the metal atoms in the transition state for reaction 20 are bridged by OH⁻, partly on the basis of analogy with reactions of known mechanisms,[31] and partly by the precedent set by the V(III)–Cr(II) reaction in ClO_4^- solution, where the high reactivity of VOH^{2+} and Cr^{2+} in an inner-sphere process has been noted.

A reaction scheme embodying these concepts is given in eq 19–20, in which hydroxide ion was arbitrarily assigned the role of a bridging ligand on the trivalent ion. The rate constants in the mechanism are related to the empirical rate parameters by the equations $f = f'K$ and $h = h'Q_a$.

$$CrCl^{2+} \rightleftharpoons Cr(OH)Cl^{+} + H^{+} \qquad K = 7 \times 10^{-6}\ M^{32} \quad (19)$$

$$V^{2+} + Cr(OH)Cl^{+} \underset{h'}{\overset{f'}{\rightleftharpoons}} VOH^{2+} + Cr^{2+} + Cl^{-} \quad (20)$$

With regard to the transition state that contains one proton more, reaction 21, we conclude that the most

$$V^{2+} + CrCl^{2+} \underset{g}{\overset{e}{\rightleftharpoons}} V^{3+} + Cr^{2+} + Cl^{-} \quad (21)$$

probable configuration of atoms is *not* bridging by Cl⁻, but that either an outer-sphere or a water-bridged mechanism operates.[33] The basis of this conclusion rests on the known relative efficiency of OH⁻ and Cl⁻ as bridging anions. The relative rate constants observed here are $f'/e \cong 10^4$ and $h'/g \cong 8 \times 10^4$. Since OH⁻ and Cl⁻ generally act as bridging groups of roughly equal effectiveness, we conclude that the low reactivity of chloride compared to hydroxide renders a chloride-bridged mechanism an unlikely feature of reaction 21.

The equilibrium quotient for reaction of V^{3+} and Cr^{2+} (eq 3) can be computed from k_2/k_1Q_1. At 25.0° and 2.50 M ionic strength the value is $k_3/k_4 = 1.7 \times 10^3$. The value computed from electrode potentials[34] that are known only approximately and in different media is *ca.* 10^3. The value of k_4 so computed (k_4 $(M^{-1}\,sec^{-1}) = 5.7 \times 10^{-4}/(0.12 + [H^+])$) is small enough that its neglect in the rate equations was justified under all conditions employed here.[35]

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[31] The $[H^+]$ dependence noted here closely parallels the chromium(II)-catalyzed reactions of chromium(III) complexes.[5] The rates of the reactions of $CrCl^{2+}$ [5b] and CrI^{2+} [5c] with Cr^{2+} are of the form $k[CrX^{2+}][Cr^{2+}]/[H^+]$. A similar reaction occurs between Fe^{2+} and $FeCl^{2+}$;[6c] the major contribution to the rate arises from a term of the form $k[FeCl^{2+}][Fe^{2+}]/[H^+]$.

[32] N. Bjerrum, *Z. Physik. Chem.*, **59**, 336 (1907).

[33] A precedent for parallel inner- and outer-sphere pathways in the same reaction was found in the work of J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

[34] W. M. Latimer, "Oxidation Potentials" 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952, quotes $E° = +0.41$ V for $Cr^{2+} = Cr^{3+} + e^-$. A considerable range of values 0.4 to 0.45 V was obtained by G. Grube and L. Schlect, *Z. Elektrochem.*, 32, 178 (1926). The value of $E° = +0.276$ V for the half-reaction $V^{2+} = V^{3+} + e^-$ was reported by I. P. Alimarin, E. R. Nikolaeva, V. I. Tikhonova, and L. V. Bobrova, *Zh. Neorg. Khim.*, 7, 298 (1962).

