that of the polymer, the initial drop in absorbance could thereby be explained. The observation from dialysis measurements that the hydrolyzed solution in question (3OH/Fe) contains some 20% of the iron in the low molecular weight form[2] accounts quite nicely for the rapid process in the $HCit^{3-}$ and H_2Cit^{2-} solutions, which are responsible for 21 and 26%, respectively, of the total absorbance change. In the H_2EDTA^{2-} solution the initial fraction is somewhat larger, 37%. It is possible that some of the surface irons in the polymer are also susceptible to rapid attack by EDTA.

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The Mechanisms of Electrolytic Reduction for Decaborane(14), $B_{10}H_{14}$, in an Aprotic Solvent. I. The First Reduction Step[1a]

Elinore B. Rupp, Donald E. Smith,[1b] and Duward F. Shriver[1c]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received April 8, 1967

Abstract: This paper presents electrochemical and spectral (esr and visible–ultraviolet) data which are interpretable in terms of a one-electron reduction of decaborane(14) to produce a radical anion. This radical undergoes rapid, first-order decay (possibly terminal–bridge hydrogen interchange) to a somewhat more stable radical anion. The latter appears to disproportionate, producing $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$. A more complex mechanism, which also involves radical anion formation, will also explain the data.

We have carried out electrochemical investigations on the reduction of decaborane(14) in an inert solvent (1,2-dimethoxyethane) in an effort to study the reduction mechanism. The reaction of decaborane with alkali metals has been reported on several occasions.[2,3] These studies have afforded some knowledge of the products of reduction and possible mechanisms. However, most aspects of the mechanisms are either unclear or without substantial proof. It seemed to us that the great selectivity of reduction potential which is available in electrochemical experiments and their analytical aspects might provide a clearer picture of the reduction process. Another aspect of the application of electrochemistry to this problem is that, in principle, appropriate electrochemical experiments can provide information on a much shorter time scale than was possible in the previous chemical investigations.[4]

Hough and Edwards have shown that the reaction of sodium amalgam with $B_{10}H_{14}$ is dependent upon reaction time[3]

$$B_{10}H_{14} + 2Na(Hg) \xrightarrow[Et_2O]{5\ hr} Na_2B_{10}H_{14}$$

$$2B_{10}H_{14} + 2Na(Hg) \xrightarrow[Et_2O]{3\ days} 2NaB_{10}H_{13} + H_2$$

Furthermore, Toeniskoetter has shown that the nature of the product is strongly dependent upon the solvent which is employed, as well as reaction time.[2]

$$2Na + B_{10}H_{14} \xrightarrow[NH_3(l)]{} Na_2B_{10}H_{14}$$

$$Na + B_{10}H_{14} \xrightarrow[Et_2O]{} NaB_{10}H_{13} + Na_2B_{10}H_{14} + \text{other products with longer reaction times (proposed } Na_2B_{10}H_{13})$$

$$Na + B_{10}H_{14} \xrightarrow[THF]{} NaB_{10}H_{13} + Na_2B_{10}H_{14}$$

In ether solutions the reaction of sodium with decaborane produces a red transient species which Toeniskoetter proposed might be a free radical, $B_{10}H_{14}^-$. This color faded slowly to a yellow-green. Upon standing, the product of 1 g-atom of hydrogen per mole of original decaborane was noted and explained in terms of the following over-all reaction

$$Na + B_{10}H_{14} \longrightarrow NaB_{10}H_{13} + 0.5H_2$$

A secondary reaction was also noted.

$$2Na + B_{10}H_{14} \longrightarrow Na_2B_{10}H_{14}$$

When the solvent was removed from the initial red solution, a white solid remained which gave back the red color when redissolved. Toeniskoetter proposed that the production of $Na_2B_{10}H_{14}$ is the result of two successive one-electron reductions

$$B_{10}H_{14} \xrightarrow{Na} NaB_{10}H_{14} \xrightarrow{Na} Na_2B_{10}H_{14}$$

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(1) (a) This work was supported by grants from the National Science Foundation and is taken in part from the Ph.D. Dissertation of E. B. Rupp, Northwestern University, Evanston, Ill., 1967; (b) to whom reprint inquiries should be addressed; (c) Alfred P. Sloan Fellow, 1967–1969.

(2) (a) R. H. Toeniskoetter, Ph.D. Thesis, St. Louis University, 1958; R. H. Toeniskoetter, G. W. Schaeffer, E. C. Evers, R. E. Hughes, and G. E. Bagley, Abstracts of Papers, 134th National Meeting of the American Chemical Society, Chicago, Ill., 1958, p 23.

