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Electrochemical Oxidation and Protonation of Octahydrotriborate Anion[1]

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In acetonitrile and dimethylformamide (DMF), $B_3H_8^-$ undergoes a one-electron oxidation at a platinum or gold anode to give $B_3H_7{\cdot}NCCH_3$ and $B_3H_7{\cdot}DMF$, respectively. Protonation of $B_3H_8^-$ in acetonitrile likewise yields $B_3H_7{\cdot}NCCH_3$, but acidification of a solution of $B_3H_8^-$ in dimethylformamide results in breakdown of the triangular boron array and yields $(CH_3)_3N{\cdot}BH_3$. Electrochemical oxidation of $B_3H_8^-$ in an aqueous potassium nitrate medium leads to complete destruction of the triborate species.

There have been relatively few investigations of the electrochemical oxidation of boron hydride anions. Gardiner and Collat[2] examined the polarographic and coulometric behavior of BH_4^- at a mercury anode in alkaline aqueous media, concluding that tetrahydroborate undergoes an eight-electron oxidation and that trihydrohydroxyborate, a product of the hydrolysis of BH_4^-, is oxidized in a three-electron process to yield molecular hydrogen. Oxidation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ at platinum electrodes in acetonitrile containing tetraethylammonium perchlorate was found by Middaugh and co-workers[3,4] to yield the corresponding radical anions, $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$, which subsequently dimerize to $B_{20}H_{19}^{3-}$ and $B_{24}H_{23}^{3-}$, respectively; in turn, the dimeric anions are oxidized to $B_{20}H_{18}^{2-}$ and $B_{24}H_{22}^{2-}$. In a study of the electrochemistry of $B_{10}H_{14}^{2-}$ in acetonitrile, Chambers, Norman, Bickell, and Cadle[5] observed that this species is oxidized to $B_{10}H_{14}$ and that $B_{10}H_{14}^{2-}$ and $B_{10}H_{14}$ interact during an electrolysis to produce $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$.

In the present research, we explored the oxidation of $B_3H_8^-$ at platinum and gold anodes in acetonitrile, dimethylformamide, and water. In contrast to the reactivity of species formed upon oxidation of the large-cage boron hydride anions in earlier work,[3-5] the product of the one-electron oxidation of $B_3H_8^-$ is stabilized in both acetonitrile and dimethylformamide through formation of an adduct with a single molecule of solvent, although the adduct formed in dimethylformamide can be oxidized further. Electrolysis of $B_3H_8^-$ in an aqueous medium results in conversion of the starting material to borates. To complement the electrochemical studies, observations concerning the protonation of $B_3H_8^-$ in acetonitrile and dimethylformamide are reported.

Experimental Section

Materials. Standard high-vacuum and Schlenk techniques described elsewhere[6] were used to handle the air- and moisture-sensitive materials. Tetramethylammonium, tetraethylammonium, and tetrapropylammonium octahydrotriborates ($R_4N^+B_3H_8^-$) were prepared by reaction of sodium borohydride with boron trifluoride etherate[7] and precipitation with the appropriate cation. These compounds were purified by recrystallization from hot methanol, and their purity was checked by ^{11}B NMR spectra recorded at 70.6 MHz on a PRFT Varian 220-MHz spectrometer and reported vs. $BF_3{\cdot}O(C_2H_5)_2$. Mass spectra were obtained on a Varian CH-7 instrument. Tetraborane(10) was taken from a stock sample of known purity.

Tetraethylammonium perchlorate (Eastman Organic Chemicals) was recrystallized from water and methyl ethyl ketone and was then dried under vacuum at 50 °C. Reagent grade acetonitrile (Mallinckrodt Chemical Co.) was dried over calcium hydride and then distilled from phosphorus pentoxide in vacuo. Dimethylformamide (Fisher Spectranalyzed material) was dried over Linde 4A molecular sieves and degassed with prepurified nitrogen followed by evacuation. Matheson prepurified nitrogen was dried over Aquasorb. Hydrogen chloride, obtained from Matheson, was dried by passage through a trap at −78 °C. Nitrosyl hexafluorophosphate ($NOPF_6$) was purchased from ROC-RIC and was manipulated in a glovebag.

