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Bromo- and Chloro-4,5-dicarba-*nido*-hexaborane(8)

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The reaction of 4,5-dicarba-*nido*-hexaborane(8), $C_2B_4H_8$, with bromine or chlorine in the presence of aluminum halide produces $BrC_2B_4H_7$ or $ClC_2B_4H_7$, respectively. The ^{11}B nmr spectra indicate that substitution occurs at the basal boron atom which is adjacent to a carbon atom. There is no indication of the formation of other isomers. The ^1H nmr and infrared spectra are consistent with this structure.

Introduction

Procedures for the synthesis of 4,5-dicarba-*nido*-hexaborane(8)[1] have been developed.[2] It may be converted to *closo*-carboranes by thermal and photochemical methods,[2,3] and deuterium exchange with several different species has been studied.[4,5] Lipscomb and his coworkers[6,7] have determined the structure of $C_2B_4H_8$ and calculated the charge distribution. Their results indicate that the two carbon atoms at the 4,5 positions have a negative charge (-0.43) while the boron atoms at the 1 (apex), 2, 3, and 6 positions have charges $+0.33$, 0.25, 0.12, and 0.12 respectively. In contrast, similar calculations show that B_5H_9 is negatively charged at the 1 position and positively charged at the base.[8] Substitution reactions and deuterium exchange with DCl occur at the 1 position of B_5H_9 in the presence of aluminum halide.[8] Since the charge distribution in the $C_2B_4H_8$ molecule differs from B_5H_9, it was of interest to determine what substitution reactions would occur with conditions similar to those used for B_5H_9. In this paper we report the chlorination and bromination of $C_2B_4H_8$ in the presence of aluminum halides.

Experimental Section

All volatile components were manipulated by means of standard high-vacuum equipment. Except for those mentioned below, all materials were reagent grade, used without further purification.

4,5-Dicarba-*nido*-hexaborane(8) was synthesized from B_5H_9 and C_2H_2 and purified by gas chromatography.[9,10] **Bromine and carbon disulfide** were dried by treating with P_4O_{10} and redistilled in the high-vacuum system. **Boron trichloride and chlorine** were distilled to remove HCl and moisture. The Cl_2 was measured as a gas using a mercury manometer which was protected with silicone oil.

Infrared spectra were recorded on a Beckman IR-5 spectrometer. A Varian A-60 was used to obtain the ^1H nmr spectra. The ^{11}B nmr spectra were recorded on a Varian 4300 at 12.8 Mc and an HA-100 at 32.1 Mc. Chemical shifts were measured by substituting external standards. Mass spectra were obtained from West Coast Technical Service, San Gabriel, Calif.

$BrC_2B_4H_7$.—Aluminum bromide was produced in a reaction tube fitted with a ground joint and stopcock by treating 2 or 3 mg of aluminum with 0.996 mmol of Br_2 in 9.05 mmol of CS_2. Then $C_2B_4H_8$ (1.03 mmol) was condensed in at $-196°$ and the mixture was warmed slowly from -78 to $-10°$ with stirring. Fractional distillation of the mixture gave 0.377 mmol of $BrC_2B_4H_7$ which passed a $-30°$ trap, but stopped at $-47°$. The new compound was identified by bromine determination by the Carius method (calcd for $BrC_2B_4H_7$: 51.8; found: 51.7) and the mass spectrum cutoff (calcd: 156; found: 156). The melting point was determined by the Stock method: -68.8, $-68.9°$. The vapor pressures which are summarized in Table I conform to the equation $\log P = (-2233/T) + 8.300$. Infrared spectrum (gas at 5 mm; 10-cm cell): 2620 cm^{-1} vs (B–H str), 1480 vs, 1460 vs, 1350 m, 1086 s, 971 m, 950 m, 906 s, 765 m, 749 m, 719 s cm^{-1}. No C–H stretch (3000–3100 cm^{-1}) was observed at this pressure. When the aluminum bromide and carbon disulfide were omitted, the yield was substantially lower. However, no other isomer of $BrC_2B_4H_7$ was detected either from the infrared or nmr spectra.

