Oxidation–Reduction Catalysis of Chromium(III) Substitution. Kinetics of the Reaction of Vanadium(II) and Chlorochromium(III) Ions and Its Reverse. An Example of Nonsteady-State Kinetics[1]

James H. Espenson and O. Jerry Parker

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010.

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Abstract: Studies have been carried out on the kinetics of three of the individual processes in the two-step sequence of reactions relating V(II), V(III), Cr(II), and Cr(III) in solutions containing chloride and/or perchlorate ions. The ions V^{2+} and $CrCl^{2+}$ react in a second-order process, with a rate constant $k_1 = e + f/[H^+]$. In chloride solution the third-order rate constant for the reaction $V^{3+} + Cr^{2+} + Cl^-$ in which $(H_2O)_5CrCl^{2+}$ is formed is given by $k_2 = g + h/[H^+]$. In perchlorate solution, the reaction of $V^{3+} + Cr^{2+}$ follows a second-order rate expression, with the rate constant $k_3 = q/(r + [H^+])$. At 25.0° and ionic strength 2.50 *M*, values (units *M* and sec) are: $e = 0.0384$, $f = 0.0025$, $g = 4.3$, $h = 0.27$, $q = 1.09$, and $r = 0.12$. The reaction of V^{2+} and $CrCl^{2+}$ did not follow steady-state kinetics unless either V^{3+} or Cr^{2+} was added, since the latter ions were formed as intermediates but reacted only relatively slowly. From the steady-state data (V^{3+} or Cr^{2+} added) the best values of k_1 were derived. Known rate constants were used to find numerical solutions for the nonsteady-state situation by a Runge–Kutta iteration process on a computer. The interrelations of the various rate steps are demonstrated. The detailed mechanism, particularly the question of inner- or outer-sphere electron transfer, is discussed with special emphasis on comparisons with reactions of established mechanism.

Ogard and Taube[2] found that a number of strong oxidizing agents catalyzed net aquation of chromium(III) complexes, such as the pentaaquochlorochromium(III) cation, $(H_2O)_5CrCl^{2+}$ (eq 1). The pro-

$$(H_2O)_5CrCl^{2+} + H_2O = Cr(H_2O)_6^{3+} + Cl^- \tag{1}$$

posed mechanism consisted of oxidation of $CrCl^{2+}$ to Cr(IV) followed by reduction back to Cr(III). Since Cr(IV) is presumably labile to substitution, chloride ion was readily released at this stage. It occurred to us that a parallel catalysis effect on chromium(III) substitution should be noted in the presence of reducing agents. The chromium(II) so formed would release the bound chloride ion and would then be reoxidized in a second step. A system was studied involving metal ions where the oxidation–reduction reaction between the aquo ions had been studied and where the equilibrium position of the Cr(III) substitution process was known. The kinetics of the reaction of V^{3+} and Cr^{2+} was studied previously,[3] and the equilibrium quotient for aquation of $CrCl^{2+}$ is known.[4]

A detailed kinetic study has been carried out on each of the three steps contributing to the following reaction scheme (the rate constants refer to constant $[H^+]$, and each shows a further dependence on $[H^+]$).

$$CrCl^{2+} + V^{2+} \underset{2}{\overset{1}{\rightleftarrows}} Cr^{2+} + Cl^- + V^{3+} \tag{2}$$

$$Cr^{2+} + V^{3+} \underset{4}{\overset{3}{\rightleftarrows}} Cr^{3+} + V^{2+} \tag{3}$$

$$\text{Net:}\ CrCl^{2+} = Cr^{3+} + Cl^- \tag{1}$$

The steady-state approximation was not satisfied in the reaction of V^{2+} and $CrCl^{2+}$; Cr^{2+} and V^{3+} so produced did not react at a high enough rate. Further verification of the proposed scheme came from detailed consideration of the nonsteady-state kinetics.

We have made independent measurements on the following processes: (1) the reaction of Cr(II) and V(III) in perchlorate solution, evaluating k_3; the reaction of Cr(II) and V(III) in solutions containing chloride as well as perchlorate ions, evaluating k_2; (3) the reaction of $CrCl^{2+}$ and V^{2+} under conditions where the first step is rate-determining, evaluating k_1; (4) the reaction of $CrCl^{2+}$ and V^{2+} under conditions where the rate constants k_2 and k_3, in addition to k_1, are important; (5) the equilibrium quotient for the over-all formation of $CrCl^{2+}$, and thereby an independent value of k_3/k_4.

