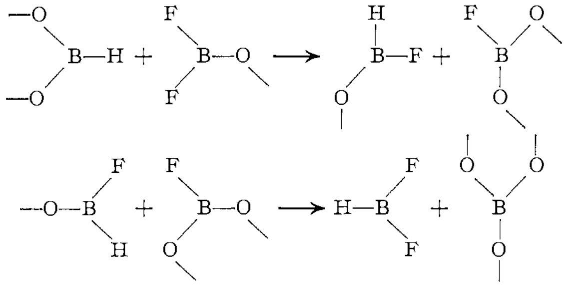
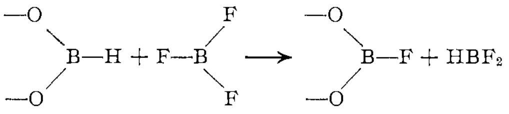
(2) Further rapid fluorine transfer from BF_3 or $-O-B<^{F}_{F}$ and $-O-B<^{O}_{F}$ groups to $^{-O}_{-O}>B-H$ or $-O-B<^{H}_{F}$ groups as exemplified by the following



In this mechanism boron atoms in BF_3 become coordinated by oxygen atoms in B_2O_3 and boron atoms in $H_3B_3O_3$ become coordinated by fluorine atoms originally in BF_3. For every B–F or B–O bond broken a new bond is formed. Thermochemical data indicate the reaction

$$2BF_3(g) + H_3B_3O_3(g) = 3HBF_2(g) + B_2O_3(s)$$

is about 1.4 kcal/mole, exothermic.[3,13] The slow decomposition of $H_3B_3O_3$ to $B_2H_6 + B_2O_3$ implies a mechanism involving transfer of H atoms from one boron to another. However, in the faster BF_3–$H_3B_3O_3$ reaction a fluorine atom is apparently transferred more rapidly than a hydrogen atom. The absence of $H^{11}BF_2$ in the products of the reaction of $H_3{}^{10}B_3O_3 + {}^{n}BF_3$ shows that the mechanism is not a simple exchange of the type



as was suggested earlier.[3]

Infrared spectra in Figures 4 and 5 suggest that the mechanism for the reaction of BCl_3 or BBr_3 with boroxine is substantially the same as that for the BF_3 reaction. However, the effect of hydrogen–halogen exchange and/or disproportionation of HBX_2 subsequent to this initial reaction is much more evident in the reaction with BCl_3 or BBr_3. The kinetic data in Table I show that the reaction rates increase in the order $BF_3 < BCl_3 < BBr_3$ and that the catalytic effect of B_2O_3 is general for all of the reactions.

Although one is tempted to correlate the reaction rate of the $H_3B_3O_3$–BX_3 reaction with the acidity of the boron atom in BX_3, it should be noted that in postulating a donor–acceptor intermediate we should consider the acceptor strength of boron atoms in both of the reacting molecules. The increase in reaction rates from the fluoride to the bromide may simply reflect the relative decrease in B–X bond strength.

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Practical Synthesis for Decahydrodecaborates

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High-yield synthesis of the decahydrodecaborate(2−) anion was achieved from the thermolysis of tetraethylammonium tetrahydroborate(1−), $(C_2H_5)_4NBH_4$, and tetraethylammonium octahydrotriborate(1−), $(C_2H_5)_4NB_3H_8$, at atmospheric pressure and 185°. The thermolysis of tetramethylammonium tetrahydroborate(1−), $(CH_3)_4NBH_4$, under similar conditions gives only trimethylamine borane, $(CH_3)_3NBH_3$, and methane, while a near equimolar mixture of $[(CH_3)_4N]_2B_{10}H_{10}$ and $[(CH_3)_4N]_2B_{12}H_{12}$ was the major product obtained from pyrolysis of tetramethylammonium octahydrotriborate(1−), $(CH_3)_4NB_3H_8$. Although $B_{10}H_{10}{}^{2-}$ was a major product, complex mixtures of products containing the $BH_4{}^-$, $B_{10}H_{10}{}^{2-}$, $B_{11}H_{14}{}^-$, and $B_{12}H_{12}{}^{2-}$ anions were obtained from the 185° pyrolysis of potassium and cesium octahydrotriborates(1−), KB_3H_8 and CsB_3H_8, respectively. No evidence was obtained for $B_9H_9{}^{2-}$ or $B_{11}H_{11}{}^{2-}$ when the pyrolysis temperatures were maintained at 185°.

