Negative-ion Mass Spectrometry of *closo*-Carboranes

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The negative-ion mass spectra of the small *closo*-carboranes, 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ exhibit much more intense $P - 1$ ions than parent ions, indicating the ease with which conjugate base anions of these cage compounds are formed. Ionization efficiency diagrams were gathered for the parent regions as well as for important fragments. These suggest that negative ions of *closo*-carboranes are formed with somewhat more difficulty than those of *nido*-carboranes which appears to reflect the lack of bridging hydrogen atoms in the former. Percentage compositions of carborane mixtures have been determined by use of a combination of mass-spectral patterns and energy-dependency information.

Mass spectrometry of carboranes has been primarily confined to positive-ion investigations.[1] In view of the lack of reasonably stable cationic species among carboranes at ambient conditions, in contrast to the plethora of stable and isolable carborane anions,[2] it is remarkable that more emphasis has not been placed on negative-ion mass spectroscopy of this important class of cage carbon–boron compounds.

In the present investigation negative-ion mass spectra of 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have been gathered and correlated. In addition, ionization efficiency curves of the major fragments have been obtained. An application of the energy-dependency information has been found in the determination of the relative percentage compositions of carborane mixtures.

EXPERIMENTAL

The carboranes 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$ were prepared and purified as previously reported.[3,4] The mass spectra were run on a Hitachi RMU-6E mass spectrometer operating in the negative mode with an accelerating voltage of 3·6 kV. The electron multiplier voltage was usually 2·5 kV and the filament emission ranged between 5 and 20 μA in the lower voltage spectra and was 70 μA in the reported 70 eV spectra.

The m/e 16 maxima (O^-) in CO_2, N_2O, CO, and NO_2 were used to calibrate [5] the energy scale in the lower voltage region and are probably accurate to 0·2—0·3 eV.

Polyisotopic spectra for each of the *closo*-carboranes 1,5-$C_2B_3H_5$, 1,2-$C_2B_4H_6$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ were obtained. Each of the parent regions have been converted to monoisotopic boron-11 spectra. For regions at masses lower than the parent region a maximum and minimum number of boron atoms, consistent with the molecular formula of the parent carborane, were assumed. Then on the basis of best monoisotopic fit of the data (for procedure see ref. 1 and refs. therein) a new maximum for the number of boron atoms was determined for each fragment. The ^{11}B monoisotopic spectra are in the Table. For a given mass a number of fragments are sometimes possible and in

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[1] J. F. Ditter, F. J. Gerhart, and R. E. Williams, 'Mass Spectrometry in Inorganic Chemistry,' Advances in Chemistry Series, No. 72, p. 191, Amer. Chem. Soc. Publ., Washington, D.C., 1968; R. E. Williams, 'Progress in Boron Chemistry,' eds. R. S. Brotherton and H. Steinberg, Pergamon Press, Elmsford, N.Y., 1970.

[2] See R. Grimes, 'Carboranes,' Academic Press, New York, 1970, for references.

[3] T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, 1964, **3**, 1686.

[4] J. R. Spielman and J. E. Scott, *J. Amer. Chem. Soc.*, 1965, **87**, 3512.

[5] L. G. Christophorou and R. N. Compton, *Health Physics*, 1967, **13**, 1277.

Relative intensities of major ^{11}B monoisotopic ions in the negative ion spectra of the *closo*-carboranes *