Table I

Vapor Pressure of $BrC_2B_4H_7$

	Temp, °C					
	0.0	18.5	28.0	40.8	55.6	65.0
P_{obsd}, mm	1.34	4.39	7.69	15.48	32.1	50.1
P_{calcd}, mm	1.36	4.42	7.70	15.44	32.3	49.8

$ClC_2B_4H_7$.—A synthetic method similar to that employed by Gaines for the chlorination of B_5H_9 was used.[11] $AlCl_3$ (0.176 g), BCl_3 (4.0 mmol), and Cl_2 (1.09 mmol) were sealed in a reaction tube with 1.19 mmol of $C_2B_4H_8$. The mixture was warmed gradually from -125 to $-30°$ during a 24-hr period. Fractional distillation of the mixture produced 0.497 mmol of $ClC_2B_4H_7$ and 0.41 mmol of recovered $C_2B_4H_8$. When the aluminum chloride was omitted, the yield was much lower (about 10%), and when both BCl_3 and $AlCl_3$ were omitted, the yield was not only poor but the mixture often exploded. No other isomer could be detected. The analysis for chlorine and the mass spectrum cutoff agreed with expected values. *Anal.* Calcd for $ClC_2B_4H_7$: Cl, 32.3. Found: Cl, 32.5. Mass spectrum calcd: 112; found: 112. Melting point values are -73.9, $-73.2°$. The vapor pressures conform to the equation $\log P = (-2113/T) + 8.275$

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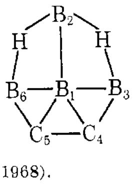
[1] The new numbering system



is used: *Inorg. Chem.*, **7**, 1945 (1968).

[2] T. Onak, R. P. Drake, and G. B. Dunks, *ibid.*, **3**, 1686 (1964).

[3] J. R. Spielman and J. E. Scott, Jr., *J. Am. Chem. Soc.*, **87**, 3512 (1965).

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

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[10] See ref 2. The authors are indebted to Dr. R. E. Williams of Space General Corp. for a generous gift of this compound.

[11] D. F. Gaines, *J. Am. Chem. Soc.*, **88**, 4528 (1966).

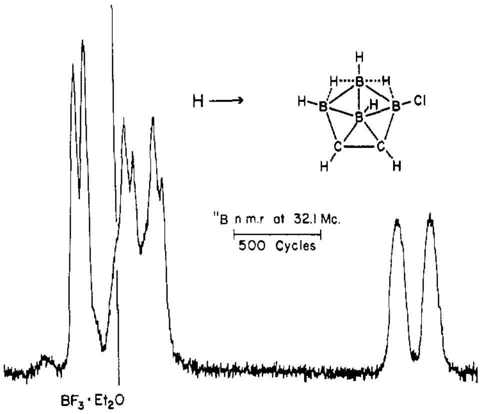

Figure 1.—The ^{11}B nmr spectrum of $ClC_2B_4H_7$.

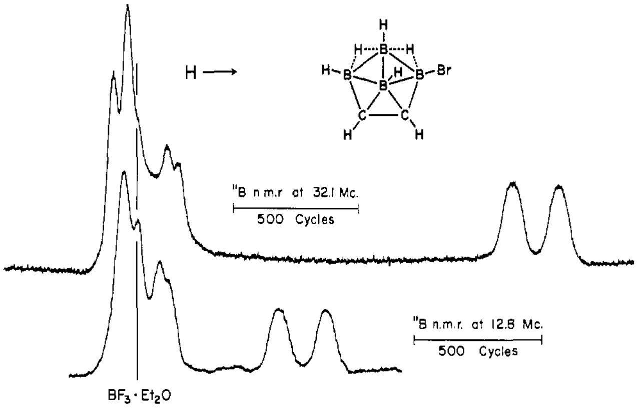

Figure 2.—The ^{11}B nmr spectra of $BrC_2B_4H_7$.

