# The Mechanisms of Electrolytic Reduction for Decaborane(14), $B_{10}H_{14}$, in an Aprotic Solvent. II. The Second Reduction Step and the Reduction of Decaboran(13)ate(−1), $B_{10}H_{13}^{-}$ [1a]

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**Abstract:** In glyme solutions, decaborane exhibits two reduction steps. Previously, it has been shown that the first step involves the formation of $B_{10}H_{15}^-$ and $B_{10}H_{13}^-$. Data are presented here which indicate that the second step originates from a one-electron reduction of $B_{10}H_{13}^-$. The resulting radical dianion, $B_{10}H_{13}^{-2}$, rapidly disproportionates to form $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ which react rapidly with bulk $B_{10}H_{14}$ to regenerate more electroactive $B_{10}H_{13}^-$. This reaction sequence corresponds to $4B_{10}H_{14} + 6e \rightleftarrows B_{10}H_{12}^{-2} + B_{10}H_{14}^{-2} + 2B_{10}H_{15}^-$ at potentials of the second reduction step. A reaction between $B_{10}H_{15}^-$ and $B_{10}H_{12}^{-2}$, generating $B_{10}H_{13}^-$, appears to contribute to the electrode reaction over the longer time scale characterizing controlled-potential electrolysis so that the net reaction under these conditions is $B_{10}H_{14} + 2e \rightleftarrows B_{10}H_{14}^{-2}$. When $B_{10}H_{13}^-$ is reduced in absence of bulk $B_{10}H_{14}$, the reaction stops with the formation of $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$.

In a previous paper[2] we have presented evidence which indicates that the first reduction step of decaborane(14) in glyme can be explained by one of two mechanisms. In both cases initial formation of a radical anion is followed by a series of steps leading to a moderately stable solution of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ in equivalent amounts. Data are presented in this paper which show that the second reduction step exhibited by $B_{10}H_{14}$ solutions is initiated by the reduction of the $B_{10}H_{13}^-$ ion, followed by a series of chemical steps, including one involving the $B_{10}H_{15}^-$ ion.

## Experimental Section

The instrumentation and techniques are identical with those presented in part I.[2]

Sodium decaboran(12)ate(2−) was prepared on a vacuum line by the method of Wilks and Carter,[3] and the composition of the sample was verified by measurement of the hydrogen evolved during synthesis. The infrared spectrum was in reasonable agreement with the literature.[3] An unsuccessful attempt was made to prepare the tetrabutylammonium salt by the addition of a tetrahydrofuran solution of $Na_2B_{10}H_{12}$ to tetrabutylammonium perchlorate in the same solvent. A precipitate of the desired salt did not form.

The electrochemical behavior of $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ was studied to provide some basis for their characterization. No attempt was made to interpret the results in terms of mechanisms. Therefore, the results are recorded without comment in this section.

Solutions of tetrabutylammonium decaboran(14)ate(2−) [$(Bu_4N)_2B_{10}H_{14}$] yield two polarographic oxidation waves and no reduction waves. The first (most cathodic) oxidation step of the $B_{10}H_{14}^{-2}$ anion exhibits a large polarographic maximum of the first kind at all concentrations studied which precludes accurate assessment of the half-wave potential. The onset of this oxidation wave occurs at about −1.4 v. The second oxidation wave is characterized by a half-wave potential ($E_{1/2}$) of −0.47 v. $(Bu_4N)_2B_{10}H_{14}$ is only sparingly soluble in glyme so that concentrations of solutions studied were much less than millimolar and were not accurately known.

Solutions of sodium decaboran(12)ate(2−) [$Na_2B_{10}H_{12}$] exhibited an oxidation wave with large maxima beginning at about −1.4 v and a second oxidation at $E_{1/2}$ = −0.47 v. A reduction at $E_{1/2}$ = −2.5 v due to the sodium ion also was observed. Although the $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ anions produced very similar oxidation polarograms, other evidence (see below) indicates that the large maxima associated with the first oxidation waves may be masking significant differences (*e.g.*, as much as ±0.1–0.2 v) in the half-wave potentials. It was observed that $B_{10}H_{12}^{-2}$ exhibited a noticeably smaller maximum than $B_{10}H_{14}^{-2}$.

Cyclic voltammograms of $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ solutions showed an irreversible oxidation wave at about −1.4 v and a reversible couple centered at about −0.5 v. These waves corresponded in potential to the observed polarographic oxidation waves. The cyclic voltammetric oxidation waves at −1.4 v were characterized by considerable distortion and erratic behavior, particularly at lower scan rates. The distortion, etc., could be minimized by using the fastest scan rates possible (~20 v/sec) at the expense of an enhanced double-layer charging current.