(3) (a) W. V. Hough and L. J. Edwards, Abstracts of Papers, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958, p 28L; (b) W. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 184.

(4) (a) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954; (b) P. Delahay, in "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, P. Delahay, Ed., Interscience Publishers, Inc., New York, N. Y., Chapter 5.

although some other processes were postulated to fit special cases.

The present work indicates that the apparently simple reduction of decaborane is in fact mechanistically complex. This paper will cover experiments designed to elucidate the first reduction step, and a following paper will describe findings relevant to the second reduction step and over-all stoichiometry of the reaction.

Experimental Section

Polarographic, cyclic voltammetric, and controlled-potential coulometric data were obtained with the aid of an all-electronic potentiostat constructed from vacuum-tube operational amplifier circuitry which is used in combination with a three-electrode cell configuration. Details of construction and performance of this type of instrument may be found in the literature.[5-8] While this instrumentation eliminates most sources of ohmic potential drop, enabling meaningful measurements in high-resistance solutions such as employed in this work, an uncompensated ohmic resistance of approximately 10^4 ohms was present in most of the work described here.[9] Quantitative data reported below are corrected for this effect.

Signal sources (initial voltage source, voltage ramp generator, and triangular wave oscillator) were constructed from standard operational amplifier circuits.[5-8,10] Readout of conventional polarograms was to a Sargent Model SR recorder. A Tektronix Model 502 oscilloscope was employed as the readout device for cyclic voltammograms. A Tektronix Model C-13 oscilloscope camera provided for permanent recording of "scope" traces. Measurement of coulombs consumed in controlled-potential electrolysis was effected with a standard operational amplifier integrator[5-8,10] which utilized circuit elements of 0.1% tolerance.

The electrolysis cell was a Sargent Model S-29390. A silver-saturated silver nitrate electrode in 1,2-dimethoxyethane (glyme) served as the reference electrode. The working electrode was a dropping mercury electrode (dme) in polarographic and cyclic voltammetric work, and a mercury pool in controlled-potential electrolysis studies. A platinum wire served as the auxiliary electrode. All electrochemical experiments were run in a base solution composed of 0.1 *M* tetrabutylammonium perchlorate (TBAP) in glyme. Preparation of solutions and polarographic experiments were performed in a dry, inert atmosphere glove box to avoid contamination of the solvent and the boron hydrides through their reaction with atmospheric oxygen. The Lucite glove box was of conventional design except for minor modifications to accommodate electrical connections, the DME assembly, and thermostat water for cell temperature control.[11] A water bath and liquid circulating pump, which were external to the drybox, allowed the polarographic cell in the drybox to be thermostated.

Polarographic and cyclic voltammetric data were obtained over the temperature range of 7-25° and the concentration range 0.5-5 m*M*. The accessible frequencies for meaningful cyclic voltammetric experiments were limited to values less than 20 Hz (scan rates less than about 40 sec^{-1}) by demands on the instrumentation imposed by the high resistance of the solutions. Even below 20 Hz, the ohmic distortion of the cyclic voltammograms[12,13] was substantial. As a result, the cyclic voltammetric data are employed only as a basis for qualitative mechanistic conclusions. All cyclic voltammetric experiments were of the multicycle, triangular wave variety.[14-16]

All experiments were run on freshly prepared solutions, as stock solutions of the hydrides in glyme were found to decompose. The tedium and expense associated with preparation and purification of solvent and electroactive materials combined with the requirement of freshly prepared solutions dictated the preparation of solutions in small quantities (25 ml). This resulted in an abnormally large uncertainty in solution concentrations of electroactive materials due to difficulties associated with weighing and handling milligram quantities of air-sensitive and/or volatile solids. Based on *a priori* estimates as well as observed reproducibility of concentration-sensitive data (*e.g.*, polarographic wave heights), the concentration uncertainty appeared to be of the order of ±5-10% (relative average deviation from the mean). This uncertainty was considered in the analysis of electrochemical data so that mechanistic conclusions demanding greater accuracy were avoided. Weighing was performed with the aid of small weighing bottles (gross weight $\simeq$ 0.3 g). After transfer to the drybox, the weighing bottle with electroactive material was dropped into 25.0 ml of 0.10 *M* TBAP in glyme. The volume of electroactive substances was neglected in calculating concentration.

