Table VIII. Hydrogenation of Unsaturated Nitriles[a]

Expt	Catalyst (mmoles)	Nitrile (mmoles)	Glpc analysis (%)
1	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	$CH_2{=}CHCN$ (90)	CH_3CH_2CN (94.4) $CH_2{=}CHCN$ (5.6)
2	$PtCl_2(PPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	$CH_2{=}CHCN$ (90)	CH_3CH_2CN (94.0) $CH_2{=}CHCN$ (6.0)
3	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	$ClCH{=}CHCN$ (90)	No hydrogenation
4	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	$CH_2{=}CCl(CN)$ (90)	No hydrogenation
5	$PtCl_2(AsPh_3)_2$ (1.5) + $SnCl_2 \cdot 2H_2O$ (15.0)	$CH_3CH{=}CHCN$ (90)	No hydrogenation

[a] At 80° under 55 atm of hydrogen in CH_2Cl_2 (150 ml) for 5 hr.

stituent attached to the olefin, a number of unsaturated nitriles were subjected to hydrogenation experiments. The results for acrylonitrile, α-chloroacrylonitrile, and a mixture of *cis*- and *trans*-β-chloroacrylonitrile are presented in Table VIII.

The catalyst composed of $PtCl_2(MPh_3)_2$ and $SnCl_2 \cdot 2H_2O$ (M = P, As) is a good catalyst for the hydrogenation of the double bond in $CH_2{=}CHCN$. The cyanide group remains intact. However, both $CH_2{=}CCl(CN)$ and *cis*- and *trans*-$CHCl{=}CHCN$ remain unreduced under the same experimental conditions. Since crotononitrile, $CH_3CH{=}CHCN$, also fails to hydrogenate, this effect is likely to arise from steric rather than electronic considerations. Substitution of groups on the α- and β-carbon atoms of acrylonitrile may be sufficient to prevent approach of a platinum–hydride species to the double bond so that subsequent transfer of hydrogen cannot occur.

Although there is some evidence for coordination of acrylonitrile to the platinum–tin catalyst, no complexes of definite composition could be isolated.

Acknowledgment. The authors wish to acknowledge the help of the Gulf Oil Corporation in the purchase of equipment for this research.

Electrochemistry of Open-Cage Boron-10 Species[1a]

J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle[1b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received May 8, 1968*

Abstract: The electron-transfer and proton-transfer reactions which interrelate the open-cage B-10 hydrides in acetonitrile have been determined. The electrochemical reduction of decaborane(14) in acetonitrile yields the dianion, $B_{10}H_{14}^{2-}$, in an irreversible two-electron step. In a similar manner, $B_{10}H_{14}$ is produced by the oxidation of $B_{10}H_{14}^{2-}$. In either case, the kinetically important reaction following charge transfer is a proton transfer between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$. The rate of this reaction is approximately $5 \times 10^4 \, M^{-1} \, sec^{-1}$ at 24 ± 2°. The over-all products of either the reduction of $B_{10}H_{14}$ or the oxidation of $B_{10}H_{14}^{2-}$ are $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ in an equimolar mixture as confirmed by ^{11}B nmr analysis. This mixture constitutes a "one-electron" oxidation state between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$. The formal reduction potential for the $B_{10}H_{14}|B_{10}H_{14}^{2-}$ couple is -0.78 ± 0.02 V *vs.* sce. The electrochemical behavior of $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ in acetonitrile is compared with that in 1,2-dimethoxyethane. A significant solvent effect on the oxidation-reduction mechanistic pathways is indicated.

The electrochemical behavior of decaborane(14) in nonaqueous solvents and the electron-transfer and proton-transfer reactions which interrelate the open-cage B-10 species in acetonitrile have been determined and compared to the behavior in monoglyme. Mechanisms for the reduction of $B_{10}H_{14}$ and the oxidation of $B_{10}H_{14}^{2-}$ are proposed, and the chemical and electrochemical kinetic parameters have been determined in acetonitrile at room temperature. The results of this study are of significance to an understanding of redox reactions of the open-cage B-10 compounds.

Previous work on the reduction of decaborane includes that of Toeniskoetter,[2] who carried out sodium reductions in ammonia, ether, and tetrahydrofuran, the work of Hough and Edwards,[3] who carried out sodium amalgam reductions in ether, and that of Rupp, Smith, and Shriver,[4] who investigated the electrochemical reduction in monoglyme (1,2-dimethoxyethane). The sodium reductions[2,3] give a mixture of products, including $Na_2B_{10}H_{14}$ and $NaB_{10}H_{13}$, which varies with solvent and reaction time. This paper reports on experiments which further characterize the reduction of decaborane. Quantitative single-sweep cyclic voltammetry and double-potential-step electrochemical measurements were carried out over a wide time scale. Although this work is in qualitative agree-

---

(1) (a) This work was supported by grants from the Research Corporation, the Petroleum Research Fund, and the National Science Foundation. (b) Phillips Petroleum undergraduate research fellow.

(2) R. H. Toeniskoetter, Ph.D. Thesis, St. Louis University, 1958.

(3) M. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 184.

(4) (a) E. B. Rupp, D. E. Smith, and D. F. Shriver, *J. Am. Chem. Soc.*, **89**, 5562 (1967); (b) *ibid.*, **89**, 5568 (1967).

ment with that of Rupp, *et al.*, regarding the net reactions,[4a] the results have forced us to different conclusions regarding the reduction mechanism in acetonitrile and indicate a significant solvent effect on the mechanistic oxidation–reduction pathways of the open-cage B-10 species.