[35] NOTE ADDED IN PROOF. A recent publication by A. Adin and A. G. Sykes [*J. Chem. Soc.*, *A*, 351 (1968)] retracts the earlier criticism[20] of the published interpretation[3] of the kinetic data for the reaction of V^{3+} and Cr^{2+} in ClO_4^- solution. These authors now express their agreement with the two-parameter rate expression (eq 13) given in the original publication.[3]

Kinetics and Oxygen Isotopic Fractionation in the Reactions of the Isomeric Chloroaquotetraamminechromium(III) Ions with Chromium(II)[1]

Sr. M. J. DeChant and J. B. Hunt

Contribution from the Department of Chemistry, The Catholic University of America, Washington, D. C. 20017. *Received December 21, 1967*

Abstract: The total loss of ammonia from *cis*- and *trans*-chloroaquotetraamminechromium(III) ions is catalyzed by chromium(II), both isomers yielding the chloropentaaquochromium(III) ion as the aquation product. Both reactions obey rate laws of the form rate = $k[Cr(II)][Cr(NH_3)_4(OH_2)Cl^{2+}]$, where $k = 1.16\ M^{-1}\ sec^{-1}$ at 25° and $E_a = 10.3$ kcal/mole for the *trans* isomer, and $k = 1.14 \times 10^{-1}\ sec^{-1}$ at 25° and $E_a = 11.2$ kcal/mole for the *cis* isomer in perchlorate media at $\mu = 1.0$. The reaction rate of the *trans* isomer is increased to a greater extent by both an increase in ionic strength and the addition of chloride ion than is the *cis* isomer. The fractionation of O^{16} compared to O^{18} in the aquo ligand has been measured for the reactions of both isomers with chromium(II). The kinetic fractionation factors, $k_{O^{16}}/k_{O^{18}}$, are 1.017 for the *trans* isomer and 1.007 for the *cis* isomer. These results are interpreted to mean that the chromium(III) complex must undergo tetragonal distortion in the formation of the activated complex.

It is generally accepted that in oxidation–reduction reactions between metal ions, in which a bridging ligand is involved, the formation of the activated complex involves rearrangements of the bonds to nonbridging ligands.[2] However, most of the evidence for such rearrangements is circumstantial, being based on differences in reaction rates for isomers or on the fact that reaction rates are influenced greatly by the identity of nonbridging ligands.[2,3] Several years ago Taube[4] recognized that the extent of bond stretching in such reactions could be evaluated directly by measurements of isotopic fractionation. Green, Schug, and Taube[4]

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[1] Based in part on the Ph.D. dissertation of Sr. M. J. DeChant, S.N.D., The Catholic University of America, Jan 1968.

[2] N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966).

[3] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

[4] (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

found very little fractionation of nitrogen isotopes in the reduction of a number of cobalt(III)–amine complexes by chromium(II), implying that the rearrangement of bonds to nonbridging ligands is unimportant in such cases.

In a recent short communication[5] we reported evidence for substantial rearrangement of the bonds to the water molecule of the *trans*-chloroaquotetraamminechromium(III) ion in its reaction with aquochromium(II) ion, an inner-sphere reaction in which the chloride ion serves as a bridge and the water molecule is a nonbridging ligand located *trans* to the bridging group. The evidence for stretching of the chromium–water bond in this reaction is a substantial fractionation of O^{16} compared to O^{18} in the water ligand as the reaction proceeds. The present paper is a detailed report of an investigation of the kinetics of and oxygen isotopic fractionation in the reactions of *cis*- and *trans*-chloroaquotetraamminechromium(III) ions with aquochromium(II). These reactions are further examples of the catalysis by chromium(II) of dissociation of chromium(III) complexes. It is generally accepted that the rate-determining step of such reactions is the transfer of an electron between the two oxidation states of chromium.[2]

The choice of reactants for this study was suggested by the recent report of Pennington and Haim[3] that the *trans*-chloroaquobis(ethylenediamine)chromium(III) ion reacts with chromous ion about 40 times as rapidly as does the *cis* isomer. The ammonia complexes have an advantage over the ethylenediamine complexes in that they may be prepared easily and precipitated quantitatively.