Solution spectra were run employing the same precautions used in solution preparation for electrochemical work. Ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer. Matched 1-cm quartz cells were used for the sample and reference solutions. A Varian Associates V-4500 esr spectrometer equipped with a 100-kHz field modulation unit and a Fieldial for regulation of the magnetic field strength and scanning rates was used to acquire esr spectra. A Varian 12-in. magnet supplied the homogeneous magnetic field. Infrared spectra were obtained with the aid of a prism-grating Beckman IR-9 spectrophotometer. The samples were in the form of Nujol mulls between KBr plates.

Eastman Red Label glyme was purified by initial drying over calcium hydride (>24 hr) followed by refluxing and distillation from a benzophenone–sodium wire mixture in a nitrogen atmosphere. An infinite reflux ratio was maintained until the blue benzophenone ketyl formed, indicating the absence of peroxides. At this point product collection was initiated with the aid of a special receiver[11] which prevented contact of purified solvent with air. All connections in the distillation apparatus were grease-free due to exclusive use of O-ring joints, silicone O rings, and Delmar–Urry stopcocks.

Linde Grade high purity dry nitrogen used for glove box, distilation column, and polarographic cell purging was purified by passing it successively through columns of silica gel, magnesium perchlorate, hot active copper, and calcium hydride. The nitrogen stream used to degas the polarographic solution was also passed through a two-stage gas bubbler containing a glyme 0.1 *M* solution of TBAP or, in some cases, pure glyme.

The TBAP, obtained from Southwestern Analytical Chemicals (polarographic grade), was recrystallized from ethanol or methanol and dried under vacuum in a drying pistol at 100°. Baker and Adamson reagent grade 70% perchloric acid was used without further purification. Tetrabutylammonium hydroxide (25% in methanol—Eastman Organic Chemicals) was used without purification. Decaborane(14) (Callery Chemical Co.) was purified by sublimation under high vacuum; mp 99.5°, lit.[17] 99.6-99.7°. The ultraviolet[18] and infrared[19] spectra agreed with the literature. Tetrabutylammonium decaboran(13)ate(1−) ($Bu_4NB_{10}H_{13}$) was prepared in a nitrogen atmosphere by a method analogous to that of Hawthorne, *et al.*[20] The infrared spectrum had a characteristic peak at 2514 and a shoulder at 2542 cm^{-1} (lit.[2] 2500 cm^{-1}) and the ultraviolet spectrum in glyme had absorption maxima at 335 and 267 mμ which agree with the literature (acetonitrile solvent).[21] A solution of the decaboran(14)ate(2−) ion was prepared on a small scale by the method of Muetterties;[22] tetrabutylammonium hydroxide was added to the aqueous solution and the resulting precipitate, $(Bu_4N)_2B_{10}H_{14}$, was collected. It was dried in a vacuum desiccator

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and stored under nitrogen; the infrared spectrum displayed maxima at 2315 (w), 2358 (vw), 2390 (w), and 2468 (s) cm^{-1}. These agree with the literature within the expected accuracy.[2] Tetrabutylammonium decaboran(15)ate(1−) ($Bu_4NB_{10}H_{15}$) was prepared from tetrabutylammonium decaboran(14)ate(2−) by the method of DuPont and Hawthorne.[23] The infrared absorptions at 2310 (w), 2355 (w), 2386 (w), and 2525 (s) cm^{-1} were in reasonable agreement with the literature.[23] In glyme solution the compound displayed a strong ultraviolet absorption at 246 mμ; this is shifted somewhat from the unpublished spectrum determined by J. A. McGinnety which displayed a single absorption at 264 mμ for a methanol solution.

Results and Discussion

Decaborane exhibits two polarographic reduction waves in solutions of 0.10 *M* TBAP in glyme. No oxidation waves are observed. Half-wave potentials ($E_{1/2}$) of the first and second reduction waves at 25° are −1.54 ± 0.03 and −2.78 ± 0.03 v *vs.* Ag-saturated $AgNO_3$, respectively. The first wave is well formed at lower concentrations ($\leq 0.8 \times 10^{-3}$ *M*) of decaborane, but exhibits a maximum of the first kind[24] at higher concentrations. The maximum increases in magnitude with increasing decaborane concentration. The first polarographic wave height at 25° corresponds to an apparent diffusion current constant[25] of 2.5 ± 0.3. Within the uncertainty of experimental data, the wave height increased linearly with decaborane concentration. Under all conditions studied, the limiting current exhibited a column height dependence which was consistent with a diffusion-controlled process; *i.e.*, plots of instantaneous limiting current *vs.* square-root of mercury column height were linear with an intercept at or near the origin.[26a] If these limiting currents contained any kinetic character,[26b] it was relatively small and masked by experimental uncertainty. Currents at the foot of the first polarographic wave were roughly independent of mercury column height. No qualitative evidence of adsorption effects (small prewaves, unusual drop oscillations, etc.) were apparent in the polarograms.