(see Table II). Infrared spectrum (gas at 13 mm; 10-cm cell): 2980 w (C–H str), 2590 vs (B–H str), 970 m, 953 m, 920 s, 770 s, 740 m, 730 m cm^{-1}. Chemically the chlorinated compound was very reactive with traces of moisture in the high-vacuum system, producing HCl and BCl_3.

TABLE II

VAPOR PRESSURE OF $ClC_2B_4H_7$

	Temp, °C								
	0.0	13.0	21.6	25.0	34.2	42.2	50.1	59.6	66.7
P_{obsd}, mm	3.3	7.7	12.8	15.4	25.5	38.0	55.4	83.9	113.1
P_{calcd}, mm	3.5	7.8	12.8	15.5	25.2	37.6	54.9	84.3	114.0

Results and Discussion

The ^{11}B nmr spectra are shown in Figures 1 and 2 and summarized in Tables III and IV along with the ^{1}H nmr spectra. The spectra are consistent with substitution at the 3-boron atom in the base adjacent to a carbon atom. In the ^{11}B nmr spectrum of the chloro compound the doublet at lowest field is the substituted boron which is split by coupling to the bridge hydrogen. The remaining assignments are based on comparison with $C_2B_4H_8$.[12] The four peaks at 4–5 ppm are probably due to the 6-boron atom overlapping the broader 2-boron. The signal from the 6-boron is split by the terminal hydrogen (J = 158 cps) and the adjacent bridge hydrogen (J = 47 cps). Only the terminal B–H splitting (J = 160 cps) is apparent for the 2-boron. The doublet at high field is the 1-boron (apex). The area ratios for peaks from low field to high are 1.03:2.00:0.97 compared to the expected 1:2:1.

TABLE III

NMR PARAMETERS FOR $ClC_2B_4H_7$

Position	^{11}B $\delta(BF_3(C_2H_5)_2O$ = 0), ppm	^{1}H τ(TMS = 10), ppm	J_{B-H}, cps
1	52.1	11.1	184
2	4	7.0	160
3	−6.5	. . .	56 (bridge)
4, 5	. . .	4.25	. . .
6	4.8	7.0	158 (term.) 47 (bridge)
H-bridge	. . .	11	. . .

TABLE IV

NMR PARAMETERS FOR $BrC_2B_4H_7$

Position	^{11}B $\delta(BF_3(C_2H_5)_2O$ = 0), ppm	^{1}H τ(TMS = 10), ppm	J_{B-H}, cps
1	50.4	11.1	185
2	2	7.0	165
3	−1.5	. . .	57 (bridge)
4, 5	. . .	4.1	. . .
6	2.2	7.0	165 (term.) 40 (bridge)
H-bridge	. . .	≃11	. . .

It is not clear from the ^{11}B spectrum of $BrC_2B_4H_7$ at 32.1 Mc whether the low-field component is made up of a singlet or doublet overlapping the 2,3,6-boron doublets. However, comparing the 12.8-Mc spectrum with the 32.1-Mc spectrum, it may be seen that while the peaks at lowest field change position, they remain the same frequency apart. Therefore they must be the 3-boron atom bonded to the bromine with the splitting due to the bridge hydrogen. The chemical shift measured at the center of this doublet is the same in the two spectra within experimental error. The rest of the low-field component can be interpreted as the overlapping signals from the other basal boron atoms, and the high-field doublet is from the apex position.

The proton nmr spectra are consistent with the proposed structures except that there is no splitting of the C–H signal from the difference in chemical environment. There is too much overlap in the bridge-hydrogen region to find the separate signals expected for the two different kinds of bridge hydrogens. However the signal is much broader than in $C_2B_4H_8$.