Chronopotentiometry. All chronopotentiometric experiments were performed at ambient temperature (27 ± 3 °C) with a three-electrode cell of conventional design.[8] Chronopotentiograms were obtained with the aid of an X-Y recorder, and transition times were measured by a technique described previously.[9]

For studies in acetonitrile, solutions were prepared by condensation of the anhydrous solvent onto weighed portions of $(CH_3)_4NB_3H_8$ and tetraethylammonium perchlorate in Schlenk-adapted volumetric glassware. Transfer of a solution into the cell, as well as all subsequent operations, was done under a nitrogen atmosphere saturated with acetonitrile vapor. Gold or platinum wire anodes were covered with Parafilm in such a way as to expose a carefully measured cylindrical area near the end of each electrode. After a series of 12–18 chronopotentiograms was recorded, the anode was cleaned by being dipped into aqua regia, washed with distilled water and acetone, and allowed to dry in air. A silver–silver chloride reference electrode in acetonitrile saturated with lithium chloride[10] was utilized; its potential was found to be −0.190 V vs. SCE (aqueous saturated calomel electrode).

Sample solutions for chronopotentiometry in dimethylformamide consisted of $(C_2H_5)_4NB_3H_8$ dissolved in solvent containing tetraethylammonium perchlorate. Because the solutions are much less air sensitive than those prepared in acetonitrile, they can be handled in ordinary volumetric glassware; however, once in the chronopotentiometric cell, the solution was deaerated and blanketed with argon. A Beckman platinum-disk anode was employed together with a cadmium amalgam reference electrode in dimethylformamide saturated with sodium chloride and cadmium chloride,[11] the potential of the latter being −0.750 V vs. SCE. To investigate the oxidation of molecular hydrogen, a solution of the supporting electrolyte in dimethylformamide was saturated with hydrogen gas prior to the chronopotentiometric measurements.

Chronopotentiometric measurements in water were carried out with $(CH_3)_4NB_3H_8$ dissolved in an aqueous 1 M potassium nitrate medium. To fabricate the working electrode, a gold wire was coated with Tygon paint (U.S. Stoneware Co., Akron, Ohio) except for an exposed cylindrical section of known area. Prepurified nitrogen was used to deaerate the solutions, and potential measurements were made with respect to an aqueous saturated calomel electrode.

Controlled-Potential Coulometry. A potentiostat/galvanostat (Model 173, Princeton Applied Research Corp.) was utilized for exhaustive, controlled-potential oxidations of $B_3H_8^-$. Current–time curves were monitored continuously with the aid of a Moseley 680 strip-chart recorder, and coulometric n values were evaluated graphically.

For electrolyses of $(CH_3)_4NB_3H_8$ in acetonitrile, a modified H-cell with greaseless fittings was used (Figure 1); it was kept at 0 °C in a shallow ice bath cut from the bottom of a plastic bleach bottle. Addition of 1.4 g of tetraethylammonium perchlorate to the large graduated vessel (D), followed by condensation of 60 ml of acetonitrile, gave a 0.1 M solution. Half of this solution was then transferred to the small graduated vessel (D′) with the aid of one of the evacuable transfer tubes (B). Introduction of a weighed amount (typically about 0.2 g) of $(CH_3)_4NB_3H_8$ into the anode compartment and connection of the parts of the cell together as shown in Figure 1, but with a plug in the place usually occupied by the reference electrode, allowed evacuation of the cell to eliminate any trace of air and moisture. Filling the cell with an inert atmosphere permitted replacement of the plug by the reference electrode. Then the two graduated vessels were inverted to fill the cell with the acetonitrile solution of tetraethylammonium perchlorate, making the cell ready for an electrolysis. When the electrolysis was finished, the solutions in the two compartments of the cell were poured back into the graduated vessels by tilting the cell, and the solution from the anode compartment was analyzed.

