Negative-ion Mass Spectrum of 2,3-Dicarbahexaborane(8)

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Summary The negative-ion mass spectrum of 2,3-dicarbahexaborane(8) has been obtained and the major anions have been shown to correlate with photochemical and thermal reaction products.

There are many reports of the positive ion mass spectra of carboranes.[1] Mass spectrometry has been used mainly for the determination of molecular weights and formulae, and to distinguish between *nido*- and *closo*-carboranes.[1,2]

In other compounds, correlations have been made between positive ions formed in the mass spectrometer and stable cations and cationic intermediates found in solution. It is unlikely that such correlations for carboranes will be extensively developed, since stable cations or cationic intermediates in carborane chemistry are extremely rare.

In contrast, a wide variety of stable carborane anions have been characterized by ^{11}B n.m.r. spectroscopy and reports of anionic intermediates are found throughout carborane chemistry.[2,3]

We have examined the negative ion mass spectrum of 2,3-dicarbahexaborane(8) and correlated this with the known chemical properties of carboranes. To our knowledge there have been no previous reports of negative ion mass spectra of carboranes.

The lower mass fragments in the spectrum are less abundant than those in the parent ion region. It is difficult to tell very much about the relative intensities of specific negative ions from this spectrum because it is complicated by the natural abundance ratio of $^{11}B:{}^{10}B$ of *ca.* 80:20.

A portion of the monoisotopic ^{11}B negative ion mass spectra at 70 eV and 8 eV are shown in the Table. The base peak in the 70 eV spectrum is the $P - 1$ anion, $C_2B_4H_7^-$ and the two major fragment ions are at m/e 73 [($C_2B_4H_5^-$ (15%)] and 61 [$C_2B_3H_4^-$ (17%)]. The relative intensities of the ions in the 8 eV spectrum are quite different from the 70 eV data. In the 8 eV spectrum the base peak is at m/e 61 and both the m/e 73 and 75 ($C_2B_4H_8^-$) ions are greatly decreased.

The photochemical and thermal reaction products of $C_2B_4H_8$ are shown in equations (1) and (2) below.[2,4,5]

$$C_2H_4H_8 \xrightarrow{h\nu} 1,2\text{-}C_2B_4H_6 + 1,6\text{-}C_2B_4H_6 + 1,5\text{-}C_2B_3H_5 \quad (1)$$

$$C_2B_4H_8 \xrightarrow{\Delta} 2,4\text{-}C_2B_5H_7 + 1,6\text{-}C_2B_4H_6 + 1,5\text{-}C_2B_3H_5 \quad (2)$$

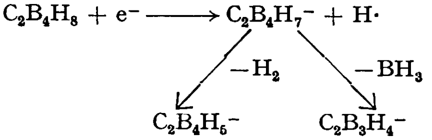
Both reactions show the conversion of the less stable *nido*-carborane, $C_2B_4H_8$ to the more stable *closo*-carboranes, $C_2B_4H_6$ and $C_2B_3H_5$. As shown in the Table, the $P - 1$ anions of these two *closo*-carboranes ($C_2B_4H_5^-$ and $C_2B_3H_4^-$) have the same formula as the two most intense peaks in the 70 eV spectrum of $C_2B_4H_8$. It has been shown in other negative ion mass spectral studies on *closo*-carboranes that these two anions ($C_2B_3H_4^-$ and $C_2B_4H_5^-$) are quite stable.[6] Thus, it seems reasonable that an analogous conversion to the more stable *P*-1 *closo*-carborane anions is occurring in the mass spectrometer.

Table. *Partial monoisotopic* ^{11}B *negative ion mass spectra of* $C_2B_4H_8$

		Relative abundance	
m/e	Formula	70 eV	8 eV
76[a]	$C_2B_4H_8^-$	2·1	
75	$C_2B_4H_7^-$	100	3·2
74	$C_2B_4H_6^-$	4·2	0·8
73	$C_2B_4H_5^-$	15·0	1·6
64[b]	$C_2B_3H_7^-$	0·3	
63	$C_2B_3H_6^-$	3	
62	$C_2B_3H_5^-$	3	2
61	$C_2B_3H_4^-$	17	100
60	$C_2B_3H_3^-$		8·1
59	$C_2B_3H_2^-$	7	24·7
58	$C_2B_3H^-$		1·4

[a] A $^{11}B:^{10}B$ ratio of 80:20 was used. [b] It is not possible to completely discard the other possible formulae for the *m/e* 64—58 ions which would contain 1 carbon and 4 boron atoms (*i.e.* *m/e* 64 = CB_4H_8 and *m/e* 58 = CB_4H_2). However, when the CB_4 formulae were assumed and the ^{10}B contributions in both the 70 and 8 eV polyisotopic spectra were subtracted, relatively large negative residues were obtained.

General correlations have been reported between photochemical reactions and positive ion mass spectrometry. In the photochemical and thermal reactions [equations (1) and (2)] presumably an electron is being excited to a high energy antibonding orbital. The analogous excited state of $C_2B_4H_7^-$, with the same total number of electrons, formed in an electron capture process as shown in equation (3) would be possible if H· is eliminated. The subsequent elimination of the two neutral molecules (BH_3 and H_2) would give rise to the two major anions found in the spectrum ($C_2B_3H_4^-$ and $C_2B_4H_5^-$ respectively).



$$\begin{tikzcd}[column sep=small] C_2B_4H_8 + e^- \arrow[r] & C_2B_4H_7^- + H\cdot \arrow[dl, "-H_2"'] \arrow[dr, "-BH_3"] & \\ C_2B_4H_5^- & & C_2B_3H_4^- \end{tikzcd} \qquad (3)$$

The formation of the known stable $C_2B_4H_7^-$ anion[7] from $C_2B_4H_8$ with sodium hydride [equation (4)] shows a further correlation of the negative ion mass spectra of $C_2B_4H_8$ with its solution chemistry.

$$C_2B_4H_8 + NaH \longrightarrow C_2B_4H_7^- \qquad (4)$$

Thus, it appears plausible to assume that should newly discovered negative ions be reasonably stable in the gas phase, then a search for them in the liquid phase may be warranted. In view of this, negative ions encountered in the mass spectrometer could provide valuable information as to what negative ions may be prepared for study in conventional 'bench top' chemistry.

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