearance potentials for several ions are given in Table III and are based on a calibrated voltage scale. SF_6, CO, O_2, H_2O and CCl_4 were used to calibrate the scale.

Table III. Appearance Potentials

Decaborane-14		Pentaborane-9	
Ion	Voltage	Ion	Voltage
$B_{10}H_{14}^-$	0.3	$B_5H_9^-$	0.3
$B_{10}H_{14}^-$	33.4	$B_5H_8^-$	0.8
$B_9H_{11}^-$	0.7	$B_4H_6^-$	2.8
$B_8H_8^-$	2.6	$B_4H_5^-$	7.9
$B_8H_8^-$	11.7	$B_4H_4^-$	4.8
$B_8H_8^-$	24.2	$B_3H_5^-$	0.3
$B_8H_8^-$	46.9		

The appearance potentials could be related to the electron affinity of the species involved and the several resonance captures could be related to differences in association of the unobserved fragment. However, since the number of possible arrangements for the unobserved fragments is very large, there is no way to make an unambiguous choice.

Finally a word should be said about the accuracy of the measurements. For values less than 5 volts the reproducibility was ±0.3 volts, for values greater than 10 volts the reproducibility was ±0.5 volt. Difficulties were encountered in the intermediate range presumably due to the clossness to the repeller voltage. Finally it should be noted that with respect to recommended[4] calibration points for negative ions, the differences among various workers for the same points was greater than our uncertainty for a single measurement. This is likely due to production products in different excited states under the conditions present in different sources.

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(2) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, 3, 699 (1964).

(3) W. N. Lipscomb, «Boron Hydrides», W. A. Benjamin, Inc., New York, 1963.

(4) F. W. McLafferty, «Mass Spectrometry of Organic Ions», Academic Press, New York, 1963. Pg. 194, Table XIV.

(5) F. W. McLafferty, «Mass Spectrometry of Organic Ions», Academic Press, New York, 1963. Pg. 195, Table XV.