Experimental Section

Materials. Decaborane(14), obtained from the Callery Chemical Co., was sublimed prior to use. Tetraethylammonium tetradecahydrodecaborate(2−), $[(C_2H_5)_4N]_2B_{10}H_{14}$ (confirmed by ^{11}B nmr spectrum[5]), was obtained by metathesis upon the addition of a $K_2B_{10}H_{14}$[5] solution to a solution of tetraethylammonium bromide. Tetraethylammonium tridecahydrodecaborate(1−) (confirmed by ^{11}B nmr spectrum[6]) and $(C_2H_5)_4NB_{10}H_{15}$ (confirmed by ^{11}B nmr spectrum[7]) were prepared immediately before each experiment by the addition of solutions of $NaB_{10}H_{13}$[8] and $NaB_{10}H_{15}$,[7] respectively, to saturated solutions of tetraethylammonium bromide. All samples were dried and stored *in vacuo* prior to use in an experiment.

Practical grade acetonitrile was distilled rapidly over P_4O_{10} (twice) and then slowly distilled over CaH_2. Monoglyme was distilled from $LiAlH_4$ immediately before use. Singly distilled dichloromethane was used. Tetraethylammonium perchlorate (TEAP) was prepared from the bromide and lithium perchlorate and recrystallized from water several times until the washings gave a negative test for bromide. It was dried *in vacuo* prior to use. "Polarographic grade" tetrabutylammonium perchlorate (TBAP), Southwestern Analytical Chemicals, was used without recrystallization. Diethylanilinium perchlorate (DEAP) was prepared following the literature directions.[9] Triply distilled mercury was used. All measurements were made at room temperature (24 ± 2°).

The above boron hydrides were found to be stable in acetonitrile under the conditions of the electrochemical experiments. This was confirmed by the electrochemical behavior and ^{11}B nmr spectral analyses.

Instruments. Most of the electrochemical measurements at stationary electrodes were performed using a potentiostat which was similar to that described by Brown, *et al.*[10] The instrument employed solid-state operational amplifiers (Philbrick Models PP35AU and PP65AU), had an output capability of 100 mA (with booster amplifiers), and had provision for compensation for most of the *iR* drop between the working electrode and the tip of the reference electrode. As reported by others,[10,11] the latter feature was found to be a necessity in obtaining quantitative electrochemical measurements at short times in high-resistance nonaqueous solutions. The square or triangular voltage signal which was applied to the working electrode was supplied by a Hewlett-Packard Model 3300A function generator equipped with a Model 3302A plug-in unit. The current–time or current–potential curves were recorded either on a Varian Model F110 XY recorder or on a Tektronix Model 564 storage oscilloscope and photographed with a Tektronix Model C-27 oscilloscope camera. Some of the electrochemical measurements were performed using apparatus which has been described elsewhere.[12,13] The constant-potential coulometer was based on a design of Underkofler and Shain[14] and employed a Heath Model EUW-19A operational amplifier module. The preparative-scale constant-potential electrolyses employed a Lambda Model LE102-FM regulated power supply.

Boron-11 nuclear magnetic resonance spectra were obtained at 32.1 MHz using a Varian Associates HA-100 spectrometer. Chemical shifts were determined relative to $BF_3 \cdot O(C_2H_5)_2$ (internal capillary tube standard). Electron spin resonance experiments were performed on a Varian Model V4500 X-band spectrometer employing 100-kc field modulation.

Electrochemical Apparatus and Techniques. A hanging mercury drop electrode (hde), which was prepared by hanging one to three drops of mercury on a mercury-plated platinum surface, was used in this study. The drops were collected from a dropping mercury electrode capillary, and the area of the hde was calculated from the weight of 50 drops. All results reported in this paper were obtained on new electrode surfaces. The reference electrode was an aqueous sce which was separated from the working electrode compartment by a fine porosity glass frit and a salt bridge containing either the solution under investigation or a solution of the supporting electrolyte. All potentials are reported *vs.* aqueous sce. The distance between the hde and the edge of the glass frit was *ca.* 5–10 mm. The counter electrode was a large platinum foil which was immersed directly in the test solution. The cell, which was similar to a design of Streuli and Cooke,[15] allowed nitrogen to be passed through a medium porosity glass frit which constituted the bottom of the electrolysis cell. A constant pressure of nitrogen on the frit, which prevented leakage of solution through the frit without passage of nitrogen through the solution, was easily obtained by manipulation of a three-way stopcock which allowed the nitrogen stream to pass over the solution during the measurement. The nitrogen stream was presaturated either with solvent or a solution identical with the test solution. The procedure used for the coulometric experiments was standard. Techniques for *in situ* electrolysis in an esr cavity have been described.[16]

The constant-potential electrolyses were carried out at a large platinum mesh working electrode (estimated area, *ca.* 60 cm²). The working electrode compartment of an H-cell contained 50 ml of solution which was 0.1–0.4 *M* in supporting electrolyte and *ca.* 0.05 *M* in the boron hydride. The electrolysis solution was separated from the carbon-rod counter electrode by a salt bridge containing supporting electrolyte. The electrolyses were interrupted periodically, and the solution in the salt bridge renewed to prevent contamination by the counter-electrode reaction products. Nitrogen, presaturated with solvent, was passed through the working electrode compartment continuously. When the current had decayed to a small fraction of the initial current, the electrolysis was stopped; the solution was drained out of the cell and immediately transferred to a glove bag filled with a dry nitrogen atmosphere. Deaerated ether (100–150 ml) was added to precipitate the TEAP and the precipitate was carefully washed with ether to remove the boron hydride salts. The filtrate (200–250 ml) was concentrated to 1–2 ml under vacuum, transferred to a nmr sample tube, and immediately subjected to high-resolution ^{11}B nmr analysis. The products were identified by comparison with authentic samples of known tetraethylammonium boron hydride salts in acetonitrile. The nmr absorption spectra were integrated using a planimeter to ascertain relative product abundances.

The chemical reductions were carried out with the sodium salt of the biphenyl radical anion using standard techniques.[17] Addition of $B_{10}H_{14}$ immediately discharged the blue color of the biphenyl radical anion. The solution was concentrated and subjected to high-resolution ^{11}B nmr analysis.