## Results and Discussion

**Reduction of Decaboran(13)ate(1−).** Tetrabutylammonium decaboran(13)ate(1−) ($Bu_4NB_{10}H_{13}$) in 0.10 *M* tetrabutylammonium perchlorate (TBAP)–glyme forms a yellow solution which exhibits one polarographic reduction wave with $E_{1/2}$ = −2.76 ± 0.03 v and one oxidation wave with $E_{1/2}$ = −0.48 ± 0.03 ($E_{1/2}$'s at 25°). With $B_{10}H_{13}^-$ concentrations greater than about 2 m*M*, a maximum of the first kind appears on both the oxidation and reduction waves which increases in magnitude with increasing $B_{10}H_{13}^-$ concentration. At 25°, polarographic wave heights indicated an apparent diffusion current constant of 2.5 ± 0.2 for the reduction wave and 1.8 ± 0.2 for the oxidation wave. Limiting currents of both waves varied linearly with concentration. In the present work, only the reduction wave was subjected to sufficient study for mechanistic interpretation.

The column height dependence of the reduction wave limiting currents indicated diffusion control[4] over a wide range of conditions (7–25°, 0.5–5 m*M* $B_{10}H_{13}^-$). The persistence of the diffusion-controlled character, which indicates that a chemical reaction preceding the charge-transfer step is unlikely,[2,5] and the magnitude of the diffusion current constant suggest a one-electron reduction of the $B_{10}H_{13}^-$ ion. This is supported by the fact that the reduction wave yielded a linear log [($i_d$ −

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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] E. B. Rupp, D. E. Smith, and D. F. Shriver, *J. Am. Chem. Soc.*, **89**, 5562 (1967).

[3] P. H. Wilks and J. C. Carter, *ibid.*, **88**, 3441 (1966); P. H. Wilks, Ph.D. Thesis, University of Pittsburgh, 1966.

[4] J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press Inc., New York, N. Y., 1966, p 86.

[5] J. Heyrovsky and J. Kuta, ref 4, pp 341–351.

$i)/i^{2/3}]$ *vs.* $E$ plot of 0.6-v slope and a nonlinear log $[(i_d - i)/i]$ *vs.* $E$ plot. Log plots were examined only at lower concentrations where the maximum was absent. These log plots are consistent with an electrode reaction involving a second-order decomposition of the primary product of a fast one-electron, charge-transfer step.[6,7] Thus, the conventional polarographic data suggest a mechanism involving a one-electron reduction of $B_{10}H_{13}^-$ to form the $B_{10}H_{13}^{-2}$ radical dianion which decomposes by a second-order process. The nonlinear log $[(i_d - i)/i]$ *vs.* $E$ plot appears to rule out the possibility of a slow charge-transfer step or an intermediate first-order decomposition of $B_{10}H_{13}^{-2}$ analogous to the first reduction step of $B_{10}H_{14}$.

A typical cyclic voltammogram of a $B_{10}H_{13}^-$ solution is shown in Figure 1. This figure illustrates the cyclic voltammetric pattern obtained after several cycles in a multicycle experiment.[8-10] The reversible couple centered at −0.5 v (waves a and e) corresponds in potential to the polarographic oxidation wave of $B_{10}H_{13}^-$ ($E_{1/2}$ = −0.47 v), while the irreversible reduction at about −2.7 v (wave b) corresponds in potential to the polarographic reduction wave of $B_{10}H_{13}^-$ ($E_{1/2}$ = −2.76 v). The coincidence of the oxidation wave at −0.5 v and the reduction wave at −2.7 v with the polarographic waves of $B_{10}H_{13}^-$, combined with their diffusion-controlled character, indicates that these processes most likely result from direct electrolysis of the bulk electroactive component, $B_{10}H_{13}^-$. This is supported by the observation that both electrode processes can occur independently; *i.e.*, the appearance of waves a and e occurs regardless of whether the potential sweep encompasses wave b, and *vice versa.* Wave a clearly represents reduction (reversible) of the $B_{10}H_{13}^-$ oxidation product. The two remaining oxidation waves (waves c and d) apparently arise from a product or products of the reduction process associated with wave b. Waves c and d do not appear unless wave b is encompassed in the potential sweep. The magnitudes of waves c and d are not reduced, relative to the other waves, by decreasing scan rate and increasing temperature which indicates that the species giving rise to these waves represent "stable" products of the $B_{10}H_{13}^-$ reduction. The cyclic voltammetric evidence that the reduction of $B_{10}H_{13}^-$ is irreversible (wave b) supports the alleged instability of the $B_{10}H_{13}^{-2}$ ion. Unfortunately, the cyclic voltammetric experiments failed to show any evidence of a reoxidation process attributable to $B_{10}H_{13}^{-2}$, so no concrete evidence for $B_{10}H_{13}^{-2}$ is provided. Apparently, the half-life of $B_{10}H_{13}^{-2}$ is much shorter than the period of the fastest triangular wave signal employed (0.1 sec) which is not unreasonable. The existence of $B_{10}H_{13}^{-2}$ as the initial product of the electrode reaction must be inferred from the one-electron character of the reduction and the above-mentioned strong evidence that the $B_{10}H_{13}^-$ ion is the electroactive species.

