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Aquation and Chromium(II)-Catalyzed Aquation Reactions of the Iodoaquo- and Chloroiodotetraamminechromium(III) Complexes

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Salts of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ and *trans*-$Cr(NH_3)_4ICl^+$ have been prepared and the stoichiometry and kinetics of their aquation reactions have been investigated. For these three ions as well as the *cis*- and *trans*-$Cr(NH_3)_4(OH)I^+$ ions, replacement of coordinated iodide by water is first order in complex concentration and occurs with retention of configuration. Rate constants and activation parameters for the hydrolysis of *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ are $k_0 = (1.75 \pm 0.12) \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 21.4 \pm 0.4$ kcal/mol, and $\Delta S^{\ddagger} = -5 \pm 1$ eu at $30.0 \pm 0.1°$, and for *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$, $k_0 = (1.12 \pm 0.03) \times 10^{-3}$ sec^{-1}, $\Delta H^{\ddagger} = 19.7 \pm 0.3$ kcal/mol, and $\Delta S^{\ddagger} = -6 \pm 1$ eu at $25.0 \pm 0.1°$. The observed first-order rate constants and activation parameters for the loss of coordinated iodide from *trans*-$Cr(NH_3)_4(OH)I^+$ are $k_{OH} = 0.367 \pm 0.003$ sec^{-1}, $\Delta H^{\ddagger} = 18.7 \pm 0.3$ kcal/mol, and $\Delta S^{\ddagger} = 5.5 \pm 1$ eu at $10.0 \pm 0.1°$; for *cis*-$Cr(NH_3)_4(OH)I^+$, $k_{OH} = 1.25 \pm 0.05$ sec^{-1}, $\Delta H^{\ddagger} = 17.0 \pm 0.6$ kcal/mol, and $\Delta S^{\ddagger} = 2 \pm 2$ eu at $10.0 \pm 0.1°$; for *trans*-$Cr(NH_3)_4ICl^+$, $k_0 = (3.28 \pm 0.05) \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 18.0 \pm 0.1$ kcal/mol, and $\Delta S^{\ddagger} = -9 \pm 0.5$ eu at $25.0 \pm 0.1°$. All rate measurements were made at unit ionic strength. The aquation of *trans*-$Cr(NH_3)_4ICl^+$ is not dependent on hydrogen ion in the concentration range 0.1–1.0 *M*. The chromium(II)-catalyzed aquation reactions of the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ ions were observed to obey the rate law $-d[\text{complex}]/dt = k_2[Cr(II)][\text{complex}]$ and to result in the formation of the iodopentaaquochromium(III) ion. Second-order rate constants and activation parameters for the chromium(II)-assisted aquations are $k_2 = 14.6 \pm 0.2$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 8.7 \pm 0.1$ kcal/mol, and $\Delta S^{\ddagger} = -24 \pm 1$ eu at $25.0 \pm 0.1°$ for *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$ and $k_2 = 165 \pm 6$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 7.1 \pm 0.1$ kcal/mol, and $\Delta S^{\ddagger} = -24 \pm 1$ eu at 25.0° for *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$, both at unit ionic strength with 1 *M* $HClO_4$.

Introduction

In this paper we report the synthesis of the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ ions and the details of both the spontaneous and the Cr(II)-catalyzed aquation reactions. The *trans*-$Cr(NH_3)_4ICl^+$ ion has also been prepared and the kinetics of aquation investigated. Although the bis-ethylenediamine complexes of chromium(III) have been studied extensively, there have been few reports concerning the tetraammine analogs.[1,2] Among the halogen derivatives, the iodo complexes should exhibit the extreme behavior: the iodo ligand should be the least strongly bound, and the possibilities of generating an intermediate of reduced coordination number and of observing isomerization should be maximized.

It has been suggested that a pentacoordinated intermediate is involved in the aquation of the $Cr(H_2O)_5I^{2+}$ ion, although the peculiarities observed for this reaction have been attributed also to the trans-activating influences of the iodide ion.[3,4] This particular example is clouded by the inability to distinguish among the five aquo ligands and by the fact that there is no possibility for isomerization to accompany the aquation. The iodoaquotetraammines, however, have only one aquo ligand at a specified geometry, and the aquation products can exist in both cis and trans forms.

Experimental Section

Materials. *cis*- and *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$.—These starting materials were prepared according to directions in the literature.[5]

trans-$[Cr(NH_3)_4(H_2O)I]I_2$.—Several approaches to the synthesis of this species were explored. A suspension of 10 g of the orange *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$ in 50 ml of 47% HI was stirred while being heated at 60° until the color had become light green. A green precipitate could also be prepared by adding 10 g of the diaquo perchlorate and 20 g of NaI to 200 ml of methanol and partially evaporating the solution on a hot plate. In each case the reaction mixtures were filtered, and the residue was washed with methanol (which dissolves residual *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$) and dried with ether. Material of a similar color was prepared by the thermal dehydration of 10 g of *trans*-$[Cr(NH_3)_4(H_2O)_2]I_3$ for several hours in an oven at 90°. Approximately 8 g of raw product was realized in each synthesis. Spectra of acidic solutions of the green materials in the region 300–650 nm revealed gross similarities characterized by an initial isosbestic point at 500 nm which moved with time to a permanent position at 535 nm. Since an isosbestic point was observed at 500 nm during the aquation of the *cis*-iodoaquo ion, it was a suspected impurity in all three preparations. This suspicion was confirmed when it was discovered that heating the filtrate from the methanol solution after the addition of another 5 g of NaI yielded a precipitate which gave a spectrum identical with that of *cis*-$[Cr(NH_3)_4(H_2O)I]I_2$. Extraction of the green material prepared from aqueous HI with 1 *M* $HClO_4$ revealed the presence of an insoluble impurity which has tentatively been identified as *trans*-$[Cr(NH_3)_4I_2]I$. Because this procedure appears to involve the least amount of isomerization and because the diiodo by-product is easily removed, this was the synthetic route employed.

Since the *cis*-iodoaquotetraamminechromium(III) chloride was observed to be more soluble than the corresponding trans isomer, the raw material was converted to the chloride salt in an attempt to isolate the trans isomer. For reasons to become evident, the procedure was not adaptable to this purpose.

