benzene (2 ml). The precipitate was filtered off, washed thoroughly with benzene and pentane, and dried under vacuum giving the product as pale yellow microcrystals (0.068 g). Nmr in $(CD_3)_2CO$: $\delta(CH_3P)$ −1.95 ppm (doublet + satellites), ^2J + $^4J(PH)$ = 12.2 Hz, $^3J(PtH)$ = 24 Hz; $\delta(CH_3Pt)$ −0.77 ppm (triplet + satellites), $^3J(PH)$ = 4.6 Hz, $^2J(PtH)$ = 60 Hz.

Other complexes were prepared similarly. Analytical data, yields, and melting points are in Table I. Nmr spectrum of $PtClCH_3[As(CH_3)_3]_2 \cdot C_2(CN)_4$ in $(CD_3)_2CO$: (CH_3As) −1.86 ppm, $^3J(PtH)$ = 17.4 Hz; $\delta(CH_3Pt)$ −0.79 ppm, $^2J(PtH)$ = 62.0 Hz.

$Pt[P(CH_3)_3]_2 \cdot C_2(CN)_4$ was prepared by the method of Baddley;[1] mp 195–215° dec. Nmr in CH_2Cl_2: $\delta(CH_3P)$ −1.75 ppm, ^2J + $^4J(PH)$ = 10.6 Hz, $^3J(PtH)$ = 35.4 Hz.

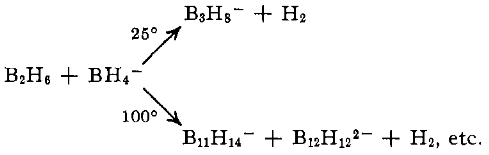
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, SHEFFIELD S3 7HF, UNITED KINGDOM

The Reaction of Pentaborane(9) with Alkali Metal Hydroborates

BY C. G. SAVORY AND M. G. H. WALLBRIDGE*

Received July 31, 1970

Several investigations have shown that both *nido*- and *closo*-borane anions are obtained by the action of a hydridic species on a neutral boron hydride. The anions formed are dependent upon the conditions used, and frequently several products are produced. Thus, diborane(6) and tetraborane(10) react with the hydroborate ion in ethereal solvents at 25 and −45°, respectively, yielding the octahydrotriborate(1−) ion,[1-5] but at higher temperatures (*e.g.*, 100°) the *nido*-$B_{11}H_{14}^-$ and *closo*-$B_{12}H_{12}^{2-}$ ions are the ultimate products.[2,3] In general all the boron hydrides from B_2H_6 to $B_{18}H_{22}$ react similarly to yield borane anions[3] although with the more stable higher hydrides proton abstraction (*via* the initial addition of a hydride ion[6]) may occur, as in the case of decaborane(14)[7-9]



$$B_2H_6 + BH_4^- \xrightarrow{25°} B_3H_8^- + H_2$$

$$B_2H_6 + BH_4^- \xrightarrow{100°} B_{11}H_{14}^- + B_{12}H_{12}^{2-} + H_2, \text{ etc.}$$

$$B_{10}H_{14} + BH_4^- \xrightarrow{25°} B_{10}H_{15}^- \longrightarrow B_{10}H_{13}^- + H_2$$

The products of the reaction of pentaborane(9) with sodium hydroborate are sharply dependent upon the reaction temperature in that at 40° the $B_3H_8^-$ ion is formed and at 60° some $B_{11}H_{14}^-$ ions may be detected, while at 100° the $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_{12}H_{12}^{2-}$ ions occur among the reaction products.[3] Other studies have shown that with the hydride ion and lithium alkyls at −78° the $B_5H_8^-$ ion is probably involved as an intermediate although the final reaction products have yet to be elucidated.[10-12] We have investigated the reaction of pentaborane(9) with lithium (and sodium) hydroborate at low temperatures (*i.e.*, up to 25°) to determine the nature of the initial products in an attempt to define more closely the important intermediates involved in the formation of the higher borane anions.

Experimental Section

Lithium hydroborate and deuterioborate were purified by Soxhlet extractions using dry ethyl ether, sodium hydroborate was recrystallized from diglyme, and pentaborane(9) was distilled *in vacuo*. Monoglyme and diglyme were dried by distillation from lithium aluminum hydride and stored over molecular sieve 4A.