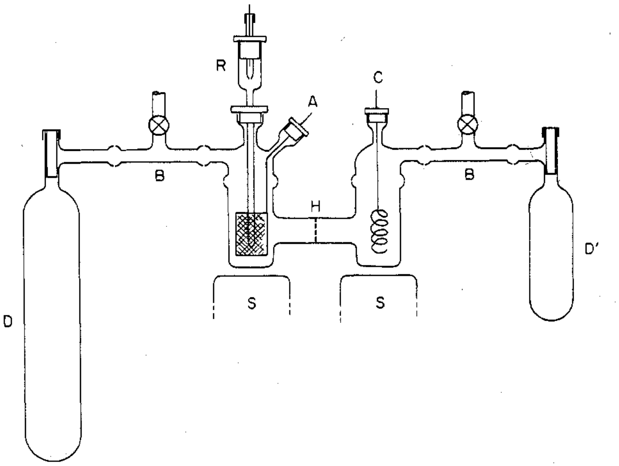

Figure 1. Cell for controlled-potential electrolyses of air-sensitive materials: A, platinum gauze anode admitted to the cell through an Ace wire adapter; B, evacuable connecting tube, composed of a Teflon stopcock attached to a tube with two Fisher-Porter 9-mm solvent seals; C, platinum wire cathode; D and D', graduated storage vessels with Teflon stopcocks and capacities of 80 and 40 ml, respectively; H, fine-porosity sintered-glass disk fused perpendicularly between two 25-mm Fisher-Porter solvent-seal joints that constitute the anode and cathode compartments of the cell; R, reference electrode, admitted to the cell by an Ace tubing adapter; S, magnetic stirrer.

Controlled-potential electrolyses in dimethylformamide were done essentially the same way as those in acetonitrile, except that dry degassed solvent was poured onto the tetraethylammonium perchlorate in the graduated vessel, rather than being condensed in, and that $(C_2H_5)_4NB_3H_8$ was used instead of $(CH_3)_4NB_3H_8$.

Electrolyses of $(CH_3)_4NB_3H_8$ in aqueous potassium nitrate media were performed at room temperature in a nitrogen-flushed H-cell of conventional design.

Reaction of $(CH_3)_4NB_3H_8$ with Hydrogen Chloride in Acetonitrile. One millimole (0.1145 g) of $(CH_3)_4NB_3H_8$ was placed in a small flask equipped with a magnetic stirring bar and attached to a vacuum line. Approximately 10 ml of acetonitrile was condensed into the flask, as was 1.00 mmol of HCl gas. Melting the acetonitrile allowed a reaction to take place which was accompanied by vigorous bubbling. Evolved gas was collected in a Toepler system, determined to be 1.04 mmol, and identified as only H_2 by mass spectral analysis. A ^{11}B NMR spectrum of the remaining solution showed only the two peaks of $B_3H_7{\cdot}NCCH_3$ at +7.7 and +34.3 ppm in a 2:1 ratio.

Removal of most of the acetonitrile solvent gave a white precipitate of $(CH_3)_4NCl$ that was filtered off. When the remainder of the solvent was removed, another white solid appeared whose mass spectrum showed acetonitrile, B_3H_7, $BH_3{\cdot}NCCH_3$, and $B_3H_5{\cdot}NCCH_3$ as major peaks. This white solid decomposed slowly above 0 °C and reacted vigorously with water to give borates.