Catalysis of trivalent metal ion substitution by the lower oxidation state of the *same* metal ion had been realized for Cr(III),[5] Fe(III),[6] and V(III)[7] complexes. The process we encountered here, where two different metal ions were involved, appeared to proceed by a similar mechanism. A second electron-transfer step was involved in this novel reaction, however, since a net reaction occurred between the aquo ions of different metals, whereas only an exchange reaction occurred when a single metal ion was involved.

Experimental Section

Materials. The reagents used in the rate studies were prepared by the following procedures. Chlorochromium(III) ion was

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2199. (b) Presented in part at 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1965.

[2] A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958).

[3] J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

[4] R. J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

[5] (a) J. B. Hunt and J. E. Earley, *ibid.*, **82**, 5312 (1960); (b) A. Adin and A. G. Sykes, *J. Chem. Soc.*, *A*, 518 (1966); (c) D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3450 (1966); (d) A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc.*, *A*, 1504 (1967); (e) D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).

[6] (a) T. J. Conocchioli and N. Sutin, *J. Am. Chem. Soc.*, **89**, 282 (1967); (b) R. J. Campion, T. J. Conocchioli, and N. Sutin, *ibid.*, **86**, 4591 (1964); (c) E. G. Moorehead and N. Sutin, *Inorg. Chem.*, **6**, 428 (1967).

[7] J. H. Espenson, *J. Am. Chem. Soc.*, **89**, 1276 (1967).

synthesized from chlorine and chromium(II) in perchloric acid solution.[8] An alternate preparation of $(H_2O)_5CrCl^{2+}$ was the addition of a trace of chromium(II) catalyst to a deoxygenated solution of chromium(III) chloride hexahydrate.[9] (The latter compound contains the ion *trans*-$(H_2O)_4CrCl_2{}^{+}$ [10]). The major product of each reaction was the desired monochloro complex, which was separated and purified by cation exchange using Dowex 50WX-8 resin and elution with 1 *F* perchloric acid. Chromium(II) perchlorate solutions were prepared and analyzed as before.[8]

Vanadyl perchlorate solutions, prepared from vanadyl sulfate and a very slight excess of barium perchlorate, were reduced to vanadium(II) with amalgamated zinc or by electrolysis at a mercury cathode. A further independent source of vanadium(II) was provided by the electrolytic reduction of a slurry of vanadium pentoxide in perchloric acid. Solutions of vanadium(III) were prepared by mixing V(II) and V(IV), with a slight excess of the former. The concentration of V(II) in stock solutions of V(II) or V(III) was analyzed by adding the appropriate volume to an excess of $Co(NH_3)_5Br^{2+}$ in perchloric acid and allowing the reaction to proceed for 10–20 min under nitrogen. The cobalt(II) so produced was analyzed spectrophotometrically as the thiocyanate complex (0.1 g/ml of ammonium thiocyanate) in 50 vol % acetone; its molar absorptivity is 1842 M^{-1} cm^{-1} at 6230 Å. Total vanadium concentrations were determined spectrophotometrically with hydrogen peroxide in sulfuric acid solution (ϵ 205 M^{-1} cm^{-1} at 4000 Å). Details of the procedure have been published.[3]

Stock solutions of V(II) and V(III) were generally prepared at 0°, and when not in use frozen and stored at −78°. A particular solution could be repeatedly frozen and thawed over a period of several weeks without detectable oxidation or formation of a detectable concentration of chloride ion.

Lithium perchlorate and barium perchlorate were prepared from the carbonates and perchloric acid and were recrystallized twice from conductivity water. Reagent grade barium chloride was recrystallized twice. Stock solutions of these salts were analyzed by titrating with base the acid rinsed from a column of cation-exchange resin. Water used in all solutions was triply distilled from alkaline permanganate in a tin-lined Barnstead still. All other chemicals were reagent grade and were used without further purification.