The method employed made use of the greater hydrolysis rate of the cis isomer. Ten grams of the raw material was dissolved in approximately 150 ml of 1 *M* $HClO_4$ and the solution was allowed to stand for 1 hr at room temperature. Owing to hydrolysis,

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[1] For example, L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

[2] (a) J. M. Dechant and J. B. Hunt, *J. Amer. Chem. Soc.*, **90**, 3695 (1969); (b) D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, **7**, 2506 (1968).

[3] M. Ardon, *ibid.*, **4**, 372 (1965).

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

[5] D. W. Hoppenjans, J. B. Hunt, and J. M. DeChant, *Chem. Commun.*, 510 (1968).

the concentration of the cis impurity was reduced relative to that of the trans species during the period of standing. The dropwise addition of 20 ml of 47% HI caused the precipitation of a substance much greener than the starting material. The *cis*- and *trans*-diaquo ions remain in solution in that they are much more soluble than the iodoaquo complex. The precipitate was collected on a filter and washed with alcohol and ether. This procedure was repeated, except that subsequent solutions were allowed to stand for only 20 min, until a solution of the precipitate in 1 *M* $HClO_4$ underwent aquation with a well-defined and permanent isosbestic point at 535 nm; yield 2 g. *Anal.* Calcd for *trans*-$[Cr(NH_3)_4(H_2O)I]I_2$: Cr, 10.0; I, 73.4; N, 10.8; H, 2.7. Found: Cr, 10.1; I, 73.3; N, 10.7; H, 2.6.

trans-**$[Cr(NH_3)_4(H_2O)I](ClO_4)_2$**.—The iodide salt was converted to the perchlorate by dissolving 4 g of the pure iodide in 50 ml of ice-cold 2 *M* $HClO_4$ followed by the slow addition of 200 ml of 70% $HClO_4$. The crude perchlorate salt was collected on a filter and washed with 2-propanol and ether. The material was recrystallized first from methanol and finally from ice-cold 2 *M* $HClO_4$ by the dropwise addition of 70% $HClO_4$; yield 2 g. *Anal.* Calcd for *trans*-$[Cr(NH_3)_4(H_2O)I](ClO_4)_2$: Cr, 11.2; I, 27.3; N, 12.1; H, 3.0. Found: Cr, 11.1; I, 26.7; N, 11.7; H, 3.0.

cis-**$[Cr(NH_3)_4(H_2O)I]I_2$**.—Ten grams of the *cis*-diaquo perchlorate was added to 50 ml of 47% HI and the suspension was stirred and heated until the color was light violet. In another experiment, 10 g of the *cis*-diaquo perchlorate and 20 g of NaI were added to 150 ml of methanol and the mixture was partially evaporated by stirring and heating. After 30 min, a dark violet precipitate was visible. In both cases, the solutions were filtered and the residues were washed with methanol and ether. By adding another 5 g of NaI to the filtrate of the methanol preparation and heating, a second crop of crystals could be obtained. No indication of isomerization was observed when either procedure was used, but, because the methanol route was more convenient and gave 50% better yields, it was employed for the bulk of this work. *Anal.* Calcd for *cis*-$[Cr(NH_3)_4(H_2O)I]I_2$: Cr, 10.0; N, 10.8; H, 2.7. Found: Cr, 9.8; N, 10.6; H, 2.7.

cis-**$[Cr(NH_3)_4(H_2O)I](ClO_4)_2$**.—Conversion of the complex from the iodide to the perchlorate salt was accomplished by carefully triturating 10 g of the purified iodide with 25 ml of 70% $HClO_4$. The slush was stirred vigorously to aid the evolution of HI and filtered. The residue was extracted with several 25-ml aliquots of methanol in which the iodoaquo perchlorate is soluble and the latter was precipitated by the very slow addition of 70% $HClO_4$ to the cold solution. The material was recrystallized from methanol and from 2 *M* $HClO_4$ by addition of 70% $HClO_4$. *Anal.* Calcd for *cis*-$[Cr(NH_3)_4(H_2O)I](ClO_4)_2$: Cr, 11.2; N, 12.1; H, 3.0; I/Cr, 1.0. Found: Cr, 11.2; N, 11.6; H, 2.9; I/Cr, 0.98.

trans-**$[Cr(NH_3)_4ICl](ClO_4)$**.—Fifteen grams of *erythro*-chloro perchlorate[6] was added to a solution of 40 ml of 47% HI and 50 ml of 70% $HClO_4$ in a lightly stoppered flask. This suspension was allowed to stand for 15 hr by which time the color had changed from violet to green. The mixture was filtered and the residue was washed with methanol until the filtrate was clear. By extracting the mixture with ten 100-ml aliquots of ice-cold 1 *M* $HClO_4$ it was possible to enrich the chloroiodo content of the residue by dissolving the more soluble aquopentaammine complex. The *trans*-chloroiodo perchlorate was recovered from the remaining residue by extracting it into ten 50-ml aliquots of methanol and precipitating it from the immediately cooled extract by the dropwise addition of concentrated $HClO_4$. The solid was collected on a filter and washed with 2-propanol and ether; yield 3 g. It was recrystallized from methanol and washed with several 10-ml aliquots of cold 1 *M* $HClO_4$, 2-propanol, and ether; yield 2 g. The final washing with 1 *M* $HClO_4$ was found to be necessary as indicated by ion-exchange results in order to remove the final traces of aquopentaamminechromium(III). *Anal.* Calcd for *trans*-$[Cr(NH_3)_4ICl](ClO_4)$: Cr, 13.6; I, 33.2; N, 14.7; H, 3.2. Found: Cr, 13.7; I, 32.9; N, 14.6; H, 3.1.

Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate solutions with zinc which was amalgamated with mercuric perchlorate. The chromium(II) solutions were stored under nitrogen which was deoxygenated by bubbling through chromium(II) perchlorate washing towers. Platinum hypodermic needles were used in handling the Cr(II) solutions.

Sodium perchlorate solutions were prepared by neutralization of perchloric acid solutions with sodium carbonate. Distilled and deionized water was used throughout and all other chemicals were reagent grade.