Reaction of $(CH_3)_4NB_3H_8$ with $NOPF_6$ in Acetonitrile. Nitrosyl hexafluorophosphate (0.608 g, 3.48 mmol) was Schlenk-transferred into a flask containing a small stirring bar. To this flask was added under nitrogen 0.390 g (3.42 mmol) of $(CH_3)_4NB_3H_8$; the two solids were mixed and the flask was attached to a vacuum line. Approximately 10 ml of acetonitrile was condensed onto this mixture of white solids at −196 °C and then warmed to melt the solvent. The solution turned bright green, with brown splotches wherever a local excess of $NOPF_6$ occurred. A brown gas was seen above the reaction mixture but disappeared rapidly. The solution was stirred at 0 °C for about 1 h until the evolution of gas ceased. Hydrogen (1.3 mmol, 76.5% of the theoretical amount expected from reaction 3 given below) was recovered and identified by means of mass spectrometry. A ^{11}B NMR spectrum of the remaining solution exhibited only peaks attributable to $B_3H_7{\cdot}NCCH_3$ and $B_3H_8^-$.

Reaction of $(C_3H_7)_4NB_3H_8$ with Hydrogen Chloride in Dimethylformamide. Into a flask, equipped with a stirring bar, in a glovebag was put 0.116 g (0.514 mmol) of $(C_3H_7)_4NB_3H_8$ and about 10 ml of dimethylformamide (degassed as it was for the electrochemical studies), and the flask was attached to a vacuum line. Dry hydrogen chloride (0.518 mmol) was condensed onto this mixture at −196 °C, and the solution was warmed to 0 °C for 90 min with no obvious reaction. After 2 h at room temperature, bubbles of H_2 were observed. A quantity of hydrogen gas (0.375 mmol) equivalent to 72% of the hydrogen chloride added was collected and identified. A ^{11}B NMR spectrum of a sample of this solution kept under nitrogen showed only the quartet attributable to $(CH_3)_3N{\cdot}BH_3$ at +6.7 ppm. Removal of this compound, as well as most of the dimethylformamide, by evacuation of the reaction flask left a solution containing a trace of $B_3H_7{\cdot}DMF$ (2:1 peak ratio at +9.1 and +15.2 ppm) along with other minor impurities. Also determined were the ^{11}B NMR spectra of $(C_2H_5)_3N{\cdot}BH_3$, $(C_3H_7)_3N{\cdot}BH_3$, and $(C_4H_9)_3N{\cdot}BH_3$, which all show quartets at +12.3 ppm rather than at +6.7 ppm.

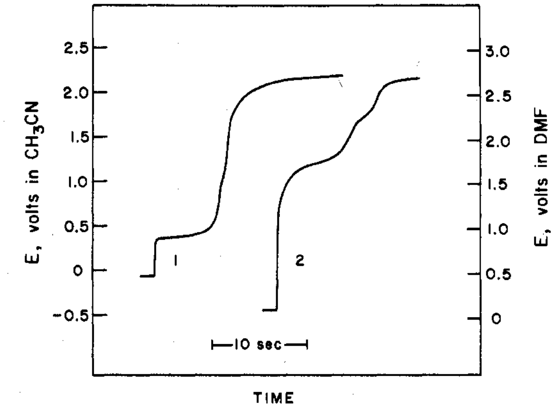

Figure 2. Curve 1: chronopotentiogram for oxidation of 0.004 98 M $(CH_3)_4NB_3H_8$ in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte at a gold wire anode at room temperature; the current was 288 μA and the electrode area and radius were 0.217 cm² and 0.0318 cm, respectively. Curve 2: chronopotentiogram for oxidation of 0.008 77 M $(C_2H_5)_4NB_3H_8$ in dimethylformamide with 0.05 M tetraethylammonium perchlorate as supporting electrolyte at a planar platinum electrode at room temperature; the current was 536 μA and the electrode area was 0.214 cm².

Reaction of B_4H_{10} with Dimethylformamide. About 0.03 ml (0.28 mmol) of tetraborane(10) was condensed into the bottom of an evacuated NMR tube attached to a stopcock. Approximately 0.75 ml of previously degassed dimethylformamide was poured on top of the stopcock. Careful opening of the stopcock allowed 90% of this solvent to move down onto the B_4H_{10} in the NMR tube. That tube was cooled to −196 °C, evacuated, sealed off, and warmed to room temperature overnight. A ^{11}B NMR spectrum of its contents showed peaks corresponding to $B_3H_7{\cdot}DMF$ and $B_3H_8^-$, as well as a broad hump at about −5.7 ppm attributed to the combined resonances of borates and BH_2^+-solvate species.