Rate Measurements. The reaction of V(III) and Cr(II) was studied as a function of chloride ion concentration. The progress of the reaction was followed spectrophotometrically at 5740 and 2500 Å by the customary procedures.[3,11] These runs were relatively rapid; under conditions chosen here, they were followed for times of 30–300 sec. In any given experiment the observed change in absorbance was dependent upon the relative amounts of chlorochromium(III) and aquochromium(III) formed. The resulting dependence of the value of $\Delta\epsilon$ upon [Cl⁻] was taken into account in computing rate constants from absorbance data.

The catalyzed aquation of chlorochromium(III) ion was studied by similar techniques. This reaction is somewhat slower, and typical reaction times were 10–40 min. Many runs contained added V(III) or Cr(II) and were studied generally at 4400 Å, whereas experiments with only V^{2+} and $CrCl^{2+}$ were studied primarily at 6090 Å.

Reaction Media. All the rate studies refer to a medium of ionic strength 2.50 *M* and a univalent anion concentration of 2.00 *M* consisting of 0.50 *M* divalent ions and 1.00 *M* univalent cations (H^+, Li^+). This medium was initially chosen in an effort to control variation of activity coefficients with the composition of the medium. It does allow one to maintain simultaneously constant ionic strength and constant anion concentration. On the other hand, the salt concentrations of such solutions are so high that we cannot claim to understand the details of activity effects therein. Moreover, we have no evidence that the activity coefficients are any more constant in this medium (or any less so) than in a medium consisting of a lower concentration of primarily univalent ions at a lower ionic strength.

Equilibrium Measurements. A few studies were carried out to evaluate the equilibrium quotient for chlorochromium(III) formation (eq 4) under the conditions of the present study: 25.0° and ionic strength 2.50 *M*.

$$Cr(H_2O)_6{}^{3+} + Cl^- = (H_2O)_5CrCl^{2+} + H_2O \qquad (4)$$

All experiments were done with $[V^{2+}]$ = 0.0200 *M* in order to hasten the approach to equilibrium. The equilibrium concentration of chlorochromium(III) in duplicate samples was determined after air oxidation of vanadium(II) by the quantitative separation of $CrCl^{2+}$ on a cation-exchange column. The $CrCl^{2+}$ was analyzed spectrophotometrically as $CrO_4{}^{2-}$ after oxidation with peroxide in alkaline solution.[12]

Results

Reaction of Chromium(II) and Vanadium(III). The electron-transfer reaction between the aquo ions was studied previously in perchlorate solution[3] although in a rather different medium (μ = 0.65 *M* previously,[3] 2.50 *M* here). The rate law at constant [H⁺] was the expected mixed-second-order equation (eq 5)[13] in which

$$-d[Cr^{2+}]/dt = k_3[V^{3+}][Cr^{2+}] \qquad (5)$$

the apparent rate constant k_3 increased with decreasing [H⁺]. Values at 25.0°, μ = 2.50 *M*, are k_3 = 0.93, 1.82, 3.18, 3.83, and 5.25 M^{-1} sec^{-1} at [H⁺] = 1.00, 0.500, 0.200, 0.133, and 0.100 *M*, respectively. The dependence of the rate constant upon [Cl⁻], as perchlorate ion was replaced by chloride, was linear within experimental error, as shown by the typical results in Figure 1.

Values of k_2, defined by eq 6,[14] were obtained from

$$-d[Cr^{2+}]/dt = k_{obsd}[V^{3+}][Cr^{2+}] = (k_3 + k_2[Cl^-])[V^{3+}][Cr^{2+}] \qquad (6)$$

plots of k_{obsd} *vs.* [Cl⁻] at each particular [H⁺]. From a least-squares fit, k_2 = 4.87 ± 0.28, 4.3 ± 0.3, 5.7 ± 0.3, 6.2 ± 0.4, and 6.8 ± 0.5 M^{-2} sec^{-1} at the five [H⁺] cited above.