Results and Discussion

Reduction of $B_{10}H_{14}$. The single-cycle current–potential (*i–E*) curves for the reduction of decaborane in acetonitrile (or dichloromethane) are in qualitative agreement with those reported in monoglyme by Rupp, *et al.*[4a] (see figure 2 of ref 4a). In acetonitrile, the initial cathodic sweep exhibits two peak-shaped waves at −1.00 and −2.06 V *vs.* sce (sweep rate, 0.2 V/sec). The reduction mechanism of the second wave, which has been studied previously,[4b] was not investigated in this work. The peak width ($E_{p/2} - E_p$) of the wave at −1.0 V is equal to 55 ± 5 mV from 0.06 to 100 V/sec. At slow sweep rates, a new redox couple is evident in the *i–E* curve at *ca.* +0.2 V. This one-electron re-

---

(5) E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

(6) J. A. Slater and A. D. Norman, unpublished observations.

(7) F. N. Tebbe and R. Schaeffer, *Inorg. Chem.*, **3**, 1638 (1964).

(8) H. Schroeder, J. R. Reiner, and T. A. Knowles, *ibid.*, **2**, 390 (1963).

(9) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

(10) E. R. Brown, T. G. McCord, D. E. Smith, and D. D. DeFord, *Anal. Chem.*, **38**, 1119 (1966).

(11) G. Lauer and R. A. Osteryoung, *ibid.*, **38**, 1106 (1966).

(12) J. R. Alden, J. Q. Chambers, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

(13) C. A. Chambers and J. Q. Chambers, *J. Am. Chem. Soc.*, **88**, 2922 (1966).

(14) W. L. Underkofler and I. Shain, *Anal. Chem.*, **35**, 1778 (1963).

(15) C. A. Streuli and W. D. Cooke, *ibid.*, **26**, 963 (1954).

(16) R. N. Adams, *J. Electroanal. Chem.*, **8**, 515 (1964).

(17) B. Pecherer, C. M. Gambrill, and G. W. Wilcox, *Anal. Chem.*, **22**, 311 (1950); N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

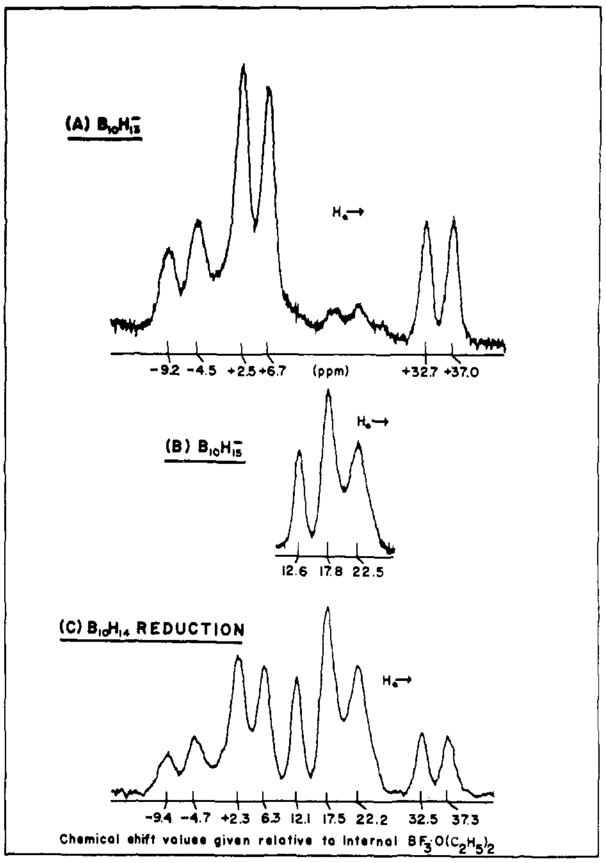

Figure 1. ^{11}B nmr analysis of electrolysis products at 32.1 Mc/sec: (A) $(C_2H_5)_4NB_{10}H_{13}$ in CH_3CN, (B) $(C_2H_5)_4NB_{10}H_{15}$ in CH_3CN, (C) $B_{10}H_{14}$ electrolysis products. See text for details.

versible couple ($E_p^a - E_p^c = 60$ mV[18,19]) is identical with the cyclic voltammogram obtained for an authentic sample of $(C_2H_5)_4NB_{10}H_{13}$ in acetonitrile and is presumably due to the oxidation of $B_{10}H_{13}^-$ (eq 1).[4a]

$$B_{10}H_{13}^- \rightleftharpoons B_{10}H_{13}\cdot + e^- \qquad (1)$$

As the sweep rate is increased, a new oxidation wave of an intermediate in the reduction process appears in the *i–E* curve at −0.6 V, and the magnitude of the $B_{10}H_{13}^-$ oxidation wave decreases. At the fastest sweep rates employed in this investigation, the magnitude of this new oxidation wave approaches the peak height of the main cathodic wave at −1.0 V. When the decaborane concentration is increased, the intermediate is relatively less prominent in the *i–E* curves. This behavior is consistent with removal of the intermediate from the diffusion layer by a second-order process. The nature of the intermediate and its removal are discussed below.

Coulometric analysis of 1–4 m*M* solutions of $B_{10}H_{14}$ at potentials between −1.2 and −1.5 V gave an *n* value of 1.1 ± 0.1 electrons per $B_{10}H_{14}$ molecule. The diffusion coefficient calculated from the peak height and the peak width[20] and from the Cottrell equation[21] is 3.3 ± 0.1 × 10^{-5} cm²/sec in acetonitrile. (This value is the average of three sets of measurements by three different workers over a 10-month period. The confidence interval represents the range of the three results.) The diffusion coefficient of decaborane in monoglyme was found to be 1.6 × 10^{-5} cm²/sec, in good agreement with the value previously reported.[4a]

