

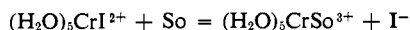
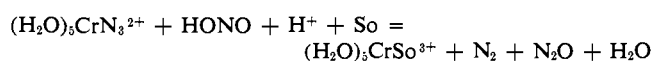
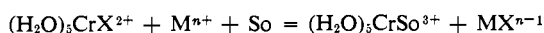
The Induced Solvolysis of Halochromium(III) and Azidochromium(III) Ions and the Spontaneous Solvolysis of Iodochromium(III) Ion in Water–Methanol Mixed Solvents¹

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Abstract: The induced solvolysis of halochromium(III) and azidochromium(III) ions in a water–methanol mixed solvent of a particular composition gives the same distribution of the two products, hexaaquochromium(III) ion and pentaquomethanolchromium(III) ion, for the different reactions. This suggests that a common intermediate, presumably pentaquochromium(III) ion, is produced in each of the reactions. The thermal solvolysis of iodochromium(III) ion gives these same relative amounts of the two products in each solvent composition studied if extrapolated to zero extent of reaction, thereby suggesting that this reaction also goes *via* the pentacoordinated intermediate. Bound water molecules in pentaquoiiodochromium(III) ion are labilized, and methanol may be introduced into the coordination shell prior to loss of iodide.

The question of whether or not a reactive intermediate pentaquochromium(III) ion is capable of existence in aqueous solution has not been settled. Although Ardon³ has presented data suggesting that aquation of pentaquoiiodochromium(III) ion proceeds *via* such an intermediate, Moore, Basolo, and Pearson⁴ have shown that these observations possibly can be explained without the necessity of the pentacoordinated intermediate. The latter authors have found that iodide ion bonded to chromium(III) causes a labilizing effect on water molecules bonded to chromium(III); they assume it is the water molecule *trans* to the iodide which is labilized. Observations relevant to the existence and reactivity of pentaquochromium(III) ion will be described in the present paper. Reactions of various complexes of chromium(III), $(\text{H}_2\text{O})_5\text{CrX}^{2+}$, where $\text{X}^- = \text{Cl}^-$, Br^- , I^- , and N_3^- , have been studied in water–methanol mixed solvents. These reactions are



with M^{n+} being Ti^{3+} , Hg^{2+} or Ag^+ , and So in each case being water or methanol. Taube and associates^{5–7} and others⁸ have used the same approach in studies on the possible production of the pentacoordinated intermediate, pentaammincobalt(III) ion, and the work reported here follows, in part, the pattern of some of these earlier studies.^{5,6} In the present study, carried out at room temperature ($25 \pm 1^\circ$), the average composition of the solvated chromium(III) product (moles of methanol bound per mole of chromium(III) ion of

charge 3+) was determined using an ion-exchange procedure⁹ for separating the bulk solvent from the mixture of the two inert, differently solvated chromium(III) ions, hexaaquochromium(III) ion and pentaquomethanolchromium(III) ion. Our observation of essentially the same value for the ratio of the amounts of these two products in the different reactions in a particular solvent is consistent with a common intermediate. As has been pointed out,⁷ such observations do not, however, prove that a common intermediate is produced.

Experimental Section

Reagents. Solutions were prepared using doubly distilled water; between the two distillations, the water was passed through an ion-exchange demineralizer (Barnstead Bantam BD-1). Analyzed reagent-grade methanol (Matheson Coleman and Bell) was used without further purification.

For use in the synthesis of bromochromium(III) ion and iodochromium(III) ion,¹⁰ a perchloric acid solution of chromium(II) perchlorate was prepared by dissolving chromium metal (United Mineral and Chemical Corp., >99.999% pure) in perchloric acid.¹¹ The halochromium(III) ions were prepared by the reaction of chromium(II) ion with bromine or triiodide ion.¹² The halochromium(III) ion was separated from the reaction mixture by an ion-exchange procedure analogous to those used previously.¹³ Chlorochromium(III) ion was obtained by ion-exchange separation of species (isomeric dichlorochromium(III) ions, chlorochromium(III) ion, and hexaaquochromium(III) ion) present in the mixture resulting from aquation and isomerization of *trans*-dichlorochromium(III) ion in dilute perchloric acid solution.^{14,15} Azidochromium(III) ion was obtained similarly from a hydrazoic acid–potassium azide buffer solution containing chromium(III) perchlorate which had been allowed to stand at room temperature for 3–4 days.¹⁶ Each of these procedures for preparing the monoligandchromium(III) species has been used previously, and in each case separation of the ion of charge 2+ ($(\text{H}_2\text{O})_5\text{CrX}^{2+}$) from the chromium(III) species of other charge was easily accomplished by ion-exchange procedures.