		1,5-$C_2B_3H_5$		1,2-$C_2B_4H_6$		1,6-$C_2B_4H_6$		2,4-$C_2B_5H_7$	
		7·0 eV	70 eV	9·5 eV	70 eV	10·5 eV	70 eV	9·0 eV	70 eV
86	$C_2B_5H_7$							2·4	4·1
85	$C_2B_5H_6$							15·1	40·3
84	$C_2B_5H_5$							5·9	10·7
83	$C_2B_5H_4$							7·5	
82	$C_2B_5H_3$								6·5
81	$C_2B_5H_2$								3·6
73	$C_2B_4H_5$			14·1	29·1	3·4	85·9		
71	$C_2B_4H_3$			4·3		5·3	4·0	*100·0*	55·5
70	$C_2B_4H_2$						2·0		
69	C_2B_4H				2·9			6·4	7·5
61	$C_2B_3H_4$	*100·0*	31·6				5·7	7·1	10·9
	CB_4H_5							7·1	
60	$C_2B_3H_3$	4·5		2·3		2·7			
59	$C_2B_3H_2$		32·7	*100·0*	*100·0*	*100·0*	*100·0*	8·7	4·3
	CB_4H_3							7·3	
58	C_2B_3H						13·3		6·0
57	C_2B_3		4·9	3·4	10·0			4·8	3·4
	CB_4H							3·7	
49	$C_2B_2H_3$							13·9	7·0
	CB_3H_4							13·9	7·0
	B_4H_5							13·9	7·0
48	$C_2B_2H_2$	5·0						8·4	
	CB_3H_3	5·0						4·9	
47	C_2B_2H			2·1		2·9	2·0	2·8	14·3
	CB_3H_2			2·2		2·7	2·0		13·9
	B_4H_3			2·0		2·6	2·0		12·6
46	C_2B_2		6·9				4·6		4·0
	CB_3H		6·6				4·2		
	B_4H_2						3·7		
45	CB_3								4·8
	B_4H								3·1
37	C_2BH_2	2·8	4·1	20·4	12·8	31·2	23·8		6·4
	CB_2H_3	2·8	4·1	20·4	6·4	31·2	14·4		6·4
	B_3H_4	2·8		20·4	4·2	31·2	9·6		6·4
36	C_2BH		5·6	7·9	3·2	7·0	1·3		3·5
	CB_2H_2		4·6	2·7	3·2		7·2		2·0
	B_3H_3				3·2		7·2		
35	C_2B		81·2		83·4	4·5	97·2		*100·0*
	CB_2H		79·9		60·8	4·3	94·8		99·6
	B_3H_2				40·5		95·7		99·6
34	CB_2				22·4		47·6		17·0
	B_3H				14·9		31·7		
33	B_3				7·5				4·7
26	C_2H_2		2·0						
25	C_2H	7·6	*100·0*	6·2	50·2	8·2	85·0		59·9
	CBH_2	7·6	99·4	6·2	50·2	8·2	62·0		
	CB_2H								60·0
	B_2H_3	7·6	99·1	6·2	50·2				60·0
	B_2H_5					8·2	62·0		
24	C_2		95·1	4·0	42·1	3·4	61·3		50·5
	CBH		70·2	2·4	29·6		70·4		35·4
	B_2H_2		45·6		17·0		54·9		20·5
23	CB		41·3		12·0		45·0		24·1
	B_2H		30·0		7·8		31·2		19·1

* Ions less than 2% of the base peak are not included.

such cases the intensity of each fragment is given in the Table as though others of the same mass are not present.

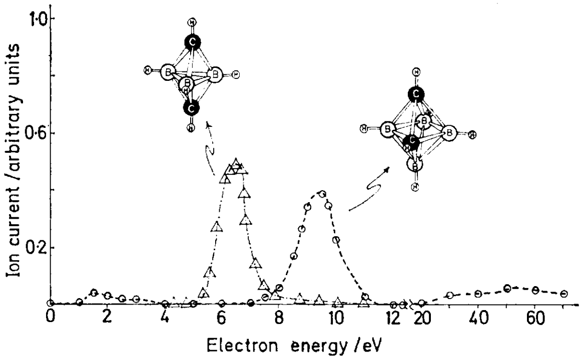

FIGURE 1 Ionization efficiency curves for (△), *m/e* 61 of 1,5-$C_2B_3H_5$; (○), *m/e* 73 of 1,2-$C_2B_4H_6$

The ionization efficiency curves (Figures 1—3) were obtained by manually varying the electron voltage while monitoring the ion current for a given ion on a potentiometric recorder. In the ionization efficiency curves, the ion current was plotted by use of arbitrary units based on the particular voltage gain of the recorder. The scale of 1—10 represents the 0·1 V full-scale pen displacement range on the recorder.

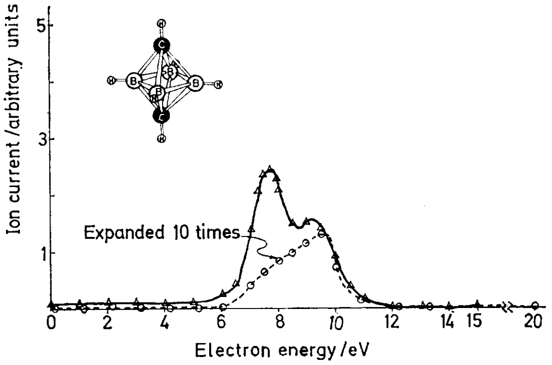

FIGURE 2 Ionization efficiency curve for fragments of 1,6-$C_2B_4H_6$: (△), *m/e* 58; (○), *m/e* 73

