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Studies of Boranes. XI. The Preparation and Properties of Hexaborane-12, B_6H_{12}[1]

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The reaction of tetramethylammonium triborohydride-8 with polyphosphoric acid *in vacuo* results in a 40% yield of tetraborane-10, small amounts of the other common boron hydrides, and a 4% yield of a new hexaborane-12, B_6H_{12}. The probable structure of this compound has been deduced from n.m.r. studies. Hexaborane-12 reacts nearly quantitatively with an excess of water to form tetraborane-10, and with dimethyl ether to form pentaborane-9.

Introduction

Knowledge of boron hydrides containing between six and nine boron atoms is very limited. Apart from the well established hexaborane-10 and nonaborane-15,[2] no other boron hydrides have been isolated in a pure form, although there have been mass spectrometric indications of B_6,[3] B_7,[3] and B_8[4,5] hydrides and a report, later withdrawn, of a nonseparable mixture of a hexaborane-12 and pentaborane-9 by Stock and Siecke.[6,7]

Reaction of tetramethylammonium triborohydride with polyphosphoric acid, under conditions similar to those used to prepare diborane from sodium borohydride and polyphosphoric acid,[8] has been found to yield tetraborane-10 in good yield as expected as a result of earlier studies.[9] The new compound, hexaborane-12, was found to be present in the higher boron hydride fractions along with nonaborane-15 and decaborane-14, but there was no evidence for the presence of hexaborane-10.

Hexaborane-12 reacts nearly quantitatively with an excess of water at 0° according to the equation

$$B_6H_{12} + 6H_2O \longrightarrow B_4H_{10} + 2B(OH)_3 + 4H_2 \qquad (1)$$

This reaction is similar to the quantitative conversion of pentaborane-11 to tetraborane-10 with water.[10] Hexaborane-12 is cleaved by dimethyl ether to pentaborane-9 and diborane.

Experimental

The high vacuum techniques used in this investigation have been described elsewhere.[7,11] The fractionation portion of the system was maintained grease-free by using mercury float valves and O-ring stopcocks (Delmar Scientific Laboratories, Inc.). In part, separation of hydride mixtures was accomplished with the aid of a low temperature fractional distillation column.[12] Tetramethylammonium triborohydride was prepared by the method of Gaines, Schaeffer, and Tebbe.[13]

Preparation and Characterization of Hexaborane-12.—In a typical preparation, a 3-l. three-necked flask was charged with about 500 ml. of polyphosphoric acid (Victor Chemical Co.) and fitted with a vacuum-tight ground rod stirrer and an addition flask for introducing solids. The reaction flask was warmed to about 40° and 10.0 g. (87.3 mmoles) of tetramethylammonium triborohydride was added to the stirred acid over a 7-hr. period and the mixture stirred for an additional 17 hr. The volatile reaction products were removed by continuous evacuation as they formed and were trapped by a series of four U-tubes cooled with liquid nitrogen. The condensable materials were subsequently separated by conventional fractional condensation techniques. The material that passed a trap at $-45°$ and condensed at $-80°$ was subjected to low-temperature fractional distillation.[12] The hexaborane-12 distilled from the column between -75 and $-62°$. Subsequent purification, when required, was accomplished by several rapid distillations into a U-tube cooled to $-63°$; the impurities (and some hexaborane-12) passed this trap. The compounds recovered included: tetraborane-10, 27.3 mmoles or 43% of the boron used; a mixture of both pentaboranes, 7.18 mmoles or 14%; hexaborane-12, about 2 mmoles or 4%; and traces of diborane and higher boron hydrides. Thus about 60% of the boron present in the triborohydride salt was recovered as volatile products.

Vapor pressures were not reliable because of rather rapid decomposition of hexaborane-12 in the liquid phase and are reported only as a guide for future investigations: $-23°$, 4.2 mm.; $-17°$, 7.0 mm.; 0°, 17.0 mm.; 25.5°, 67.0 mm. The extrapolated boiling point is between 80 and 90° and the melting point is $-83°$ (Stock ring method).[14]

The elemental analysis of hexaborane-12 was obtained by thermal decomposition of a weighed sample to hydrogen and boron in a sealed quartz tube. The hydrogen evolved was measured with an automatic Toepler pump, and boron was determined by dissolving the residue in nitric acid and titrating the D-mannitol complex using the identical pH method. The molecular weight was determined by rapid measurement of the vapor density.