Experimental Section

Preparations and Materials. The salt *cis*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$ was prepared by a modification[6] of the method of Werner and Surber.[7] *cis*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ was prepared from the chloride salt by careful trituration with concentrated $HClO_4$ during which most of the chloride ion was expelled as HCl gas. The perchlorate was recrystallized from the minimum amount of water by the addition of 70% $HClO_4$. As prepared, the *cis*-chloroaquo perchlorate was contaminated by a small amount of $[(NH_3)_5CrCl](ClO_4)_2$. This impurity was removed by dissolving the salt in methanol, in which the chloropentaammine complex is virtually insoluble, and reprecipitating the salt from the filtered solution with 70% $HClO_4$. *trans*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ and *trans*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$ were prepared by the methods of Hoppenjans, Hunt, and DeChant.[6] The distinction between the *cis* and *trans* isomers was made on the basis of their spectra, the spectrum of the *trans* complex being very similar to that of the *trans*-$Cr(en)_2Cl(OH_2)^{2+}$ ion.[8]

Care was taken to ensure that no organic solvent other than methanol was used in the preparation and drying of compounds used in the fractionation studies, since some other common solvents, *e.g.*, ethanol and diethyl ether, yield fragments of mass 46 in the mass spectrometer.

Chromium(II) perchlorate solutions were prepared by the dissolution of high-purity chromium metal (United Mineral and Chemical Corp.) in deaerated 4 *M* $HClO_4$. When the metal had dissolved completely, the solution was diluted to the desired concentration by the addition of deaerated distilled water and was stored under nitrogen prepurified by passage through chromium(II) perchlorate solutions. The chromium(II) concentration was determined by reaction with excess deaerated iodate solution followed by titration of the excess iodate (as I_2) with a standard sodium thiosulfate solution.[9] The total chromium content was measured spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide.[10] The chromium(II) solutions contained less than 1% chromium(III).

Kinetic Measurements. Reaction vessels were square silica spectrophotometer cuvettes fitted with self-sealing rubber serum caps and with an attached side arm also fitted with a serum cap. A solution of the chromium(III) complex was prepared by adding a weighed amount of the solid complex together with the appropriate quantities of perchloric acid and sodium perchlorate to a volumetric flask and diluting to the mark with distilled water. The desired amount of the complex solution (about 5 ml) was pipetted into the main body of the cuvette. The serum caps were fitted into place, and oxygen was removed from the cuvette by means of a stream of nitrogen. The desired quantity of chromium(II) perchlorate solution (0.5 ml or less) was added to the side arm of the cuvette from a microburet fitted with a hypodermic needle. A thermistor probe in the form of a hypodermic needle was inserted through the serum stopper into the complex solution to monitor its temperature, and the cuvette was brought to the desired temperature by immersion in a water bath. The faces of the cell were quickly cleaned, and the cell was shaken vigorously to mix its contents and initiate reaction. The cell was placed in the thermostated (±0.1°) cell compartment of a Cary Model 15 recording spectrophotometer, and recording of absorbance *vs.* time was begun within 5 sec after mixing.

The chloride salts of the tetraammine complexes were used for some of the kinetic runs, which were done before procedures were devised for preparing the perchlorate salts. To test the effect of the free chloride ion on reaction rates, hydrochloric acid was substituted for part of the perchloric acid in some runs.

Since chromium(II) is not consumed in the reactions under study, pseudo-first-order rate constants were obtained from plots of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time t and at the end of the reaction, respectively. For both complexes investigated the absorbance continued to change very slowly because of dissociation of $CrCl^{2+}$ after the primary reaction was complete,[3] and A_∞ was taken to be the absorbance measured after *ca.* 7–10 half-lives. Plots of log $(A_t - A_\infty)$ *vs.* time were linear up to at least 85% reaction.