Analytical Methods.—Hydrogen and nitrogen analyses were performed by the analytical services group[7] at the University of Iowa. Chromium was oxidized to chromate with alkaline peroxide and measured either spectrophotometrically by its absorbance[8] at 375 nm or potentiometrically[9] by titration of acidified solutions against standard ferrous ammonium sulfate using a combination platinum–calomel electrode. The chromium(II) concentration of chromous solutions was determined by reaction with excess potassium iodate followed by titration of the remaining iodate against standard thiosulfate in the presence of excess iodide.[10] Complexes to be analyzed for halogen were digested in base and neutralized prior to analysis. Ionic chloride and iodide were determined potentiometrically by titration against standard silver nitrate using a combination silver–mercurous sulfate electrode.[11] A Model 26 Radiometer pH meter was used for all potentiometric titrations. In some cases, iodide was measured by its absorption[12] at 225 nm.

Spectra.—A Cary Model 14 recording spectrophotometer was used to measure the ultraviolet and visible spectra of the various complexes. Changes in the spectra during the measurement were significant for some of the complexes; thus the values reported were measured as follows. Samples were weighed in small volumetric flasks and diluted to the mark with 1 *M* $HClO_4$. Aliquots of these solutions were transferred to cuvettes and several scans were recorded at specified time intervals. The chromium and iodide concentrations of the remainder of the solutions were determined spectrophotometrically. The A_0 values at any given wavelength were determined from the intercept of the plots $\ln(A_t - A_\infty)$ *vs.* time. The A_∞ could be calculated by using the chromium or iodide concentrations and the known extinction coefficient of the products or could be observed spectrophotometrically by allowing the aquation reaction to proceed to completion. Extinction coefficients for the reacting complexes were calculated from the A_0 values and the measured chromium and iodide concentrations.

Kinetics.—The loss of iodide ion from the various complexes in acid solution was followed spectrophotometrically in both the visible and the ultraviolet regions of the spectrum. For runs made in the visible region, samples were weighed into 1-cm quartz cells. The cells were fitted with serum caps and deaerated with a stream of prepurified nitrogen for about 10 min in the dark. During this time, 3.1 ml of a deaerated solution of perchloric acid, adjusted to unit ionic strength with $NaClO_4$, was withdrawn into a syringe and the syringe was immersed in a water bath held at the temperature of the run. It required less than 30 sec to remove the syringe from the bath, transfer the solution to the cell, and mix and introduce the cell into the thermostated cell compartment of the Cary 14.

For the measurements in the ultraviolet region the procedure was the same except that the samples were not weighed and a 0.1-cm cell was used.

Although the experiments were carried out in a nitrogen atmosphere, spectra of solutions of the products in which the initial concentration of reactant was $(2.3 \pm 0.5) \times 10^{-2}$ *M* revealed

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[6] M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **299**, 15 (1959).

[7] Funds for this service derive directly from the Graduate College, University of Iowa.

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

[9] A. I. Vogel, "Quantitative Inorganic Analysis," 34th ed, Longmans, Green and Co., London, 1961, p 311.

[10] H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

[11] D. Jaques, *J. Chem. Educ.*, **42**, 429 (1965).

[12] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).

TABLE I

SPECTRAL DATA FOR TETRAAMMINECHROMIUM(III) COMPLEXES

Spectral maxima		Spectral minima	
λ, nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}
cis-$Cr(NH_3)_4(H_2O)I^{2+}$			
546	62.3 ± 0.9	483	30.0 ± 0.3
471	34.0 ± 0.5	446	18.0 ± 0.1
295	(3.44 ± 0.05) × 10^3	278	(3.05 ± 0.05) × 10^3
244	(6.51 ± 0.02) × 10^3		
215	9 × 10^3	236	6.4 × 10^3
trans-$Cr(NH_3)_4(H_2O)I^{2+}$			
590	37.4 ± 0.2	509	14.0 ± 0.3
472	33.6 ± 0.1	449	20.3 ± 0.2
294	(2.88 ± 0.03) × 10^3	281	(2.7 ± 0.1) × 10^3
243	(5.9 ± 0.1) × 10^3	228	(5.4 ± 0.1) × 10^3
trans-$Cr(NH_3)_4ICl^{+}$			
620	60.2 ± 0.2	527	4.2 ± 0.1
480	27.5 ± 1.0	458	17.2 ± 0.1
310 sh	(2.9 ± 0.1) × 10^3	244	(3.6 ± 0.2) × 10^3
260	(8.4 ± 0.2) × 10^3		

the presence of 10^{-5}–10^{-6} M I_2 and I_3^-. The addition of a small amount of $S_2O_3^{2-}$ to these solutions changed the spectra to those which could be accounted for in terms of the chromium(III) complexes alone. At the visible wavelength chosen for the study, small amounts of I_2 and I_3^- do not absorb. Consequently, good agreement between kinetic measurements made in both the presence and the absence of added $S_2O_3^{2-}$ would be predicted and was observed.

To follow the loss of iodide ion from *cis*- and *trans*-$Cr(NH_3)_4(OH)I^{2+}$, 5.938 ml of a NaOH solution, adjusted to unit ionic strength with $NaClO_4$, was added to a 2-cm cylindrical quartz cell. The cell was fitted with a serum cap and placed in the thermostated sample compartment of the rapid-mixing apparatus.[13] After 15 min and immediately prior to the run, the complex was dissolved in several milliliters of cold 1 M $NaClO_4$ which had been acidified to a pH of approximately 5. This solution was withdrawn into a spring-driven rapid-mixing syringe[13] and a specific volume, which varied between 0.31 and 0.38 ml, was fired into the NaOH solution. Transmittance *vs.* time data were recorded on a Moseley 7101A strip chart recorder.