The product of the k_2 reaction path was shown to be $CrCl^{2+}$ by its known absorption spectrum.[15] The concentration of $CrCl^{2+}$ in product solutions was estimated from the decrease in absorbance at 6090 Å, comparing the value at the end of the run with that after equilibrium was attained, 10–20 hr. Several experiments are shown in Table I. The observed values for $[CrCl^{2+}]/([CrCl^{2+}] + [Cr^{3+}])$ at the completion of the run can be com-

Table I. Product Distribution in the Reaction of V^{3+} and Cr^{2+} in Chloride Solution (25.0°, I = 2.50 M[15])

		Fraction $CrCl^{2+}$	
[H⁺], *M*	[Cl⁻], *M*	Obsd (no.)[a,b]	Calcd
1.00	0.90	0.86 (8)	0.834
0.500	0.25	0.34 (1)	0.371
0.500	0.478	0.53 (1)	0.531
0.500	0.75	0.90 (2)	0.640

[a] Number of independent runs under a given set of conditions in which the analysis of $CrCl^{2+}$ was carried out. [b] Corrected for the $CrCl^{2+}$ remaining at equilibrium.

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(8) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

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(10) (a) E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, 80, 5015 (1958); (b) I. G. Dance and H. C. Freeman, *Inorg. Chem.*, **4**, 1555 (1965); (c) B. Morosin, *Acta Cryst.*, 21, 280 (1966).

(11) J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

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

(13) It was noted here as well as in the original study[3] of the reaction in perchlorate solution that the second-order rate constants in runs with excess V(III) were higher, often as much as 10% above the average of runs with Cr(II) in excess. All of the Cr(II) and V(III) solutions were reanalyzed by independent methods, and a number of rate runs were analyzed for the reagent in excess after completion of the run; no errors were found (within 2%). The rate effect may be due to an undetected systematic error in analysis, or it may represent a small but genuine kinetic effect. Since the effect is barely beyond experimental error, it will not be considered further; the rate constants reported here refer to runs with excess Cr(II) or a small excess of V(III).

(14) Chloride complexing of V^{3+} is negligible up to 1 *M* Cl⁻: S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

(15) (a) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965), (b) J. E. Finholt, K. G. Caulton, and W. J. Libbey, *ibid.*, **3**, 1801 (1964).

pared with the ratio $k_2[\mathrm{Cl}^-]/(k_2[\mathrm{Cl}^-] + k_3)$ which is the theoretical value according to eq 2 and 3. Except for one unaccountably discrepant result, the observed and calculated values agreed well enough with this assumption, demonstrating that the chloride-dependent path does not have a component leading to $\mathrm{Cr(H_2O)_6}^{3+}$.

Chlorochromium(III) and Vanadium(II) Steady-State Data. The rate equations resulting from the two-step mechanism presented above (eq 2 and 3), neglecting k_4 as justified later, are

$$\frac{-\mathrm{d}[\mathrm{CrCl}^{2+}]}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{CrCl}^{2+}][\mathrm{V}^{2+}] + k_2[\mathrm{Cl}^-](\mathrm{d}[\mathrm{Cr}^{2+}]/\mathrm{d}t)}{k_3 + k_2[\mathrm{Cl}^-]} \quad (7)$$

$$\frac{\mathrm{d}[\mathrm{Cr}^{3+}]}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{CrCl}^{2+}][\mathrm{V}^{2+}] - k_3(\mathrm{d}[\mathrm{Cr}^{2+}]/\mathrm{d}t)}{k_3 + k_2[\mathrm{Cl}^-]} \quad (8)$$

When the steady-state approximation for the intermediates Cr^{2+} and V^{3+} becomes valid, the equations become

$$\frac{-\mathrm{d}[\mathrm{CrCl}^{2+}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Cr}^{3+}]}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{CrCl}^{2+}][\mathrm{V}^{2+}]}{k_3 + k_2[\mathrm{Cl}^-]} \quad (9)$$

The steady-state relation was not generally valid in the present work, however. In terms of the two-step mechanism shown above, Cr^{2+} and V^{3+} were formed (k_1) at a rate higher than they reacted (k_2 and k_3). The resulting concentrations of these ions were sufficiently high that appreciable fractions of the total chromium and of the total vanadium at any instant were present as Cr^{2+} and V^{3+}.