A linear plot was found for $\log[(i_d - i)/i]$ *vs.* potential (E) with a slope of 0.06 v, while a plot of $\log[(i_d - i_d)/i^{2/3}]$ *vs.* E was noticeably nonlinear. These plots were taken from polarograms of the less concentrated (<1 m*M*) $B_{10}H_{14}$ solutions where maxima were not apparent.

The foregoing conventional polarographic evidence strongly suggests a primary reduction step involving a one-electron reduction of the decaborane molecule[26,27]

$$B_{10}H_{14} + e \longrightarrow B_{10}H_{14}\cdot^- \qquad (1)$$

An important characteristic of the conventional polarographic results concerning the existence of reaction 1 is the fact that the limiting current of the first decaborane reduction wave is diffusion controlled. This diffusion-controlled character, which is also evident in the cyclic voltammetric data (see below), is maintained for temperatures between 7 and 25°, concentrations between 0.5 and 5 m*M*, and in the presence of a tenfold excess of $B_{10}H_{13}^-$. This total absence of kinetic character of the limiting current under widely varying conditions appears to preclude the possibility of a chemical reaction preceding the charge-transfer step[26,28] such as

$$B_{10}H_{14} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H^+ + B_{10}H_{13}^- \qquad (2)$$

where the electroactive species is H^+ or $B_{10}H_{13}^-$. The most reasonable conclusion one can draw is that the $B_{10}H_{14}$ molecule is the electroactive species. This combined with the one-electron character of the electrode reaction forces the conclusion that a monoanion radical is the initial product of the electrolysis step. However, cyclic voltammetry, esr spectra, and a variety of other data indicate that this radical anion is short-lived.

As described in the introductory section, a radical anion has been invoked by Toeniskoetter. He reported that the initial reduction product of $B_{10}H_{14}$ with sodium in diethyl ether was a red species which he reasoned to be a radical. He was able to obtain a solution of similar color by mixing $B_{10}H_{14}$ and $B_{10}H_{14}^{-2}$, and the eventual evolution of 1 mole of hydrogen for each mole of decaborane was observed. However, no positive experimental evidence points to the existence of a radical anion other than the electrochemical results presented here. To gain more evidence on this point, we performed some esr observations on the reaction product of $B_{10}H_{14}$ with $B_{10}H_{14}^{-2}$.

An equimolar mixture of $B_{10}H_{14}$ and $(Bu_4N)_2B_{10}H_{14}$ was placed in a vacuum line reactor and benzene-free glyme distilled into the tube. On melting of the ether (*ca.* −65°) an intense purple color formed. If a sample of the reaction mixture was refrozen and sealed off at this stage, a weak esr signal could be observed with the sample maintained at a low temperature (*e.g.*, −92°). The weak signal consisting of a single broad peak with no hyperfine structure is shown in Figure 1 (modulation 9.4, $g = 2.0$, signal width 115 gauss). On warming, the purple color faded in unison with a decay of the esr signal. Continued warming to ambient temperature produced a yellow solution. Thus, we have confirmatory evidence for a radical species in this system. The width of the line may be due to the presence of several nonequivalent boron and hydrogen sites plus the random distribution of ^{10}B and ^{11}B isotopes.

Figure 2 shows some typical cyclic voltammograms observed with decaborane in glyme–0.1 *M* TBAP after application of several triangular wave cycles (*i.e.*, approximately the steady-state pattern[14]) in a multicycle experiment in which the triangular wave potential does not encompass the second reduction step. The potential of the irreversible cathodic wave (wave B) corresponds to the first polarographic reduction wave of decaborane. This wave appears regardless of whether the potential sweep encompasses the more anodic processes (waves A, C, D), confirming that it originates from the bulk electroactive component, $B_{10}H_{14}$. The

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[23] J. A. DuPont and M. F. Hawthorne, *Chem. Ind.* (London), 76 (1966).

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[25] The diffusion current constant, I, is defined here as $I = i_l/C_0{}^* m^{2/3} t^{1/6}$ where i_l is the *instantaneous* plateau current at the end of drop life (μa), $C_0{}^*$ is the concentration of the electroactive material in the bulk solution (mmoles/l.), m is the mercury flow rate (mg/sec), and t is the drop life (sec).