Following the reaction between chromium(II) and the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ ions involved weighing the samples into 2-cm cylindrical quartz cells, capping with serum caps, and deaerating for at least 15 min. Following this, 5.938 ml of deaerated 1 M $HClO_4$ was withdrawn from a reservoir and added to the cell *via* syringe. Deaeration was continued throughout this process and for several minutes beyond. For runs at 15 and 20°, the cell was cooled in an ice bath for ~20 sec following the addition of the acid. It was then placed in the thermostated sample compartment of the spectrometer and allowed to reach temperature equilibrium. A specific volume which varied between 0.27 and 0.37 ml of the chromium(II) solution was then added *via* the rapid-mixing syringe. Except for those runs at 25° where the time was less, an average of 20 min elapsed between the addition of the acid to the cell and the addition of the chromium(II) solutions. Spontaneous aquation during this time was insignificant for the trans isomer but it was appreciable for the cis isomer. Based on qualitative observations, the reaction between chromium(II) and either *cis*- or *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ is too slow to contribute to the color change associated with the reduction of the iodo complexes. Several runs were made by means of an alternate procedure in which only a small time elapsed between dissolution and initiation of the reduction without observable effect on the results.

It is also important to note, that even in the case of the cis complexes, *no* evidence was obtained for the loss of ammine ligands during the aquation reactions.

Results and Discussion

Identification of Complexes.—Identification of the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ and *trans*-$Cr(NH_3)_4Cl(I)^+$ species was made on the basis of their mode of formation and decomposition, their behavior on a cation-exchange resin (Dowex 50W-X2), chemical analysis, and absorption spectra. Details of the latter are presented in Table I where it is evident that the extent of splitting of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition due to the tetragonal field of the ligands is in the predicted order.[14]

Aquation Reactions.—When the *trans*-$[Cr(NH_3)_4ICl]ClO_4$ is dissolved in 1 M $HClO_4$, a color change from green to violet occurs within several minutes followed by a much slower color change from violet to orange. This observation is consistent with the stoichiometry proposed in the equation

$$trans\text{-}Cr(NH_3)_4ICl^+ \xrightarrow[H_2O]{\text{rapid}} \underset{\text{violet}}{trans\text{-}Cr(NH_3)_4(H_2O)Cl^{2+}} + I^- \xrightarrow[H_2O]{\text{slow}} \underset{\text{orange}}{trans\text{-}Cr(NH_3)_4(H_2O)_2^{3+}} + Cl^- \quad (1)$$

By assuming that this is the case, isosbestic points would be initially expected at 566 ± 1 nm (ε 17.5 ± 0.5 M^{-1} cm^{-1}), 493 ± 3 nm (ε 15.0 ± 0.6 M^{-1} cm^{-1}), and a region of near tangency from 465 to 470 nm (ε 17.8 ± 0.5 M^{-1} cm^{-1}). In practice, isosbestic points were observed at 568 ± 1 nm (ε 18.6 ± 0.2 M^{-1} cm^{-1}), 493 ± 1 nm (ε 14.4 ± 0.1 M^{-1} cm^{-1}), 234 ± 1 nm [ε (7.2 ± 0.2) × 10^3 M^{-1} cm^{-1}], and 218 ± 1 nm [ε (11.5 ± 0.3) × 10^3 M^{-1} cm^{-1}] with a region of tangency at about 467 nm (ε 17.3 ± 0.2 M^{-1} cm^{-1}).

The sharp definition of the isosbestic points in the ultraviolet region was maintained throughout the duration of the observed color change, but a slight decrease in absorbance, attributed to the second step of eq 1, was observed at 568 nm at a time corresponding to approximately 90% reaction.

Since isosbestic points would be observed at 590, 487, and 440 nm if *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ were the sole product of the reaction, its presence in only small amounts would not be reflected by significant shifts in the isosbestic points expected for the presence of only the *trans*-chloroaquo ion. Fortunately, its participation in the reaction could be discounted in other ways. The visible spectrum of a solution of *trans*-$Cr(NH_3)_4ICl^+$ following the primary aquation reaction closely resembles that of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. Unlike this ion, *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ absorbs strongly in the ultraviolet region such that the residual absorbance of a solution of the chloroiodo ion at 295 nm should be sensitive to even small amounts of the iodoaquo complex. In this way the ratio of $Cr(NH_3)_4(H_2O)Cl^{2+}$ to $Cr(NH_3)_4(H_2O)I^{2+}$ in the solution of the products was estimated to be between 30 and 40. The spread represents the uncertainty in the contribution of I_2 and I_3^- to the final absorbance.

Although a number of ion-exchange experiments were performed, only a qualitative confirmation of the stoi-

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[13] R. C. Thompson and G. Gordon, *J. Sci. Instrum.*, **41**, 480 (1964).

[14] C. J. Ballhausen and C. K. Jørgensen, *Kgl. Dan. Vidensk. Selsk. Mat. Fys. Medd.*, 29 (1955).

chiometry could be obtained. Solutions of the chloroiodo ion were allowed to stand for at least 6 half-lives before they were added to the resin. During this procedure, formation and volatilization of I_2 and column-catalyzed aquation of any *trans*-iodoaquo species that may have been present were undetermined and were opposing sources of error. Nevertheless, the initial effluent was found to contain an average of 92% of the iodide originally coordinated to chromium and there was no evidence of iodide in the +2 band.

In view of the above data and since spectral and rate differences between the cis and trans isomers of these complexes are large, reaction paths which involve isomerization can be safely discounted. We conclude that aquation of the *trans*-chloroiodo ion proceeds according to eq 1 more than 96% of the time.