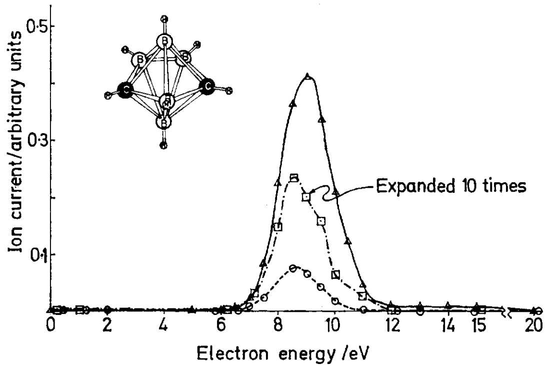

FIGURE 3 Ionization efficiency curve for fragments of 2,4-$C_2B_5H_7$: (□), *m/e* 61; (△), *m/e* 71; (○), *m/e* 85

DISCUSSION

1,5-$C_2B_3H_5$.—For $C_2B_3H_5$ at low voltage (7 eV) the spectrum is dominated by the $C_2B_3H_4^-$ ion which is probably formed by dissociative resonance capture (1).

$$C_2B_3H_5 + e^- \longrightarrow C_2B_3H_4^- + H\cdot \qquad (1)$$

At high voltage (70 eV) the 'ion-pair' process probably dominates the spectrum and allows a reasonable production of $C_2B_3H_4^-$ as the dominant ion *via* 'ion-pair' formation (2). The ionization efficiency curve

$$C_2B_3H_5 + e^- \longrightarrow C_2B_3H_4^- + H^+ + e^- \qquad (2)$$

(Figure 1) for the $C_2B_3H_4^-$ ion shows a maximum at 6·5 eV which is remarkably close to the voltage maximum of this ion in the $C_2B_4H_8$ spectrum.[6]

1,2-$C_2B_4H_6$.—The spectra of 1,2-$C_2B_4H_6$ at both high (70 eV) and low (2—15 eV) (Table) voltages are dominated by the fragment ion region at *m/e* 56—60, although the *P* — 1 peak attributed to $C_2B_4H_5^-$ is also substantial. The fragment ion most prevalent in the spectrum is the one assigned to the $C_2B_3H_2^-$ ion. Even when the *P* — 1 peak ($C_2B_4H_5$) is maximized at 9·5 eV, as determined by voltage-dependency curves (Figure 1), the $C_2B_3H_2^-$ ion still dominates.

Coincidentally, the difference in formulae between the

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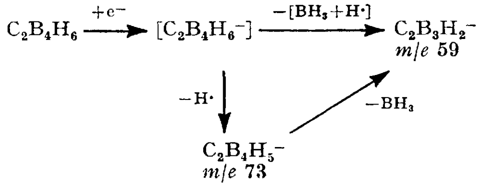
[6] C. Brown, K. Gross, and T. Onak, *Chem. Comm.*, 1972, 68; *J. Amer. Chem. Soc.*, 1972, in the press.

prevalent parent group ion $C_2B_4H_5^-$ and the base $C_2B_3H_2^-$ ion corresponds to a borane (BH_3) group. The production of borane units is not without precedent in polyboron mass spectrometry;[1,6,7] therefore, one of the routes shown in Scheme 1 to $C_2B_3H_2^-$ may well obtain for the production of these ions from 1,2-$C_2B_4H_6$.

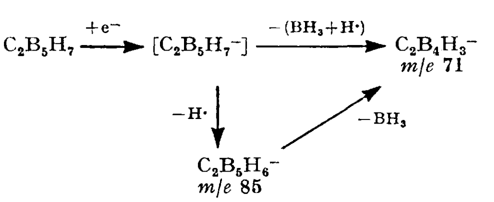
1,6-$C_2B_4H_6$.—The negative-ion spectra of 1,6-$C_2B_4H_6$ at both 70 and 10 eV are very similar to that of the 1,2-isomer so that similar fragmentation routes are, at first, implied. However, the ionization efficiency curve (Figure 2) for *m*/*e* 73 ($C_2B_4H_5^-$) is slightly different from that for the 1,2-isomer; therefore, the extra observed maximum indicates that the *m*/*e* 73 ion (which may or may not be the same ion in both isomers) is formed by more than one process. This eV region is in the dissociative electron-capture area. The additional process of formation may account for the somewhat different values for the intensity ratios found for mass 73 : 59 in comparing the 1,2- with the 1,6-$C_2B_4H_6$ isomers. A voltage-dependency diagram at *m*/*e* 59 contains two distinct maxima at 7·7 and 9·1 eV and is similar in shape to the diagram for $C_2B_4H_8$ at *m*/*e* 61.[6] The presence of the intense *m*/*e* 59 fragment indicates that Scheme 1 may also apply to the 1,6-isomer of $C_2B_4H_6$.