Introduction

The absence of an economical method for synthesis of salts of decahydrodecaborate(2−) from diborane or hydroborates has been conspicuous.[1] Preparation of these salts can be accomplished using decaborane as a starting material[2] with nearly quantitative conversion of decaborane to $B_{10}H_{10}{}^{2-}$, but formation of $B_{10}H_{10}{}^{2-}$ from lower boron hydride derivatives has been observed only in small quantities while other species (B_9, B_{11}, B_{12}) were major products.[3] The dodecahydrododecaborate(2−) ion ($B_{12}H_{12}{}^{2-}$), on the other hand, is easily derived from nonboron–boron-bonded parents.[4,5]

The requirement for decaborane as a starting material has been a limiting factor in consideration of deca-

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hydrodecaborate(2−) rather than dodecahydrododecaborate(2−) for any practical applications. Decaborane is difficult to synthesize in the laboratory and the economics of decaborane production are presently unattractive.

Discussion

The controlled thermolysis of either tetraethylammonium octahydrotriborate(1−) or tetrahydroborate(1−) gives tetraethylammonium decahydrodecaborate(2−) in excellent yield. Whereas pyrolysis of these salts at 200–250° yielded more complex mixtures of products containing only small amounts of the $B_{10}H_{10}^{2-}$ salt,[3] this reaction product is predominant at 185°. The hydrogen loss at 185° is quite slow in comparison to that at the higher temperatures. The data obtained are consistent with the reactions in eq 1 and 2.

$$10(C_2H_5)_4NBH_4 \xrightarrow{185^\circ} [(C_2H_5)_4N]_2B_{10}H_{10} + 8(C_2H_5)_3N + 11H_2 + 8C_2H_6 \tag{1}$$

$$10(C_2H_5)_4NB_3H_8 \xrightarrow{185^\circ} 3[(C_2H_5)_4N]_2B_{10}H_{10} + 4(C_2H_5)_3N + 23H_2 + 4C_2H_6 \tag{2}$$

Under similar reaction conditions, tetramethylammonium octahydrotriborate(1−) undergoes thermolysis to yield tetramethylammonium decahydrodecaborate(2−), tetramethylammonium dodecahydrododecaborate(2−), and trimethylamine borane. The data are in agreement with the stoichiometry represented by eq 3. Tetramethylammonium hydroborate

$$9(CH_3)_4NB_3H_8 \xrightarrow{185^\circ} [(CH_3)_4N]_2B_{10}H_{10} + [(CH_3)_4N]_2B_{12}H_{12} + 5(CH_3)_3NBH_3 + 5CH_4 + 15H_2 \tag{3}$$

gave only small amounts of polyhedral hydroborates with trimethylamine borane a major product.

$$(CH_3)_4NBH_4 \xrightarrow{185^\circ} CH_4 + (CH_3)_3NBH_3 \tag{4}$$

The potassium and cesium salts of octahydrotriborate(1−) also gave relatively simple product mixtures at 185°. In contrast to the small amounts of $B_{10}H_{10}^{2-}$ reported from higher temperature pyrolysis,[3] this is a major product of slow pyrolysis. The hydroborates are coproducts, and the only materials evidenced, other than $K_2B_{10}H_{10}$ and $Cs_2B_{10}H_{10}$, were $CsB_{11}H_{14}$, $KB_{11}H_{14}$, and $K_2B_{12}H_{12}$.

Complete separation of the products from the 185° pyrolysis of CsB_3H_8 was not effected. However, $B_{11}H_{14}^-$ was precipitated as the water-insoluble tetramethylammonium salt[6] and only the $B_{10}H_{10}^{2-}$ and BH_4^- remained in solution. Although the decahydrodecaborate(2−) salt was the major product, significant quantities of tetradecahydroundecaborate(1−) were always found. Since essentially all of the cesium was present as $CsBH_4$, $Cs_2B_{10}H_{10}$, and $CsB_{11}H_{14}$, the slow pyrolysis is best represented by the equations for the two competing reactions

$$4CsB_3H_8 \xrightarrow{185^\circ} Cs_2B_{10}H_{10} + 2CsBH_4 + 7H_2 \tag{5}$$

$$5CsB_3H_8 \xrightarrow{185^\circ} CsB_{11}H_{14} + 4CsBH_4 + 5H_2 \tag{6}$$

The KB_3H_8 pyrolysis yielded less decahydrodecaborate(2−) than the other octahydrotriborate(1−) salts studied. The amount of $K_2B_{12}H_{12}$ formed was nearly equal to that of $K_2B_{10}H_{10}$ in all of the experiments. $KB_{11}H_{14}$ accounted for only a minor amount of the potassium and no other materials were present in detectable quantities except for KBH_4. Thus, the two major pyrolysis reactions are represented by eq 7 and 8.