Anal. Calcd. for B_6H_{12}: B, 84.3; H, 15.7; mol. wt., 77.0. Found: B, 84.2; H, 15.7; mol. wt., 76.6 (vapor density).

The mass spectrum of hexaborane-12 was obtained using a Consolidated Electrodynamics Corp. Model 21-620A spectrometer. The spectrum of the parent group is given in Table I. Decomposition during measurement makes determination of peaks at lower masses unreliable.

The ^{11}B and ^1H n.m.r. spectra of a pure sample of hexaborane-12 were obtained using a Varian Model 4300B spectrometer operating at 19.3 and 60 Mc./sec., respectively (Fig. 1, Table II). The sample was maintained at or below $-10°$ using standard Varian accessories.

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[1] (a) For X see D. F. Gaines and R. Schaeffer, *J. Phys. Chem.*, in press; (b) for a preliminary report see D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc.*, 267 (1963).

[2] A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962), and references therein.

[3] S. G. Gibbins and I. Shapiro, *J. Am. Chem. Soc.*, **82**, 2968 (1960).

[4] B. Keilin and I. Shapiro, *ibid.*, **76**, 3864 (1954).

[5] For a review see I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, "Borax to Boranes," Advances in Chemistry, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, p. 139 ff.

[6] A. Stock and W. Siecke, *Ber.*, **57**, 566 (1924).

[7] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[8] R. O. Buttlar, Doctoral Dissertation, Indiana University, 1962, p. 20.

[9] R. Schaeffer and F. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

[10] J. L. Boone and A. B. Burg, *ibid.*, **80**, 1519 (1958).

[11] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[12] J. E. Dobson and R. Schaeffer, to be published.

[13] D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

[14] Reference 11, p. 95.

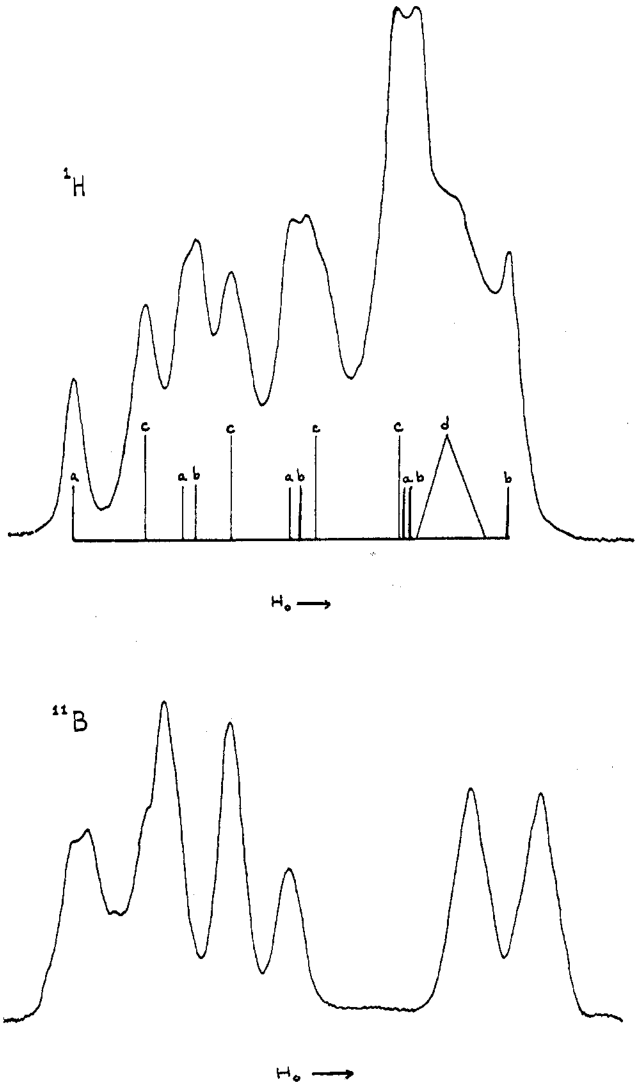


Fig. 1.—The ^1H and ^{11}B n.m.r. spectra of hexaborane-12.