Results and Discussion

Studies in Acetonitrile. Solutions of $(CH_3)_4NB_3H_8$, ranging in concentration from 0.0028 to 0.0185 M in anhydrous acetonitrile containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte, were examined chronopotentiometrically with gold and platinum wire electrodes. As shown in Figure 2, curve 1, an anodic chronopotentiogram exhibits a wave for oxidation of $B_3H_8^-$ at approximately +0.4 V vs. the silver–silver chloride reference electrode in acetonitrile saturated with lithium chloride;[10] the small wave near +1.1 V is associated with the formation of a gold oxide film on the electrode due to a trace of water in the solvent. With a freshly cleaned electrode, the transition time for the $B_3H_8^-$ wave first increases and then decreases during a series of measurements at a fixed current density; such behavior was previously noted for the oxidation of BH_4^- in aqueous alkaline media,[12] but as yet there has been no satisfactory explanation of the phenomenon. Experimental data for the concentrations of $B_3H_8^-$ specified above and for a range of transition times from 1.4 to 22 s gave a chronopotentiometric constant ($i\tau^{1/2}/AC$) of 616 ± 29 A s$^{1/2}$ cm/mol. Based on the fact that the oxidation of $B_3H_8^-$ is a one-electron process (determined, as described below, by means of controlled-potential coulometry), a diffusion coefficient of (5.2 ± 0.5) × 10^{-5} cm^2/s at room temperature was evaluated for $B_3H_8^-$ according to a procedure discussed elsewhere.[13] Such a diffusion coefficient is consistent with the value of 3.3 × 10^{-5} cm^2/s found for the much larger $B_{10}H_{14}$ molecule in acetonitrile.[5]

Controlled-potential electrolyses of solutions of $B_3H_8^-$ proceeded smoothly, with a normal exponential current decay, at both +0.75 and +1.25 V. Evolution of hydrogen gas (whose identity was determined by mass spectrometry) was evident in the anode compartment, whereas smaller amounts of a different gas (presumably a mixture of ethene and ethane) were evolved at the cathode. Soon after the start of electrolysis, the solution in the cathode compartment began to turn yellow, darkening slightly during the remainder of the experiment. Integration of current–time curves revealed that $B_3H_8^-$ undergoes a one-electron oxidation. A ^{11}B NMR spectrum of a sample of solution from the anode compartment exhibited only the two peaks (areas 2:1 at +7.7 and +34.3 ppm, respectively) corresponding to $B_3H_7{\cdot}NCCH_3$. Therefore, the process taking place appears to be

$$B_3H_8^- \xrightarrow{CH_3CN} B_3H_7{\cdot}NCCH_3 + {}^1/_2H_2 + e^- \qquad (1)$$

Independent syntheses of $B_3H_7{\cdot}NCCH_3$ according to the reactions

$$B_3H_8^- + HCl \xrightarrow{CH_3CN} Cl^- + H_2 + B_3H_7{\cdot}NCCH_3 \qquad (2)$$

$$B_3H_8^- + NOPF_6 \xrightarrow{CH_3CN} PF_6^- + NO + B_3H_7{\cdot}NCCH_3 + {}^1/_2H_2 \qquad (3)$$

substantiate the conclusion that the electrochemical oxidation of $B_3H_8^-$ results in elimination of a hydrogen atom to form the known Lewis acid, B_3H_7. This, in turn, reacts with the Lewis base, acetonitrile, used as solvent to yield $B_3H_7{\cdot}NCCH_3$. We saw no evidence for the anodic formation of a radical such as $B_3H_8{\cdot}$ in acetonitrile; no products resulting from disproportionation or coupling of a boron radical were found, and no current-reversal chronopotentiogram for the reduction of $B_3H_8{\cdot}$ was observed.