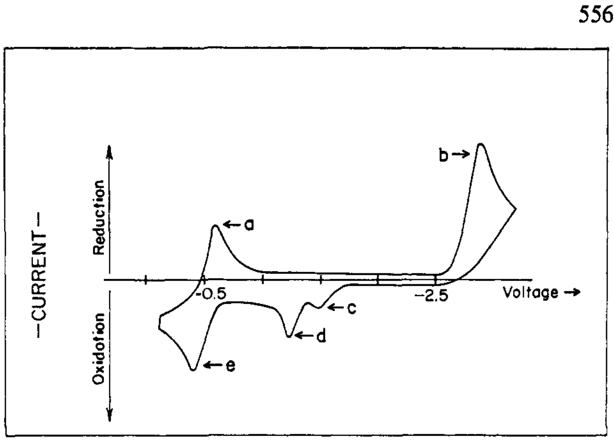

Figure 1. Cyclic voltammogram of $B_{10}H_{13}^-$ (system: 0.74 × $10^{-3}$ *M* $Bu_4NB_{10}H_{13}$, 0.1 *M* TBAP in 1,2-dimethoxyethane, 25°; applied: multicycle triangular wave potential, scan rate = 1.9 v/sec). This figure shows the cyclic voltammetric pattern after application of several triangular wave cycles (approximately steady-state pattern). The ordinate is uncalibrated.

Definite evidence for the existence of $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ as stable products of the $B_{10}H_{13}^-$ reduction is provided by a controlled-potential electrolysis experiment. Complete controlled-potential electrolysis of $Bu_4NB_{10}H_{13}$ solutions at potentials corresponding to the plateau of the polarographic reduction wave (−3.0 v) consumed 1.1 faradays per mole of $B_{10}H_{13}^-$. A polarogram of the resulting solution shows an oxidation wave with a large maximum beginning at −1.4 v and a second oxidation wave with $E_{1/2}$ = −0.5 v. A cyclic voltammogram of the same solution exhibits a pair of erratic oxidation peaks at about −1.4 and −1.2 v, and a reversible couple centered at −0.5 v. The solution exhibits an ultraviolet spectrum with distinct shoulders at 260 and 300 mμ. Addition of $Bu_4NB_{10}H_{15}$ to this solution caused the appearance of a polarographic reduction wave at $E_{1/2}$ = −2.75 v, while the maximum on the polarographic oxidation wave at −1.4 v increased. Finally, at higher concentrations of $Bu_4NB_{10}H_{13}$, a white precipitate formed in the course of the electrolysis which was identified as $(Bu_4N)_2B_{10}H_{14}$ by polarography and infrared spectra. The ultraviolet absorption at 260 mμ exhibited by the solution suggests the existence of $B_{10}H_{12}^{-2}$ as a coproduct with $B_{10}H_{14}^{-2}$. Although a saturated solution of $(Bu_4N)_2B_{10}H_{14}$ shows a small shoulder at this wavelength which may contribute to the observed absorption, it cannot account for the observed intensity. The most likely source of this ultraviolet peak appears to be the $B_{10}H_{12}^{-2}$ ion. The polarographic oxidation waves exhibited by the solution after electrolysis serve as evidence for the presence of $B_{10}H_{12}^{-2}$ and/or $B_{10}H_{14}^{-2}$ but fail to establish that both ions are present due to the similarities in their polarographic characteristics. The most definitive electrochemical evidence indicating that both $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ are products of the $B_{10}H_{13}^-$ reduction is provided by the cyclic voltammograms. Waves c and d of Figure 1 suggest the presence of two stable products which are oxidizable in the vicinity of −1.2 to −1.4 v, the same potential range where the $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ ions are oxidized. We believe these two waves are attributable to $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$, despite the fact that they do not exhibit erratic behavior of the same magnitude[11] which characterizes the corresponding cyclic voltammetric waves produced by authentic $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ solutions. The erratic behavior

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(6) V. Hanus, *Chem. Zvesti,* **8,** 702 (1954).

(7) R. I. Gelb, Ph.D. Thesis, The University of Wisconsin, Madison, Wis., 1966.

(8) A. Sevcik, *Collection Czech. Chem. Commun* , **13,** 349 (1948)

(9) H. Matsuda, *Z. Elektrochem.,* **61,** 489 (1957).

(10) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.,* **84,** 806 (1962).

(11) Waves c and d begin to exhibit erratic behavior at concentrations of $B_{10}H_{13}^-$ of about 5 m*M* or larger.