[26] J. Heyrovsky and J. Kuta, ref 24: (a) p 86; (b) pp 341–351.

[27] J. Heyrovsky and J. Kuta, ref 24: (a) pp 97–98; (b) pp 129–130.

[28] (a) In order to rationalize our data in terms of a mechanism involving reaction 2 preceding the charge-transfer step, one would demand an H^+–$B_{10}H_{13}^-$ recombination rate which exceeds the estimated collision frequency (*cf.*, ref 26 and 28b); (b) L. Onsager, *J. Chem. Phys.*, 2, 599 (1934).

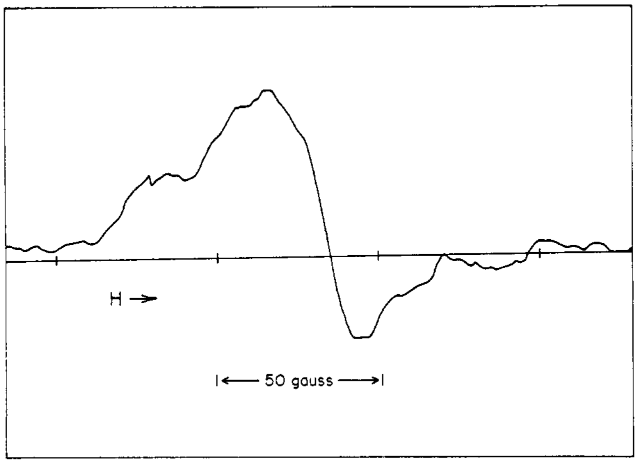

Figure 1. Derivative esr spectra of the $B_{10}H_{14}$–$B_{10}H_{14}^{-2}$ reaction mixture at −92°.

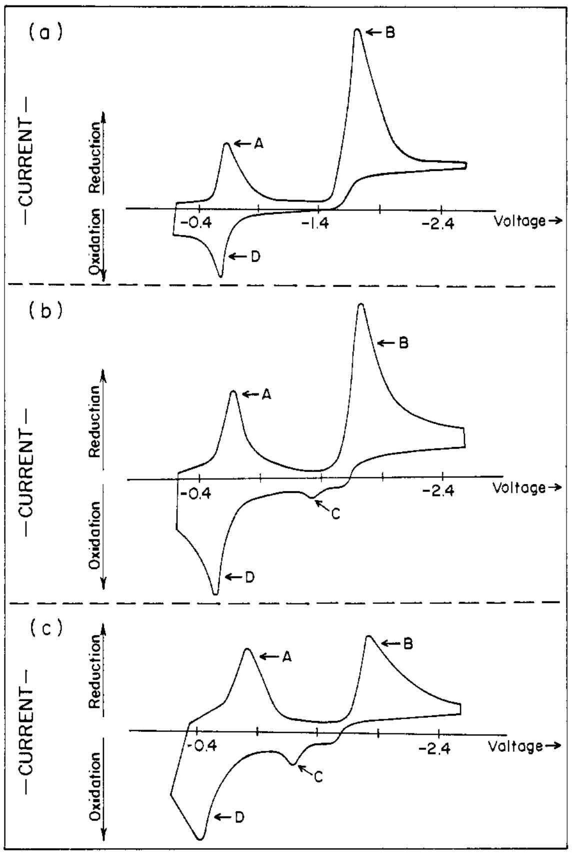

Figure 2. Cyclic voltammograms of decaborane (system: 0.49 × 10^{-3} *M* decaborane, 0.1 *M* Bu_4NClO_4, in 1,2-dimethoxyethane at 7°; applied: multicycle triangular wave potential, scan rates (a) 0.88 v/sec, (b) 1.9 v/sec, (c) 5.5 v/sec). This figure shows cyclic voltammograms after application of several triangular wave cycles (approximately steady state). The ordinate is uncalibrated. The voltammograms are not corrected for *iR* drop.