TABLE I

MASS SPECTRUM OF THE PARENT GROUP OF HEXABORANE-12

m/e	I (rel.)	m/e	I (rel.)
65	12.7	72	95.1
66	22.0	73	64.7
67	25.8	74	60.4
68	28.4	75	41.8
69	42.7	76	31.0
70	70.2	77	6.6
71	100.0	78	1.1

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF HEXABORANE-12

		BH		BH_2	
^{11}B	δ^a (±0.5) p.p.m.	−23.5	+22.7	−9.9	
	J (±3) c.p.s.	160	158	129	
^1H	δ^b (±0.1) p.p.m.	−4.70	−1.73	−3.70	+0.83 (BHB)
	J (±3) c.p.s.	160	160	128	

[a] With reference to $BF_3 \cdot O(C_2H_5)_2$. [b] With reference to $Si(CH_3)_4$.

The gas phase infrared spectrum of hexaborane-12 was obtained using a 5-cm. cell, at 17 mm. pressure, with a Perkin-Elmer Infracord Model 137. Principal absorptions occurred at 3.86 (vs), 3.98 (s), 5.17 (m), 6.67 (s), 7.45 (m), 8.56 (m), 9.46 (s), 9.75 (sh), 10.6 (m), 11.2 (m), and 13.4 (w) μ.

The volatility and stability of the hexaborane-12 obtained in this study suggest that it is not the compound reported by Stock[15] as B_6H_{12} (?), which was more volatile than pentaborane-9 and could not be separated from it. Hexaborane-12 is much less volatile than pentaborane-9 and is easily separated from it. Gibbins and Shapiro,[3] on the basis of mass spectral studies of a sample contaminated with hexaborane-10 as well as B_7 and B_8 hydrides, reported the existence of a very unstable hexaborane thought to contain either 12 or 14 hydrogens. Since their evidence for the compound was both meager and inconclusive, no comparison with the present B_6H_{12} can be made.

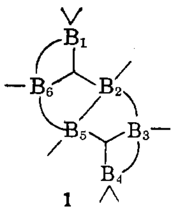
Reaction of Hexaborane-12 with Water.—In a typical reaction, 0.097 mmole of hexaborane-12 was shaken with about 1 ml. of water for 60 sec. at 0°. The reaction was then quenched by cooling with liquid nitrogen and the reaction vessel attached to the vacuum line. There was 0.382 mmole of hydrogen produced. Tetraborane-10, 0.090 mmole, was separated from water by fractionation through a trap at $-80°$ and identified by its vapor pressure of 10.8 mm. at $-63°$ (lit.[16] 10.8) and its mass spectrum.[5] The hydrogen and tetraborane-10 recovered amounted to yields of 98.5 and 92.8%, respectively.

Reaction of Hexaborane-12 with Dimethyl Ether.—Hexaborane-12, 0.068 mmole, was mixed with 0.38 mmole of dimethyl ether and allowed to stand for 3 hr. at room temperature in the gas phase. During this time a small amount of noncondensables formed. Fractionation yielded 0.050 mmole of pentaborane-9 (identified by its mass spectrum) and about 0.03 mmole of diborane.

Discussion

The ^{11}B n.m.r. spectrum of hexaborane-12 (Fig. 1, Table II) indicates that there are equal numbers of three different kinds of boron in the molecule: two doublets arising from two types of BH and a triplet due to BH_2. The downfield doublet, which partially overlaps with the triplet, shows some unresolved fine structure that probably arises from bridge hydrogen coupling. (The spectrum of hexaborane-10 consists of two simple doublets in a ratio of 1:5.)[17] The ^1H n.m.r. spectrum is consistent with the ^{11}B spectrum. The peaks labeled a and b correspond to the low- and high-field doublets in the ^{11}B spectrum, respectively, and those labeled c correspond to the triplet. The bridge hydrogen region, d, corresponds approximately to four hydrogens as required.

In view of the n.m.r. data, the most probable structure for hexaborane-12 appears to be the 4212 formulation (1) proposed by Lipscomb,[18] in which the 1,4 borons give rise to the triplet in the ^{11}B spectrum, the 2,5 borons produce the upfield doublet, and the 3,6 borons give the low-field doublet. The 4212 formulation can give rise to another structure (2).[18] This structure



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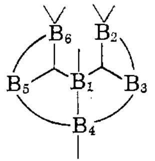
[15] Reference 7, p. 77.