SCHEME 1

2,4-$C_2B_5H_7$.—The spectrum of 2,4-$C_2B_5H_7$ at 9·0 eV is similar to those of the $C_2B_4H_6$ carboranes in that the C_2B_{n-1} ion (n = number of boron atoms in parent molecule) region predominates. The ions of most interest appear to be at *m*/*e* 85 ($C_2B_5H_6^-$), *m*/*e* 71 ($C_2B_4H_3^-$), and a number of smaller fragments (*m*/*e* 61, 59, 49, 47, 35, 34, 25, 24, and 23) which cannot be unambiguously assigned. Electron energy-dependency diagrams (Figure 3) run at *m*/*e* 85, 71, and 61 reveal that all these ions have maxima around 9·0 eV. This may indicate that each of the ions have a common precursor. That is, once a hydrogen is abstracted from the $C_2B_5H_7$, the fragmentation into the smaller ions at *m*/*e* 71 and 61 occurs with a smaller energy requirement than the initial process. To account for the intense *m*/*e* 71 peak the routes shown in Scheme 2 are suggested.

It is noteworthy that, as with the $C_2B_4H_6$ isomers, as well as with the *nido*-carborane[6] $C_2B_4H_8$, loss of borane units is strongly indicated. Although this is expected with compounds containing three attached hydrogens, as in 2,4-$C_2B_4H_8$ [boron atom (5) has two bridging hydrogen atoms as well as a terminal hydrogen atom] the loss of BH_3 units from the *closo*-carboranes is unexpected. For this to occur rearrangements are necessary, or an alternate mechanism is operating in which two of the hydrogen atoms are split off before or after a BH unit departs.



SCHEME 2

The presence of $P - 1$ ions in greater abundance than parent ions is consistent with the observation of slightly acidic hydrogens in the *closo*-carboranes. With butyllithium it is known that the cage C–H hydrogen can be abstracted [reaction (3)] and these ions have much the same structural features as the parent carborane.[8-10] It is quite likely, then, that the P − 1 ions of the *closo*-carboranes in the negative-ion mass spectra have the same structural features of the parent system, except for a loss of a H–C_{cage} hydrogen atom. Production of negative ions from *closo*-carboranes are formed with somewhat more difficulty than in *nido*-compounds.[6] The latter contain bridging hydrogen atoms which are probably more acidic[11] than cage CH hydrogen atoms; therefore the conjugate base anions ($P - 1$) are more easily formed.

$$C_2B_nH_{2+n} + C_4H_9Li \longrightarrow [Li^+C_2B_nH_{1+n}^-] + C_4H_{10} \quad (3)$$

One significant aspect of the above work is the observation that both $C_2B_5H_7$ and the two $C_2B_4H_6$ isomers produce fragmentation to the $C_2B_4H_x^-$ and $C_2B_3H_x^-$ ion regions, respectively, but that $C_2B_3H_5$ does not appear to fragment to any great extent. This may imply that a C_2B_2 (or CB_3) carborane ion is not particularly stable and suggests that the C_2B_3 (or 5-atom carbon–boron framework) may be the smallest stable carborane framework potentially capable of reasonable existence.

Utilization of Negative-ion Mass Spectrometry for Identification and Percentage Composition of a Carborane Mixture.—Because the negative-ion spectra of different carborane systems exhibit, in some cases, grossly different voltage dependences, it appeared that this spectroscopic tool might have an application in the identification and determination of the percentage composition of a mixture containing carboranes. A $C_2B_4H_8$–$C_2B_5H_7$ (1 : 19) mixture was subjected to analysis. At 70 eV both spectra were superimposed as expected, whereas at 6·8 eV only the pattern of $C_2B_4H_8$ was visible. Selection of certain masses at random for percentage-composition determination gave an average of 4·9% $C_2B_4H_8$ which is remarkably close to the known

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[7] D. F. Munro, J. E. Ahnell, and W. S. Koski, *J. Phys. Chem.*, 1968, **72**, 2682; R. E. Enrione and R. Rosen, *Inorg. Chim. Acta*, 1967, 1169.

[8] R. R. Olsen and R. N. Grimes, *Inorg. Chem.*, 1971, **10**, 1103.

[9] R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, 1970, **92**, 5072.

[10] R. E. Kesting, K. F. Jackson, E. B. Klusmann, and F. J. Gerhart, *J. Appl. Polymer Sci.*, 1970, **14**, 2525.

[11] T. Onak and G. B. Dunks, *Inorg. Chem.*, 1966, **5**, 439.

composition (5·0%). Further, the sensitivity of negative-ion mass spectrometry is such that it is obvious that as low as 0·001% $C_2B_4H_8$ could be detected and identified, and an approximate percentage composition determined in a similar mixture of materials.

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