A solution containing mercury(II) perchlorate and perchloric acid was prepared by dissolving reagent grade mercury(II) oxide

(1) Based upon the Ph.D. thesis of S. P. Ferraris, University of Colorado, 1969. Supported in part under National Science Foundation Grants GP-680 and GP-7185X.

(2) N.A.S.A. Predoctoral Fellow (1965–1968); University of Colorado Fellowship (1968–1969).

(3) M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).

(4) P. Moore, F. Basolo, and R. Pearson, *ibid.*, **5**, 223 (1966).

(5) F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **79**, 255 (1957).

(6) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(7) G. E. Dolbear and H. Taube, *ibid.*, **6**, 60 (1967).

(8) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *ibid.*, **6**, 1027 (1967).

(9) J. C. Jayne and E. L. King, *J. Amer. Chem. Soc.*, **86**, 3989 (1964).

(10) In general, the coordinated water molecules will be omitted in naming the chromium(III) complex ions.

(11) J. P. Fackler, Jr. and D. G. Holah, *Inorg. Chem.*, **4**, 954 (1965).

(12) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

(13) F. A. Guthrie and E. L. King, *ibid.*, **3**, 916 (1964); T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

(14) H. S. Gates and E. L. King, *J. Amer. Chem. Soc.*, **80**, 5011 (1958).

(15) J. D. Salzman and E. L. King, *Inorg. Chem.*, **6**, 426 (1967).

(16) T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).

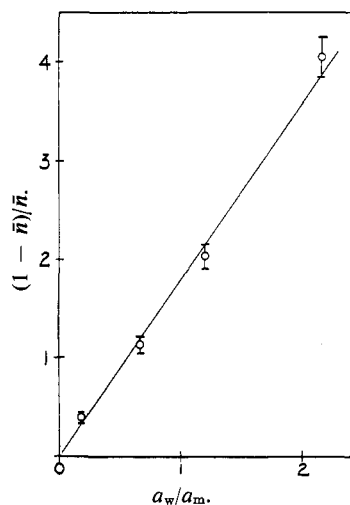


Figure 1. $(1 - \bar{n})/\bar{n}$ vs. a_w/a_m . The slope of the line (1.8) is identified as k_1/k_2 . (The uncertainty designations correspond to an uncertainty of $\pm 4\%$ in \bar{n} .)

in excess perchloric acid. A solution containing silver(I) perchlorate and perchloric acid was prepared in an analogous way from precipitated silver(I) oxide. Hydrated thallium(III) perchlorate was the source of thallium(III) ion. Sodium nitrite was the source of nitrous acid; the reaction mixtures were acidic enough to convert nitrite ion to nitrous acid.

The mixed solvents containing a known concentration of perchloric acid (range 0.02–0.10 *M*) were prepared by a combination of gravimetric and volumetric techniques. The various solutions used in the experiments were prepared from these mixed solvents immediately before use; neither the chromium(III) complex nor the inducing reagent (mercury(II), silver(I), thallium(III), or nitrous acid) was in the methanol-containing solvent for more than a few minutes before the reactant solutions were mixed.

Reagent grade Dowex 50W resins (in the hydrogen ion form) were used. For the preparative work, X-12 resin (100–200 mesh) was used; for analysis of the reaction mixtures (separation of species of charge 3+ from the solvent mixtures), X-8 resin (50–100 mesh) was used. Resin was purified by treatment with alkaline peroxide and with ~ 3 *M* hydrochloric acid.