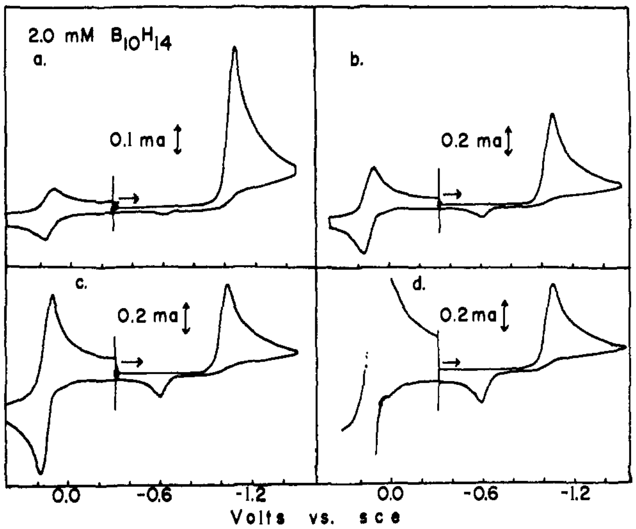

Figure 2. Effect of addition of $(C_2H_5)_4NB_{10}H_{13}$ on the cyclic voltammogram of 2.0 × 10^{-3} *M* $B_{10}H_{14}$–0.1 *M* TEAP in acetonitrile: (a) no $B_{10}H_{13}^-$ added, (b) 2 × 10^{-3} *M*, (c) 6 × 10^{-3} *M*, and (d) 14 × 10^{-3} *M* $B_{10}H_{13}^-$ (sweep rate, 1.0 cps; hde area, 0.063 cm²).

Product identification was established unequivocally by ^{11}B nmr spectral analysis of the electrolysis products of 0.2–0.5-g samples of decaborane. The results of a typical experiment are shown in Figure 1. The spectrum of the products is clearly the superposition of the spectra of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$. Integration of the peak areas gives a 1:1 ratio of intensities. A similar product spectrum was obtained when the electrolysis was carried out in monoglyme and when the reduction was carried out chemically using the sodium salt of the biphenyl radical anion as a reducing agent. Thus the over-all reduction mechanism is given by

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

The $B_{10}H_{15}^-$ species was found to be electroinactive at mercury in acetonitrile which accounts for the lack of a $B_{10}H_{15}^-$ peak in the cyclic voltammograms. Although these conclusions regarding the over-all reaction are the same as those of Rupp, *et al.*,[4a] for monoglyme solutions, the ^{11}B nmr data presented here provide a notably more direct and unequivocal demonstration of the product, $B_{10}H_{15}^-$.

Addition of the $(C_2H_5)_4NB_{10}H_{13}$ salt to the $B_{10}H_{14}$ solution stabilizes the intermediate wave in the *i–E* curves. This experiment is shown in Figure 2. As the concentration of $B_{10}H_{13}^-$ is increased (a–d of Figure 2), the oxidation wave at −0.6 V becomes more prominent, and of course, the $B_{10}H_{13}^-$ oxidation wave at +0.2 V increases. At the highest $B_{10}H_{13}^-$ to $B_{10}H_{14}$ ratio examined, a 7:1 molar ratio, the oxidation wave of the intermediate was clearly evident in the *i–E* curves at sweep rates of 0.02 V/sec. Addition of the $(C_2H_5)_4NB_{10}H_{15}$ salt to the solution had *no effect* on the lifetime of the intermediate. Evidently, the intermediate species is in equilibrium with $B_{10}H_{13}^-$ on the time scale of the electrochemical experiment, but not with the stable form of $B_{10}H_{15}^-$.

---

[18] The criterion of reversibility used here is that the anodic and cathodic peak potentials (E_p^a and E_p^c) are separated by *ca.* 60/*n* mV; see ref 19.

[19] R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).

[20] Reference 19, eq 47 and 52.

[21] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, p 60.

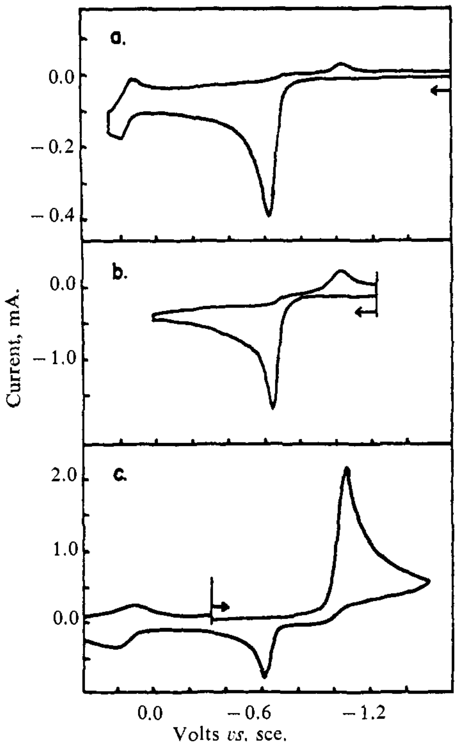

Figure 3. Cyclic voltammograms of $B_{10}H_{14}^{2-}$ and $B_{10}H_{14}$ in 0.1 *M* TEAP–acetonitrile (electrode area, 0.063 cm^2): (a) 2.0 × 10^{-3} *M* $B_{10}H_{14}^{2-}$, sweep rate, 4.0 V/sec; (b) 2.0 × 10^{-3} *M* $B_{10}H_{14}^{2-}$; sweep rate, 24 V/sec; (c) 2.0 × 10^{-3} *M* $B_{10}H_{14}$; sweep rate, 40 V/sec.

Oxidation of $B_{10}H_{14}^{2-}$. The characteristics of the electrochemical oxidation of $B_{10}H_{14}^{2-}$ (as the $(C_2H_5)_4N^+$ salt) are critical to an understanding of the redox reactions of the open-cage B-10 species in acetonitrile. Cyclic voltammograms of $B_{10}H_{14}^{2-}$ in acetonitrile (Figure 3) are almost the mirror images of those for the reduction of $B_{10}H_{14}$. The initial potential sweep exhibits two oxidation waves, one at *ca.* −0.6 V and a second at +0.2 V. The first wave is identical in all respects with the oxidation wave of the intermediate in the reduction of $B_{10}H_{14}$ observed at fast sweep rates. The peak width ($E_p - E_{p/2}$) of this wave was 41 ± 5 mV for sweep rates from 0.06 to 100 V/sec. The second wave at +0.2 V can again be identified with the oxidation of $B_{10}H_{13}^-$ (eq 1).