Stoichiometric Measurements. To establish reaction stoichiometry, reaction mixtures prepared in the same manner as for kinetic measurements, but in larger quantities, were suspended in sealed flasks in a thermostated bath for *ca.* 7 half-lives. Reaction was then quenched by air oxidation of the chromium(II), and the chromium complexes in the solution were separated by ion exchange on a column of Dowex 50W-X8, 100–200 mesh, H^+ form.

Isotopic Fractionation Studies. To ensure uniform isotopic content of the complex compounds used for isotopic fractionation studies, the compounds were prepared on a large scale (*ca.* 200 g) and mixed thoroughly, and all samples of a given compound used in the fractionation studies were taken from the same preparation. The reaction vessel for the fractionation studies was a multi-necked round-bottom flask fitted with a sealed stirrer, a self-sealing rubber stopper through which the chromium(II) solution could be inserted, a stopcock for the admission of oxygen, entrance and exit tubes for nitrogen, and a thermistor probe by means of which the temperature was monitored. A weighed portion of the ammine complex (*cis*- or *trans*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$) was placed in the reaction flask, and slightly more 2 *M* $HClO_4$ than was required for a saturated solution was added. The vessel was purged of oxygen with a stream of prepurified nitrogen, and the solution was brought to the desired temperature in a water bath. Reaction was initiated by the addition of a measured volume of chromium(II) perchlorate solution.

The reaction was quenched after 2 or more half-lives by oxidation of the chromium(II) in a vigorous stream of pure oxygen gas. The solution was cooled to *ca.* −20°, upon which the NH_4^+ ion formed in the reaction precipitated almost quantitatively as NH_4ClO_4, which was removed by filtration. The filtrate was cooled to *ca.* −15° in a methanol–Dry Ice bath and was saturated with HBr gas, upon which *cis*- or *trans*-$[Cr(NH_3)_4(OH_2)Cl]Br_2$ precipitated. When this precipitation procedure was tested on synthetic mixtures, >99% of the *trans* isomer and >96% of the *cis* isomer were recovered, and neither $CrCl^{2+}$ nor the dimeric species from the oxidation of Cr^{2+} precipitated under such conditions. The spectra of the retrieved tetraammine complexes matched those of the starting materials very closely.

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[5] J. M. DeChant and J. B. Hunt, *J. Am. Chem. Soc.*, 89, 5988 (1967).

[6] D. W. Hoppenjans, J. B. Hunt, and M. J. DeChant, submitted for publication.

[7] A. Werner and H. Surber, *Ann.*, 405, 220 (1914); G. G. Schlessinger, "Inorganic Laboratory Preparations," The Chemical Publishing Co., Inc., New York, N. Y., 1962, p 226.

[8] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, 1, 20 (1962).

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

[10] G. W. Haupt, *J. Res. Natl. Bur. Std.*, 48, 414 (1952).

The bromide salts were washed with methanol and dried in air and *in vacuo* to remove the methanol and any crystal water. Quantitative removal of bound water was achieved by heating the *cis* compound at 135° for *ca.* 50 hr and the *trans* compound at 128° for *ca.* 50 hr under high vacuum. The evolution of water from the bromide salts was accompanied by the evolution of some ammonia (about 2–3% of the total weight loss). The ammonia–water mixture was separated by distillation under high vacuum through a glass coil immersed in a methanol–Dry Ice bath, which trapped out the water quantitatively, reducing the ammonia contaminant to a level undetectable in a mass spectrometer.

"Zero-time" samples of the complexes were dissolved in 2 *M* $HClO_4$ and precipitated as the bromide salts with HBr. Bound water was removed from these control samples by the same procedure described above for samples retrieved from reaction mixtures. However, the *cis* bromide retrieved from the reaction mixture was found to decompose more rapidly than did *cis*-$[Cr(NH_3)_4Cl(OH_2)]Br_2$ prepared from the starting material, a difference in behavior which was remedied by precipitating the zero-time samples from a solution containing a small amount of ammonium bromide.