Repeated spectral scans of an acidic solution of *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$ during the aquation reaction revealed six isosbestic points at 500 ± 1 nm (ϵ 36.7 ± 0.3 M^{-1} cm^{-1}), 474 ± 1 nm (ϵ 33.2 ± 0.4 M^{-1} cm^{-1}), 465 ± 1 nm (ϵ 29.0 ± 1.3 M^{-1} cm^{-1}), 444 ± 1 nm (ϵ 18.2 ± 0.2 M^{-1} cm^{-1}), 236 ± 1 nm (ϵ (6.44 ± 0.6) × 10^3 M^{-1} cm^{-1}), and 216 nm (ϵ 8.8 × 10^3 M^{-1} cm^{-1}). If *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$ is the only cationic product, isosbestic points would be predicted at 498 ± 2 nm (ϵ 35.5 ± 0.5 M^{-1} cm^{-1}), 476 ± 1 nm (ϵ 32.0 ± 1.0 M^{-1} cm^{-1}), 464 ± 3 nm (ϵ 25.0 ± 0.5 M^{-1} cm^{-1}), and 447 ± 2 nm (ϵ 17.5 ± 0.5 M^{-1} cm^{-1}). Isomerization to the *trans*-iodoaquo species or aquation to the *trans*-diaquo species would have been detected most readily in the spectral region at about 500 nm where the extinction coefficient of the *cis*-diaquo species (35.5 M^{-1} cm^{-1}) is appreciably higher than that of the *trans*-iodoaquo (14.5 M^{-1} cm^{-1}) or the *trans*-diaquo complex (23.4 M^{-1} cm^{-1}) but slightly lower than that observed (36.7 M^{-1} cm^{-1}). The observed extinction coefficients for this region of the spectrum closely approximated those measured for the *cis*-diaquo ion. Significant contributions from the alternate reaction paths can also be discounted on the basis of the chromatographic results. Product solutions of the *cis*-iodoaquo ion exhibited only one orange +3 band on Dowex 50W-X2 resin. Elution of this band with 1.5 M $HClO_4$ resulted in 96% recovery of the chromium(III) present initially, and the extinction coefficients measured here, within experimental error, were those determined for the *cis*-diaquo ion. Combined with the information that aquation of the *trans*-iodoaquo species is approximately an order of magnitude slower than that of the cis isomer and that isomerization of the *cis*- and *trans*-diaquo complexes is slower still,[15] we are led to the conclusion that aquation of the *cis*-iodoaquo ion occurs with retention of configuration.

Essentially the same argument presented for the aquation of the *cis*-iodoaquo ion applies to the reaction of *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$. If only the *trans*-diaquo complex is produced in this reaction, isosbestic points should be observable at 535 ± 1 nm (ϵ 18.1 ± 0.3 M^{-1} cm^{-1}), 481 ± 2 nm (ϵ 24.5 ± 0.5 M^{-1} cm^{-1}), 459 ± 3 nm (ϵ 23.2 ± 0.5 M^{-1} cm^{-1}), and 447 ± 3 nm (ϵ 20.6 ± 0.6 M^{-1} cm^{-1}). Isosbestic points were observed at 535 ± 1 nm (ϵ 19.0 ± 0.2 M^{-1} cm^{-1}), 482 ± 3 nm (ϵ 24.0 ± 0.7 M^{-1} cm^{-1}), 235 ± 1 nm [ϵ (5.6 ± 0.1) × 10^3 M^{-1} cm^{-1}], and 216 nm (ϵ 8.1 × 10^3 M^{-1} cm^{-1}) with a region of near tangency from 456 to 450 nm (ϵ 20.8 ± 0.3 M^{-1} cm^{-1}). The isosbestic points at 235 and 216 nm involve reactant and free iodide while the rest involve reactant and product complexes. This information and that obtained from ion-exchange experiments analogous to the above rule out any significant contribution of reaction paths other than simple aquation with retention of configuration.

Loss of iodide from *cis*- and *trans*-$Cr(NH_3)_4(OH)I^+$ also occurs with retention of configuration. The starting materials were generated by dissolution of either *cis*- or *trans*-$[Cr(NH_3)_4(H_2O)I](ClO_4)_2$ in basic solution. The spectra which were recorded after acidifying the completely hydrolyzed solutions were identical with those observed for the respective *cis*- and *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ species. It was possible to precipitate the diaquo complexes from these solutions as perchlorates and chemical analysis confirmed the spectral observations. It was concluded that the hydrolysis of the *cis*- and *trans*-hydroxoiodo complexes produces the corresponding hydroxoaquo or dihydroxo complex depending on the pH.

Preliminary rate data for the aquation of *cis*- and *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ and for *trans*-$Cr(NH_3)_4(Cl)I^+$ were obtained by recording the visible or ultraviolet spectra of acidic solutions of the complexes until no further change was observed. The *cis*- and *trans*-diaquo ions and, to a lesser degree, the *trans*-chloroaquo ion are relatively inert at the conditions of the experiment such that agreement between A_∞(calcd) and A_∞(obsd) was excellent when small corrections for the absorbance of I_2 and I_3^- were made. Rate constants (k_{obsd}), defined by the relation

$$-d[\text{complex}]/dt = k_{obsd}[\text{complex}] \qquad (2)$$

and evaluated from the equation

$$\ln\left[\frac{A_0 - A_\infty}{A_t - A_\infty}\right] = k_{obsd}t \qquad (3)$$

were found to be independent of the wavelength chosen. The equality between the rate of increase in absorbance at 225 nm (due to the formation of I^-) and the rate of decrease in absorbance at, for example, 295 nm (due to the disappearance of the reactant complex) is required by the stoichiometry proposed for the reactions of the *cis*- and *trans*-iodoaquo complexes. Due to the absorbance of the chloroaquo ion at 225 nm, a similar check on the stoichiometry of the chloroiodo ion was not possible.

First-order rate constants for the aquation of the *cis*- and *trans*-iodoaquo isomers are given in Table II. It is evident from the data that both reactions are accelerated by an increase in pH such that the variation of the observed first-order rate constants with hydrogen ion concentration can be expressed as

$$k_{obsd} = k_0 + k_2'/[H^+] \qquad (4)$$

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(15) D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, **8**, 505 (1969).

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF *cis*- AND *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$ COMPLEXES IN PERCHLORIC ACID[a]

$[H^+]$, M	10^4k_{obsd}, sec^{-1} 25.0°	30.0°	35.0°	40.0°
		Cis[b]		
1.010	11.3 10.7[c]	19.8 ± 0.3	35.7 ± 0.4	
0.1050	12.5 ± 0.4	22.6 ± 0.3	38.2	
0.0578	13.3 13.7 ± 0.1[c]	24.3 ± 0.1	41.2 ± 0.6	
0.0259	15.1 ± 0.3	29.2 ± 0.5	50.6 ± 0.2	
0.0165	17.7 ± 0.4	33.2 ± 0.5 33.0 ± 0.3[d,e]		
0.0129			66.4 ± 1.0	
		Trans[b]		
1.050		2.1		
1.003			3.52	6.31 ± 0.07
0.1050		3.61 ± 0.3[e]	7.75 ± 0.2	13.3 ± 0.7 14.2 ± 0.2[d]
0.0578		5.6 ± 0.1 5.80[d]	10.9 ± 0.3	2.05 ± 0.3
0.0259		10.3 ± 0.2	20.6 ± 0.1	37.9 ± 0.1
0.0165		15.1	30.3 ± 0.7	57.4 ± 1.6

[a] At unit ionic strength adjusted with $NaClO_4$. The uncertainties represent deviations from the mean for replicate samples. [b] For measurements on the cis complex at 550 nm, $C_0 = (1.9–0.8) \times 10^{-2}$ M; for the trans complex at 590 nm, $C_0 = (3.2–1.2) \times 10^{-2}$ M; for measurements at 295 nm, $C_0 = (3.2–1.2) \times 10^{-3}$ M for both the cis and trans complexes. Within experimental error, k_{obsd} was found to be independent of initial concentration (C_0). [c] At 295 nm. [d] At 296 nm. [e] In the presence of ~10^{-5} M $S_3O_3^{2-}$.

