our nmr spectra with those published for these ions, and the reaction therefore appears to be significantly different from that which occurs between pentaborane(9) and hydride ion.[10-12]

The reactions reported here offer an alternative synthesis of the $B_9H_{14}^-$ ion in reasonable yield; the only other reported preparations of this ion have always involved the degradation of decaborane(14) in alkaline solution.[14] Furthermore, since it is known that pentaborane(9) reacts with the hydroborate ion at 120° to form the *closo*-$B_{12}H_{12}^{2-}$ ion,[3] these results substantiate the tentative suggestion made elsewhere[23] that the $B_9H_{14}^-$ ion is a probable intermediate in this reaction scheme.

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[23] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, p 87.

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The Effect of Halide Ions on the Rate of Aquation of *trans*-Iodoaquotetraamminechromium(III)

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Ardon[1] has reported that chloride ion and bromide ion replace iodide ion in the iodopentaaquochromium(III) ion without intermediate formation of hexaaquochromium(III). His results were interpreted in terms of an SN1 mechanism in which the solvent and ambient ions compete for a pentaaquochromium(III) intermediate. During a subsequent investigation,[2] it was learned that if iodopentaaquochromium(III) is allowed to aquate in $H_2{}^{18}O$, the product hexaaquochromium(III) contains two labeled water molecules. Since the rate of water exchange of the hexaaquochromium(III) species is slow, this information is inconsistent with the explanation offered by Ardon.

A new mechanism which involves a strong trans labilization by iodide ion was proposed.[2] The incorporation of ambient anions into the first coordination sphere of the chromium(III) product can be explained in terms of this mechanism which is given in eq 1 and 2.

$$(H_2O)_5CrI^{2+} + X^- \longrightarrow (H_2O)_4CrIX^+ + H_2O \qquad (1)$$

$$(H_2O)_4CrIX^+ + H_2O \longrightarrow (H_2O)_5CrX^{2+} + I^- \qquad (2)$$

The demonstration of direct anation reactions in aqueous solution and of the existence of pentacoordinated intermediates sufficiently long-lived to discriminate between various entering ligands is not so common as to make further investigation in this direction unwarranted.[3] Results of our study[4] of the reactions of *trans*-$Cr(NH_3)_4(Cl)(I)^+$ suggested that the reactions of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ could be similar to that reported for $Cr(H_2O)_5I^{2+}$. Thus, in the present investigation we wish to report the effect of added halide ions on the rate of decomposition of *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ and the nature of the reaction products.

Experimental Section

trans-$[Cr(NH_3)_4(H_2O)I][ClO_4]_2$ was prepared and purified according to the method of Hoppenjans.[4] The complex contained varying amounts of water of crystallization such that the Cr:I:N molar ratio was taken as a measure of purity. *Anal.* Calcd for *trans*-$[Cr(NH_3)_4(H_2O)I][ClO_4]_2$: Cr:I:N, 1:1:4. Found: Cr:I:N, 1:1.03:3.96.

The rate of decomposition of the *trans* complex was measured spectrophotometrically at 590 nm which corresponds to the position of the low-energy absorption maximum for *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$. Although *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$ also absorb at this wavelength, color changes associated with the slow aquation[5] of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ will be negligible. The pseudo-first-order rate constants were determined by means of our nonlinear least-squares fitting program.[6]

Ion-exchange chromatography using Dowex 50W-2X with 1 and 2 *M* hydrogen ion eluent was employed to separate the products of the aquation reactions. In all experiments, a comparison of the sum of the separated products with the amount of reactant showed better than 96% recovery.

Results and Discussion

The pseudo-first-order rate constants for the reaction of *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ ion were measured in the presence of varying chloride ion concentrations and are illustrated in Figure 1. The observed rate constant can be expressed by the following equation: $k_{obsd} = k_1 + k_2(Cl^-)$. Values for k_1 of 6.6×10^{-4} and 1.45×10^{-3} sec^{-1} at hydrogen ion concentrations of 1.0 and 0.1 *M*, respectively, compare favorably with values reported elsewhere.[4] The values of k_2 are $3.1_3 \times 10^{-4}$ and $3.6_3 \times 10^{-4}$ M^{-1} sec^{-1} at hydrogen ion concentrations of 1.0 and 0.1 *M*, respectively.

The observed rate constants for various anionic media are presented in Table I. Chloride and bromide

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR REACTIONS OF *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ AS A FUNCTION OF THE AMBIENT ANION AT UNIT IONIC STRENGTH AND 40°

1.0 *M* acid	10^4k_{obsd}, sec^{-1}	1.0 *M* acid	10^4k_{obsd}, sec^{-1}
$HClO_4$	6.6 ± 0.03	HBr	7.5 ± 0.03
HCl	9.7 ± 0.07	HI	6.5 ± 0.12

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[1] M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).