Because electrochemical oxidation and protonation of $B_3H_8^-$ in acetonitrile both lead to the same product, namely, $B_3H_7{\cdot}NCCH_3$, these two processes might have certain mechanistic similarities. We suggest that anodic oxidation can be visualized as removing one electron from the boron–boron bond of $B_3H_8^-$, followed by expulsion of a bridging hydrogen atom and by formation of the central three-center bond in the B_3H_7 moiety, the latter becoming coordinated with a molecule of solvent. In the protonation reaction, it is proposed that the solvated proton, $H{:}N^+{\equiv}CCH_3$, attacks the boron–boron bond of $B_3H_8^-$, allowing the proton to combine with a bridging hydrogen and leading to formation of the central three-center bond in $B_3H_7{\cdot}NCCH_3$. Inasmuch as no further electrochemical reaction of $B_3H_7{\cdot}NCCH_3$ is observed, we conclude that the three-center bond and the hydrogen-bridge bond of this species are much less susceptible to oxidation than the boron–boron bond of $B_3H_8^-$.

Studies in Dimethylformamide. Chronopotentiometric oxidation of $B_3H_8^-$ in dimethylformamide yields the two waves shown in Figure 2, curve 2, indicating that at least two processes take place. Controlled-potential electrolyses at +1.6 and +2.0 V vs. the cadmium amalgam reference electrode in dimethylformamide[11] at 0 °C led to evolution of hydrogen gas in the anode compartment and to yellowing of the solution in the cathode compartment. Graphical analysis of the current–time curves demonstrated that the first chronopotentiometric wave seen in Figure 2, curve 2, corresponds to the one-electron oxidation of $B_3H_8^-$ to yield $B_3H_7{\cdot}DMF$ and hydrogen

$$B_3H_8^- \xrightarrow{DMF} B_3H_7{\cdot}DMF + {}^1/_2H_2 + e^- \qquad (4)$$

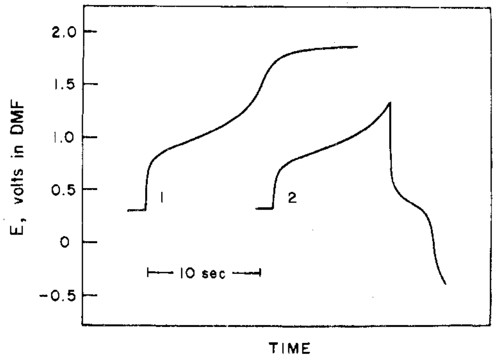

Figure 3. Anodic and current-reversal chronopotentiograms for a 0.05 M solution of tetraethylammonium perchlorate in dimethylformamide saturated with hydrogen gas obtained with a planar platinum electrode at room temperature; the area of the electrode was 0.214 cm^2 and the current was 38.6 μA.

Evidence for the presence of $B_3H_7{\cdot}DMF$ was the appearance of two peaks of areas 2:1 at +9.1 and +15.2 ppm, respectively, in a ^{11}B NMR spectrum of a sample of solution from the anode compartment. We confirmed the identity of $B_3H_7{\cdot}DMF$ by comparing it to a sample synthesized from B_4H_{10} and dimethylformamide

$$B_4H_{10} + DMF \rightarrow B_3H_7{\cdot}DMF + [BH_3{\cdot}DMF] \rightarrow (CH_3)_3N + \text{borates} \qquad (5)$$

Investigation of the second stage of oxidation of $B_3H_8^-$ in dimethylformamide entailed exhaustive electrolysis at +2.3 V. A ^{11}B NMR spectrum of the solution from the anode compartment exhibited only a broad hump at −5.7 ppm, the region in which borates and BH_2-complexed species resonate.[14] Coulometric data indicated that approximately 4.5 electrons are involved in the overall oxidation of $B_3H_8^-$. Apparently, the $B_3H_7{\cdot}DMF$ undergoes an oxidation in which at least three electrons are transferred and in which there may be breakdown of the dimethylformamide portion of the molecule. However, because these products have little interest chemically and are difficult to separate, we have not investigated the oxidation of $B_3H_7{\cdot}DMF$ in any more detail.