Analytical Procedures. Chromium analysis, where required, was performed by first converting the chromium to chromate(VI) ion with alkaline peroxide; the light absorption was then measured at 372 nm.¹⁷ Analysis for methanol bound to chromium(III) was made by the procedure used previously.⁹ Methanol is oxidized to carbon dioxide by a mixture of cerium(IV) and chromium(VI) in ~ 12 *M* sulfuric acid. As usually carried out in this study, 0.05 to 0.006 mmol of methanol was analyzed with an accuracy of $\pm 3\%$.

The Induced Solvolysis of Halochromium(III) Ion.—Acidic solutions of halochromium(III) ion in the binary solvent were mixed at room temperature with acidic solutions of thallium(III), mercury(II), or silver(I) perchlorate in a binary solvent of the same composition. In most experiments, comparable volumes of the two solutions were used; the final volume was 150–300 ml, and the stoichiometric concentration of chromium(III) was 10^{-4} to 10^{-3} *M*. In experiments with mercury(II) in excess, the green color of chlorochromium(III) ion changed to the blue-violet of a mixture of hexa-aquo-chromium(III) ion plus penta-aquomethanolchromium(III) ion in ~ 10 min; with bromo- and iodo-chromium(III) ion the reaction occurred upon mixing. The reaction of thallium(III) with iodo-chromium(III) occurred upon mixing. The reaction of silver(I) ion with chlorochromium(III) ion was very slow ($\sim 25\%$ completion in 2 hr), and this reaction was not studied. The reactions of silver(I) with bromo- and iodo-chromium(III) ion were complete in 5–12 min. The reaction of nitrous acid with azido-chromium(III) ion was slow;^{17a} after 5–20 min, the unreacted nitrous acid was consumed with excess sulfamic acid.

(17) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

(17a) NOTE ADDED IN PROOF. R. C. Thompson and E. J. Kaufmann (*J. Amer. Chem. Soc.*, in press) have studied the rate of this reaction; they have confirmed the stoichiometry assumed here.

In experiments containing an excess of metal ion, hydrochloric acid was added to the mixture after reaction was complete in order to complex (or precipitate) the metal ion before the ion-exchange procedure. In the experiments using silver(I) ion, the precipitated silver(I) halide was filtered from the solution before the ion-exchange procedure. The excess inducing metal ion (mercury(II) or thallium(III)) or the unreacted chromium(III) complex was eluted from the resin phase with 0.50 *M* perchloric acid and/or 0.10 *M* hydrochloric acid. The column then was rinsed with ~ 0.10 *M* perchloric acid (an aqueous solution) to remove completely the free solvent methanol. After the rinse, the chromium(III) species of charge 3+ (hexa-aquo-chromium(III) ion and penta-aquomethanol-chromium(III) ion) were eluted with 3 *M* sulfuric acid and analyzed for total chromium and total methanol. It was demonstrated that aqation of methanolchromium(III) species during the rinsing procedure was not appreciable ($<10\%$).

The experimentally measured quantity, \bar{n} , the average number of methanol molecules bound per chromium(III) ion, is related to the relative amounts of hexa-aquo-chromium(III) ion and penta-aquomethanolchromium(III) ion

$$[\text{Cr}(\text{OH}_2)_6(\text{OHMe})^{3+}]/[\text{Cr}(\text{OH}_2)_6^{3+}] = \bar{n}/(1 - \bar{n})$$

if only these two differently solvated chromium(III) ions are present. This was checked in a reaction between silver(I) ion and iodo-chromium(III) ion; the differently solvated chromium(III) species produced were separated from one another using the ion-exchange procedure developed by Mills.¹⁸ Only hexa-aquo-chromium(III) ion and penta-aquo-chromium(III) ion were found in an elution in which 95% of the chromium(III) was recovered.

The results of the experiments did not depend upon the order of mixing or upon the relative amounts of inducing reagent and chromium(III) complex. In the reaction of mercury(II) ion with chlorochromium(III) ion, variation of the ratio (moles of mercury(II))/(moles of chlorochromium(III)) from 0.77 to 9.1 had no appreciable effect upon the derived value of \bar{n} .