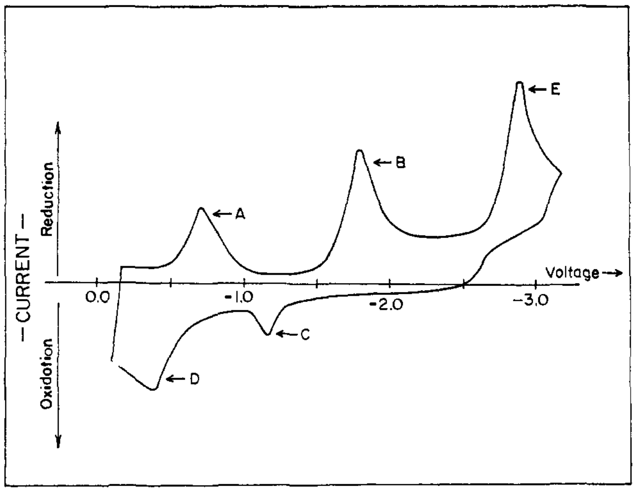

Figure 2. Cyclic voltammogram of decaborane encompassing entire working potential range (system: 0.49 × $10^{-3}$ $M$ $B_{10}H_{14}$, 0.1 $M$ TBAP in 1,2-dimethoxyethane, 25°; applied: multicycle triangular wave potential, scan rate = 5.5 v/sec). This figure shows approximately steady-state pattern as in Figure 1.

of the cyclic voltammetric waves probably originates in convective mass transport (solution stirring) which is also responsible for the polarographic maxima.[12,13] The alleged solution stirring is induced by diffusive mass transport of the depolarizers,[12,13] $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$. Since mass transport conditions associated with these ions differ drastically between the case where they are generated as products of $B_{10}H_{13}^{-}$ reduction and the case where they are transported from the bulk of the solution, a corresponding difference in the magnitude of the stirring effects is not surprising. Finally, the effect of $Bu_4NB_{10}H_{15}$ on the polarographic behavior of the solution obtained by controlled-potential reduction of $B_{10}H_{13}^{-}$ also suggests the existence of $B_{10}H_{12}^{-2}$ as a stable product. The appearance of a polarographic reduction wave attributable to $B_{10}H_{13}^{-}$ ($E_{1/2} = -2.75$ v) upon addition of $B_{10}H_{15}^{-}$ is best interpreted in terms of a reaction between $B_{10}H_{15}^{-}$ and $B_{10}H_{12}^{-2}$. This reaction is discussed at greater length below.

The only reduction mechanism which appears reasonably consistent with the foregoing results for solutions of $Bu_4NB_{10}H_{13}$ is

**Mechanism I**

$$B_{10}H_{13}^{-} + e \rightleftharpoons B_{10}H_{13}^{-2} \tag{Ia}$$

$$2B_{10}H_{13}^{-2} \longrightarrow B_{10}H_{12}^{-2} + B_{10}H_{14}^{-2} \tag{Ib}$$

which corresponds to the over-all reaction

$$2B_{10}H_{13}^{-} + 2e \longrightarrow B_{10}H_{12}^{-2} + B_{10}H_{14}^{-2} \tag{1}$$

Reaction Ia represents a charge-transfer step of sufficient rapidity that Nernstian conditions are maintained in the polarographic experiments. Reaction Ib represents a bimolecular disproportionation of the $B_{10}H_{13}^{-2}$ radical dianion yielding $B_{10}H_{12}^{-2}$ and $B_{10}H_{14}^{-2}$ as stable[14] products.

**Second Reduction Step of Decaborane.** The second polarographic reduction wave of decaborane solutions in 0.1 $M$ TBAP–glyme is characterized by an $E_{1/2}$ of $-2.78 \pm 0.03$ v *vs.* Ag–saturated $AgNO_3$.[2] The wave exhibits a column height dependence which is consistent with a diffusion-controlled process[4] under all conditions studied (7–25° temperature range, 0.5–5 m$M$ concentration range). The apparent diffusion current constant at 25° is $1.3 \pm 0.3$, a value which is only about one-half that expected for a one-electron process.[15] The ratio of the height of the second reduction wave to that of the first wave was $0.55 \pm 0.10$ under all conditions employed. Within experimental uncertainty, the height of the second reduction wave exhibited a linear concentration dependence. This wave yielded a linear plot of log $[(i_d - i)/i^{2/3}]$ *vs.* $E$ of 0.6-v slope, while a log $[(i_d - i)/i]$ *vs.* $E$ plot was nonlinear.

A typical cyclic voltammogram (multicycle, steady-state[8-10]) of decaborane in which the potential sweep encompasses the second reduction wave of $B_{10}H_{14}$ is shown in Figure 2. The significance of waves A, B, and D appears to be the same as indicated earlier (part I).[2] Wave E corresponds in potential to the second polarographic reduction wave of decaborane. The irreversibility of the second reduction step is apparent from the cyclic voltammogram. Wave C is discussed below.