Product identification was carried out as described above. The ^{11}B nmr spectrum of the electrolysis products was essentially identical with that of Figure 1C, a superposition of the $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ spectra in a 1 : 1 molar ratio. The over-all oxidation is given by

$$2B_{10}H_{14}^{2-} \longrightarrow B_{10}H_{13}^- + B_{10}H_{15}^- + 2e^- \quad (3)$$

Thus equal molar amounts of $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ correspond to a "one-electron" oxidation state between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$.

At fast sweep rates (>0.2 V/sec) a reduction wave appears in the cyclic voltammogram of a $B_{10}H_{14}^{2-}$ solution at *ca.* −1.0 V. This intermediate wave is identical with the first reduction wave observed in the cyclic voltammogram of the $B_{10}H_{14}$ solution (see Figure 3). The coincidence of the potentials of the intermediate waves with the $B_{10}H_{14}^{2-}$ oxidation wave and the $B_{10}H_{14}$ reduction wave and the agreement of the $E_p - E_{p/2}$ values in each case strongly suggest that the intermediates are two-electron and not one-electron products. If one-electron waves, producing the $B_{10}H_{14}\cdot^-$ species, are assumed, then the coincidence of the oxidation and reduction peak potentials of the radical anion with those of the $B_{10}H_{14}^{2-}$ and $B_{10}H_{14}$, respectively, has to be explained. Furthermore, the relative potentials of the waves in Figure 3 would imply that the $B_{10}H_{14}\cdot^-$ is unstable to disproportionation in acetonitrile if initial one-electron products are assumed. In this case, the intermediate in the oxidation of $B_{10}H_{14}^{2-}$, assumed to be $B_{10}H_{14}\cdot^-$, would be reduced at −1.0 V to $B_{10}H_{14}^{2-}$. This contradicts the assumption of an initial one-electron product in the reduction of $B_{10}H_{14}$ at this potential. Thus the assumption of one-electron waves leads to a contradiction and indicates that $B_{10}H_{14}^{2-}$ is the intermediate formed in the reduction of decaborane in acetonitrile.

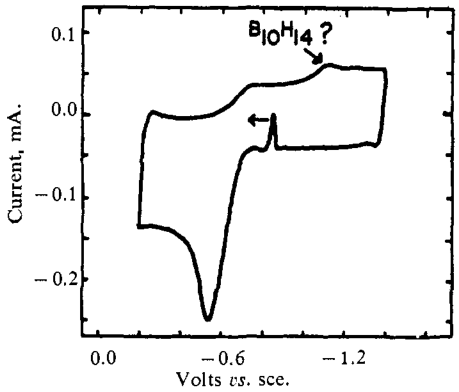

Figure 4. Cyclic voltammogram of $B_{10}H_{14}^{2-}$ in monoglyme, *ca.* 0.5 × 10^{-3} *M* $B_{10}H_{14}^{2-}$–0.1 *M* TBAP (sweep rate, 240 V/sec; hde area, 0.048 cm^2).

This argument cannot be applied to the behavior of $B_{10}H_{14}$ in monoglyme since the electrochemistry of $B_{10}H_{14}^{2-}$ is different in this solvent. A peak is not observed on the cathodic segment of cyclic voltammograms of $B_{10}H_{14}^{2-}$ monoglyme solutions which can be identified unequivocally with the reduction of $B_{10}H_{14}$. This observation is consistent with the work of Rupp, Smith, and Shriver.[22] However, the peak potentials and the peak widths are approximately the same in the two solvents. The width ($E_p - E_{p/2}$) of the $B_{10}H_{14}^{2-}$ oxidation peak in monoglyme was 50 ± 5 mV for sweep rates from 1 to 50 V/sec. Figure 4 shows a cyclic voltammogram of $B_{10}H_{14}^{2-}$ in monoglyme. At the fastest sweep rates that can be employed in this solvent, a small reproducible wave can be detected in the region where $B_{10}H_{14}$ is reduced. However, in acetonitrile the $B_{10}H_{14}$ peak is prominent at this sweep rate. This is the principal experimental difference in the electrochemical behavior of the B-10 species in the two solvents, acetonitrile and monoglyme, and has not been adequately explained. It is not unreasonable that preferential solvation of a $B_{10}H_{14}\cdot^-$ species in monoglyme, compared to acetonitrile, could account for this difference. The mechanism proposed below (eq 4 and 5) is consistent with the *reduction* of $B_{10}H_{14}$ in monoglyme. However, on the basis of the available experimental evidence, *in monoglyme* the mechanism proposed below cannot be distinguished from the mechanism proposed by Rupp, *et al.*, Scheme II.[4a]

---

(22) D. E. Smith, private communication.

Addition of $(C_2H_5)_4NB_{10}H_{13}$ to the $B_{10}H_{14}^{2-}$ solution increases the lifetime of the intermediate, $B_{10}H_{14}$, in acetonitrile. Addition of $N(C_2H_5)_4B_{10}H_{15}$ does not affect the lifetime of the intermediate.

Proposed Mechanisms. The following mechanisms, eq 4 and 5, are proposed to describe the electrochemical behavior of $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$, respectively.

Reduction of $B_{10}H_{14}$

$$B_{10}H_{14} + 2e^- \longrightarrow B_{10}H_{14}^{2-} \tag{4a}$$

$$B_{10}H_{14} + B_{10}H_{14}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{13}^- + \{B_{10}H_{15}^-\} \tag{4b}$$

$$\{B_{10}H_{15}^-\} \xrightarrow{k_2} B_{10}H_{15}^- \tag{4c}$$

Oxidation of $B_{10}H_{14}^{2-}$

$$B_{10}H_{14}^{2-} \longrightarrow B_{10}H_{14} + 2e^- \tag{5a}$$

$$B_{10}H_{14} + B_{10}H_{14}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B_{10}H_{13}^- + \{B_{10}H_{15}^-\} \quad (5b) = (4b)$$

$$\{B_{10}H_{15}^-\} \xrightarrow{k_2} B_{10}H_{15}^- \quad (5c) = (4c)$$

Supporting Evidence. In addition to the argument above, the following results or observations are in agreement with the proposed mechanisms.