Infrared spectra were recorded using a Perkin-Elmer 457 grating Infracord, and the ^{11}B nmr spectra were recorded using a Varian HA-100 instrument operating at 32.1 MHz. Mass spectra were obtained from an AEI MS9 spectrometer with a source temperature of 50–60° and an ionizing voltage of 70 eV.

Reaction of Pentaborane(9) with Lithium Hydroborate.— Initial experiments were carried out to determine the stoichiometry of the reaction. Thus when pentaborane(9) (0.258 g, 4.0 mol) was condensed onto lithium hydroborate (0.0774 g, 3.52 mmol) in monoglyme (or diglyme) under vacuum and the reaction mixture was allowed to warm slowly from −196° to room temperature, some pentaborane(9) (0.022 g, 0.34 mmol) was recovered from the reaction flask by distillation giving a molar ratio of reactants as $B_5H_9:LiBH_4 = 1.04$. Separate control experiments established that about half of the monoglyme had to be removed to recover all the volatile component, *viz.*, B_5H_9. A typical procedure was as follows. Pentaborane(9) (0.743 g, 11.6 mmol) was distilled onto a solution of lithium hydroborate (0.257 g, 11.6 mmol) in monoglyme (20 ml) at −196° under vacuum. The mixture was warmed to −78° and stirred for 4 hr over which time no hydrogen was evolved. Further stirring over 36 hr at 25° led to the evolution of hydrogen (161 ml, 7.2 mmol) together with small amounts of diborane (0.040 g, 1.4 mmol) and pentaborane(9) (0.073 g, 1.16 mmol). The pentaborane(9) appeared to be liberated during the course of the reaction because none could be recovered in the early stages of the reaction. Although hydrogen was still being evolved after 36 hr, the rate of evolution was extremely slow, and after a further 50 hr only another 4 ml (0.18 mmol) had been recovered. The diborane and pentaborane(9) were separated by vacuum distillation and identified from their ir and mass spectra. Treatment of an aliquot of the residual solution with aqueous tetramethylammonium hydroxide (~20 ml) yielded a white solid precipitate (0.42 g) which was shown to be $(CH_3)_4NB_9H_{14}$. The solid was analyzed by combustion at 800° in an oxygen stream. *Anal.* Calcd for $C_4H_{26}NB_9$: C, 25.95; H, 14.15; N, 7.54. Found: C, 26.47; H, 15.06; N, 7.16. A further aliquot of the above solution was treated with 1,4-dioxane to precipitate an oil which changed slowly to a solid on shaking. The ^{11}B nmr spectrum of the solid (in diglyme) was consistent with its being predominantly $LiB_9H_{14} \cdot diox$. Concentration of the filtrate precipitated another solid consisting mainly of $LiB_3H_8 \cdot diox$ (identified from the ^{11}B nmr spectrum). On redissolving this solid in monoglyme and treating the solution with aqueous tetramethylammonium

---

* To whom correspondence should be addressed.

(1) D. F. Gaines, R. Schaeffer, and F. Tebbe, *Inorg. Chem.*, **2**, 526 (1963).

(2) H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **85**, 3885 (1963).

(3) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1457 (1964).

(4) R. W. Parry, R. W. Rudolph, and D. F. Shriver, *ibid.*, **3**, 1479 (1964).

(5) W. V. Hough and L. J. Edwards, *Advan. Chem. Ser.*, **No. 32**, 190 (1961).

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

(7) G. W. Schaeffer, unpublished results; see ref 6.

(8) W. V. Hough and L. J. Edwards, *Advan. Chem. Ser.*, **No. 32**, 192 (1961).

(9) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

(10) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).

(11) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

(12) H. D. Johnson, R. A. Geanangel, and S. G. Shore, *ibid.*, **9**, 908 (1970).