The isotopic content of the water was determined by equilibrating the weighed water sample with a carefully measured quantity of carbon dioxide, separating the carbon dioxide-water mixture by fractional distillation, and determining the isotopic composition of the carbon dioxide in an isotopic ratio mass spectrometer.[11] The isotopic composition of the complexed water was calculated from that of the carbon dioxide using the formula of Dostrovsky and Klein.[12]

Water-Exchange Experiments. To evaluate the extent to which isotopic exchange between the aquo ligands of the tetraammine complexes and the solvent could have interfered with the fractionation experiments, O^{18}-enriched water was substituted for ordinary water in experiments using the same procedure described above for the fractionation experiments. The water bound to the retrieved tetraammine complexes was removed by pyrolysis and analyzed for O^{18} content by the method of Anbar and Guttman.[13]

Results and Discussion

The ion-exchange separation of the product solutions from the chromium(II)-catalyzed reactions of both isomers yielded three chromium-containing fractions: a green fraction identified from its spectrum[14] as the chloropentaaquochromium(III) ion and accounting for about 95% of the tetraammine complex used, a blue fraction identified as the hexaaquochromium(III) ion and accounting for about 5% of the tetraammine complex used, and a green fraction which was not removed from the column with 2 *M* $HClO_4$. The latter fraction contained approximately the amount of chromium originally added as Cr^{2+} and was undoubtedly the binuclear species which is formed in the oxidation of Cr^{2+} by O_2.[15] The principal net change in the reactions studied is then described by the equation

$$\textit{cis-}\text{ or }\textit{trans-}Cr(NH_3)_4(OH_2)Cl^{2+} + 4H_3O^+ \longrightarrow (H_2O)_5CrCl^{2+} + 4NH_4^+ \quad (1)$$

That $Cr(OH_2)_6^{3+}$ is also found in product solutions is to be expected, since the loss of chloride ion from the $Cr(OH_2)_5Cl^{2+}$ ion is catalyzed by Cr^{2+}. Thus the reactions which we have studied are exactly analogous to the chromium(II)-catalyzed aquation reactions of the *cis*- and *trans*-chloroaquobis(ethylenediamine)chromium(III) ions.[3] The spontaneous aquation reactions, *i.e.*, loss of chloride or ammonia, of both complexes are much too slow to interfere with the chromium(II)-catalyzed reactions.[16]

In Table I the kinetic data for the reactions of chloroaquotetraammine complexes with chromium(II) are summarized. Second-order rate constants, k, were calculated using the equation $k = k_{obsd}/[Cr^{2+}]$, where k_{obsd} is the observed first-order rate constant. Each entry for k in Table I is the average of two or more determinations, and multiple determinations of k under a given set of conditions agreed within 3%. The values of k for both complexes are independent of both $[Cr^{2+}]$ and $[H^+]$. In perchlorate solutions, *i.e.*, in the absence of free chloride ion, both complexes then obey the rate law

Table I. Second-Order Rate Constants for Chromium(II)-Catalyzed Reactions[a]

(a) *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+} + Cr^{2+}$

$10^3[Cr^{2+}]$, *M*	Initial $[H^+]$, *M*	$10^1[Cl^-]$, *M*	k, M^{-1} sec^{-1}
3.48	1.0	0	1.16
7.60	1.0	0	1.17
8.90	1.0	0	1.13
7.66	1.0	0.52	1.20
7.60	1.0	2.4	1.30
7.60	1.0	4.0	1.37
7.60	1.0	10.0	1.77
7.60	1.0	0	1.58[b]
7.60	1.0	0	1.94[c]
7.60	1.0	0	2.33[d]
8.90	1.0	0.6	1.19
5.12	0.60	0.6	1.18
5.12	0.34	0.6	1.21
5.12	0.16	0.6	1.18
4.5–21.0	1.0	0	0.620[e]
6.0–8.9	1.0	0	2.02[f]