1. Equations 4 and 5 fit the over-all stoichiometry of eq 2 and 3 and the $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$ addition experiments.

2. The chemical equilibrium following the electron-transfer step is consistent with known acid–base properties of the boron hydrides. Decaborane is a moderately strong acid[23] and $B_{10}H_{15}^-$ can be prepared by protonation of $B_{10}H_{14}^{2-}$ with HCl in alcohol.[24]

3. All of the species in these equations are known boron hydrides except for $\{B_{10}H_{15}^-\}$. The nature of its decay is not of importance to the mechanisms, but it might be significant that the ^{11}B nmr spectrum of the stable $B_{10}H_{15}^-$ species is a narrow triplet which is not of the "decaborane type" and does not resemble the nmr spectrum of the $B_{10}H_{14}^{2-}$ species from which it was formally produced by the simple addition of a proton.

4. No esr signals were observed when the electrolysis was performed in the cavity of an esr spectrometer in the presence of a large excess of $B_{10}H_{13}^-$, conditions under which the intermediate wave could easily be detected electrochemically at slow sweep rates.

The observation of a broad esr signal upon mixing $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ at low temperature[4a] does not invalidate eq 4 and 5. At low temperature the rates of proton transfer should be slow enough that an equilibrium amount of the radical anion, $B_{10}H_{14}\cdot^-$, could be detected by esr spectroscopy. However, at room temperature the equilibrium (eq 6) lies to the left and the species on the left are rapidly removed by eq 4b.

$$B_{10}H_{14} + B_{10}H_{14}^{2-} \rightleftharpoons 2B_{10}H_{14}\cdot^- \tag{6}$$

5. Addition to the electrolysis solution of a proton donor, which can compete with $B_{10}H_{14}$ to protonate $B_{10}H_{14}^{2-}$ in eq 4b, alters the electrochemical reduction of $B_{10}H_{14}$. When an acid such as N,N-diethylanilinium (bH^+) perchlorate, which is electroinactive in acetonitrile at potentials more positive than −1.3 V, is added to the solution in a 5 molar excess, the reduction wave height at −1.0 V increases by a factor of almost 2. The E_p value is only slightly changed. The over-all reduction process under these conditions is given by

$$B_{10}H_{14} + bH^+ + 2e^- \longrightarrow B_{10}H_{15}^- + b \tag{7}$$

The product was confirmed by constant-potential electrolysis followed by ^{11}B nmr spectrometry.

6. A large number of double-potential-step experiments[25,26] were performed to measure the lifetime of the intermediate in the reduction of $B_{10}H_{14}$. In this experiment the potential is stepped from a point more negative than the cathodic wave (*e.g.* −0.2 V in Figure 2a) to a point past the wave at which the intermediate is produced (*e.g.*, −1.4 V in Figure 2a) for a time τ, and then back to the original potential where the intermediate is oxidized. The ratio of the anodic and cathodic currents (i^a/i^c) is a function of the lifetime of the intermediate. The resulting i^a/i^c values were compared to theoretical working curves calculated by the method of Feldberg and Auerbach[27] for a variety of mechanisms including those of Rupp, *et al.*[4a] In no case was the agreement satisfactory although the data clearly indicate that a second (or higher) order chemical process is involved in the decay of the intermediate. Because of the number of variables (τ, $[B_{10}H_{14}]$, k_1, k_{-1}, and k_2), working curves were not constructed for the proposed mechanism (eq 4), but the results could be rationalized in terms of it. Assuming a small "steady-state" concentration of $\{B_{10}H_{15}^-\}$ in eq 5, the rate law for the chemical reactions following the electron-transfer step is given by

$$\text{rate} = \frac{k_1k_2[B_{10}H_{14}][B_{10}H_{14}^{2-}]}{k_2 + k_{-1}[B_{10}H_{13}^-]} \tag{8}$$

When the experimental values of i^a/i^c were fitted to working curves calculated assuming an irreversible reaction between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$ (*i.e.* in eq 4b, $k_{-1} = 0$), the rate constants obtained always decreased with time. This is consistent with the proposed mechanism since, as the electrolysis time increases, the concentration of $B_{10}H_{13}^-$ builds up in the diffusion layer and the second term in the denominator of eq 8 becomes more important. By working under conditions such that the backward reaction might be ignored (*i.e.* short times and large values of i^a/i^c), the rate constant, k_1, was estimated to be $4.6 \pm 1.1 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. This value is the average of 30 separate measurements, and the limits are given at the 95% confidence level. In view of the uncertainty in the assumptions and the difficulty in the measurements (the i^a/i^c values are on the knee of the working curves), this value should be taken as an approximation only.

7. The electrochemical behavior is generally consistent with the proposed mechanism, but the presence of the fast chemical "annihilation" reaction following charge transfer makes a detailed kinetic analysis of the two-electron charge-transfer step difficult. Intramolecular hydrogen rearrangements, coupled to the electron-transfer steps, must be involved in the over-all process since decaborane is known to have four bridging hydrogens[28] and $B_{10}H_{14}^{2-}$ probably has two.[29] The

---

[23] G. A. Guter and G. W. Schaeffer, *J. Am. Chem. Soc.*, **78**, 3546 (1956).

[24] J. A. Dupont and M. F. Hawthorne, *Chem. Ind.* (London), 405 (1962).

[25] T. Kambara, *Bull. Chem. Soc. Japan*, **27**, 523 (1954).

[26] W. M. Schwartz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

[27] S. W. Feldberg and C. Auerbach, *Anal. Chem.*, **36**, 505 (1964).