The second term of eq 4 is consistent with a two-step mechanism which would involve the *cis*- and *trans*-hydroxoiodo ions as follows

$$\begin{tikzcd}
Cr(NH_3)_4(H_2O)I^{2+} \arrow[r, shift left, "K_1"] & Cr(NH_3)_4(OH)(I)^{+} + H^{+} \arrow[l, shift left] \arrow[d, "k_{OH^-}", "H_2O"'] \\
Cr(NH_3)_4(H_2O)_2^{3+} \arrow[r, shift left] & Cr(NH_3)_4(H_2O)(OH)^{2+} + I^{-} \arrow[l, shift left, "H^+"']
\end{tikzcd} \qquad (5)$$

According to this scheme, k_2' can be expressed as

$$k_2' = K_1k_{OH^-} \qquad (6)$$

Once the equilibrium, K_1, has been displaced totally to the right, k_{obsd} should be independent of pH and equal to k_{OH^-}. This was verified by a series of rate measurements at 300 nm in the pH range 9–13, the results of which are shown in Table III. It is seen from Table III that k_{obsd} does not increase significantly with increasing $[OH^-]$ over the pH range 9–13, although k_{obsd} does increase substantially when $[OH^-]$ is increased from *ca.* 0.1 to 1.0 M.

Values of k_0 and k_2' were determined by fitting the data of Table II to eq 4. These results are shown in Table IV along with the additional results which were extrapolated from the data of Table III. Values for K_1 were calculated from the corresponding values of k_2' and k_{OH^-} and are compared in Table IV with those measured directly for some analogous tetraammines of chromium(III). Chloride ion and iodide ion have essentially the same effect on the acidity of the complex when substituted for water in the diaquo ion but are less effec-

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE BASE HYDROLYSIS OF THE *cis*- AND *trans*-$Cr(NH_3)_4(OH)I^+$ SPECIES[a]

$[OH^-]$, M	$10^{-1}k_{obsd}$, sec^{-1} 5.0°	10.0°	15.0°
		Cis	
1.050	12.6 ± 0.2		
0.1015	7.05 ± 0.04	13.3	21.6 ± 0.3
0.0099	6.67 ± 0.06	12.2 ± 0.4	20.9 ± 0.4
Buffer[b]			21.6 ± 0.4
		Trans	
1.050		5.09 ± 0.5	
0.1015	1.95	3.62	6.55
0.0099	1.92	3.69 ± 0.3	
Buffer[b]			6.52 ± 0.2

[a] Rates measured at unit ionic strength adjusted with $NaClO_4$. Initial concentrations of cis and trans complexes were ~10^{-4} M. Progress of the reactions were followed at 300 nm. The uncertainties represent average deviations from the mean for replicate runs. [b] $NH_4OH–NH_4ClO_4$ buffer, pH 9.2, $\mu = 1$ M.

TABLE IV

RATE CONSTANTS FITTED TO THE EQUATION

$$k_{obsd} = k_0 + k_2'[H^+] = k_0 + k_{OH}K_1/[H^+]$$

Temp, °C	10^4k_0,[a] sec^{-1}	10^5k_2, M sec^{-1}	k_{OH},[b] sec^{-1}	pK_1[c]
		cis-$Cr(NH_3)_4(H_2O)I^{2+}$		
25	11.2 ± 0.3	1.05 ± 0.04	6.43	5.8
30	20.2 ± 0.4	2.20 ± 0.12	10.8	5.7
35	34.7 ± 0.3	4.07 ± 0.10	17.7	5.6
		trans-$Cr(NH_3)_4(H_2O)I^{2+}$		
30	1.75 ± 0.12	2.20 ± 0.04	3.71	5.2
35	3.25 ± 0.13	4.47 ± 0.04	6.30	5.2
40	5.36 ± 0.27	8.55 ± 0.08	10.0	5.1

[a] The uncertainties correspond to one standard deviation and are calculated directly by our nonlinear least-squares computer program. [b] Extrapolated from data collected at lower temperatures. [c] The pK values at 25.0° for the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ ions and for the *cis*- and *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ ions are 5.1, 4.4, 5.8, and 5.4, respectively: R. A. LaRossa and J. B. Hunt, unpublished results.

tive than hydroxide ion in this respect. The larger dependence of k_{obsd} on acidity in the case of the *trans*-iodoaquo isomer is seen to be primarily an effect of the greater acidity of this ion. Also apparent from Table IV is the acceleration in the rate of loss of iodide caused by removal of a proton from the coordinated water molecule. By comparing k_0 and k_{OH^-} at 30.0°, we note that the loss of I^- from the *cis*- and *trans*-hydroxoiodo complexes is faster than from the aquo ions by factors of 5200 and 21,000, respectively.

If the additional acceleration observed for runs in 1 *M* NaOH is due to the formation of amido species, the pH at which this reaction path becomes important is significantly higher than was observed for the pentaammine series.[16] This would be the case if loss of iodide from $\text{Cr(NH}_3)_3(\text{NH}_2)(\text{OH})\text{I}$ is less rapid than from $\text{Cr(NH}_3)_4(\text{NH}_2)\text{I}^+$ or if $\text{Cr(NH}_3)_4(\text{OH})\text{I}^+$ is a weaker acid than is $\text{Cr(NH}_3)_5\text{I}^{2+}$. Electrostatic arguments tend to favor the latter explanation. Because $\text{Cr(NH}_3)_3(\text{NH}_2)(\text{OH})\text{I}$ is neutral and $\text{Cr(NH}_3)_4(\text{NH}_2)\text{I}^+$ bears a positive charge, the neutral species should lose iodide ion more rapidly than the positively charged species. On the other hand, $\text{Cr(NH}_3)_4(\text{OH})\text{I}^+$ would be expected to be a weaker acid than $\text{Cr(NH}_3)_5\text{I}^{2+}$ owing to the difference in charge.