[16] A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923).

[17] R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 333 (1959).

[18] W. N. Lipscomb, *J. Phys. Chem.*, **65**, 1064 (1961), and references therein.

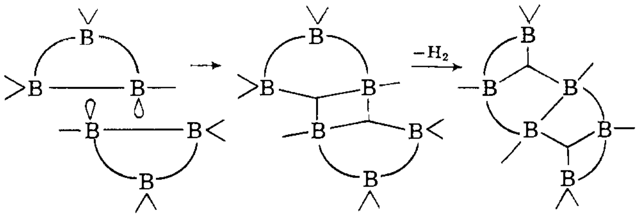
may be expected to be somewhat less stable because of probable interference between hydrogens on borons 2 and 6. This structure would make it necessary to postulate accidental overlap of the n.m.r. signals from borons 1 and 4 to account for the upfield doublet. Furthermore, the high-field doublet occurs at too low a field by some 15 p.p.m. or more for a typical apical boron such as is found in pentaborane-9 or hexaborane-10.[17]



2

It has been suggested that decomposition of triborohydride-8 salts by anhydrous protonic acids may occur by attack of a proton on triborohydride-8 ion to form a mixture of hydrogen, diborane, and triborane-7 (perhaps through triborane-9 as an intermediate).[9] Tetraborane-10 may then form by reaction of diborane with triborane-7.[9,19,20]

The formation of hexaborane-12 with the unusual open structure could be envisioned as occurring through combination of two triborane-7 units to yield hexaborane-14, which then loses hydrogen and rearranges to hexaborane-12. Alternatively, triborane-7 may react with tetraborane-10 or another higher hydride present in relatively substantial concentration. Although there is no experimental evidence to support such a simple process, it seems highly likely that triborane-7 is involved since the product is not obtained from other sources.



It is interesting to note that this is the first example of a boron hydride in which the structure is based not upon the most compact icosahedral fragment possible, but rather upon a more open form. Since isomeric forms of lower boranes are unknown, such a structure could be produced either directly as a result of a favorable mechanism or indirectly by rearrangement to the more thermodynamically stable form.

Using bond energies of Gunn and Green,[21] the heat of atomization of hexaborane-12 (formulated as a 4212 structure in terms of the semitopological theory of Lipscomb)[18] is calculated as 1411.7 kcal./mole and the standard heat of formation is then +14.7 kcal./mole.

The degradation of hexaborane-12 to pentaborane-9 in the presence of dimethyl ether can be thought of as occurring through base-catalyzed elimination of a borane group to give a B_5H_9 fragment (perhaps solvated) which rearranges to the stable pentaborane-9 framework.

Further chemical studies of hexaborane-12 are in progress.

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(19) R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

(20) R. E. Enrione and R. Schaeffer, *ibid.*, **18**, 103 (1961).

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

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Iodine Cations and Oxycations. I. Solutions of Iodic Acid in Sulfuric Acid

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Solutions of iodic acid in sulfuric acid have been studied by means of cryoscopic and conductometric measurements. No evidence was obtained for the formation of the iodyl cation IO_2^+ or the iodic acidium ion $H_2IO_3^+$, and it appears that iodic acid is converted to solvated and polymerized forms of iodyl hydrogen sulfate, $IO_2 \cdot HSO_4$.

Introduction

Of the four common halogens iodine is the most electropositive and thus is the most likely to form compounds in which it is present as a cation or as a cationic radical. A few classes of compounds are known in which iodine is apparently present in the form of a cation and in many other compounds the presence of cations or oxycations containing iodine has been suggested.[1] The participation of iodine cations or oxycations as transient intermediates in many reactions of iodine compounds in aqueous solution has also been postulated.[2] In very few cases, however, has definite information been obtained on the exact nature of these ions. Arotsky and Symons have recently summarized the evidence for the iodine cation I^+.[3]

Sulfuric acid has proved to be a useful solvent for the stabilization of many cations which are too electrophilic to exist in more basic solvents. The even

(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p. 1239.

(2) K. J. Morgan, *Quart. Rev.* (London), **8**, 123 (1954).

(3) J. Arotsky and M. C. R. Symons, *ibid.*, **14**, 282 (1962).