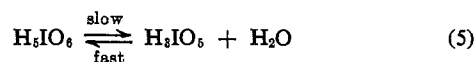


BrO_3^- .¹¹ and NO_3^- .¹¹ It has been suggested^{11,15,16} that the oxygen exchange of these oxy anions proceeds *via* a bimolecular nucleophilic attack (of water or chloride ions) on the protonated species: H_2ClO_3^+ , H_2BrO_3^+ , and H_2NO_3^+ .

In oxy anions of larger central atom the rate of oxygen exchange is more likely controlled by the rate of elimination of water molecules from the oxy anions. Thus, the relatively fast oxygen exchange of iodate, which is assumed to exist in water mainly as H_2IO_4^- , has been suggested¹¹ to proceed *via* the rapid equilibrium, $\text{H}_2\text{IO}_4^- \rightleftharpoons \text{IO}_3^- + \text{H}_2\text{O}$. The high rate of oxygen exchange observed in periodic acid and the fact that the reaction is not catalyzed by chloride ions (an effective catalyst in the exchange of bromate and nitrate) indicate that this exchange also proceeds *via* a monomolecular dissociation reaction



This is similar to the mechanism for the dehydration of H_4IO_6^- given by Kustin and Lieberman,⁵ who suggested that the dissociation of the water molecule is assisted by hydrogen bonding to the solvent water.

It is plausible to assume that the oxygen exchange of telluric and xenic acids also proceeds *via* a dissociative mechanism. The relatively fast oxygen exchange of these compounds, *via* a dissociative rate-determining step, may be understood by considering the nature of the central atom–oxygen bond. Tellurium, iodine, and

(16) T. C. Hoering, R. C. Butler, and H. O. McDonald, *J. Am. Chem. Soc.*, **78**, 4829 (1956).

xenon occupy the fifth row of the periodic table and are the largest nonmetallic elements that form oxy compounds. Owing to their large radii, these elements may form compounds of high coordination number, and it is in these compounds that the oxygen exchange was found to be fastest. Interatomic-distance data for the I–O bond in oxygen–iodine compounds have been quoted and discussed by Pauling.¹⁷ The I–O bond in the octahedral (IO_6) configuration was shown to have a small amount of double bond character. It is, however, much less than in the I–O bond of the tetrahedral iodine compounds or in X–O bonds of the other nonmetallic oxy compounds with low coordination number. The high lability of the I–O bond in periodate may thus be associated with the relatively weak double bond character of the octahedrally coordinated iodine. Similar arguments hold for tellurate and xenate. On these grounds it may be expected that oxygen exchange of perxenic acid [$\text{Xe}(\text{OH})_6$] with water will be even faster than for xenic acid.

Generally, the rate of exchange in a series of isoelectronic oxy compounds decreases as the charge of the central atom increases.¹ It is interesting to note that the contrary is observed on comparing the rates of oxygen exchange of periodic acid and its isoelectronic neighbor in this series, $\text{Te}(\text{OH})_6$; apparently the rule does not apply to oxy compounds of large central atoms in their high coordination state where the nature of the X–O bond is altered to a great extent.

(17) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, Chapter 7.

A New Boron Hydride, B_8H_{18} ¹

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A new unstable hydride of boron has been prepared by treatment of tetramethylammonium triborohydride-8 with polyphosphoric acid. A number of physical and chemical properties are reported for the compound. Two possible structures are suggested with some preference for a model based on linkage of two B_4H_9 units through a B–B bond.

The reaction to triborohydride ion with polyphosphoric acid has previously been shown to yield a number of boron hydrides; in particular, it constitutes a useful preparative method for tetraborane-10 and hexaborane-12.² This reaction has now been shown to yield octaborane-18 as a trace product.

Unlike the recently discovered octaborane-12,^{3,4} the existence of which had been indicated by mass

(1) Studies of Boranes. XVII; for paper XVI of this series, see R. Schaeffer, Q. Johnson, and G. Smith, *Inorg. Chem.*, **4**, 917 (1965).

(2) D. F. Gaines and R. Schaeffer, *ibid.*, **3**, 438 (1964).

(3) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964).