[28] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, p 7.

[29] Reference 28, p 182.

experimental results do not permit conclusions regarding the mechanistic details of these possible reactions.

The experimental current function, defined by the left-hand side of eq 9,[20] increases by about 50% from a

$$\frac{i_p}{ACv^{1/2}} = 298(\alpha n_a)^{1/2} n D^{1/2} \qquad (9)$$

one-electron value when the sweep rate increases (see Figure 5). At these sweep rates the time scale of the electrochemical experiment competes with the lifetime of the intermediate species. It is tempting to explain the increase by an over-all two-electron process and a one-electron rate-controlling step with an αn_a value of 0.5, *i.e.*

$$B_{10}H_{14} \xrightarrow{e^-,\ \text{slow}} B_{10}H_{14}\cdot^- \xrightarrow{e^-,\ \text{fast}} B_{10}H_{14}^{2-} \qquad (10)$$

However, the shapes of the waves (both oxidation and reduction) are inconsistent with this interpretation. The αn_a and $(1 - \alpha)n_a$ values, calculated from the peak widths, are 0.86 and 1.17, respectively, at sweep rates from 1.0 to 200 V/sec. The dependence of the half-peak potentials on sweep rate yields the same numbers. These values suggest that the rate-controlling step is a two-electron transfer. However, this process is unlikely in view of the instability of the radial anion, $B_{10}H_{14}\cdot^-$, and the conceptual unattractiveness of a two-electron rate-controlling charge transfer. At sweep rates greater than 500 V/sec, where the time scale of the electrochemical experiment is much shorter than the lifetime of the intermediate, the peak widths definitely increase. This increase might be a manifestation of one-electron charge-transfer control (eq 10).

The formal reduction potential, $E°'$, for the $B_{10}H_{14}|B_{10}H_{14}^{2-}$ couple is -0.78 ± 0.02 V *vs.* sce in acetonitrile. This value was estimated by the average of E_p^a and E_p^c plus a small term due to the asymmetry of the oxidation and reduction waves. It is not corrected for a liquid junction potential. At the slowest sweep rates employed, 0.004 V/sec, the half-peak potential is approximately equal to the $E°'$ value. Evidently, at slow sweep rates the over-all process begins to have characteristics of a quasi-reversible charge-transfer reaction, followed by a complex kinetic step.

The decrease of the current function at the fastest sweep rates (greater than 200 V/sec) has not been adequately explained. Experiments on model systems and dummy cells showed that the decrease is not due to an instrumental difficulty.[30] The chronoamperometric constant exhibited similar behavior at short times. There is low-temperature nmr evidence which indicates that decaborane is strongly solvated in acetone[31] and ether[32] solvents. One can speculate that the dissociation of a decaborane–solvent "complex" might contribute to the irreversible character of the over-all electrode process and the decrease of the current function at fast sweep rates.

Conclusions

The electron-transfer and proton-transfer reactions which interrelate the open-cage B-10 species in acetonitrile have been elucidated. They are given by eq 4 and 5. The kinetically important step following charge transfer both in the reduction of $B_{10}H_{14}$ and the oxidation of $B_{10}H_{14}^{2-}$ is a proton-transfer reaction between $B_{10}H_{14}$ and $B_{10}H_{14}^{2-}$. The rate constant for this reaction in acetonitrile is approximately $5 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at 24 ± 2°. At short times the initial two-electron process is charge-transfer controlled in acetonitrile. The formal reduction potential of the $B_{10}H_{14}|B_{10}H_{14}^{2-}$ couple is -0.78 ± 0.02 V *vs.* sce.

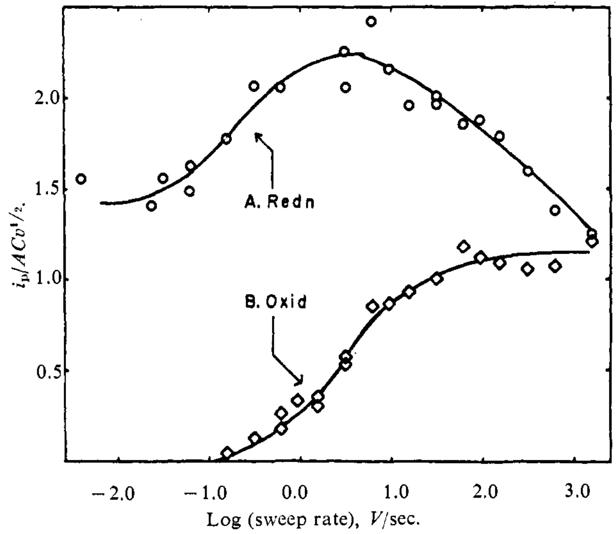

Figure 5. Dependence of the current function on the sweep rate (system, $1.1 \times 10^{-3}\ M\ B_{10}H_{14}$–0.1 M TEAP in acetonitrile; hde area, 0.048 cm²): (A) reduction of $B_{10}H_{14}$; (B) oxidation of the intermediate (units: i_p in A, A in cm², C in M, v in V/sec).

Comparison of the mechanism proposed in this study to the results of previous work on sodium[2] and sodium amalgam[3] reductions of decaborane reveals interesting similarities. The reduction in acetonitrile resembles that observed in liquid ammonia which gave $B_{10}H_{14}^{2-}$ as the only product.[2] On the other hand, in ether Toeniskoetter[2] observed a transient red color during the reduction which was possibly due to the radical anion, $B_{10}H_{14}\cdot^-$, and subsequently a mixture of products, including $NaB_{10}H_{13}$ and $Na_2B_{10}H_{14}$, was obtained. Hough and Edwards found that in ether the product after 5 hr was $Na_2B_{10}H_{14}$, which reacted further to yield $NaB_{10}H_{13}$. Besides the differences in solvents, the time scale of the reactions appears to be one of the principal features which differentiates the electrochemical and sodium reductions. In recent years the chemistry of hydrocarbon anions in ethereal solvents has been shown to involve both "tight" and "weak" ion pairs.[33] It is likely that part of the time-scale difference in the electrochemical and chemical reduction arises because of stabilization of the $B_{10}H_{14}^{2-}$ and $B_{10}H_{14}\cdot^-$ species by ion-pair formation with sodium ions and that ion-pair formation will play a significant role in the chemistry of boron hydride anions in solution. Finally, these observations and the differences between the electro-

---

(30) The constant peak width and the lack of a marked concentration dependence of the current function suggest that an adsorption process is not involved in the two-electron step in the concentration range investigated in this study, 0.5–4.5 × $10^{-3}\ M\ B_{10}H_{14}$; see R. H. Wopschall and I. Shain, *Anal. Chem.*, **39**, 1514 (1967).