reversible couple producing waves A and D and the species giving wave C represent products of the first decaborane reduction step (wave B). This is indicated by the observation that waves A, C, and D do not appear unless wave B is included in the potential sweep. The fact that wave C decreases in magnitude with decreasing scan rate indicates that the species responsible for this oxidation wave is a transient intermediate. This is confirmed further by the fact that wave C decreases with increasing temperature. Increasing decaborane concentration also suppresses the magnitude of wave C, relative to the other waves, suggesting that the species in question is decomposing through a second- (or higher) order reaction. The magnitude and other characteristics of wave C are not influenced significantly by whether or not waves A and D are included in the potential sweep. This shows that the electrode reaction associated with waves A and D neither serves as the origin nor influences the demise of the species producing wave C. All of the qualitative characteristics of wave C are attributable to the oxidation of a transient intermediate formed by the first reduction step of $B_{10}H_{14}$ which is decomposing by a second-order process. Thus, it is reasonable to assign this wave to the oxidation of the $B_{10}H_{14}^-$ radical anion. Unlike wave C, waves A and D show characteristics attributable to a product of the reduction of $B_{10}H_{14}$ which is stable in the time scale of the cyclic voltammetric experiment. These waves appear to originate in the $B_{10}H_{13}^-$ anion as waves of identical characteristics (potential, magnitude, etc.) are observed with authentic $B_{10}H_{13}^-$ solutions (see part II[29]). Wave D presumably corresponds to the oxidation of $B_{10}H_{13}^-$, while wave A arises from the reverse reaction. The fact that waves attributable to $B_{10}H_{13}^-$ appear in the cyclic voltammetry indicates $B_{10}H_{13}^-$ is a rapidly formed product of the first reduction step of $B_{10}H_{14}$.

We have assigned wave C of Figure 2 to the transient radical species, $B_{10}H_{14}^-$. However, as outlined below, the species responsible for wave C probably is not the primary reduction product, since the most likely interpretations of the electrochemistry require an even less stable primary species, $\{B_{10}H_{14}^-\}$

$$B_{10}H_{14}^- + e \rightleftarrows \{B_{10}H_{14}^-\} \qquad \text{(Ia)}$$

$$\{B_{10}H_{14}^-\} \rightleftarrows B_{10}H_{14}^- \qquad \text{(Ib)}$$

It is also explained below that the data are accommodated by invoking subsequent disproportionation of the $B_{10}H_{14}^-$ radical to form the stable $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ anions

$$2B_{10}H_{14}^- \rightleftarrows B_{10}H_{13}^- + B_{10}H_{15}^- \qquad \text{(Ic)}$$

Reactions Ia–c (mechanism I) correspond to the overall reaction.

$$2B_{10}H_{14} + 2e = B_{10}H_{13}^- + B_{10}H_{15}^- \qquad \text{(I)}$$

The substantial overvoltage separating the reduction step (wave B, Figure 2) and the oxidation step (wave C, Figure 2) which are assigned to the $B_{10}H_{14}$–$B_{10}H_{14}^-$ redox couple gives rise to the suggestion that the species producing wave C, presumably $B_{10}H_{14}^-$, is not the initial product of the electron-transfer step, $\{B_{10}H_{14}^-\}$. The existence of a unimolecular transformation of the primary electrolysis product (reaction Ib) not only rationalizes the overvoltage, but also the linear polarographic log $[(i_d - i)/i]$ *vs.* E plot of 0.06-v slope and the foot-of-wave column height data. These results are consistent with a rapid, reversible charge-transfer step followed by unimolecular decomposition of the prod-

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(29) D. E. Smith, E. B. Rupp, and D. F. Shriver, *J. Am. Chem. Soc.*, **89**, 5568 (1967).

uct.[30] If the second-order decomposition (reaction Ic) were directly coupled to a reversible one-electron charge-transfer step, a linear log $[(i_d - i)/i^{2/3}]$ *vs.* E plot of 0.06-v slope should have been observed.[31,32] Mechanism I can accommodate the linear log $[(i_d - i)/i]$ *vs.* E plot provided conditions are such that reaction Ic does not influence the surface concentrations of the primary electrolysis product, $\{B_{10}H_{14}^-\}$.[33] This will be true, provided: (a) reaction Ib is irreversible, or (b) reaction Ib has some reversible character, but reactions Ia and c are sufficiently rapid that an equilibrium (or near-equilibrium) with respect to reaction Ib cannot be achieved under polarographic conditions. In principle, cyclic voltammetric confirmation of the existence of two forms of the ion radical could be obtained by increasing the triangular wave frequency until the period approached the half-life of the alleged $\{B_{10}H_{14}^-\}$ species. Under such conditions an oxidation wave due to $\{B_{10}H_{14}^-\}$ would appear, forming a reversible couple with wave B (Figure 2). Such a wave was not observed at the fastest scan rates available in this work. Unfortunately, the aforementioned limitations imposed on the instrumentation by the high resistance of the solvent precluded the use of reasonably fast scan rates which is possible under more ideal conditions.[34]