[2] P. Moore, F. Basolo, and R. G. Pearson, *ibid.*, **5**, 223 (1966).

[3] See also the effect of spontaneous solvolysis of iodopentaaquochromium(III) in water–methanol solvents (S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, **92**, 1215 (1970)) where data are presented in favor of a presumed pentaaquochromium(III) intermediate.

[4] D. W. Hoppenjans, G. Gordon, and J. B. Hunt, *Inorg. Chem.*, in press.

[5] D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *ibid.*, **7**, 2506 (1968).

[6] The square of the difference between the observed and calculated absorbance values in terms of the approximate rate law is minimized and the corresponding standard deviations are calculated directly by means of this Fortran IV program: R. C. Thompson and G. Gordon, *ibid.*, **5**, 502 (1966).

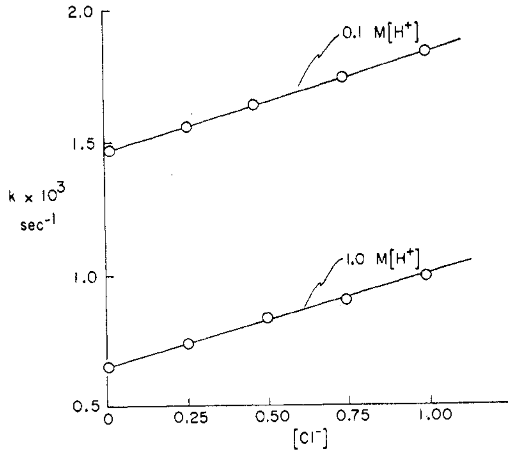

Figure 1.—The effect of added chloride ion on the rate of aquation of *trans*-$Cr(NH_3)_4(OH_2)I^{2+}$ at unit ionic strength and 40°.

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*-$Cr(NH_3)_4(H_2O)I^{2+}$, in the presence of chloride and bromide ions, were separated by ion-exchange chromatography. In addition to *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$, a considerable amount of *trans*-$Cr(NH_3)_4(H_2O)X^{2+}$ ($X = Cl^-$ or Br^-) was detected. More halo complex was found than can be accounted for by the corresponding anation reactions of *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$. 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)	% $Cr(NH_3)_4$-$(H_2O)X^{2+}$ [a]	% $Cr(NH_3)_4$-$(H_2O)_2{}^{3+}$ [a]
trans-$Cr(NH_3)_4(H_2O)I^{2+}$	1 *M* HCl	22	78
trans-$Cr(NH_3)_4(H_2O)_2{}^{3+}$	1 *M* HCl	3	97
trans-$Cr(NH_3)_4(H_2O)I^{2+}$	1 *M* HBr	13	87
trans-$Cr(NH_3)_4(H_2O)_2{}^{3+}$	1 *M* HBr	2	98
cis-$Cr(NH_3)_4(H_2O)I^{2+}$	1 *M* HCl[b]	7	93
cis-$Cr(NH_3)_4(H_2O)_2{}^{3+}$	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*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ ion is produced when *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$ aquates in 1.0 *M* hydrochloric acid.

The spontaneous aquation reactions of the *cis*- and *trans*-$[Cr(NH_3)_4(H_2O)I][ClO_4]_2$ 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−) Salts[1]

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At the beginning of an electrochemical study of the $B_{11}H_{11}{}^{2-}$ ion, $Cs(CH_3)_4NB_{11}H_{11}$ 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 $B_{10}H_{10}{}^{2-}$. The reported nmr spectrum[2b] was thus that of a mixture, not that of $B_{11}H_{11}{}^{2-}$ alone.

Results

Electrochemistry.—A solution containing about 1 m*M* $Cs(CH_3)_4NB_{11}H_{11}$ 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 $B_{11}H_{11}{}^{2-}$. Controlled-potential electrolysis of purified $[(C_2H_5)_4N]_2B_{11}H_{11}{}^{2-}$ at 0.20 V required the expected 1.0 equiv/mol.

Nmr.—The reported ^{11}B nmr spectrum of $B_{11}H_{11}{}^{2-}$ 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 ^{11}B nmr spectrum of $[(C_2H_5)_4N]_2B_{11}H_{11}$ 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 $Cs(CH_3)_4NB_{11}H_{11}$ suggested that the ion undergoes the same type of oxidation as the $B_{10}H_{10}{}^{2-}$ 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

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(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).