The results of this work show that the only products of the reaction of bromine and chlorine with $C_2B_4H_8$ are 3-$BrC_2B_4H_7$ and 3-$ClC_2B_4H_7$, respectively. Either substitution does not occur at other positions or if it does the products are unstable. Similar reactions in B_5H_9 occur at the apex position which is sterically unhindered and carries the greatest electron density. Although the steric environment of the apex boron atom of $C_2B_4H_8$ is like that of B_5H_9, substitution occurs at the basal boron which has a higher electron density than the apex. The carborane *o*-$B_{10}H_{10}C_2H_2$ is different structurally from these compounds, but it has been shown that similar bromination reactions occur at the

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9,12 positions.[13,14] These results all indicate that the course of these reactions is determined by the charge distribution of the molecule.

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Thermodynamic Properties for the Dissociation of Bisulfate Ion and the Partial Molal Heat Capacities of Bisulfuric Acid and Sodium Bisulfate over an Extended Temperature Range[1,2]

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Heat of solution measurements of sodium sulfate in water and dilute aqueous hydrochloric acid solutions were made at several temperatures between 0 and 100° to obtain the thermodynamic properties of the aqueous bisulfate ion. From the temperature dependence of these heats the standard partial molal heat capacities for bisulfuric acid ($H \cdot HSO_4$) and sodium bisulfate were determined. Values of -4142 ± 69 cal mol^{-1} and -22.90 ± 0.20 cal mol^{-1} deg^{-1} were obtained for $\Delta H°$ and $\Delta S°$, respectively, at 25° for the dissociation of the aqueous bisulfate ion. New values of the dissociation constant, K^0, of the bisulfate ion were evaluated from 0 to 150° from the calorimetric data. Previous values of K^0 obtained from equilibrium measurements over this temperature range were analyzed by the third-law method and shown to be in satisfactory agreement with the thermal measurements.

Introduction

The integral heat method of obtaining partial molal heat capacities of pure substances has been described in some preceding papers of this series.[4-7] As used previously, the standard heats of solution of some salt are determined at convenient temperature intervals over a range of temperatures. The temperature dependence of the standard heat of solution can then be calculated as can, ultimately, the partial molal heat capacity of the ions which are formed on dissolution. In this communication we describe the extension of this method to obtain accurate thermal data on a species, the bisulfate ion, which cannot be formed in the pure state, but only in equilibrium amounts and in the presence of other ions. In principle, measurements on $HSO_4^-(aq)$ can be obtained either from dissolving sulfuric acid in water or from dissolving a soluble sulfate salt in dilute solutions of a strong acid. The heat obtained is then due to the sum of the heat of solution and the heat of the association or dissociation of HSO_4^-. A number of considerations led to the choice of allowing sodium sulfate to react with dilute hydrochloric acid solutions, not the least of which was the smaller heat of solution of sodium sulfate compared to sulfuric acid or one of its hydrates. Consequently more of the observed heat is due to the bisulfate ion and not to the solution process.

One hundred and sixty-eight separate heats of solution of solid sodium sulfate have been made in water and dilute solutions of hydrochloric acid at various ionic strengths between 4.34 and 95.00°. From these data and the accepted value of the dissociation constant of $HSO_4^-(aq)$ at 25° it was possible to determine the thermodynamic properties for the dissociation process over an extended interval of temperature. From the temperature dependence of $\Delta H°$ of dissociation and the previously reported[8] heat capacities of $Na_2SO_4(aq)$ and $H_2SO_4(aq)$, the standard partial molal heat capacities of $NaHSO_4(aq)$ and $H \cdot HSO_4(aq)$ have been obtained. Finally, it has been possible to reexamine the previously obtained thermodynamic functions for the dissociation of $HSO_4^-(aq)$ from extensive equilibrium measurements[9-11] and check their consistency with the thermal data.

Experimental Section

Apparatus.—The submarine-type heat of solution calorimeter (CS-2) which was used to make these measurements has been previously described.[7] The calorie was taken as 4.1840 abs J.

Materials.—The sodium sulfate used to make these calorimetric measurements was prepared from Baker Analyzed reagent grade sodium sulfate in the anhydrous form. The salt was dissolved in

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[1] This communication constitutes paper XII of a series of communications from these laboratories on the thermodynamic properties of high-temperature aqueous solutions.

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