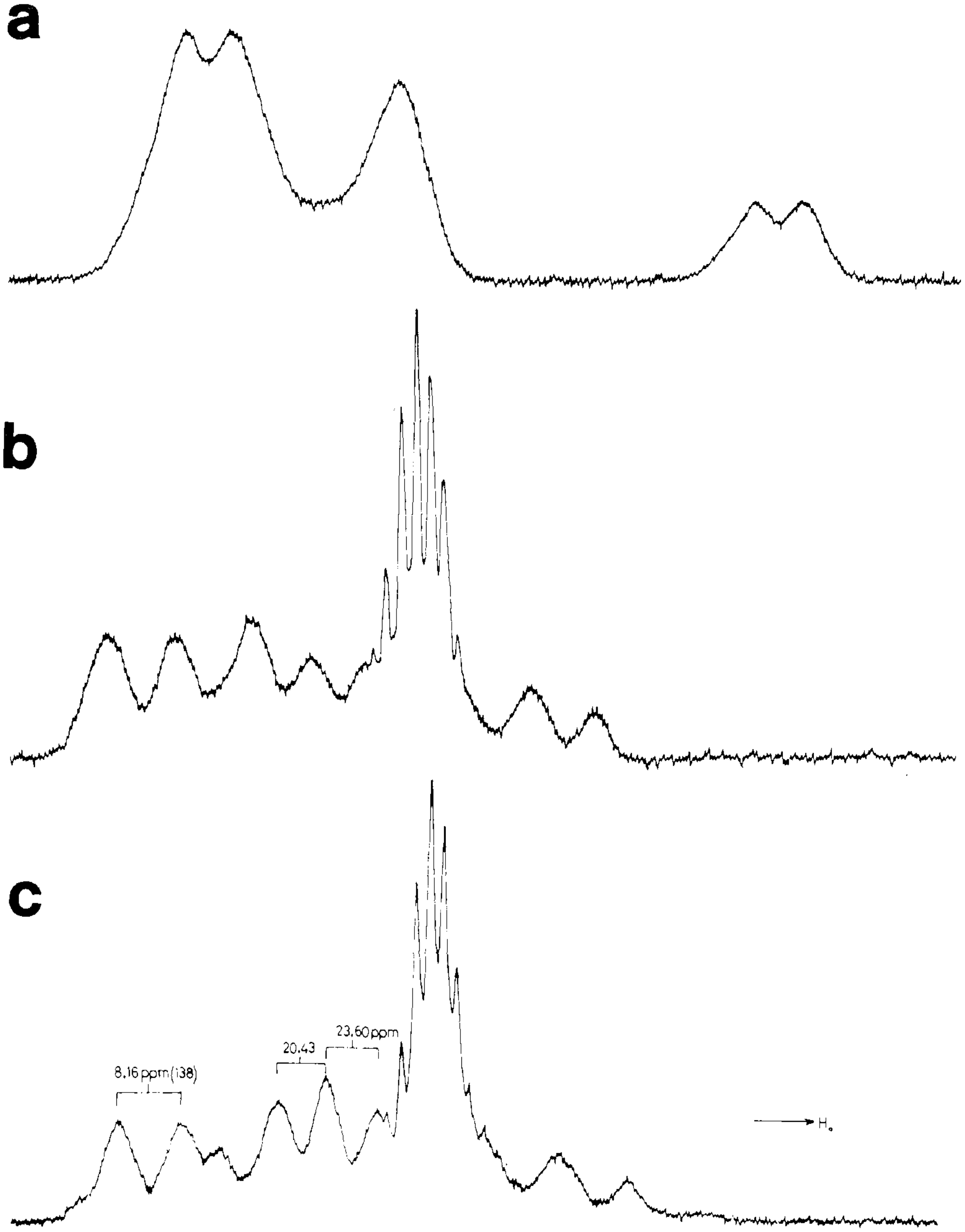


Figure 1.—The 32.1-MHz ^{11}B nmr spectra from the reaction of $LiBH_4$ with B_5H_9 in diglyme solution at (a) −78°, (b) 0°, and (c) 25°.

hydroxide, a white solid precipitate was obtained. This solid was also analyzed using a high-temperature combustion method. *Anal.* Calcd for $C_4H_{20}NB_3$: C, 41.08; H, 17.51; N, 12.25. Found: C, 41.50; H, 17.77; N, 11.90.

