



Figure 1.—The effect of added chloride ion on the rate of aquation of $\text{trans-Cr}(\text{NH}_3)_4(\text{OH}_2)\text{I}^{2+}$ at unit ionic strength and 40° .

ions substantially accelerate the rate of aquation in comparison to the rate in perchloric acid. The rate of aquation in HI is essentially the same as in perchloric acid.

The products of the spontaneous aquation of *cis*- and *trans*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$, in the presence of chloride and bromide ions, were separated by ion-exchange chromatography. In addition to $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, a considerable amount of $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$ or Br^-) was detected. More halo complex was found than can be accounted for by the corresponding anation reactions of $\text{trans-Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$. A comparison of these results is shown in Table II.

TABLE II
THE EFFECT OF HALIDE IONS ON THE PRODUCTS OF THE AQUATION AND ANATION REACTIONS AT 40°

| Complex | Added anion (X) | % $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$ ^a | % $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ ^a |
|--|----------------------|--|--|
| <i>trans</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ | 1 M HCl | 22 | 78 |
| <i>trans</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ | 1 M HCl | 3 | 97 |
| <i>trans</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ | 1 M HBr | 13 | 87 |
| <i>trans</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ | 1 M HBr | 2 | 98 |
| <i>cis</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ | 1 M HCl ^b | 7 | 93 |
| <i>cis</i> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$ | 1 M HCl ^b | 3 | 97 |

^a Reported as per cent recovered material at unit ionic strength.

^b Measured at 35° .

The increased rate in HCl and HBr and the fact that a considerable amount of the halo complex is produced suggests that the halide ion is incorporated into the first coordination sphere of chromium prior to the loss of iodide. These results also suggest a strong *trans* labilization of the coordinated water molecule by coordinated iodide. This conclusion is reinforced by the fact that only a small amount of *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ ion is produced when *cis*- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ aquates in 1.0 M hydrochloric acid.

The spontaneous aquation reactions of the *cis*- and *trans*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}][\text{ClO}_4]_2$ in oxygen-18-enriched water are in progress to determine the extent of labilization of coordinated water molecules.

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Purification, Voltammetry, and Boron-11 Nuclear Magnetic Resonance Spectra of Undecahydro-*closo*-undecaborate(2-) Salts¹

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At the beginning of an electrochemical study of the $\text{B}_{11}\text{H}_{11}^{2-}$ ion, $\text{Cs}(\text{CH}_3)_4\text{NB}_{11}\text{H}_{11}$ was prepared and purified by the published procedure.² Boron analyses and ir and nmr spectra matched the reported data. Subsequent experiments showed the product to be impure, containing about 10% of an impurity which was probably $\text{B}_{10}\text{H}_{10}^{2-}$. The reported nmr spectrum^{2b} was thus that of a mixture, not that of $\text{B}_{11}\text{H}_{11}^{2-}$ alone.

Results

Electrochemistry.—A solution containing about 1 mM $\text{Cs}(\text{CH}_3)_4\text{NB}_{11}\text{H}_{11}$ and 0.1 M tetraethylammonium perchlorate in acetonitrile was examined voltammetrically at a stationary platinum electrode, with a saturated aqueous calomel reference electrode. An anodic wave with $E_{p/2} = +0.05$ V was observed, followed by a smaller wave at $+0.35$ V. Controlled-potential-electrolyzed solutions showed the expected decrease in the 0.05-V wave but no change in the 0.35-V wave.

After recrystallizations as the tetraethylammonium salt, the anodic wave at $+0.35$ V did not appear, and a single anodic wave with $E_{p/2} = 0.05$ V was observed for $\text{B}_{11}\text{H}_{11}^{2-}$. Controlled-potential electrolysis of purified $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{B}_{11}\text{H}_{11}^{2-}$ at 0.20 V required the expected 1.0 equiv/mol.