$$4KB_3H_8 \xrightarrow{185^\circ} K_2B_{10}H_{10} + 2KBH_4 + 7H_2 \tag{7}$$

$$5KB_3H_8 \xrightarrow{185^\circ} K_2B_{12}H_{12} + 3KBH_4 + 8H_2 \tag{8}$$

It is obvious that the tetraethylammonium octahydrotriborate(1−) is unique in these 185° thermolysis studies, since decahydrodecaborate(2−) is formed almost exclusively. Since the metal tetrahydroborates undergo no decomposition at these temperatures and are end products of the pyrolyses, it is reasonable to conclude that formation of polyhedral hydroborates from the quaternary salts depends upon the initial cleavage of an alkyl and hydrogen with formation of the alkane. But further reaction of the trialkylamine borane alone would result in formation of trialkylammonium salts. For example, the thermolysis of trialkylamine borane in the presence of diborane under pressure yields trialkylammonium dodecahydrodecaborates.[5] Thus, it is probable that the formation of the decahydrodecaborate(2−) is due to the interaction of the amine borane with the quaternary salt, *e.g.*

$$(C_2H_5)_4NBH_4 + 2(C_2H_5)_3NBH_3 \longrightarrow (C_2H_5)_4NB_3H_8 + 2(C_2H_5)_3N + H_2 \tag{9}$$

The fact that the methyl system proceeds by a different course can be explained on the basis that the trimethylamine is more volatile than the ethyl derivative and does not remain in the reaction medium. On the other hand, the formation of methane and trimethylamine borane from tetramethylammonium hydroborate(1−) is very rapid at 185°. A slower cleavage of the ethyl group and hydrogen may permit the interaction suggested in eq 9.

Experimental Section

Materials.—Alkylammonium octahydrotriborates and CsB_3H_8 were synthetized by conventional methods[3,7] and purified by recrystallization; $(C_2H_5)_4NB_3H_8$ and $(CH_3)_4NB_3H_8$ were recrystallized from hot methanol and CsB_3H_8 was recrystallized from a warm water solution. KB_3H_8 was prepared by dissolving an equimolar amount each of analytical grade KI (Fisher) and $(CH_3)_4NB_3H_8$ in warm acetonitrile. Formation of insoluble $(CH_3)_4NI$ was immediately observed. After the mixture was stirred for several hours, the solution was filtered and the filtrate was evaporated. The crude KB_3H_8 was twice recrystallized from a CH_3CN–CH_2Cl_2 solvent pair. $(C_2H_5)_4NBH_4$ and $(CH_3)_4NBH_4$ were used as received from Ventron Corp.

Authentic samples of $[(C_2H_5)_4N]_2B_{10}H_{10}$, $(C_2H_5)_4NB_{11}H_{14}$, and $[(C_2H_5)_4N]_2B_{12}H_{12}$ were prepared from $[NH_4]_2B_{10}H_{10}$,[8] $NaB_{11}H_{14}\cdot 2.5C_4H_8O_2$,[6] and $Na_2B_{12}H_{12}\cdot C_4H_{10}O_2$,[5] respectively, by metathesis in water.

Analytical.—Infrared spectra were obtained on a Perkin-Elmer

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Model 21 spectrophotometer. Mass Spectra were obtained on a Consolidated Engineering Co. Type 21-103B mass spectrometer. X-Ray diffraction patterns were obtained on a Norelco X-ray diffraction instrument. Elemental analyses of boron, carbon-hydrogen, and nitrogen were obtained by the micro-Schöniger, micro-Pregl, and micro-Dumas combustion methods, respectively.

Thermolysis Results. Tetrahydroborates.—(a) Tetraethylammonium tetrahydroborate(1−), 5.96 g (41 mmoles), was placed in a nitrogen-filled 100-cc steel cylinder provided with a needle valve. The cylinder was appropriately attached to a vacuum line and evacuated. The reactor was heated by an air oven and the air blanket was held at 185° for 16 hr. Volatile products were passed through a −80° trap to a Toepler pump and into a calibrated volume. The total amount of noncondensable material was 80 mmoles (theoretical for eq 1 is 78 mmoles). The composition of the gas was determined by mass spectral analysis as 56% H_2 and 43% C_2H_6; theory for eq 1 is 58 and 42%, respectively. The −80° trap contained only triethylamine identified by its vapor tension (65 mm pressure at 25°) and infrared analysis. The residual solid was added to 20 ml of warm CH_3CN, cooled to near 0°, and immediately filtered to remove the trace of $B_{12}H_{12}^{2-}$; 0.08 g of the white crystalline product was isolated while the $B_{10}H_{10}^{2-}$ soluble fraction recovered by volatilization of the acetonitrile weighed 1.36 g.