The ratio of rate constants, $k(\text{cis})/k(\text{trans})$, for the loss of Cl^- from the isomers of $\text{Co(en)}_2\text{XCl}^{2+}$ is usually greater than unity if X is an electron-releasing ligand and the mechanism is dissociative.[17] For example, the ratio $k(\text{cis})/k(\text{trans})$ for the hydroxochlorobis(ethylenediamine)cobalt(III) ions is 7.5 but only 0.6 for the chloroaquo isomers.[18,19] It is interesting to observe, therefore, that the ratio $k(\text{cis})/k(\text{trans})$ for the $\text{Cr(NH}_3)_4(\text{OH})\text{I}^+$ ions is only 3 while this ratio for the corresponding iodoaquo ions is about 10. A similar result was observed for the chloroaquo and chlorohydroxo complexes.[20]

First-order rate constants corresponding to the replacement of the first halide in *trans*-$\text{Cr(NH}_3)_4(\text{Cl})\text{I}^+$ are given in Table V. The lack of a sufficiently acidic ligand in this complex could explain the lack of acid dependence of the rate in the 0.1–1.0 *M* HClO_4 range. As such, the values presented represent the sums of the rate constants for loss of both the iodo and chloro ligands. The ratio $k(\text{I}^-)/k(\text{Cl}^-)$ should be accurately reflected by the ratio of chloroaquo found in the product solution. Based on the residual absorbance in the near-ultraviolet region, this ratio was estimated to be between 30 and 40. Compared to the values reported for the ratios d ln (RI)/d ln (RCl) of 300 for R = $\text{Cr(H}_2\text{O)}_5$,[21] about 150 for R = $\text{Cr(NH}_3)_5$[16,21] and *cis*- and *trans*-$\text{Cr(NH}_3)_4(\text{H}_2\text{O})$,[20] 190 for R = *trans*-$\text{Cr(NH}_3)_4(\text{OH})$,[20] and 340 for R = *cis*-$\text{Cr(NH}_3)_4(\text{OH})$,[20] this seems somewhat low. However, if the rate of release of Cl^- from the *trans*-chloroiodo ion is just half its known rate of release from the *trans*-dichloro ion, the ratio would be only 75.[2b] There is reason to believe this ratio should be smaller. The rapid water exchange observed for the iodopentaaquochromium(III) ion has been attributed to a strong iodide trans effect.[4] The evidence at hand suggests that the situation is similar in the present case so that loss of chloride from the *trans*-chloroiodo ion would be accelerated by the trans iodide. In an attempt to demonstrate this effect, the stoichiometry of the aquation of the *trans*-chloroiodo ion is being examined in greater detail and will be published separately.[22] Based on a value of 35 for the ratio $k(\text{I}^-)/k(\text{Cl}^-)$, calculated values of $k(\text{I}^-)$ and $k(\text{Cl}^-)$ at 25.0° would be 3.2×10^{-3} and 9×10^{-5} sec^{-1}, respectively.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF THE *trans*-$\text{Cr(NH}_3)_4\text{ICl}^+$ ION[a]

Temp, °C	[H⁺], *M*	10^3k_{obsd}, sec^{-1}
20.0	1.003	1.88 ± 0.02
	0.105	1.93 ± 0.02
25.0	1.003	3.34 ± 0.03[b]
	1.003	3.23 ± 0.05
	0.105	3.27 ± 0.05
30.0	1.003	5.60 ± 0.2[c]
	1.003	5.35 ± 0.2
	1.003	5.60 ± 0.2[b]

[a] Measured at 630 nm and unit ionic strength adjusted with NaClO_4. Initial complex concentrations were in the range 0.75–2.1 m*M*. The uncertainties represent average deviations for replicate runs. [b] At 258 nm. [c] At 620 nm.

Chromous Reactions.—Equation 7 represents the stoichiometry observed for the reaction of chromium(II) with the *cis*- and *trans*-iodoaquo ions. Thus, a

$$\text{Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+} + \text{Cr(II)} + 4\text{H}^+ \longrightarrow \text{Cr(H}_2\text{O})_5\text{I}^{2+} + 4\text{NH}_4^+ + \text{Cr(II)} \qquad (7)$$

deaerated solution of either ion with Cr(II) underwent a rapid color change to bright green. Depending on how long these solutions were allowed to stand before being exposed to the laboratory atmosphere, ion-exchange chromatography revealed either two or three bands. The bands were identified as the $\text{Cr(H}_2\text{O})_5\text{I}^{2+}$, the $\text{Cr(H}_2\text{O})_6^{3+}$, and the $(\text{H}_2\text{O})_4\text{Cr(OH)}_2\text{Cr(H}_2\text{O})_4^{4+}$ ions. The *cis*-$\text{Cr(NH}_3)_4(\text{H}_2\text{O})_2^{2+}$ species formed fairly rapidly by aquation of *cis*-$\text{Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ reacted slowly with chromium(II) and was frequently observed on the column.

Kinetic measurements of the Cr(II) reactions were made at 650 nm the position of the long-wavelength maximum of the iodopentaaquo ion.[23] The concentration ranges covered were as follows: chromium(II), $(1.1\text{–}5.3) \times 10^{-3}$ *M;* chromium(III), $(0.7\text{–}1.7) \times 10^{-2}$ *M;* hydrogen ion, 1.0 *M*. The data found in Table VI are consistent with the single-term rate law

$$-\text{d[complex]}/\text{d}t = k_2[\text{Cr(II)}][\text{complex}] \qquad (8)$$

with $k_2(\text{trans}) = 165 \pm 5\ M^{-1}\ \text{sec}^{-1}$ and $k_2(\text{cis}) = 14.6 \pm 0.4\ M^{-1}\ \text{sec}^{-1}$ at 25.0°.