(4) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

spectrographic studies,^{5,6} there are no previous reports of an octaborane having as high a hydrogen content as octaborane-18. An octaborane thought to be octaborane-14 and its n.m.r. spectrum were reported to be among the products of the discharge reaction of diborane.⁷ It has recently been suggested that the substance isolated in 1933 by Burg and Schlesinger was probably B_8H_{15} rather than an octaborane as originally suggested.^{8,9}

Experimental

Preparation and Isolation of Octaborane-18. The reaction of tetramethylammonium triborohydride with polyphosphoric acid was carried out in exactly the

(5) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **76**, 3864 (1954).

(6) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, "Advances in Chemistry Series, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, p. 127.

(7) J. F. Ditter, H. B. Landesman, and R. E. Williams, National Engineering Science Co., Pasadena, Calif., Technical Report AF04 (611)5156, 1961.

(8) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).

(9) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

manner previously described for the preparation of hexaborane-12.² The reaction flask was maintained under vacuum by continuous pumping to remove hydrogen and volatile products. Condensable products were trapped in a series of "U" traps cooled with liquid nitrogen. After reaction had apparently ceased, all products were distilled into a trap held at -65° . After an extended period of continuous pumping (about 5 hr.), this trap retained some hexaborane-12, octaborane-18, and nonaborane-15; separation was accomplished using a low-temperature fractionation column from which octaborane-18 slowly distilled when the temperature at the point of exit was about -62° .¹⁰ At least one further fractionation was required to obtain pure product. The impure product condenses as a glassy solid at the level of the liquid nitrogen surface surrounding the trapping tube; the pure product condenses as a white solid. Since decomposition of the compound is rapid at temperatures at which vapor pressures are too low to measure by conventional methods, the melting behavior and ^{11}B n.m.r. spectrum were used as criteria of purity. Owing to the minute yield of octaborane-18 obtained, no preparations were undertaken using less than about 10 g. of tetramethylammonium triborohydride; the yield of octaborane-18 from this size preparation is about 30 mg.

Analysis. Samples of pure octaborane-18 were transferred to a small weighing tube, weighed as rapidly as possible, and transferred into a pre-ignited and weighed quartz pyrolysis apparatus. The latter consisted of a small U-trap leading to a spiral connected by a ground taper to the input valve of the Toepler system. After the sample had been transferred to the small U-trap, the quartz decomposition tube was sealed from the weighing tube, the spiral heated with a torch to a dull red glow, and the sample allowed to slowly distil into the spiral with continuous Toeplering to remove the hydrogen as formed. After complete vaporization of the sample, the entire apparatus was thoroughly flamed to decompose any residues which had not reached the hot spiral. Hydrogen was measured volumetrically and the boron determined by weighing as the element (except that in one analysis the residue was dissolved in nitric acid and the boric acid titrated using the identical pH method as the *d*-mannitol complex). Three satisfactory analyses (judged by a mass balance of 98% or greater) were carried out.

Anal. Calcd. for B_8H_{18} : H, 17.33; B, 82.67. Found: H, 17.32, 17.37, 17.70; B, 82.68, 82.63, 82.30.

The mass balance in the analysis eliminates the possibility of the material containing elements other than boron and hydrogen. The last value given above was obtained by titration and is particularly crucial in this regard.

Molecular Weight. Since octaborane-18 has a very low vapor pressure at room temperature and is stable for only very short periods at higher temperatures, the standard techniques for measuring vapor density could not be used. Two attempts to measure the vapor pressure lowering in tetraborane-10 as solvent were unsuccessful, apparently owing to decomposition of B_8H_{18} . Hence, the flash evaporation method de-

veloped by Burg and Kratzer was used with only minor variation.⁹ Photographic negatives of the mercury surfaces were enlarged to prints about three times actual size. Measurements were made from the wet print pressed flat between glass plates. From the first of two determinations it became apparent that an equilibrium pressure was not attained owing to very rapid decomposition at the temperature necessary to ensure complete vaporization of a reasonable size sample. However, it was found that the pressure rise was a linear function of time. The data were fitted to a linear regression equation by the method of least squares; the zero-time intercept from this equation was assumed to be the pressure before decomposition had occurred and was used to calculate the molecular weight. Molecular weights from two determinations were 106 and 104, respectively; the calculated molecular weight of B_8H_{18} is 104.7. Blurred manometer levels caused by vibration from the stirrer motor cause the result of the first determination to be regarded as least reliable. Evaluation of the 95% confidence interval of the intercept from the second determination places limits of 96 to 113 upon molecular weight.