Several factors suggest that electron transfer to $B_{10}H_{13}^{-}$ is responsible for the second decaborane reduction step. The conclusive evidence that $B_{10}H_{13}^{-}$ is a product of the first reduction step, the nearly identical potentials (polarographic $E_{1/2}$'s and cyclic voltammetric peak potentials) associated with the reduction wave of $B_{10}H_{13}^{-}$ and the second reduction wave of decaborane and, finally, the similarities in shape of these waves (log plots), are observations leading to this hypothesis. Other reasonable possibilities such as addition of the second electron to the anion radical

$$B_{10}H_{14}^{-} + e \longrightarrow B_{10}H_{14}^{-2} \tag{2}$$

or onset of a simultaneous transfer of two electrons to the decaborane molecule

$$B_{10}H_{14} + 2e \longrightarrow B_{10}H_{14}^{-2} \tag{3}$$

have been considered. However, one final observation seems to eliminate them from consideration. Because rates of heterogeneous electron-transfer processes depend exponentially on potential,[16] transfer of a second electron at a stage preceding the decomposition of the anion radical, as in reactions 2 and 3, would negate the effects of the chemical decomposition of $B_{10}H_{14}^{-}$ on the limiting current.[17,18] Thus, the second polarographic wave would be expected to have a magnitude consistent with a one-electron process, *i.e.*, a height equal to that of the first wave. For this reason, the fact that the second polarographic reduction wave of decaborane is diffusion controlled, yet only 50–60% as large as the first wave, cannot be accommodated by a reaction scheme involving reactions 2 or 3. This observation is perfectly consistent with a mechanism involving electron transfer to $B_{10}H_{13}^{-}$, in view of the fact that the reaction leading to $B_{10}H_{13}^{-}$ yields an equivalent amount of the electroinactive $B_{10}H_{15}^{-}$ ion.

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(12) J. Heyrovsky and J. Kuta, ref 4, Chapter 19.

(13) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

(14) The term "stable" implies a negligible decomposition over the 2–4-hr time period associated with the most time-consuming experimental observations.

(15) J. Heyrovsky and J. Kuta, ref 4, pp 97–98.

(16) J. Heyrovsky and J. Kuta, ref 4, Chapter 14.

(17) J. Koutecky in "Proceedings of the First International Polarographic Congress, Prague," Vol. 1, Prirodoved. vydavatelstvi, Prague, 1951, p 826.

(18) A. A. Vlcek, *Collection Czech. Chem. Commun.*, **22**, 1736 (1957).

If one accepts electron transfer to $B_{10}H_{13}^-$ as the origin of the second wave, then decomposition of the reduction product, $B_{10}H_{13}^{-2}$ (reaction Ib), is expected to follow the electron-transfer step on the basis of evidence presented above. This assumption receives some confirmation in the fact that the second polarographic reduction wave of decaborane exhibits a linear log $[(i_d - i)/i^{2/3}]$ plot of 0.6-v slope which agrees with the behavior of the $B_{10}H_{13}^-$ reduction wave and is consistent with a disproportionation of the initial reduction product, $B_{10}H_{13}^{-2}$.

Although the foregoing results strongly suggest that reactions Ia and b are operative in the second reduction step of decaborane, other evidence indicates that the reaction path is complicated by several additional chemical reactions coupled to the charge-transfer step. The more varied $B_{10}$ species present in the decaborane reduction process give rise to the additional chemical reactions which could not occur in the reduction of $B_{10}H_{13}^-$ solutions where the distribution of $B_{10}$ compounds is simpler. Evidence has already been given for a rapid reaction between $B_{10}H_{14}$ and $B_{10}H_{14}^{-2}$ which presumably involves the steps.[2,19,20]

$$B_{10}H_{14} + B_{10}H_{14}^{-2} \rightleftarrows 2B_{10}H_{14}^- \qquad (4)$$

$$2B_{10}H_{14}^- \longrightarrow B_{10}H_{13}^- + B_{10}H_{15}^- \qquad (5)$$

Thus, in the electrolytic reduction process one expects that unreacted $B_{10}H_{14}$ can react with the reduction product, $B_{10}H_{14}^{-2}$, through reactions 4 and 5. A similar reaction between $B_{10}H_{14}$ and $B_{10}H_{12}^{-2}$ was also investigated in this work. Upon mixing equivalent amounts of $B_{10}H_{14}$ and $Na_2B_{10}H_{12}$, a yellow solution which exhibited polarographic waves characteristic of a $Bu_4NB_{10}H_{13}$ solution formed immediately. The magnitude of the polarographic wave supports the stoichiometry