The esr experiment indicated that the decomposition of the more stable radical anion, $B_{10}H_{14}^-$ (purple color at low temperatures), leads to a yellow solution. The nature of this product was investigated electrochemically and spectroscopically. Exhaustive controlled-potential electrolysis of decaborane at potentials corresponding to the plateau of the first reduction wave (*e.g.*, at ~2.0 v) consumed a charge of 1.0 faraday per mole of decaborane, indicating that the reduction retains a one-electron character over the long time scale of the controlled-potential electrolysis (~1–2 hr). In the course of the electrolysis the solution changed from colorless to yellow. Polarograms of the resulting solution exhibited a reduction wave with $E_{1/2} = -2.77$ v and an oxidation wave of comparable magnitude at $E_{1/2} = -0.48$ v. This polarogram was characteristic of $B_{10}H_{13}^-$ in all respects,[29] except the magnitudes of the waves were about one-half as large as expected if all the decaborane had been converted to $B_{10}H_{13}^-$. Also, a cyclic voltammogram of this solution was qualitatively identical with that of $B_{10}H_{13}^-$.[29] An ultraviolet spectrum of the same solution exhibited peaks at 335 and 246 mμ. The 335-mμ band is characteristic of $B_{10}H_{13}^-$. Finally, it was observed that the polarographic, cyclic voltammetric, and ultraviolet spectral behavior just described for the glyme solution obtained by controlled-potential electrolysis of decaborane at −2.0 v was reproduced by a solution obtained upon mixing solutions of decaborane and $(Bu_4N)_2B_{10}H_{14}$. One concludes that $B_{10}H_{13}^-$ is a stable product of the electrochemical and chemical reductions of decaborane.

While the identification of $B_{10}H_{13}^-$ in the electrolysis solution appears unequivocal, another B_{10} species must be present to explain the over-all stoichiometry of reduction. That is, the complete reduction of $B_{10}H_{14}$ leads to $B_{10}H_{14}^{-2}$,[2,29] so the hydrogen-deficient $B_{10}H_{13}^-$ must be accompanied by a hydrogen-rich species. Another indication of more than one product is the polarographic evidence cited above that only half of the $B_{10}H_{14}$ is converted to $B_{10}H_{13}^-$ upon exhaustive reduction of $B_{10}H_{14}$ at −2.0 v. On the basis of the 246-mμ ultraviolet absorption peak and other less direct data, we believe that $B_{10}H_{15}^-$ is the other B_{10} species. We were initially puzzled by the lack of evidence for a second species in the polarograms or cyclic voltammograms of the yellow solution resulting from electrolysis of $B_{10}H_{14}$. Therefore, we investigated 1 m*M* $B_{10}H_{15}^-$ solutions and found them polarographically inactive which explains our failure to electrochemically detect the presence of a second B_{10} species. Thus, invoking the presence of $B_{10}H_{15}^-$ as a reduction product in these solutions is not contradictory to the polarographic data, and mechanism I fits all observations. Since the cyclic voltammograms of $B_{10}H_{14}$ indicate rapid formation of the stable product, $B_{10}H_{13}^-$ (waves A and D, Figure 2), rapid formation of the coproduct, $B_{10}H_{15}^-$, also is required by mechanism I. Mechanism I demands that equimolar mixtures of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ are stable, a fact we found to be true over the time scale of the electrochemical observations (≤2–3 hr). However, slow evolution of hydrogen (eventually 1 equiv per mole of B_{10} species) was observed over longer periods (~1 day).

On considering alternatives to mechanism I, it appears that certain features of this mechanism must be retained. Namely, we believe that any alternative mechanism should be consistent with the same over-all reaction and it should incorporate a radical anion of $B_{10}H_{14}$ as a transient intermediate. These restrictions are suggested by the rather convincing and varied supporting evidence. The least certain aspect of mechanism I relates to the mode of decomposition of the intermediate species. It is at this point that alternative mechanisms can be devised.

With these restrictions in mind, one possible alternative involves the steps shown in mechanisms IIa–d.