The infrared and X-ray diffraction patterns of the insoluble salt were identical with those of the authentic $[(C_2H_5)_4N]_2B_{12}H_{12}$ sample, while those of the soluble fraction were identical with those of $[(C_2H_5)_4N]_2B_{10}H_{10}$.

Anal. Calcd for $[(C_2H_5)_4N]_2B_{12}H_{12}$: B, 32.24; C, 47.76; H, 13.03; N, 6.96. Found: B, 31.9; C, 47.7; H, 13.3; N, 7.0. Calcd for $[(C_2H_5)_4N]_2B_{10}H_{10}$: B, 28.54; C, 50.75; H, 13.32; N, 7.39. Found: B, 28.5; C, 51.1; H, 13.3; N, 7.4.

The yield of $B_{10}H_{10}^{2-}$ based on boron charged was 94+%.

(b) Tetramethylammonium tetrahydroborate(1−), 3.35 g (28.2 mmoles), was similarly heated at 185°. Although the gas evolution was essentially complete in less than 1 hr, the reactor was heated for 16 hr to assure complete reaction. The evolved reaction gas, 97 mole % CH_4 by mass spectral analysis, was measured at 36.3 mmoles. The material collected in the −80° trap was recovered, 2.44 g, and subsequently identified, by infrared, as $(CH_3)_3NBH_3$. The residual solids recovered from the reactor, 0.23 g, were a mixture of higher polyhedral boranes, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^{-}$, and $B_{12}H_{12}^{2-}$. To a water solution of this residue 0.5 g of $(C_2H_5)_3NHCl$ was added. A white crystalline precipitate was formed, and this was filtered and dried. The material was identified by its X-ray and infrared patterns as $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

Octahydrotriborates.—(a) Crystalline $(C_2H_5)_4NB_3H_8$, 1.24 g (7.27 mmoles), was heated at 185° for 16 hr. The apparatus and techniques were the same as those used for the hydroborates. The evolved gases were passed through a −80° trap and two −196° traps connected in series. The total amount of −196° noncondensable gas was 16.8 mmoles (theoretical for eq 2 is 16.7 mmoles). The material collected in the −196° trap was identified by mass spectral analysis as pure ethane and measured to be 2.88 mmoles (theoretical for eq 2 is 2.91 mmoles). The −80° trap contained $(C_2H_5)_3N$ exclusively, identified by vapor tension measurement and mass spectrographs.

The residual solid, 0.823 g (theoretical 0.825 g if all $B_{10}H_{10}^{2-}$), was added to 20 ml of methanol and heated to reflux. The crystalline insoluble fraction obtained on cooling was filtered out and dried, 0.09 g (10.9%). The X-ray and infrared patterns were identical with those of the authentic sample of $[(C_2H_5)_4N]_2B_{12}H_{12}$. The soluble fraction was recovered by volatilization of the methanol. This was then added to 10 ml of water at 50° and cooled, and a second crystalline insoluble material was recovered. The X-ray and infrared patterns of the water-insoluble fraction, 0.031 g (3.7 wt %), were identical with those of $(C_2H_5)_4NB_{11}H_{14}$. The water-soluble fraction, 0.65 g (79% recovery based on eq 2), was pure $[(C_2H_5)_4N]_2B_{10}H_{10}$ identified by X-ray, infrared, and elemental analyses.

Anal. Calcd for $[(C_2H_5)_4N]_2B_{12}H_{12}$: B, 32.34; C, 47.76; H, 13.01; N, 6.96. Found: B, 32.4; C, 46.2; H, 13.4; N, 6.85. Calcd for $(C_2H_5)_4NB_{11}H_{14}$: B, 45.16; C, 36.5; H, 13.02; N, 5.32. Found: B, 44.5; C, 35.7; H, 13.2; N, 5.7. Calcd for $[(C_2H_5)_4N]_2B_{10}H_{10}$: B, 28.54; C, 50.75; H, 13.32; N, 7.39. Found: B, 28.6; C, 49.5; H, 13.3; N, 7.6.