Nmr.—The reported ¹¹B nmr spectrum of $\text{B}_{11}\text{H}_{11}^{2-}$ consists of two doublets of relative areas 10:1 at 35.0 and 47.4 ppm, respectively, upfield from external methyl borate.^{2b} After purification which removed the electrochemical impurity, the small doublet at 47.4 ppm no longer appeared. The 32-MHz ¹¹B nmr spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{B}_{11}\text{H}_{11}$ in acetonitrile consists of a single doublet at 35.0 ppm, with $J = 125$ Hz. Each component of the doublet has a width at half-height of approximately 45 Hz.

Discussion

The appearance of two waves in the voltammetry of the $\text{Cs}(\text{CH}_3)_4\text{NB}_{11}\text{H}_{11}$ suggested that the ion undergoes the same type of oxidation as the $\text{B}_{10}\text{H}_{10}^{2-}$ ion, *viz.*, a one-electron oxidation followed by dimerization and subsequent oxidation of the dimer at a more anodic potential.³ The second wave would be smaller than

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Taken from the Ph.D. Thesis of R. J. Wiersema, University of Kansas, 1969.

(2) (a) F. Klanberg and E. L. Muetterties, *Inorg. Syn.*, **11**, 25 (1968); (b) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966); (c) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, p 92.

(3) R. L. Middaugh and F. Farha, Jr., *J. Amer. Chem. Soc.*, **88**, 4147 (1966).

the first if the kinetics of the dimerization were not sufficiently rapid. If this were the case, electrolysis at 0.20 V should require 1.0 equiv/mol. After the electrolysis, only the second wave should appear, and it should be as large as the original first wave, assuming that the dimerization went to completion. This behavior was not observed.

The preparation of $B_{11}H_{11}^{2-}$ involves the synthesis of $CsB_{11}H_{14}$ and its conversion to $Cs_2B_{11}H_{13}$, followed by pyrolysis to $Cs_2B_{11}H_{11}$. Varying amounts of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ are also formed in the pyrolysis. The data summarized in Table I indicate that the extraneous

TABLE I
VOLTAMMETRY AND ^{11}B CHEMICAL SHIFTS
OF IONS IN THE SYNTHESIS OF $B_{11}H_{11}^{2-}$

| Ion | $E_{p/2}^a$ | ^{11}B chem shift ^b |
|---------------------|-------------|----------------------------------|
| $B_{11}H_{14}^-$ | +1.6 | +35 |
| $B_{11}H_{13}^{2-}$ | -0.45 | +38.4 (10), +49.6 (1) |
| $B_{10}H_{10}^{2-}$ | +0.4 | +19 (1), +48 (4) |
| $B_{12}H_{12}^{2-}$ | +1.4 | +33.5 |
| $B_{11}H_{11}^{2-}$ | +0.05 | +35.0 ^c |

^a Anodic wave at stationary Pt electrode, in volts; aqueous saturated calomel electrode reference, in acetonitrile containing 0.10 M $(C_2H_5)_4NClO_4$; scan rate 4 V/min. ^b 32-MHz ^{11}B nmr chemical shift in acetonitrile, in ppm upfield from $B(OCH_3)_3$; relative areas in parentheses. ^c Literature³ report: 35.0 (10), 47.4 (1).

wave in the voltammetry and the high-field doublet in the nmr spectrum of the $Cs(CH_3)_4NB_{11}H_{11}$ obtained are probably due to the presence of some $B_{10}H_{10}^{2-}$.

Either stationary-electrode voltammetry or ^{11}B nmr can be used to detect easily more than 5% $B_{10}H_{10}^{2-}$ in $B_{11}H_{11}^{2-}$. Detection of contamination by $B_{12}H_{12}^{2-}$ remains difficult because of the extreme oxidative stability of $B_{12}H_{12}^{2-}$ and the similarity of its ^{11}B nmr and ir spectra to those of $B_{11}H_{11}^{2-}$. Amounts greater than 10% $B_{12}H_{12}^{2-}$ in $B_{11}H_{11}^{2-}$ can be detected by nmr.