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The acid dependence of the rate was not investigated. The acidity of the iodoaquo ions and the ability of the hydroxo ligand to compete with the iodo ligand as an electron bridge is insufficient to cause a significant acid dependence except at high pH values. For example, no acid dependence was observed for the Cr(II) reduction of either *cis*- and *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ [24] or *cis*- and *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ [2a] in the range 0.1–1.0 *M* $HClO_4$.

Competition from the subsequent aquation of the iodopentaaquo ion can be ruled out by consideration of the known rate constants for this reaction. This hydrolysis reaction results in a decrease in absorbance at 650 nm and is described by the rate law given in eq 9

$$-\frac{d \ln [CrI^{2+}]}{dt} = k' = k_1 + \frac{k_2}{[H^+]} + \frac{k_3[Cr(II)]}{[H^+]} \qquad (9)$$

with $k_1 = 8.41 \times 10^{-5}$ sec^{-1}, $k_2 = 3.43 \times 10^{-5}$ *M* sec^{-1},[21] and $k_3 = 2.2 \times 10^{-2}$ sec^{-1} [25] at 25.0° and unit ionic strength. In terms of the present investigation in which the maximum Cr(II) concentration was 5.3 × 10^{-3} *M* and $[H^+] = 1.0$ *M*, the maximum value of k' would be 2.37 × 10^{-4} sec^{-1}. Corresponding values of k_{obsd} for the reactions of the *cis*- and *trans*-iodoaquo ions, calculated from the data in Table VI, are 7.6 × 10^{-2} and 0.90 sec^{-1}, respectively. Hence, little interference is to be expected. An experimental check of this was made by following the reactions at 572 nm where color changes associated with the reactions of the iodopentaaquo ion are minimal. A significant difference from the information obtained at 650 nm was observed for the cis isomer at 15° (Table VI), but the effect was not repeated at 20°. Several additional runs were made at the long-wavelength maxima of the cis and trans isomers where a decrease in absorbance was observed. These were in substantial agreement with the remainder of the data.

Nevertheless, plots of ln $(A_\infty - A_t)$ *vs.* time for the *cis*-iodoaquo ion were often characterized by a slight initially negative curvature. This was observed at all the wavelengths studied and persisted through variations in the experimental procedure and methods of purification. The observations are consistent with the presence of a reactive trace impurity (perhaps a triammine derivative) but no corroborating evidence was obtained.

It has been generally accepted that the nonbridging ligands in inner-sphere redox reactions must undergo rearrangement in the formation of the activated complex and that in the case of chromium this is more easily accomplished with oxygen than with nitrogen. This has been demonstrated recently for the chromium(II) reduction of the *cis*- and *trans*-chloroaquotetraamminechromium(III) ions where it was further shown that rearrangement of the nonbridging ligands is most severe in the trans position.[2a] Thus, it is not surprising to find that, as in analogous systems, the *trans*-iodoaquo ion is the most reactive of the isomers and that the reduction of both isomers is more rapid than the reduction of the iodopentaammine complex.[2a,21] It may also be observed that the ratio of the rate of reduction *via* an iodo bridge to that *via* a chloro bridge, k_{I^-}/k_{Cl^-}, is not independent of these considerations. Proceeding from the pentaammines[21] to the cis and the trans tetraamines, [1a] k_{I^-}/k_{Cl^-} equals 96, 128, and 142, respectively.

TABLE VI

SECOND-ORDER RATE CONSTANTS FOR THE Cr(II)-CATALYZED AQUATIONS[a]

Temp, °C	10^3[Cr(II)], *M*	k_2, M^{-1} sec^{-1}
	cis-$Cr(NH_3)_4(H_2O)I^{2+}$	
15.0	5.31	8.41 ± 0.4
	5.18	8.65 ± 0.1
	3.97	8.36
	2.89	8.32 ± 0.1[b]
	1.91	8.90 ± 0.3
	1.91	10.2 ± 1.0[c]
20.0	5.25	11.4 ± 0.2
	4.35	11.8 ± 1.3
	3.91	11.1
	1.93	12.0 ± 0.2
	1.93	11.8 ± 0.2[c]
25.0	5.31	14.8 ± 0.4
	4.21	14.7 ± 0.3
	3.95	14.1
	trans-$Cr(NH_3)_4(H_2O)I^{2+}$	
15.0	5.25	107 ± 3
	5.31	102[d]
	3.97	106
	2.89	102 ± 1
	2.01	98 ± 5
	1.91	105[c]
	1.17	100 ± 3
20.0	5.25	131 ± 3
	3.98	134
25.0	5.31	170 ± 5
	3.94	166 ± 4
	1.08	151 ± 8

[a] Initial $[H^+]$ was 1 *M* $HClO_4$ and rates were measured at 650 nm. The initial chromium(III) complex concentration was varied between 0.7 and 1.7 × 10^{-2} *M*. The uncertainties represent average deviations for replicate runs. [b] At 550 nm. [c] At 572 nm. [d] At 590 nm.

Activation Parameters.—The following activation parameters were calculated by means of our nonlinear least-squares program. For the aquation reactions, $\Delta H^{\ddagger} = 19.7 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -6 \pm 1$ eu for *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$, $\Delta H^{\ddagger} = 21.4 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -5 \pm 1$ eu for *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$, $\Delta H^{\ddagger} = 17.0 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = 2 \pm 2$ eu for *cis*-$Cr(NH_3)_4(OH)I^+$, $\Delta H^{\ddagger} = 18.7 \pm 0.1$ kcal/mol and $\Delta S = 5.5 \pm 1$ eu for *trans*-$Cr(NH_3)_4(H_2O)I^+$, and $\Delta H^{\ddagger} = 18.0 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = 9 \pm 0.5$ eu for *trans*-$Cr(NH_3)_4ICl^+$; for the Cr(II) reduction of *cis*-$Cr(NH_3)_4(H_2O)I^{2+}$ $\Delta H^{\ddagger} = 8.7 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -24 \pm 1$ eu, and $\Delta H^{\ddagger} = 7.1 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -24 \pm 1$ eu for the Cr(II) reduction of the *trans*-$Cr(NH_3)_4(H_2O)I^{2+}$.

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