The Spontaneous Solvolysis of Iodo-chromium(III) Ion. The spontaneous solvolysis of iodo-chromium(III) ion has been studied at room temperature in solvents of approximately the same composition as were used in the induced solvolysis studies. In these experiments, initial stages of the ion-exchange procedure (analogous to that already described) were carried out at $\sim 0^\circ$. In most of the experiments, unreacted iodo-chromium(III) ion was eluted from the column with cold ($\sim 0^\circ$) aqueous 0.5 *M* perchloric acid. In some experiments, however, the unreacted iodo-chromium(III) ion was eluted from the column with cold ($\sim 0^\circ$) 0.75 *M* perchloric acid in the same mixed solvent as used in the experiment. (The results were the same as those in which the unreacted iodo-chromium(III) ion was eluted with an aqueous solution.) With the unreacted iodo-chromium(III) ion removed, the remainder of the procedure, the rinsing with 0.10 *M* perchloric acid and the elution of chromium(III) species of charge 3+ with 3 *M* sulfuric acid, was performed at room temperature (as in analysis of experiments on the induced solvolysis). The objective of these experiments was evaluation of \bar{n} for product species, extrapolated to zero extent of reaction. It was anticipated that the labilizing effect of coordinated iodide, demonstrated by Moore, Basolo, and Pearson,⁴ would cause methanol to be incorporated into the first coordination shell of the reactant iodo-chromium(III) ion. The effect of this reaction is absent from this extrapolated value of \bar{n} of the product species. Although direct demonstration of the presence of iodo-methanolchromium(III) ion in the reaction mixture would be desirable, the relevant data cannot be obtained by the procedures employed in this study. The labilizing effect of the coordinated iodide allows any coordinated methanol to be replaced by water during the aqueous rinsing procedure in which free solvent methanol is eliminated.

Results

The results of 88 different experiments on the induced solvolysis of certain chromium(III) complexes in acidic water-methanol solution are summarized in Table I. Although seven different reactions were studied, the variation in the observed values of \bar{n} for a particular solvent composition is within the experimental error, which is judged to be $\pm 4\%$. The dependence of these observed values of \bar{n} upon solvent composition is presented in Figure 1 (a plot of $(1 - \bar{n})/\bar{n}$ vs. a_w/a_m , where

(18) C. C. Mills, III, and E. L. King, forthcoming publication.

a_w and a_m are the activities of water and methanol, respectively). (Values of the ratio of activities used were interpolated from those tabulated in an earlier study⁹ for 30°.)

Table I. Value of \bar{n} = (Bound CH_3OH)/(Total Cr^{III}) in Chromium(III) Species Produced in Induced Solvolysis^{a-c}

Reaction	Z^d			
	0.28	0.46	0.64	0.87
$\text{Ti}^{3+} + \text{CrI}^{2+}$	0.204 (2)	0.318 (2)	0.462 (2)	0.74 (2)
$\text{Hg}^{2+} + \text{CrI}^{2+}$	0.203 (2)	0.335 (2)	0.473 (2)	0.72 (2)
$\text{Hg}^{2+} + \text{CrBr}^{2+}$	0.199 (4)	0.330 (4)	0.467 (2)	0.71 (2)
$\text{Hg}^{2+} + \text{CrCl}^{2+}$	0.194 (12)	0.337 (6)	0.470 (13)	0.72 (4)
$\text{Ag}^+ + \text{CrI}^{2+}$	0.206 (3)	0.323 (3)	0.467 (2)	0.74 (2)
$\text{Ag}^+ + \text{CrBr}^{2+}$	0.195 (2)	0.339 (2)	0.471 (2)	
$\text{HONO} + \text{CrN}_3^{2+}$	0.201 (2)	0.323 (3)	0.476 (2)	0.72 (2)

^a Room temperature ($25 \pm 1^\circ$); $\sim 0.10 M \text{HClO}_4$. ^b The exact solvent composition in individual experiments varied over a range of 0.02 (at $Z \cong 0.28$) to 0.08 (at $Z \cong 0.87$) unit of Z . These experimental values were corrected to the value appropriate for the solvent compositions given in the column heading. (The correction is ~ 0.008 unit in \bar{n} per 0.01 unit in Z .) ^c Number in parentheses gives number of independent experiments. ^d Z = mole fraction of methanol considering only solvent components (Z = (moles of methanol)/(moles of methanol + moles of water)).