$$B_{10}H_{14} + B_{10}H_{12}^{-2} \longrightarrow 2B_{10}H_{13}^- \qquad (6)$$

That these chemical reactions of the reduction products, $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$, with decaborane play a role in the mechanism of the second decaborane reduction step is confirmed by cyclic voltammetric evidence. A comparison of Figures 1 and 2 shows that the oxidation processes in the vicinity of $-1.2$ to $-1.4$ v differ substantially in these two cases. Two oxidation waves appear in this potential range in the cyclic voltammogram of $B_{10}H_{13}^-$ solutions (waves c and d, Figure 1) while only one arises in the $B_{10}H_{14}$ cyclic voltammogram (wave C, Figure 2). Unlike waves c and d of Figure 1, wave C of Figure 2 shows characteristics attributable to a transient intermediate.[2] This fact would be consistent with an assignment of this wave to the oxidation of either $B_{10}H_{14}^{-2}$, $B_{10}H_{12}^{-2}$, or $B_{10}H_{14}^-$. Each compound is reduced in this potential range, and in view of reactions 4–6 and the previously noted instability of $B_{10}H_{14}^-$, each anion is expected to be unstable under the experimental conditions. Regardless of the identity of the species giving rise to this wave,[21] one must postulate a rapid decomposition of both $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ in the presence of $B_{10}H_{14}$ to accommodate the difference between the oxidation waves under consideration in Figures 1 and 2. Reactions 4–6 fulfill this requirement. Additional cyclic voltammetric evidence for these reactions is provided by the fact that inclusion of wave E (Figure 2) in the potential sweep tends to decrease the magnitude of wave B (the first reduction step). The effect becomes particularly pronounced when the anodic limit of the potential sweep does not exceed potentials much more positive than the foot of wave B. Under such conditions wave B is virtually undetectable after a few cycles as shown in Figure 3. This behavior is typical of a mechanism in which the product of the second reduction step (wave E) reacts chemically with the species being reduced at the first step (wave B), the type of process which would result from reactions 4–6. The attenuation of wave **B** is enhanced by maintaining the anodic limit of the potential sweep as close to the foot of wave B as possible because this minimizes the fraction of the triangular wave period during which neither decaborane reduction step occurs and unreacted decaborane can diffuse from the bulk of the solution to the electrode surface to contribute to wave B during the following cycle. These effects on the cyclic voltammograms indicate that reactions 4–6 are very rapid; *i.e.*, their half-lives are less than the period of the applied triangular wave potential signal. The fact that the limiting current of the second polarographic reduction wave is diffusion controlled also suggests that these reactions are "rapid."

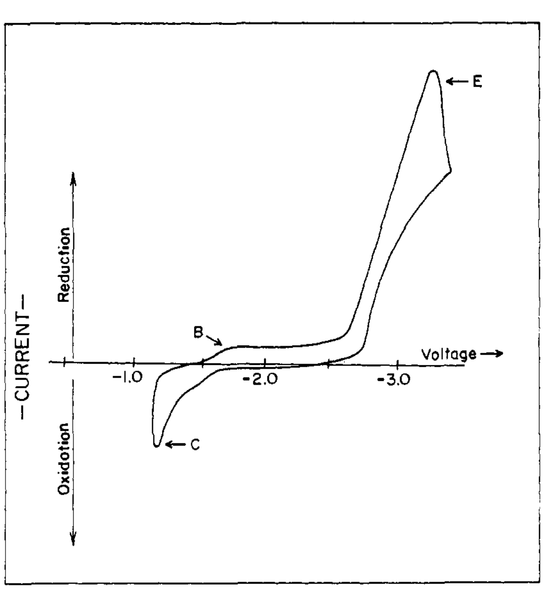

Figure 3. Cyclic voltammogram of decaborane showing attenuation of first reduction wave by inclusion of second step (system: $1.0 \times 10^{-3}$ *M* $B_{10}H_{14}$, 0.1 *M* TBAP in 1,2-dimethoxyethane, 25°; applied: multicyclic triangular wave potential; scan rate = 5.5 v/sec). This figure shows approximately steady-state pattern as in Figure 1.

Although reactions 4–6 appear to play a significant role in the mechanism of the second reduction step of decaborane, it should be noted that they have no effect on the over-all stoichiometry of this process. The

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(19) (a) R. H. Toeniskoetter, Ph.D. Thesis, St. Louis University, St. Louis, Mo., 1958; (b) 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.

(20) No evidence, pro or con, is available on whether the less stable radical anion, $\{B_{10}H_{14}^-\}$, which was proposed to explain electrochemical data,[2] is involved in this chemical process.

(21) The erratic behavior of the corresponding cyclic voltammetric oxidation wave of authentic $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ precludes a definitive assignment of wave C of Figure 2.

sum of reactions Ia, Ib, and 4–6 is

$$2B_{10}H_{14} + 2e \rightleftharpoons B_{10}H_{13}^- + B_{10}H_{15}^- \tag{7}$$

which is the over-all process associated with the first reduction step. The reaction sequence in question simply represents an alternative path for the first electron transfer whereby $B_{10}H_{14}$ is reduced chemically by the products of $B_{10}H_{13}^-$ reduction. One still expects the net reaction at the second reduction step to correspond to the reduction of $B_{10}H_{13}^-$ in accord with reaction 1. Removal of $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ by reactions 4–6 cease when the $B_{10}H_{14}$ concentration in the diffusion layer is rendered negligible by chemical and electrochemical reduction, permitting the stoichiometry of reaction 1 to manifest itself. Thus, provided transfer of the second electron entails only reactions Ia, Ib, and 4–6, the over-all stoichiometry of the reduction of decaborane at potentials of the second reduction step will be the sum of reactions 1 and 7

$$4B_{10}H_{14} + 6e \rightleftharpoons B_{10}H_{12}^{-2} + B_{10}H_{14}^{-2} + 2B_{10}H_{15}^- \tag{8}$$

This corresponds to a net transfer of 1.5 electrons per decaborane molecule which is in reasonable accord with the finding that the second polarographic reduction wave of decaborane is only about 0.5–0.6 that expected for a one-electron transfer. The rate processes corresponding to reactions Ia, Ib, and 4–6 also appear to adequately explain the various other aspects of the polarographic and cyclic voltammetric response of this system.