(31) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, 81, 4496 (1959).

(32) J. A. Slater and A. D. Norman, unpublished observation.

(33) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961); N. Hirota, *J. Phys. Chem.*, 71, 127 (1967); M. C. R. Symons, *ibid.*, **71**, 172 (1967); R. Chang and C. S. Johnson, Jr., *J. Am. Chem. Soc.*, **88**, 2338 (1966).

chemical behavior in monoglyme[4a,b] and acetonitrile suggest that solvent effects may play a significant rôle in determining the mechanistic pathways of boron hydride oxidation and reduction processes.

Acknowledgment. William O'Deen built the potentiostat described in the Experimental Section. Helpful discussions of this work with D. E. Smith and S. W. Feldberg are also acknowledged.

The Preparation and Mass Spectrometry of Triphosphine-5

T. P. Fehlner

Contribution from the Department of Chemistry and the Radiation Laboratory,[1] *University of Notre Dame, Notre Dame, Indiana 46556.* *Received April 26, 1968*

Abstract: A convenient photochemical method for the preparation of triphosphine-5, P_3H_5, is described. The purification and the determination of some of the physical properties of this unstable compound are reported. The fragmentation pattern and appearance potentials of selected ions have been determined using a mass spectrometer with molecular beam sampling. The latter results allow the phosphorus–hydrogen and phosphorus–phosphorus bond energies and the proton affinity of phosphine to be estimated. This compound, which is an intermediate in the thermal decomposition of diphosphine-4, thermally decomposes at 300°K to yield diphosphine-4 and tetraphosphine-6. This reaction is the prototype for a generalized chain growth step in the net polymerization of diphosphine-4.

The formation of triphosphine-5, P_3H_5, as an intermediate in the thermal decomposition of diphosphine-4 has been reported previously.[2] This unstable compound is of considerable interest as it contains two phosphorus–phosphorus bonds. Evidence suggesting its existence has appeared several times in the past. The unidentified white solid melting at $-34°$ observed by Evers and Street in liquid diphosphine-4 was no doubt P_3H_5.[3] In a series of reports Baudler and coworkers have presented a substantial amount of evidence for the existence of triphosphine and higher hydrides of phosphorus.[4] Some mass spectrometric evidence has also been presented by others.[5] However, none of these workers has isolated and studied triphosphine-5, and we now wish to report on the preparation, isolation, and characterization of this compound.

Results and Discussion

Preparation. Triphosphine-5 was originally prepared by the pyrolysis of diphosphine-4 in a special reactor (see below). Although the yields were fair, the method proved unsatisfactory as a preparative method as the removal of the unreacted diphosphine-4 could not be accomplished without destroying a majority of the triphosphine-5 product. This simply reflects the instability of this compound, especially in the liquid phase. With this method we were never able to obtain triphosphine-5 with less than 40% diphosphine-4. Consequently we sought a preparation procedure that would minimize the contamination of the crude product with P_2H_4. Along with other workers, we had noted that diphosphine-4 decomposition was enhanced by ordinary daylight.[4,6,7] By photolyzing diphosphine-4 in a bulb and analyzing the products, it was easily shown that triphosphine-5 was a product of the photodecomposition. A circulating flow reactor described in the Experimental Section was then developed to prepare larger quantities of this compound. The trick in the preparation is that by the proper choice of cold baths, nearly pure (95%) triphosphine-5 can be obtained.[8]

Phosphine is also produced in the photolytic reaction, and after a period of time the reactor line became contaminated with solid material. The yield of phosphine and triphosphine-5 as a function of irradiation time is shown in Figure 1. Both compounds were measured utilizing a modified codistillation–fractionation apparatus.[9] Calibration relating peak area to moles was carried out for phosphine, but the yields for triphosphine-5 are estimates based on peak areas. Unexpectedly, this apparatus was not useful for the purification of triphosphine-5 due to problems of decomposition.

There are a few enlightening clues as to the nature of the photolysis reaction. First, in some earlier studies on diphosphine-4,[10] the action of light on diphosphine-4

---

[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-599.

[2] T. P. Fehlner, *J. Amer. Chem. Soc.*, **88**, 2613 (1966).

[3] E. C. Evers and E. H. Street, Jr., *ibid.*, **78**, 5726 (1956).

[4] M. Baudler and L. Schmidt, *Naturwissenschaften*, **46**, 577 (1959); M. Baudler, H. Ständeke, M. Borgardt, and H. Strabel, *ibid.*, **52**, 345 (1965); M. Baudler, H. Ständeke, M. Borgardt, H. Strabel, and J. Dobbers, *ibid.*, **53**, 106 (1966).

[5] P. Royen, C. Rocktäschel, and W. Mosch, *Angew. Chem.*, **76**, 860 (1964).

[6] E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956).

[7] S. R. Gunn and L. G. Green, *ibid.*, **65**, 779 (1961).

[8] It should be emphasized that experiments in dark reactors showed that triphosphine-5 is also produced by pyrolytic decomposition.

[9] G. H. Cady and D. P. Seigwarth, *Anal. Chem.*, **31**, 618 (1959).

[10] T. P. Fehlner, *J. Amer. Chem. Soc.*, **89**, 6477 (1967).