(b) *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+} + Cr^{2+}$

$10^2[Cr^{2+}]$, *M*	Initial $[H^+]$, *M*	$10^1[Cl^-]$, *M*	10^1k, M^{-1} sec^{-1}
0.89	1.0	0	1.14
1.31	1.0	0	1.13
1.72	1.0	0	1.16
3.95	1.0	0	1.17
4.62	1.0	0	1.14
3.95	0.22	0	1.12
3.95	0.41	0	1.13
3.95	0.61	0	1.19
4.62	1.0	2.0	1.17
4.62	1.0	6.0	1.28
4.56	1.0	8.0	1.33
4.62	1.0	10.0	1.38
4.99	1.0	0	1.39[b]
4.99	1.0	0	1.61[c]
4.99	1.0	0	1.82[d]
1.7–5.3	1.0	0	0.621[e]
0.4–1.7	1.0	0	2.15[f]

[a] 25.0°, $\mu = 1$, unless otherwise noted. [b] $\mu = 2.0$. [c] $\mu = 3.0$. [d] $\mu = 4.0$. [e] 15.0°. [f] 35.0°.

$$\text{rate} = k[Cr(NH_3)_4Cl(OH_2)^{2+}][Cr^{2+}] \quad (2)$$

It is seen, however, that the rate constants for the *trans* complex are increased significantly in the presence of free chloride ion, the increase in k being linear in $[Cl^-]$, within experimental error. The complete rate law for the *trans* complex over the range of experimental conditions is then

$$\text{rate} = (k_1 + k^2[Cl^-])[Cr^{2+}][\textit{trans-}Cr(NH_3)_4Cl(OH_2)^{2+}] \quad (3)$$

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

(12) I. Dostrovsky and F. S. Klein, *Anal. Chem.*, 24, 414 (1952).

(13) M. Anbar and S. Guttman, *Intern. J. Appl. Radiation Isotopes*, **5**, 233 (1959).

(14) J. E. Finholt, K. G. Caulton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

(15) R. Kolaczkowski and R. A. Plane, *ibid.*, 3, 322 (1964).

(16) D. W. Hoppenjans, J. B. Hunt, and C. Gregoire, submitted for publication.

where $k_1 + k_2[Cl^-] = k$ of eq 2. The rate constant for the *cis* isomer is increased also by the addition of chloride ion, but to a much smaller extent than the *trans*. The rate constants for both isomers increase as the ionic strength increases, but again the effect is much more pronounced in the case of the *trans* isomer.

The activation parameters, calculated from the data of Table I for solutions of $\mu = 1.0$ and $[Cl^-] = 0$, are $E_a = 11.2 \pm 0.5$ kcal mole^{-1}, $\Delta H^{\ddagger} = 10.6$ kcal mole^{-1}, and $\Delta S^{\ddagger} = -27.6 \pm 1.5$ cal deg^{-1} mole^{-1} for the *cis* complex, and $E_a = 10.3 \pm 0.5$ kcal mole^{-1}, $\Delta H = 9.7 \pm 0.5$ kcal mole^{-1}, and $\Delta S^{\ddagger} = -26.0 \pm 1.5$ cal deg^{-1} mole^{-1} for the *trans* complex.

The results of the oxygen isotopic fractionation experiments are presented in Table II. In this table N_0 and N_t represent the ratio $[O^{18}]/[O^{16}]$ for the particular chloroaquotetraammine complex at zero time and after the reaction was quenched (at time t), respectively. As an indication of the precision of the measurements on which these ratios are based, the ratios $[O^{18}]/[O^{16}]$ measured for two zero time samples from the same batch of the *trans* complex were 0.001989 and 0.001991.