The influence of an additional chemical reaction on these systems becomes apparent when we compare data on controlled-potential electrolysis with the above results. When the solution resulting from exhaustive controlled-potential electrolysis of decaborane at $-2.0$ v (first reduction step) was subjected to further electrolysis at $-3.0$ v (second reduction step), an additional $1.2 \pm 0.1$ faradays per mole of decaborane was consumed, or a total of 2.2 faradays for the stepwise reduction. Similarly, exhaustive controlled-potential electrolysis of a fresh decaborane solution at $-3.0$ v consumed 2.0 faradays per mole of decaborane. In both cases, the electrochemical and spectral characteristics of the solutions resulting from electrolysis at $-3.0$ v showed evidence for only the $B_{10}H_{14}^{-2}$ ion, some of which precipitated as $(Bu_4N)_2B_{10}H_{14}$ allowing unequivocal identification by infrared. In other words, regardless of whether one effects complete electrolysis of decaborane at $-3.0$ v or in a stepwise manner, first at $-2.0$ v and then at $-3.0$ v, the same product is obtained and a total of two electrons per decaborane molecule is consumed. Thus, the over-all reaction under controlled-potential electrolysis conditions appears to be

$$B_{10}H_{14} + 2e \longrightarrow B_{10}H_{14}^{-2} \tag{9}$$

This result can be reconciled with the polarographic and cyclic voltammetric results by postulating a chemical reaction in which the electroinactive $B_{10}H_{15}^-$ ion is converted to a reducible $B_{10}$ molecule so that all of the original $B_{10}$ material can accept a second electron. This reaction must occur at a rate which is too slow to contribute significantly to the over-all reaction in the polarographic time scale (2–10 sec), but rapid enough to proceed essentially to completion in the time required for exhaustive controlled-potential electrolysis (1–2 hr). The most likely possibility appears to be the reaction

$$B_{10}H_{12}^{-2} + B_{10}H_{15}^- \longrightarrow B_{10}H_{13}^- + B_{10}H_{14}^{-2} \tag{10}$$

which will enable uptake of an additional 0.5 electron per $B_{10}$ molecule by formation of reducible $B_{10}H_{13}^-$ from inactive $B_{10}H_{15}^-$. Evidence that such a reaction proceeds at a reasonable rate is provided by the appearance of a small $B_{10}H_{13}^-$ polarographic reduction wave upon adding $B_{10}H_{15}^-$ to a solution allegedly containing $B_{10}H_{14}^{-2}$ and $B_{10}H_{12}^{-2}$ which was obtained by exhaustive electrolysis of $Bu_4NB_{10}H_{13}$. The formation of $B_{10}H_{13}^-$ also serves as additional evidence for the presence of $B_{10}H_{12}^{-2}$ as a product of the $B_{10}H_{13}^-$ reduction. Since the solution was already saturated in $(Bu_4N)_2B_{10}H_{14}$ prior to addition of $B_{10}H_{15}^-$, confirmation of its formation in the reaction of $B_{10}H_{15}^-$ and $B_{10}H_{12}^{-2}$ was not possible.

The tendency of the second polarographic reduction wave of decaborane to exhibit a magnitude slightly exceeding one-half that of the first wave may be taken as an indication that reaction 10 is contributing slightly to the polarographic results.[22] Thus, the half-life associated with reaction 10 may be no more than two to five times the polarographic drop life.

Attempts to confirm the foregoing results regarding reaction 10 by mixing $Na_2B_{10}H_{12}$ and $(Bu_4N)B_{10}H_{15}$ solutions were inconclusive due to sodium ion interference with the small polarographic reduction wave of $B_{10}H_{13}^-$. Because of spectral similarities of the compounds involved, ultraviolet measurements did not afford further information on this reaction.

To summarize, the experimental evidence is best accommodated by a reaction mechanism for the decaborane reduction at potentials of the second reduction step which involves the reactions shown in Mechanism II. Reactions IIa–IIe simply represent the combination of mechanism I (part I)[2] for the first electron addition and the basic steps proposed for the reduction of $B_{10}H_{13}^-$. Reactions IIf–h represent chemical interactions which could not occur in the reduction of $B_{10}H_{13}^-$ solutions due to the simpler distribution of $B_{10}$ species. Reactions labeled "fast" are alleged to have half-lives comparable with or shorter than the periods of the triangular wave potentials employed in the cyclic