Reaction with Carbon Monoxide. A 0.13-mmole sample of octaborane-18 was condensed into a 1-l. bulb, carbon monoxide added to a pressure of about 1 atm., and the system then warmed to room temperature. The liquid octaborane appeared to slowly evaporate. After about 1 hr. no liquid phase or visible residue remained. After 4 hr. the contents of the bulb were slowly passed through a series of liquid nitrogen cooled traps. Fractionation of the condensable products yielded 0.05 mmole of BH_3CO , 0.05 mmole of B_4H_{10} , 0.08 mmole of $\text{B}_4\text{H}_8\text{CO}$, traces of unidentified material of lower volatility, and 0.04 mmole of unreacted B_8H_{18} .

Reaction with Hydrogen. A 0.36-mmole sample of octaborane-18 was allowed to decompose in the presence of hydrogen under the same conditions as employed for carbon monoxide reaction. In contrast to that experiment a considerable amount of yellow residual liquid remained after 1 hr. at room temperature. After 4 hr. the products were fractionated and found to contain 0.10 mmole of B_2H_6 , 0.39 mmole of B_4H_{10} , and 0.04 mmole of B_8H_{12} ; no undecomposed B_8H_{18} was found.

^{11}B N.m.r. Spectrum. The ^{11}B n.m.r. spectrum of octaborane-18 was obtained using a Varian DP60 nuclear magnetic resonance spectrometer operating at 19.3 Mc./sec. A neat sample of octaborane-18 was used and was maintained with standard Varian accessories at approximately -20° to avoid decomposition during the measurement.

The ^{11}B n.m.r. spectrum consisted of a well-isolated high-field doublet ($\delta = 40.9$ p.p.m., $J = 148$ c.p.s.) and a low-field group which appeared to be the result of an overlapping doublet ($\delta = 3.7$, $J = 122$ c.p.s.) and triplet ($\delta = 7.1$ p.p.m., $J = 124$ c.p.s.). The integrated areas of the low-field and high-field groups were equal over a range of transmitter power of about 30 db.

Discussion

The thermal instability of this compound, although not as extreme as that of octaborane-12, prevents easy

(10) J. Dobson and R. Schaeffer, design to be published.

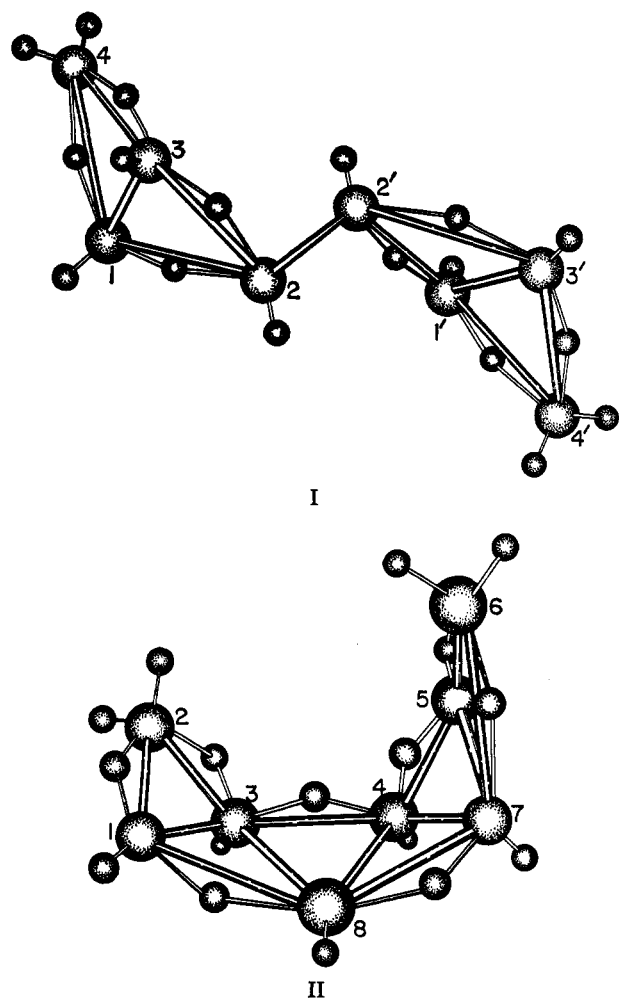


Figure 1. Suggested structures for B_8H_{18} : I, bitetraboronyl model; II, "beltline" model.