Consider the alterations in reaction conditions that would force the reaction to conform more closely to the steady-state relation. Addition of a high concentration of *one* of the intermediates, say V^{3+}, would maintain the concentration of the other intermediate, Cr^{2+}, at a considerably lower level than when V^{3+} was not added, since Cr^{2+} is converted to CrCl^{2+} or Cr^{3+} by its reactions with V^{3+}. An estimate of the V^{3+} concentration required to cause deviations of no more than 5%[16] can be made, assuming an approximate value of 0.06 M^{-1} sec^{-1} for k_1. For the steady-state approximation to be valid within 5% accuracy,[16] the inequality in eq 10 must

$$\frac{[\mathrm{Cr}^{2+}]_{\mathrm{ss}}}{[\mathrm{CrCl}^{2+}]_0} = \frac{k_1[\mathrm{V}^{2+}]_0\{\exp(-k_1[\mathrm{V}^{2+}]_0t)\}}{(k_3 + k_2[\mathrm{Cl}^-])[\mathrm{V}^{3+}]} \leq 0.05 \quad (10)$$

hold. For example, at $[\mathrm{H}^+] = 0.100\ M$, the known rate constants employed in eq 10 allowed one to calculate that $[\mathrm{V}^{3+}]$ must be larger than *ca.* $0.23[\mathrm{V}^{2+}]_0$. In runs with $[\mathrm{V}^{2+}]_0 = 0.066\ M$, $[\mathrm{V}^{3+}]$ must be $\geq 0.015\ M$. Runs 14–20 in Table II had $[\mathrm{V}^{3+}] = 0.020\ M$ and met this criterion. Experiments 9–13 with $0.015 \leq [\mathrm{Cr}^{2+}] \leq 0.074\ M$ also met this arbitrary 5% requirement.

Table II summarizes the kinetic data under steady-state conditions. The pseudo-first-order dependence of rate upon $[\mathrm{CrCl}^{2+}]$ was indicated by the linearity of plots of log $(D_t - D_\infty)$ *vs.* time (D = absorbance) over at least 80% reaction in each run, from the slopes of which the second-order rate constant k_1 was computed.

$$k_1 = 2.303[\mathrm{V}^{2+}]^{-1}\left\{\frac{-\mathrm{d}\log(D_t - D_\infty)}{\mathrm{d}t}\right\} \quad (11)$$

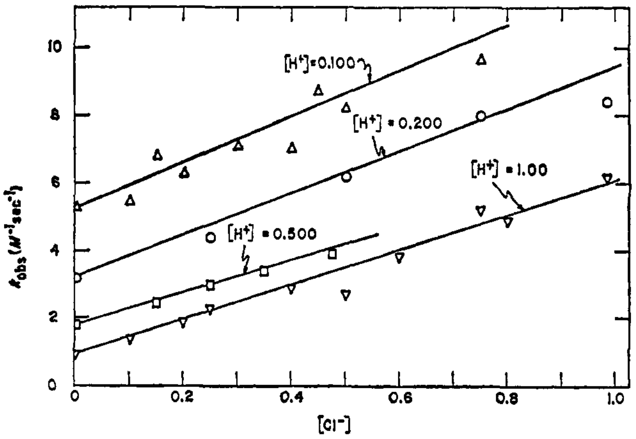

Figure 1. Illustrating the chloride dependence of the observed second-order rate constants for the reaction of V^{3+} and Cr^{2+}.

Most experiments were carried out at 4400 Å, with some runs at 6090 and 6200 Å. A run at λ 5780 Å (run 20, Table II), an isosbestic wavelength for Cr^{3+} and CrCl^{2+}, gave no absorbance change, indicating that notable concentrations of V^{3+} and Cr^{2+} were not formed in the course of the experiment.

Table II. Apparent Second-Order Rate Constants at Various Concentrations (M)[a] (25.0°, μ = 2.50 M[15] at 4400 Å)

Run	$[\mathrm{V}^{2+}]_0$	$[\mathrm{Cr}^{2+}]_0$	$[\mathrm{V}^{3+}]_0$	$[\mathrm{H}^+]$	k_1, M^{-1} sec^{-1}
1	0.100	0.784		1.00	0.0409
2	0.0760	0.080		1.00	0.0417
3	0.0760	0.080		1.00	0.0403
4	0.0760	0.080		0.500	0.0428
5	0.0608	0.040		0.250	0.0485
6	0.0608	0.040		0.200	0.0514
7	0.0608	0.040		0.200	0.0500
8	0.0608	0.040		0.125	0.0577
9	0.0304	0.015		0.100	0.0641
10	0.0304	0.015		0.100	0.0616
11	0.0760	0.020		0.100	0.0652
12	0.0760	0.040		0.100	0.0681
13	0.0760	0.074		0.100	0.0616
14	0.0657		0.020	0.100	0.0629
15	0.0657		0.020	0.100	0.0619
16	0.0657		0.020	0.100	0.0631
17	0.0657		0.020	0.100	0.0628
18	0.0657		0.020	0.100	0.0621[b]
19	0.0657		0.020	0.100	0.0617[c]
20	0.0657		0.020	0.100	*d*
21	0.0608	0.040		0.062	0.0708