**Mechanism II**

$$B_{10}H_{14} + e \longrightarrow \{B_{10}H_{14}^-\} \text{ (first electron addition)} \tag{IIa}$$

$$\{B_{10}H_{14}^-\} \xrightarrow{\text{fast}} B_{10}H_{14}^- \tag{IIb}$$

$$2B_{10}H_{14}^- \xrightarrow{\text{fast}} B_{10}H_{13}^- + B_{10}H_{15}^- \tag{IIc}$$

$$B_{10}H_{13}^- + e \longrightarrow B_{10}H_{13}^{-2} \text{ (second electron addition)} \tag{IId}$$

$$2B_{10}H_{13}^{-2} \xrightarrow{\text{fast}} B_{10}H_{14}^{-2} + B_{10}H_{12}^{-2} \tag{IIe}$$

$$B_{10}H_{14} + B_{10}H_{14}^{-2} \xrightarrow{\text{fast}} 2B_{10}H_{14}^- \tag{IIf}$$

$$B_{10}H_{14} + B_{10}H_{12}^{-2} \xrightarrow{\text{fast}} 2B_{10}H_{13}^- \tag{IIg}$$

$$B_{10}H_{12}^{-2} + B_{10}H_{15}^- \xrightarrow{\text{slow}} B_{10}H_{13}^- + B_{10}H_{14}^{-2} \tag{IIh}$$

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[22] The expected effect of such a process on the polarographic mercury column height dependence[5] was not observed in this work. However, it is quite possible that a slight kinetic effect on the column height dependence was masked by experimental uncertainty which was larger than usual due to the erratic behavior of the dropping mercury electrode at the very cathodic potentials of the second reduction step.

voltammetric experiments, *i.e.*, much shorter than the polarographic drop life. The label "slow" implies a reaction with a half-life which is somewhat longer than the polarographic drop life, but much shorter than the time required for controlled-potential electrolysis. The existence of a "slow" chemical step complicates matters in that a statement of the effective over-all reaction differs for the polarographic and controlled potential electrolysis time scales. For polarographic and cyclic voltammetric conditions, reactions IIa–g are important and the over-all stoichiometry is given by reaction 8. For the times involved in controlled-potential electrolysis, all reactions in Mechanism II are important and the over-all process simplifies to reaction 9.

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# A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls[1,2]

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**Abstract:** The phosphorus-31 chemical shifts are reported for 25 compounds of the type $(R_nPh_{3-n}P)M(CO)_5$, where R is alkyl, *n* is 0, 1, 2, or 3, and M is Cr, Mo, or W. The $^{183}W-^{31}P$ spin-spin coupling is observed for all the tungsten compounds, and a linear correlation exists between these coupling constants and the carbonyl stretching frequencies in the respective compounds. In addition, the novel compound *trans*-tributylphosphinetriphenylphosphinemolybdenum tetracarbonyl is described. Its $^{31}P$ nmr spectrum exhibits phosphorus–phosphorus spin-spin coupling.

It has become evident in the past few years that $^{31}P$ nmr studies can be of great value in the investigation of bonding and structure in coordination compounds. In the first paper in this field Meriwether and Leto[4] outlined various effects that may influence the chemical shift of phosphorus. Subsequent papers[5–18] have dealt with these effects and additional problems such as the influence of valency on chemical shift[11] or the effect of *cis–trans* isomerism on heavy metal–phosphorus coupling constants.[5,14,15,18]

In an attempt to provide additional pertinent information, monosubstituted tertiary phosphine complexes of the group VI metal carbonyls were investigated. These compounds are relatively easy to prepare and allow comparisons of variation in chemical shift with changing atomic weight of the metal while the valency and stereochemistry remain constant. The effect of changing the organic substituents on phosphorus can also be noted. In addition, useful information can be obtained from $^{183}W-^{31}P$ spin–spin coupling constants.

## Experimental Section

The phosphorus-31 nmr measurements of concentrated dichloromethane solutions in 15-mm tubes were recorded with a Varian Associates DP60 nmr spectrometer. Calibrations were made using a 2-mm tube of 85% phosphoric acid inside the 15-mm sample tube. Chemical shifts are accurate to ±0.5 ppm and phosphorus–tungsten coupling constants to ±8 cps. Dilution of the solutions caused no noticeable chemical shift changes. Addition of excess tertiary phosphine to the solution of a complex compound resulted in an extra peak for the uncomplexed ligand with the same chemical shift as the pure ligand and no change in chemical shift of the complexed phosphine. This indicates that ligand exchange is not rapid enough to cause chemical shift averaging of complexed and free ligand. Several test solutions of the complexes were allowed to stand in air for 1 day. The nmr spectrum remained identical after this period. This indicates that paramagnetic impurities which might form on decomposition of the compounds do not noticeably affect the chemical shifts.

Proton nmr spectra were recorded of approximately 20% dichloromethane solutions with a Varian Associates A-60A spectrometer using tetramethylsilane as an internal reference.

The infrared spectra of the carbonyl region were obtained from cyclohexane solutions of the compounds with a Perkin-Elmer Model 621 double-beam spectrometer using a sodium chloride cell with sample thickness of 0.012 mm. The intense bands are accurate to $\pm 1\ cm^{-1}$ and the weak bands to about $\pm 5\ cm^{-1}$.

Microanalyses were performed by Galbraith Laboratories of Knoxville, Tenn., Midwest Microlabs of Indianapolis, Ind., and Dr. Franz Kasler of the University of Maryland.

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