The reaction of sodium hydroborate with pentaborane(9) in ethereal solvents such as monoglyme proceeded very similarly to those with the lithium salt, and the same borane anions were isolated.

Results and Discussion

Preliminary experiments showed that pentaborane(9) and lithium hydroborate react in a 1:1 molar ratio in monoglyme at low temperatures without the evolution of hydrogen. However, hydrogen is liberated slowly at room temperature, and 0.5–0.7 mol [per mole of pentaborane(9) used] may be collected, the volume varying slightly from one experiment to another. During the reaction the solution gradually turns yellow, and a very small amount of white solid precipitates which may be removed by filtration.

Treatment of the filtered solution with solid tetraalkylammonium halides precipitated only trace amounts of borane anions as deduced from the ir spectra of the recovered solids which showed only very weak absorptions in the 2500-cm^{-1} region from the B–H bonds present. In view of the results given below this is probably due to the limited solubility of the added halide in the solvent. In contrast, addition of aqueous tetramethylammonium hydroxide caused some effervescence and an immediate white precipitate which could be recrystallized from water. The ^{11}B nmr spectrum of the precipitate (in DMSO solution) showed three doublets centered at δ 8.21, 20.44, and 23.50 ppm (relative to $BF_3 \cdot (C_2H_5)_2O$ =

0) with $J_{\mathrm{B-H}}$ values of 138, 130, and 139 Hz, respectively, which is essentially identical with the spectrum reported for the $B_9H_{14}^-$ ion.[13] The presence of the $B_9H_{14}^-$ ion was further substantiated from the uv spectrum which showed a single absorption at $\lambda_{\max}$ 272 mμ with ε 3.95 × 10^3 (literature values for $B_9H_{14}^-$ are 271 mμ and 3.98 × 10^3, respectively[14]). These results, together with the elemental analysis, identify the solid as tetramethylammonium tetradecahydrononaborate(1−), $(CH_3)_4NB_9H_{14}$.

The $B_9H_{14}^-$ ion may also be recovered from the original solution by the addition of dioxane, a white solid being formed after shaking. Although this solid was not analyzed, it is reasonable to assume that it is a dioxanate solvate of LiB_9H_{14} since the ^{11}B nmr spectrum of the solid (in diglyme) was identical with that obtained from the $(CH_3)_4NB_9H_{14}$. Further, the clear filtrate (A), obtained after removing the white solid, deposited another white solid as the solvent was gradually removed. After filtering and dissolving this second solid in monoglyme the ^{11}B nmr spectrum of the resulting solution corresponded exactly with the reported spectrum of the octahydrotriborate(1−) anion, $B_3H_8^-$.[15,16] The presence of the $B_3H_8^-$ ion in the filtrate (A) was confirmed by the addition of aqueous tetramethylammonium hydroxide which precipitated a white solid, which was recrystallized from methanol and shown to be $(CH_3)_4NB_3H_8$ from a comparison of the ir and ^{11}B nmr spectra with those reported for the $B_3H_8^-$ ion[1,15] and by elemental analysis.

The course of the reaction may, in part, be followed by variations in the ^{11}B nmr spectrum. Thus when equimolar quantities of lithium hydroborate and pentaborane(9) in diglyme are sealed in an nmr tube at −196° and the spectrum is recorded as the solution warms to −78° in the probe, the distinctive feature is that no signals attributable to either of the reactants are observed. Instead a multiplet (not well resolved at −78°), together with two doublets, is obtained (Figure 1a), and while the multiplet remains essentially unchanged throughout the reaction, the two doublets disappear as the temperature is raised to 0° (Figure 1b) and then further to 25° (Figure 1c). The multiplet becomes clearly resolved into a septet at 25°, and this, together with the shift and coupling constant (Table I), indicates that this signal arises from the $B_3H_8^-$ ion, the two outer signals of the nonet being unresolved as reported previously.[15-17] In addition, our observed relative intensities of 17:31:57:70:57:31:11 agree well with the expected values,[15] the small difference in the intensities of the outermost peaks being due to some overlap with other signals in the spectrum. The three doublets arising from the presence of the $B_9H_{14}^-$ ion also appear in the final spectrum, and the only remaining signals (which in terms of relative integrated intensities account for about 20% of the total boron content) are those with δ +13.9 ppm, which appears to be a singlet but may be a more complex signal if overlap with other signals occurs, and a signal centered at δ +39.5 ppm, which appears to be a triplet. We are unable to assign these signals at present. We have confirmed, by separate experiments, that there is no evidence for the presence of the $B_3H_8^-$ ion when only pentaborane(9) is dissolved in diglyme, since it is known that the ion does exist in diglyme solutions of tetraborane(10).[17]