(b) Pure $(CH_3)_4NB_3H_8$, 5.36 g (46.7 mmoles), was similarly heated at 185° for 16 hr. The gas evolving from the reaction did not contain any $(CH_3)_3N$ but was composed only of H_2 and CH_4, 68 and 32 mole %, respectively, as established by mass spectral analysis of a gas sample. The white solid which sublimed into a −80° cold trap was identified as pure $(CH_3)_3NBH_3$ weighing 1.72 g (theoretical for eq 3 is 1.89 g). The residual solid was extracted with 20 ml of water to separate the insoluble $B_{12}H_{12}^{2-}$ fraction; 1.41 g of $[(CH_3)_4N]_2B_{12}H_{12}$ was recovered and evaporation of water gave a soluble fraction weighing 1.35 g. The X-ray and infrared patterns of the insoluble and soluble fractions were identical with those of authentic samples of $[(CH_3)_4N]_2B_{12}H_{12}$ and $[(CH_3)_4N]_2B_{10}H_{10}$, respectively.

Anal. Calcd for $[(CH_3)_4N]_2B_{12}H_{12}$: B, 44.8; C, 33.1; H, 12.5; N, 9.6. Found: B, 44.1; C, 32.7; H, 12.6; N, 9.7. Calcd for $[(CH_3)_4N]_2B_{10}H_{10}$: B, 40.6; C, 36.0; H, 12.8; N, 10.6. Found: B, 39.2; C, 35.9; H, 12.6; N, 10.8.

As an additional check on the completeness of separation of $B_{12}H_{12}^{2-}$ from the $B_{10}H_{10}^{2-}$ salt, the addition of $(C_2H_5)_3NHCl$ was made to a water solution of the $[(CH_3)_4H]_2B_{10}H_{10}$ soluble fraction separated above. No trace of the insoluble $[(C_2H_5)_3NH]_2B_{12}H_{12}$ was observed.

(c) After heating a sample of pure CsB_3H_8 (5.02 g, 29 mmoles) for 16 hr, 4.95 g of residual solid was recovered from the reactor. The presence of principally BH_4^- and $B_{10}H_{10}^{2-}$ was clearly indicated by comparing the X-ray diffraction pattern and infrared spectrum to those of authentic $CsBH_4$ and $Cs_2B_{10}H_{10}$ samples. Weak additional lines in the X-ray indicated the presence of another substance. By addition of $(CH_3)_4NCl$ to a water solution of the pyrolysis residue, a crystalline precipitate was obtained. After filtering and drying, 1.046 g of product was recovered having an infrared spectrum and X-ray pattern characteristic of $(CH_3)_4NB_{11}H_{14}$. Separation of the two remaining components, $CsBH_4$ and $Cs_2B_{10}H_{10}$, by extraction with water was not successful. Evaporation of the filtrate gave a white solid which exhibited no X-ray or infrared evidence of polyhedral borates other than $B_{10}H_{10}^{2-}$.

(d) Pyrolysis of a pure sample of KB_3H_8, 8.9 g (112.0 mmoles), at 185° produced 182 mmoles (theoretical for eq 7 is 196 mmoles, theoretical for eq 8 is 179 mmoles) of molecular hydrogen. The pyrolysis residue was dissolved in 50 ml of water, and 15.4 g (112 mmoles) of $(C_2H_5)_3NHCl$ was added. The reaction mixture was cooled to 0°, and the mixture was stirred for 30 min. The insoluble crystalline product was recovered by filtration and dried. Characterization of this material by infrared and X-ray showed a mixture consisting mainly of $[(C_2H_5)_3NH]_2B_{12}H_{12}$ contaminated with $(C_2H_5)_3NHB_{11}H_{14}$. Separation of these was achieved by extraction with 50 ml of methanol giving 2.9 g (8.35 mmoles) of the $B_{12}H_{12}^{2-}$ derivative while recovery of the methanol-soluble fraction gave 0.47 g (2.0 mmoles) of $(C_2H_5)_3NHB_{11}H_{14}$.

Addition of a 40% $(C_2H_5)_4NOH$–water solution to the water-soluble fraction obtained above did not yield an immediate precipitate. The solution was concentrated slightly and cooled to 0°. Upon standing overnight, 2.95 g (7.8 mmoles) of crystalline $[(C_2H_5)_4N]_2B_{10}H_{10}$ was recovered.

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