The structure of $B_{11}H_{11}^{2-}$ is presumably very similar to that of $B_9C_2H_{11}$, with which it is isoelectronic.^{2b} The structure of the dimethyl derivative of $B_9C_2H_{11}$ indicates that five-, six-, and seven-coordinate borons would all be present in a capped decaborane-like structure.⁴ The observation of a single doublet in the nmr spectrum could be explained by an accidental equivalence of chemical shifts or by a polyhedral rearrangement that is fast on the nmr time scale. Experiments

(4) C. Tsai and W. E. Streib, *J. Amer. Chem. Soc.*, **88**, 4513 (1966).

on compounds with closed B_7 , B_9 , B_{10} , and B_{12} polyhedral structures all indicate a sufficiently high barrier to such a polyhedral rearrangement that such rearrangements should be slow on the nmr time scale.⁵ The only other case of a closed polyhedral borane anion having nonequivalent borons in its ground-stage geometry but showing a single nmr chemical shift is the $B_8H_8^{2-}$ ion.⁶ In the absence of a logical reason why rearrangements in $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ should have much lower barriers than those in $B_7H_7^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$, we prefer to say that $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ represent cases in which borons of different coordination numbers in the same molecule are spectroscopically equivalent at 32.0 MHz.

Experimental Section

Purification of $Cs_2B_{11}H_{11}$.—Both $Cs_2B_{11}H_{11}$ and $Cs(CH_3)_4NB_{11}H_{11}$ prepared by the published procedure² contained small amounts of $B_{10}H_{10}^{2-}$ which could not be removed by repeated recrystallizations from water. The procedure below could be applied to either of these compounds.

The crude product of the pyrolysis of $Cs_2B_{11}H_{13}$ (ca. 5.5 g) was dissolved in 150 ml of warm water and filtered through Celite to remove colloidal material. While still hot, the filtrate was passed through a sodium ion exchange column. The warm solutions both before and after passing through the column were protected by nitrogen atmosphere. The effluent (about 250 ml) was evaporated under reduced pressure to about 75 ml and treated with an aqueous solution of tetraethylammonium bromide. The resulting precipitate was collected by filtration and dried at room temperature under vacuum. The $[(C_2H_5)_4N]_2B_{11}H_{11}$ was then recrystallized repeatedly from an acetonitrile-water mixture until no waves other than the oxidation wave at +0.05 V were observed by stationary-electrode voltammetry at platinum in acetonitrile, and no peaks due to $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ could be observed in the ^{11}B nmr spectrum. About half of the $CsB_{11}H_{13}$ pyrolyzed was realized as pure $[(C_2H_5)_4N]_2B_{11}H_{11}$.

Electrochemistry.—Voltammetry was carried out using a stationary platinum-inlay electrode in acetonitrile containing 0.10 M $(C_2H_5)_4NClO_4$ at a scan rate of 4 V/min. The potentiostat was built according to a design of M. D. Hawley.⁷

Exhaustive electrolysis was carried out at a Pt gauze electrode, using a Kepco OPS 40-0.5 power supply. Current was monitored as a voltage across a precision resistor in series with the working electrode, using a strip chart recorder.

Nmr.—Spectra were run on a Varian HA-100 spectrometer operated at 32 MHz. An external capillary of $B(OCH_3)_3$ was used as a reference. Spectra were calibrated by use of an audio side band.

(5) Reference 2c, Chapter 3.

(6) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

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Correspondence

The Structure of Bis(tri-*n*-butyltin) Sulfate. Solid-State Monomer or Polymer?

Sir:

Stapfer, Leung, and Herber¹ have reported recently

Mössbauer and infrared data for $[(n-C_4H_9)_3Sn]_2SO_4$

(1) C. H. Stapfer, K. L. Leung, and R. H. Herber, *Inorg. Chem.*, **9**, 970 (1970).

and have concluded the compound has a monomeric structure I and not a polymeric structure II in the solid state. We feel these data do not warrant such a conclusion.

First, we briefly discuss data for the closely related compounds $[(CH_3)_3Sn]_2SO_4$, $[(CH_3)_3Sn]_2SeO_4$, and $[(CH_3)_3Sn]_2CrO_4$.²⁻⁴ The ir spectra indicate T_d sym-