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE ^{11}B NMR SPECTRA FROM THE REACTION OF PENTABORANE(9) WITH LITHIUM HYDROBORATE IN DIGLYME

	δ,[a] ppm	$J_{\mathrm{B-H}}$, Hz	Integrated ratio[b]
Figure 1a	13.4 (d)	114	3.9
	29.1 (m)	...	2.0
	60.2 (d)	110	1.0
Figure 1b	8.9 (d?)	179	1.0
	20.1 (d?)	147	1.1
	29.9 (m)	32	2.5
	39.9 (t?)	167	1.2
Figure 1c	8.16 (d)	138	1.5
	13.90 (s?)	...	0.9
	20.43 (d)	131	3.1
	23.60 (d)	140	
	29.5 (m)	33	4.8
	39.5 (t?)	170	1.7
B_5H_9 (in diglyme)	13.30 (d)	161	4.0
	52.7 (d)	176	1.0

[a] Shifts relative to $(C_2H_5)_2O \cdot BF_3 = 0$. The assignments of the signals are given as s (singlet), d (doublet), t (triplet), and m (multiplet), with the recorded value being that for the center of each set of signals. [b] These figures may contain a small error due to the overlapping of several signals.

The mechanism of formation of the $B_9H_{14}^-$ ion is not clear, but the hydroborate ion does appear to enter fully into the reaction since, when lithium tetradeuterioborate was used, the ^{11}B nmr spectrum of the equimolar reaction mixture B_5H_9–$LiBD_4$ was initially similar to that in Figure 1a except that the doublets at δ +14.6 and +63.0 ppm and the multiplet at δ +31.0 ppm were less well resolved indicating that some distribution of deuterium had occurred. Again on standing at 25° the multiplet signal remained (but without any increase in resolution) while the other signals changed and became similar to those in Figure 1c as hydrogen and HD were evolved. The traces of diborane and pentaborane(9) recovered were shown to be partially deuterated from their ir spectra,[18,19] and the mass spectra of the two vapors indicated the presence of $B_2H_3D_3$ and $B_5H_4D_5$.[20,21] Further, we have been unable to detect any intermediates such as $B_5H_8^-$ [10,12] or $B_6H_9^-$ [22] from a comparison of

---

[13] N. N. Greenwood, H. J. Gysling, J. A. McGinnety, and J. D. Owen, *Chem. Commun.*, 505 (1970).

[14] L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, **85**, 2674 (1963).

[15] R. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).

[16] D. Marynick and T. Onak, *J. Chem. Soc. A*, 1160 (1970).

[17] R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

[18] H. J. Hrostowski and G. C. Pimentel, *J. Amer. Chem. Soc.*, **76**, 998 (1954).

[19] W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

[20] W. S. Koski and J. C. Kaufmann, *ibid.*, **24**, 221 (1956).

[21] J. F. Ditter, E. B. Klusmann, J. C. Perrine, and I. Shapiro, *J. Phys. Chem.*, **64**, 1682 (1960).

[22] H. D. Johnson, S. G. Shore, N. L. Mock, and J. C. Carter, *J. Amer. Chem. Soc.*, **91**, 2131 (1969).

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.

Acknowledgments.—We are grateful to Drs. R. E. Williams and J. F. Ditter of the Aerojet-General Corp. for a gift of pentaborane(9) and to Mr. P. Tyson for assistance in recording the nmr spectra. We thank the Science Research Council for research grants in support of this work and for the award of a studentship.

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IOWA, IOWA CITY, IOWA 52240

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

BY ROBERT BUCHACEK, DONALD W. HOPPENJANS,
AND GILBERT GORDON*

Received August 10, 1970

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

---

* To whom correspondence should be addressed.

[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).