Results of the spontaneous solvolysis of iodochromium(III) ion in acidic water-methanol solution are presented in Figure 2 (a plot of \bar{n} for the mixture of product species vs. the fraction of the iodochromium(III) which had reacted). The data fall on approximately straight lines, with the data at two different electrolyte concentrations at $Z = 0.47$ defining two different lines. The straight lines in the figure were calculated by the method of averages. The intercepts and the values of \bar{n} obtained at these solvent compositions in the induced solvolysis experiments are presented in Table II. The agreement is within the probable error of establishing the intercept.

Table II. Limiting Value of \bar{n} in Thermal Solvolysis of Pentaquoiodochromium(III) Ion in Mixed Solvents

Z	\bar{n}^a	\bar{n}^b
0.27	0.21	0.20
0.47	0.29, 0.30	0.32
0.65	0.49	0.47

^a Intercept in Figure 2. ^b Value obtained under assumption of SN1 mechanism with $k_1/k_2 = 1.8$.

Discussion

Data obtained from the induced solvolysis studies in each solvent suggest strongly that a common intermediate is generated in each of the several reactions. The ratio of the rate constants for the two reactions which consume the intermediate, assumed to be pentaquochromium(III) ion,¹⁹ can be obtained from Figure

(19) S. T. Spees, Jr., J. R. Perumareddi, and A. W. Adamson (*J. Amer. Chem. Soc.*, **90**, 6626 (1968)) have performed calculations based on crystal-field theory which suggest that reactions of chromium(III) species giving a pentacoordinated intermediate would have an activation energy greatly in excess of the values observed for such reactions. These authors conclude, therefore, that ligand exchange reactions of chromium(III) do not occur *via* a pentacoordinated intermediate.

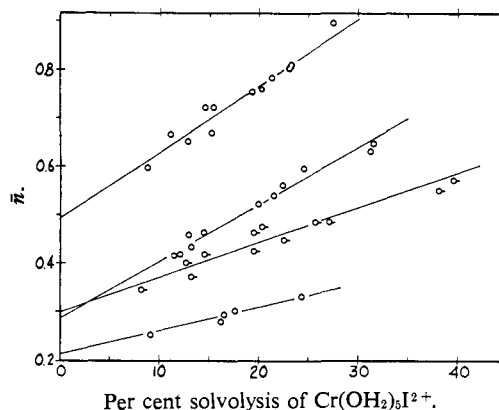
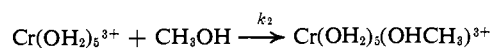
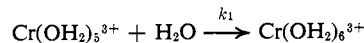
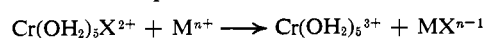


Figure 2. \bar{n} of chromium(III) product in thermal aquation of pentaquoiodochromium(III) ion. Series with intercept 0.49 ($Z = 0.65$); series with intercepts ~ 0.295 ($Z = 0.47$) (upper line $I = 0.15$; lower line $I = 0.10$); series with intercept 0.21 ($Z = 0.27$).

1. The reaction sequence



leads to the relationship between \bar{n} and solvent composition

$$\frac{(1 - \bar{n})}{\bar{n}} = \frac{k_1/\gamma^{\pm w}}{k_2/\gamma^{\pm m}} \left(\frac{a_w}{a_m} \right)$$

in which $\gamma^{\pm w}$ and $\gamma^{\pm m}$ are the activity coefficients of the transition states for the reactions with rate constants k_1 and k_2 , respectively. The data fall on a reasonably straight line, which indicates that there is little dependence of $\gamma^{\pm m}/\gamma^{\pm w}$ upon solvent composition. The slope of this line can be identified as k_1/k_2 if $\gamma^{\pm m}/\gamma^{\pm w} = 1$; therefore, $(k_1/k_2) = 1.8$. This value, the kinetic discrimination of pentaquochromium(III) ion for water over methanol, can be contrasted with the equilibrium discrimination: $6/Q_1 \cong 9$, where $Q_1/6$ is the statistically corrected value of the equilibrium quotient for replacement of one water molecule in hexaquochromium(III) ion by methanol.⁹ That the kinetic discrimination factor is closer to unity than the equilibrium discrimination factor is consistent with the presumed high reactivity of pentaquochromium(III) ion.