[a] In all these experiments, $[\mathrm{CrCl}^{2+}]_0$ was 0.0120 M. [b] Studied at 6090 Å. [c] Studied at 2600 Å. [d] Studied at 5780 Å which is an isosbestic point for CrCl^{2+} and Cr^{3+}; under these conditions there was essentially no change in the observed absorbance.

The variation in $[\mathrm{V}^{2+}]$ was not large although there was a twofold variation in the runs at $[\mathrm{H}^+] = 0.100$ M (runs 9 and 10). The first-order dependence upon $[\mathrm{V}^{2+}]$ is indicated by those experiments. The non-steady-state data considered later in detail encompassed a much wider range of $[\mathrm{V}^{2+}]$, and confirmed this aspect of the rate expression, as assumed in eq 7. The rate constant k_1 was independent of whether Cr^{2+} or V^{3+} was added and independent as well of its concentration. The regular variation of k_1 with $[\mathrm{H}^+]$ will be considered in detail in a later section.

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(16) A measure of the validity of the steady-state approximation is given by the maximum fraction of the concentration of CrCl^{2+} or V^{2+}, whichever is lower, that was converted to intermediate.

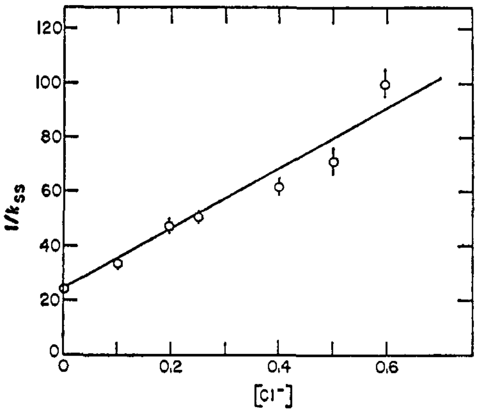

Figure 2. Illustrating the chloride dependence of the observed second-order rate constant for the reaction of V^{2+} and $CrCl^{2+}$ at 25.0° and $[H^+] = 1.00\ M$ under steady-state conditions. In each run, $[CrCl^{2+}]_0 = 0.012$, $[V^{2+}]_0 = 0.076$, and $[Cr^{2+}]_0 = 0.08\ M$. The solid line is that predicted from combination of three independently known rate constants, according to eq 12, and corresponds to the values $k_1 = 0.0409\ M^{-1}\ sec^{-1}$, $k_2 = 4.87\ M^{-1}\ sec^{-1}$, and $k_3 = 0.93\ M^{-1}\ sec^{-1}$.

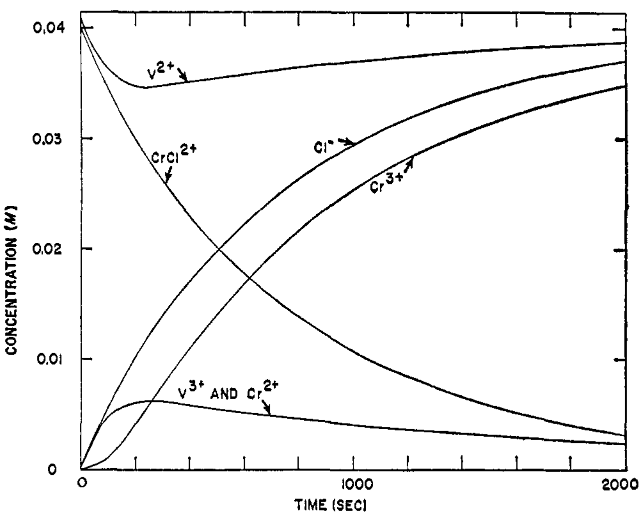

Figure 3. Concentrations of reactants, products, and intermediates as a function of time in a typical nonsteady-state experiment with $[V^{2+}]_0 = 0.0410$ and $[CrCl^{2+}]_0 = 0.0403\ M$ at $[H^+] = 1.00\ M$ and 25.0°. Lines shown here give the theoretical values computed from the assumed model with given rate constants, according to the Runge–Kutta computation.