$$B_{10}H_{14} + e \rightleftharpoons \{B_{10}H_{14}^-\} \qquad \text{(IIa)}$$

$$\{B_{10}H_{14}^-\} \longrightarrow B_{10}H_{14}^- \qquad \text{(IIb)}$$

$$B_{10}H_{14}^- + B_{10}H_{14} \longrightarrow B_{10}H_{15}\cdot + B_{10}H_{13}^- \qquad \text{(IIc)}$$

$$B_{10}H_{15}\cdot + e \longrightarrow B_{10}H_{15}^- \qquad \text{(IId)}$$

Basically, this mechanism differs from mechanism I by the path of decomposition of $B_{10}H_{14}^-$. Reactions IIa and IIb have the same significance as reactions Ia and Ib. Reaction IIc represents a protonation of the anion radical by the parent compound. Reaction IId represents the reduction of the $B_{10}H_{15}\cdot$ radical immediately following reaction IIc. Implicit in this mechanism is the assumption that the standard potential of reaction IId is much more positive ($\gtrsim$0.2 v) than that of reaction IIa. Otherwise, this sequence of steps would not suffice to explain experimental observations such as the one-electron character and/or the linear log $[(i_d - i)/i]$ *vs.* E plot. Considerable precedent for this assumption is found in the electrochemical behavior of compounds ranging from organic ion radicals[35–40] to the oxygen molecule[41–44] where the pro-

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tonated anion radical is invariably more easily reduced than the parent compound. Precedent has also been found in organic electrochemistry for protonation of ion radicals by the parent compound when the parent compound contains an acidic proton.[45] Although the extrapolation of these established results to decaborane electrochemistry is a long one, the possibility of reactions IIc and d at least is suggested. The possibility is made realistic by the acidic character of $B_{10}H_{14}$.[46]

Although mechanism II suffices to explain the experimental observations, it is tempting to suggest that it is overly complex and that the unimolecular rearrangement step (reaction IIb) is unnecessary. One is led to this suggestion because reaction IIb is not required to explain the linear $\log[(i_d - i)/i]$ *vs.* E plot. A mechanism consisting of reactions IIa, c, and d is adequate to rationalize this result[47] as well as most of the other observations. However, such a simplified mechanism fails to provide a simple explanation for the overvoltage separating waves B and C (Figure 2) in the cyclic voltammograms. One cannot attribute wave C to the oxidation of $B_{10}H_{15}^-$ or $B_{10}H_{15}\cdot$. The former is clearly electroinactive, and the latter cannot achieve significant concentrations in the diffusion space because of the requirement that it is immediately reduced following reaction IIc. Thus, within the framework of the proposed mechanism, $B_{10}H_{14}^-$ is the only species remaining to which wave C can be assigned. Thus, the overvoltage between waves B and C can be explained only by invoking the existence of reaction IIb or, alternatively, by proposing that the charge-transfer step (reaction IIa) is irreversible which is unlikely as indicated below.

Experiments on the effect of proton donors on the decaborane electrochemistry have been performed to further substantiate or rule out the possibility of mechanism II. Although significant effects have been observed, analysis of the data indicates that it does not provide conclusive evidence on this point. Thus, at present we believe both mechanisms I and II represent reasonable rationales of the experimental data, but we tend to prefer I because of its simplicity.

A number of other mechanisms have been considered, all of which have been rejected as inconsistent with one or more aspects of the experimental data. One worth mentioning, since it represents a well-known classical explanation of certain aspects of the data, involves the steps

$$B_{10}H_{14} + e \xrightarrow[\alpha \simeq 1]{\text{slow}} B_{10}H_{14}^- \qquad \text{(IIIa)}$$

$$2B_{10}H_{14}^- \longrightarrow B_{10}H_{13}^- + B_{10}H_{15}^- \qquad \text{(IIIb)}$$

Reaction IIIa represents a slow, essentially irreversible,[48] charge-transfer step characterized by a charge-transfer coefficient of nearly unity. Reaction IIIb is identical with reaction Ic. Although this mechanism accommodates much of the data (column height dependences, overvoltage between waves B and C, linear $\log[(i_d - i)/i]$ *vs.* E plots, product composition, etc.), we reject it as unlikely because it requires a charge-transfer coefficient, α, of nearly unity[48b] to explain the 0.06-v slope of the $\log[(i_d - i)/i]$ *vs.* E plot. Such an α value recently has been shown difficult to rationalize theoretically[49] and is inconsistent with the well-formed reoxidation wave (wave C) in the cyclic voltammograms.[50]

Finally, we wish to point out that a first-order decay of the alleged $\{B_{10}H_{14}^-\}$ radical to produce a more stable radical might be explained in terms of bridge to terminal hydrogen interchange. It is thought that $B_{10}H_{14}^{-2}$ differs from $B_{10}H_{14}$ in terms of the relative numbers of bridging and terminal hydrogens. Thus, the unstable radical anion might resemble $B_{10}H_{14}$ and the more stable radical anion might resemble $B_{10}H_{14}^{-2}$. There is evidence that such a process can be rapid (*e.g.*, $B_3H_8^-$ and $Al(BH_4)_3$).[51]

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