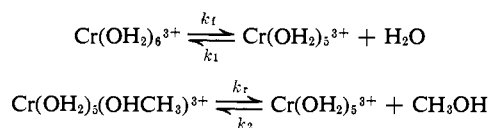
The value for k_1/k_2 obtained in the studies of induced solvolysis can be used to probe the question of whether or not the exchange of oxygen-18 between solvent water and hexaquochromium(III) ion occurs *via* the intermediate pentaquochromium(III) ion. To do this, consideration is given also to the rate of establishment of equilibrium²⁰ and the position of equilibrium⁹ in the solvent exchange reaction



If this latter reaction proceeds by way of the intermediate, and not by a transition state of coordination number seven, the complete mechanism for the solvent exchange reaction includes the two reactions with rate

(20) R. J. Baltisberger and E. L. King, *ibid.*, **86**, 795 (1964).

constants k_f and k_r



in addition to those involving the rate constants k_1 and k_2 , which are the reverse of the two reactions given above. In this case the value of k_f is related to k' , the first-order rate constant for the approach to equilibrium (k of ref 20), in the following way

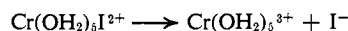
$$k_f = k' \frac{1 + (k_1/k_2)(a_w/a_m)}{1 + a_w/(Q_1 a_m)}$$

in which it is assumed that Brønsted activity coefficient factors are unity; Q_1 is the equilibrium quotient for the overall reaction. The value of k_f calculated from the data of the present study ($k_1/k_2 = 1.8$, assumed to be valid for 30°), the data of Baltisberger and King (k'),²⁰ and the data of Jayne and King ($Q_1 \cong 0.60$ at 30°)⁹ is $\sim 1.25 \times 10^{-5} \text{ sec}^{-1}$ (extrapolated to pure water) at 303°K. This should also be the value of k_{ex} (the first-order rate constant for oxygen-18 exchange) if each of the exchange reactions (water for water and methanol for water) occurs by way of the pentacoordinated intermediate. The value of k_{ex} ²¹ extrapolated to 30° is $\sim 3.4 \times 10^{-5} \text{ sec}^{-1}$. Since this value is greater than the value derived under the limiting assumption that the methanol for water exchange goes exclusively by way

(21) J. P. Hunt and R. A. Plane, *J. Amer. Chem. Soc.*, **76**, 5960 (1954).

of the pentacoordinated intermediate, one must conclude that the ¹⁸O exchange does not go predominantly by way of such an intermediate. Taking the derived constants at being error free, one would conclude that the fraction of the oxygen-18 exchange proceeding *via* the pentacoordinated intermediate cannot exceed ~ 0.4 ($= 1.25 \times 10^{-5} / 3.4 \times 10^{-5}$). If, however, one were to assign a generous margin of error to the several experimentally observed quantities upon which this calculation is based, the conclusion is possible that both ligand exchange reactions (water for water and methanol for water) may occur by the S_N1 mechanism. This is as far as one can go in drawing conclusions regarding the mechanism for the oxygen-18 exchange from these data.

Iodide ion is a better leaving group than water, its aquation from iodochromium(III) ion being ~ 35 -fold faster than the rate of oxygen-18 exchange (which is corrected statistically for this calculation). Ardon's conclusion³ that the thermal aquation of pentaquoiodochromium(III) ion proceeds by an S_N1-type mechanism with



as the first step is supported by the agreement between the limiting values of \bar{n} in the present thermal solvolysis studies and the values observed in the induced solvolysis studies. The increase in \bar{n} with increasing extent of reaction supports the suggestion of Moore, Basolo, and Pearson⁴ regarding the labilizing effect of coordinated iodide. It does not demand, however, that iodide labilize only the *trans* water.