According to eq 9, the steady-state rate constant should be a function of $[Cl^-]$ according to the equation

$$k_{ss} = \frac{k_1 k_3}{k_2[Cl^-] + k_3} \qquad (12)$$

In experiments without added chloride ion, the term k_3 generally was the main denominator term, leading to a value of $k_{ss} \cong k_1$. A number of steady-state runs (0.080 M added Cr^{2+}) were also performed containing added Cl^-, in the range of up to 0.60 M Cl^- at t_0, with $[H^+] = 1.00\ M$. Figure 2 shows a plot of $1/k_{ss}$ *vs.* $[Cl^-]$ and compares the data obtained with the predictions of eq 12 based on the independently known values of k_1, k_2, and k_3. The agreement is considered to be satisfactory, giving additional support to the rate law and mechanism proposed.

Chlorochromium(III) and Vanadium(II) Nonsteady-State Data. The reaction of V^{2+} and $CrCl^{2+}$ was also studied without added vanadium(III) or chromium(II). Initial concentrations were varied as follows: $CrCl^{2+}$, 0.005–0.091 M; V^{2+}, 0.010–0.082 M. Plots of log $(D - D_\infty)$ *vs.* time were not linear but were curved upward near the start of a run and downward as the reaction neared completion. An attempt was made to learn whether the decrease in the apparent value of k_1 (eq 11) as the reaction progressed in the early stages could be attributed to a side reaction that consumed V^{2+}. The V^{2+} content of samples removed from the reaction solution was analyzed by the spectrophotometric method based on $Co(NH_3)_5Br^{2+}$. The amount of cobalt(II) produced by this reaction was the same (±2%), within experimental error, at all points during the run. In fact, the experiment measured not $[V^{2+}]$, but the sum $[V^{2+}] + [Cr^{2+}]$, and showed the constancy of total reducing strength.

Rate runs were performed at 5780–5800 Å, an isosbestic point for Cr^{3+} and $CrCl^{2+}$. In such experiments the absorbance first fell with time, passed through a gradual minimum, and then rose to very nearly its starting value. Since the molar absorptivities of the proposed intermediates Cr^{2+} and V^{3+} differ from those of the major species, their formation at appreciable concentration will manifest itself spectrally. At λ 5780 Å, for example, conversion of V^{2+} (ϵ 3.8) to V^{3+} (ϵ 5.6) and conversion of $CrCl^{2+}$ (ϵ 13.1) to Cr^{2+} (ϵ 2.3) rather than to Cr^{3+} (ϵ 13.1) would lead to the observed minimum in absorbance with time. According to this same scheme, the sum $[V^{2+}] + [Cr^{2+}]$ would be constant, thereby accounting for the observed constancy of reducing strength.

A computer program utilizing the Runge–Kutta method was employed to solve the differential equations in an iterative technique to calculate concentrations and absorbance as a function of time, given values for the rate constants k_1, k_2, and k_3, the initial concentrations, and the molar absorptivity of each species.[17,18] The value of k_1 used in these computations was that derived from the steady-state experiments at the appropriate $[H^+]$.

Consider a particular run having $[CrCl^{2+}]_0 = 0.0403$ and $[V^{2+}]_0 = 0.0410\ M$ at 1.00 M H^+, shown in Figure 3. The intermediates V^{3+} and Cr^{2+} rose to a maximum value; 15.3% of the initial $CrCl^{2+}$ and V^{2+} had been converted to Cr^{2+} and V^{3+} at the maximum. In the early portion of each experiment, when $[V^{3+}]$ and $[Cr^{2+}]$ were yet increasing, $[V^{2+}]$ was decreasing substantially. The decrease in $[V^{2+}]$ would alone account for the unexpected curvature in the pseudo-first-order plots. The effect was accentuated in the absorbance values; gradual conversion of V^{2+} (ϵ 3.3) to V^{3+} (ϵ 5.4) caused the apparent rate constant to decrease with time. Very late in the run, $-d[Cr^{2+}]/dt$ became of the same order of magnitude as $-d[CrCl^{2+}]/dt$, accounting for the downward curvature noted near the end of each run.