manipulation and consequently hampers characterization. In light of this it is important to present the arguments based on the experimental data for the formula B_8H_{18} . These are (1) volatility suggests either a B_7 , B_8 , or B_9 hydride; (2) the ^{11}B n.m.r. spectrum requires a molecule containing an even number of boron atoms; (3) the molecular weight limits at 95% confidence of 96 to 113, in conjunction with reproducible analyses showing a hydrogen:boron ratio between 2.24 and 2.29, also exclude a B_7 or B_9 hydride (analyses require a molecular weight for B_7H_{15} of 92.7, for B_9H_{21} 118.1; in fact, these lie outside the 99% confidence limits of the molecular weights, which are 94 to 117); (4) of the possible octaboranes both octaborane-16 and octaborane-20 are incompatible with the analytical hydrogen:boron ratio whereas octaborane-18 is in good agreement.

The basic question to be answered about octaborane-18 concerns its structure. The high hydrogen content virtually eliminates a molecule based upon a compact icosahedral fragment. In light of the experimental data presently available, at least two reasonable structures can be proposed, with no clear-cut argument strongly against either one.

A bitetraboronyl molecule (I), Figure 1, which conceptually could be formed by condensation of two tetraborane-10 molecules at the B-2 is possible. A belt-

line icosahedral fragment (II), Figure 1, conceptually formed by removal of the 5 and 8 borons from the decaborane-14 structure is also possible.

Structure I is favored by the ^{11}B n.m.r. spectrum, which indicates the presence of an equivalent pair of borons having two terminal hydrogens, a second pair of borons having one terminal hydrogen, and a set of four borons having one terminal hydrogen. Further support for this structure is the almost exact agreement between the chemical shifts of the corresponding types of boron in I and tetraborane-10, the only difference being the slight downfield shift attributed to the two borons linked by the isolated boron-boron single bond. A precedent for this structure is also available in the known hydride decaborane-16, although the inherent stability of the B_5H_9 framework may render it a special case. Formation of substantial B_8H_{12} by decomposition in the presence of hydrogen could result from loss of the two BH_3 groups opposite the boron-boron bond followed by rearrangement.

Structure II is also in agreement with the ^{11}B n.m.r. data in respect to the number of borons having one and two terminal hydrogens but differs in that it contains three pairs of equivalent borons having a single terminal hydrogen. It is necessary to assume accidental overlap of doublets arising from the 1, 5 and 3, 7 borons to fit the observed spectrum. It may be somewhat simpler to explain on the basis of this structure the formation of hexaborane-12 in the decomposition of octaborane-18 in the presence of hydrogen, since the proposed structure of hexaborane-12 may be obtained directly from II by the removal of BH_3 groups from the 2- and 6- positions.

It will be noted that the two proposed structures are not as different as they may first appear, but differ only in the placement of two bridge hydrogens. Thus, subject to the ease and symmetry of their cleavage, it would not seem unlikely to obtain the observed decomposition products from either structure, although the formation of B_8H_{12} from I requires more rearrangement than from II. Further structural studies are underway in the laboratory of Professor W. N. Lipscomb.

The reactions with hydrogen and with carbon monoxide shed little light upon the structure. The reaction with carbon monoxide produced B_4H_8CO in high yield, 0.08 vs. 0.09 mmole of B_8H_{18} consumed, as well as a reasonable yield of B_4H_{10} (0.05 mmole) as might be expected if I decomposed into B_4H_8 and B_4H_{10} fragments. The products of decomposition in the presence of hydrogen would then be expected to be almost entirely B_4H_{10} since B_4H_8CO , which presumably decomposes through B_4H_8 , can be converted to B_4H_{10} in fairly good yield by decomposition in a large excess of hydrogen. That this was not the case, and also the much higher production of polymeric yellow solids in the latter reaction, may indicate that carbon monoxide does not play a passive role in the decomposition and does not serve only as a trapping agent for B_4H_8 .

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