Molecular hydrogen produced by reaction 4 might be oxidized to hydrogen ion, which should, in turn, react with $B_3H_8^-$. As shown by the chronopotentiograms in Figure 3, dissolved molecular hydrogen does undergo electrochemical oxidation at +0.8 V. However, apparently almost all of the H_2 formed in reaction 4 escapes from the dimethylformamide solution before oxidation can take place, because the coulometric *n* value for oxidation of $B_3H_8^-$ at either +1.6 or +2.0 V is very close to unity. Yet any hydrogen ion which is formed by oxidation of molecular hydrogen interacts slowly with $B_3H_8^-$ (see eq 6), as described in the Experimental Section,

$$2B_3H_8^- + 2H^+ + 3DMF \rightarrow 3(CH_3)_3N{\cdot}BH_3 + \text{borates} \qquad (6)$$

to give the same products yielded by the reaction of diborane with dimethylformamide.[15] It is believed that diborane reduces dimethylformamide first to $(CH_3)_2NCH_2OB_2H_5$, and from that stage to $(CH_3)_2NCH_3$ and B_2H_4O, which disproportionates to borates and diborane. The trimethylamine formed would then complex the diborane to yield $(CH_3)_3N{\cdot}BH_3$. Since $(CH_3)_3N{\cdot}BH_3$ rather than $(C_2H_5)_3N{\cdot}BH_3$ was isolated from the oxidation of $(C_2H_5)_4NB_3H_8$ in 0.1 M tetraethylammonium perchlorate, the $(CH_3)_3N$ could have come only from reduction of dimethylformamide by the product of the reaction of $B_3H_8^-$ with hydrogen ion.

Perhaps the most interesting aspect of the dimethylformamide system is the difference between protonating $B_3H_8^-$ (reaction 6) and oxidizing that same species (reaction 4). When $B_3H_8^-$ is oxidized in dimethylformamide, hydrogen is

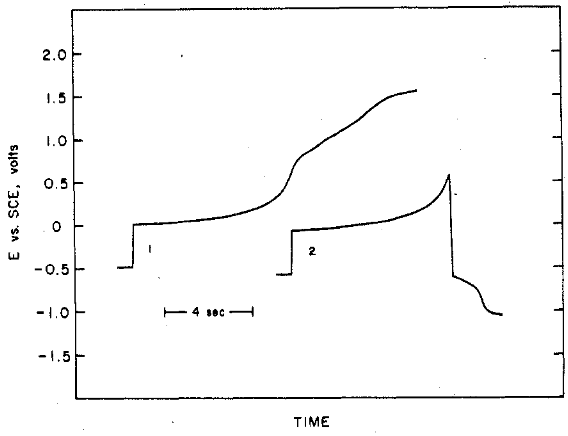

Figure 4. Anodic and current-reversal chronopotentiograms for 5.92×10^{-4} M $(CH_3)_4NB_3H_8$ in aqueous unbuffered 1 M potassium nitrate solution obtained with a gold wire electrode at room temperature; the current was 360 μA and the electrode area and radius were 0.355 cm² and 0.0318 cm, respectively.

lost with the resultant formation of the $B_3H_7\cdot DMF$ species. On the other hand, the B_3H_9 believed to be formed from protonation of $B_3H_8^-$ in dimethylformamide slowly reduces the solvent. Such is not the case in acetonitrile, for B_2H_6 (and, one would expect, B_3H_9) reacts with the solvent to form $BH_3\cdot NCCH_3$ which slowly trimerizes to yield $(CH_3CH_2)_3N_3B_3H_3$.[16]