Table II. Oxygen Isotopic Fractionation in the Reactions of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ with Aquochromium(II)

W_t/W_0[c]	N_t/N_0[d]	$k_{O^{16}}/k_{O^{18}}$
	(a) *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [a]	
0.283	1.0216	1.0174
0.218	1.0270	1.0178
0.214	1.0266	1.0173
0.197	1.0277	1.0171
0.195	1.0274	1.0168
0.190	1.0291	1.0176
0.177	1.0271	1.0157
0.159	1.0333	1.0182
0.118	1.0355	1.0168
	Average	1.0172 ± 0.0005
	(b) *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [b]	
0.169	1.0097	1.0055
0.157	1.0104	1.0056
0.149	1.0117	1.0061
0.146	1.0139	1.0072
0.122	1.0166	1.0078
0.118	1.0164	1.0076
0.0967	1.0161	1.0068
0.0966	1.0182	1.0076
0.0741	1.0162	1.0063
	Average	1.0067 ± 0.0007

[a] [Complex] = 0.28 *M*; initial $[H^+] = 2.0$ *M*; $\mu = 2.8$; $T = 15°$. [b] [Complex] = 0.36 *M*; initial $[H^+] = 2.5$ *M*; $\mu = 3.6$; $T = 15°$. [c] Fraction of starting material remaining at time t. [d] $N_t = [O^{18}]/[O^{16}]$ for tetraammine complex at time t; $N_0 = [O^{18}]/[O^{16}]$ for tetraammine complex at zero time.

It is seen that the ratio N_t/N_0 increased steadily as the extent of reaction increased, a trend which is particularly noticeable for the *trans* complex.

The results of the water-exchange experiments rule out the possibility of fractionation due to exchange with the solvent. A sample of the *trans* complex, containing water of normal isotopic abundance initially, was found to have undergone no detectable exchange with the solvent (eightfold enriched in O^{18}) during the 2-hr deaeration period, 2 half-lives of the Cr(II)-catalyzed reaction, and the same separation and drying procedure used in the fractionation experiments. A sample of the *cis* complex was found to have exchanged to the extent of only 5% during similar treatment. Further, the preparation of the *cis* complex involved long contact with water, so that the complex was probably in isotopic equilibrium with normal water at the beginning of the fractionation experiments, and therefore any exchange during the deaeration process would not have affected the results significantly.

In Table II we have chosen to designate the isotopic fractionation factor as $k_{O^{16}}/k_{O^{18}}$, where $k_{O^{16}}$ and $k_{O^{18}}$ are the rate constants for ions of the complex containing O^{16} and O^{18}, respectively. Since ions containing the different isotopes must obey the same rate equation, it can be shown easily that $k_{O^{16}}/k_{O^{18}} = \mathrm{d}\ln[O^{16}]/\mathrm{d}\ln[O^{18}]$, where the latter quotient is the definition of the fractionation factor given by Green, Schug, and Taube.[4b] It can be shown also that

$$\frac{k_{O^{16}}}{k_{O^{18}}} = 1 - \frac{\ln(N_t/N_0)}{\ln(N_t/N_0) + \ln([O^{16}]_t/[O^{16}]_0)} \tag{4}$$

which was the equation used in calculating the fractionation factors quoted in Table II. Since these experiments were done with material of ordinary isotopic composition, the oxygen in both the starting material and retrieved material was about 99.8% O^{16}. The fraction $[O^{16}]_t/[O^{16}]_0$ is then approximated very closely by W_t/W_0, the fraction of the original complex remaining at time t. The fraction W_t/W_0 was calculated from weights of the starting material and the retrieved material, rather than from rate data, since temperature control was not very precise (±1°) in the fractionation experiments.

It is seen from Table II that there is a substantial fractionation of O^{16} compared to O^{18} in the reaction of the *trans* isomer and a smaller but significant fractionation of O^{16} compared to O^{18} in the reaction of the *cis* isomer. Thus, the *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion reacts about 1.7% faster with Cr^{2+} when O^{16} rather than O^{18} is present in the aquo ligand, whereas the *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion reacts about 0.7% faster when O^{16} is present.