Studies in Water. Although the situation in water is believed to be similar to that encountered in dimethylformamide, the species involved are so much less stable that our conclusions are more tenuous. A chronopotentiogram for the oxidation of $B_3H_8^-$ at a gold anode in an unbuffered aqueous potassium nitrate medium exhibits three waves, as shown in Figure 4, curve 1. It is suggested that the first wave at +0.1 vs. SCE corresponds to the reaction

$$B_3H_8^- \xrightarrow{H_2O} B_3H_7\cdot OH_2 + {}^1/_2H_2 + e^- \qquad (7)$$

because bubbles of hydrogen gas form at the surface of the anode. If the current is reversed at the transition time of the first wave for oxidation of $B_3H_8^-$ (Figure 4, curve 2), a cathodic wave appears at −0.7 V, signaling the reduction of hydrogen ion formed by oxidation of molecular hydrogen at the electrode surface during oxidation of $B_3H_8^-$.

Conceivably, the second, greatly attenuated wave at +0.85 V might arise from oxidation of $B_3H_7\cdot OH_2$ to a hydrated form of BH_2^+. However, both of these species are exceedingly unstable in an aqueous solution, being rapidly converted to borates. Formation of a gold oxide film on the surface of the anode is responsible for the third wave at +1.1 V.

Controlled-potential coulometric oxidations of $B_3H_8^-$ at +0.5 and +1.0 V showed the transfer of at least 6 equiv/mol of $B_3H_8^-$. This result varied with the initial concentration of $B_3H_8^-$ and with the pH of the solution. Apparently, the H^+ produced by oxidation of the H_2 generated in reaction 7 reacts vigorously with $B_3H_8^-$ to form what can be visualized as an aqueous solution of diborane—a very unstable, highly reducing mixture.[17] Therefore, although it is unrealistic to attempt to reach quantitative conclusions from the coulometric data, it is clear that an oxidation of $B_3H_8^-$ takes place in an aqueous medium. However, because water is a protic solvent, sufficient complications occur to make further investigations unwarranted at this time.

Registry No. $(CH_3)_4NB_3H_8$, 12386-10-6; $B_3H_7\cdot NCCH_3$, 59796-67-7; $(CH_3)_3N\cdot BH_3$, 75-22-9; $B_3H_7\cdot DMF$, 59803-46-2; $(C_2H_5)_3N\cdot BH_3$, 1722-26-5; $(C_3H_7)_3N\cdot BH_3$, 15201-50-0; $(C_4H_9)_3N\cdot BH_3$, 2080-00-4; B_4H_{10}, 18283-93-7; acetonitrile, 75-05-8; dimethylformamide, 68-12-2; $(C_3H_7)_4NB_3H_8$, 59796-66-6; $(C_2H_5)_4NB_3H_8$, 12555-74-7.

References and Notes

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Contribution from the Union Carbide Corporation,
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The Kinetics of the Boron Plus Nitrogen Reaction

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The reaction kinetics between boron and nitrogen have been examined in the temperature range of 1479 to 1823 K, using amorphous (probably α-phase) boron and β-rhombohedral boron. The evidence indicates the reaction mechanism is most likely topochemical yielding BN with α-B as the starting material. When β-B is the starting material, a two-step reaction series occurs with an homogeneous reaction to form B_6N followed by a topochemical reaction to yield BN.

Introduction

The direct boron–nitrogen reaction was selected to test the applicability of a proposed gas–solid reaction mechanism. Listed in Table I are some solid–diatomic gas reaction mechanisms encountered and their distinguishing kinetic features. These are the mechanisms that are operative for reactions going to completion. A topochemical mechanism is defined as a reaction that is rate limited by the process occurring at the interface between the product and a solid reactant. Thin-film mechanisms are not included. The mechanisms are listed in Table I as if only one reaction step were rate limiting. It is also possible to obtain a reaction with multiple rate-limiting steps that is not easily catalogued by these classifications. It was the original intent of the work reported here to test a reaction other than a metal–hydrogen reaction for applicability of the reactant-phase diffusion model.