The form of the rate laws and the appearance of $(H_2O)_5CrCl^{2+}$ as a reaction product strongly suggest that the reactions under study involve an electron-transfer reaction between chromium(II) and chromium(III) as the rate-controlling step and that the chloride ion serves as a bridging group in the electron-transfer step.[2,3] At least in perchlorate media, the major difference between the reactions of the two isomers is that the *trans* complex has a water molecule *trans* to the bridging group, whereas the *cis* complex has its water molecule *cis* to the chloride bridge and an ammonia molecule *trans* to the bridge. The consequences of this difference in geometry were anticipated in the results of Pennington and Haim[3] for the analogous ethylenediamine complexes, *i.e.*, we expected that the *trans* isomer would react more rapidly with Cr^{2+} than would the *cis* isomer, as had been the case for the ethylenediamine complexes. However, there is a quantitative difference between the ammonia and ethylenediamine complexes which merits discussion. From Table I it is seen that *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ reacts about ten times as rapidly as does *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, whereas Pennington and Haim[3] found that *trans*-$Cr(en)_2(OH_2)Cl^{2+}$

reacted about 40 times as rapidly as did *cis*-$Cr(en)_2(OH_2)Cl^{2+}$.

Pennington and Haim[3] have suggested that the difference in reaction rates for *cis* and *trans* isomers could be explained by assuming that the bond to the ligand *trans* to the bridging groups must be stretched in formation of the activated complex, a feat which could be accomplished more readily with oxygen, rather than nitrogen, in the *trans* position. A slight extension of this idea can be used to explain the fact that the difference in rates between the isomers is larger for the ethylenediamine complexes than for the ammine complexes. If the bond to the *trans* ligand must be stretched, then the formation of the activated complex for *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ would require also that either some bonds in the chelate ring be distorted or, more likely, that the conformation of the ring be changed. The latter requirement would not exist in the case of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. For this reason the ammine complexes may provide better information about the effect of the character of individual bonds.

The isotopic fractionation factors quoted in Table II provide direct evidence that the bond to the *trans* ligand is stretched in forming the activated complex, at least when the reactant is *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. A much smaller, but still significant, stretching of the Cr–O bond for *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is also indicated. The picture of the activation process provided by the fractionation factors is essentially that anticipated by previous workers.[1,17] If it is assumed that the electron-transfer step is adiabatic, that the Franck-Condon principle is applicable, and that the d_{z^2} orbital of chromium(III) is used to accept the incoming electron, then the activation process would involve the lowering of the energy of the d_{z^2} orbital.[18] This could be accomplished by elongation of the complex along the *z* axis, *i.e.*, along the direction of the bridging group and the *trans* ligand. Lowering of the energy of the d_{z^2} orbital would also be aided by elongation of the bonds to the *cis* ligands, but to a much smaller extent.

Although the isotopic fractionation factors which we have measured provide evidence for substantial participation of the *trans* ligand in the activation process, it seems unlikely that the rearrangement required of the *trans* ligand is anywhere close to that required of the bridging ligand. The fractionation factor which we have obtained for the *trans* water molecule is less than half that reported by Diebler, Dodel, and Taube[19] for the bridging water molecule in the reduction of $Co(NH_3)_5OH_2^{3+}$ by Cr^{2+}. The latter reaction involves a large free-energy change, and less over-all bond rearrangement in the formation of the activated complex would be expected than for the reactions which we have studied.

The effect of free chloride ion on the rate of reaction of the *trans* complex deserves further mention. The form of the chloride-dependent term of the rate law (*cf.* eq 3) implies a second path for the reaction for which the activated complex has the composition $[(H_2O)Cr(NH_3)_4Cl \cdot Cr(H_2O)_x \cdot Cl]^{3+}$. The role of the free chloride ion is probably that of a nonbridging ligand attached to Cr^{2+}. A similar role for ambient chloride ion has been suggested by Taube and King[20] to explain the catalysis by chloride ion of isotopic exchange between $CrCl^{2+}$ and Cr^{2+}. If this explanation of the role of free chloride ion is correct, then some $(H_2O)_4CrCl_2^+$ should be formed in the reaction. However, a comparison of our rate data with those of Espenson and Slocum[21] reveals that both isomers of $(H_2O)_4CrCl_2^+$ would be expected to disappear as rapidly as they were formed under the conditions of our experiments.

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