(17) We are grateful to Dr. T. W. Newton for help in formulating the program, and to Dr. J. P. Birk for adapting it to the problem in question in a form suited to the IBM 360 computer.

(18) The FORTRAN IV listing of this program as used on an IBM 360 has been deposited as Document No. 9948 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

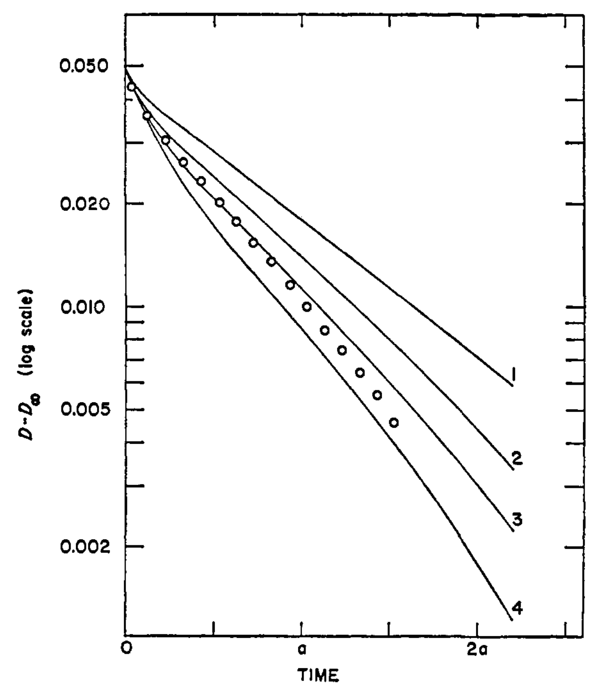

Figure 4. Observed and calculated absorbance values (2-cm optical path) in a nonsteady-state experiment on V^{2+} + $CrCl^{2+}$ plotted as ($D - D_\infty$) (log scale) *vs.* time. Conditions: $[V^{2+}]_0$ = 0.0410 and $[CrCl^{2+}]$ = 0.0403 *M* at $[H^+]$ = 1.00 *M* and 25.0°. Calculated lines are given for three other nonsteady-state runs at different $[V^{2+}]$ successively higher by a factor of 2: (1) 0.0103, (2) 0.0205, (3) 0.0410 (data depicted), (4) 0.082. The time scales are successively shorter by factors of 2, the values of *a* in runs 1–4 being 3200, 1600, 800, and 400 sec.

A comparison of calculated and observed absorbance values in four experiments at varying $[V^{2+}]$ is given in Figure 4, where the time scale has been normalized to compensate exactly for variation in $[V^{2+}]$ (*i.e.*, were the steady-state approximation valid, all four plots would be linear and would coincide precisely). In addition, the data for one run are shown superimposed on the theoretical line, the latter computed from the "best" values of the rate constants and molar absorptivities. Considering the uncertainties associated with these quantities, the fit of calculated and observed values is considered good. The fit could be made essentially perfect by adjustments in the various parameters within their experimental errors.

The computer program could be applied quite effectively to the previously cited data at the $CrCl^{2+}$–Cr^{3+} isosbestic point, 5800 Å. Using the known molar absorptivities, in a run with $[CrCl^{2+}]_0$ = 0.0200, $[V^{2+}]_0$ = 0.0820, $[Cl^-]_0$ = 0, and $[H^+]$ = 1.00 *M*, the observed $[Cr^{2+}]_{max}$ was 0.0051 *M* at *ca.* 210 sec, compared to the computed value of 0.0058 *M* at 220 sec. (Estimated errors in experimental $[Cr^{2+}]_{max}$ and t_{max} are 10% and 20 sec.) In the identical experiment, but with added chloride, $[Cl^-]_0$ = 0.400 *M*, observed $[Cr^{2+}]_{max}$ = 0.0036 *M* at *ca.* 160 sec, and calculated $[Cr^{2+}]_{max}$ = 0.0040 *M* at 180 sec.

Several Runge–Kutta computations were performed for runs which presumably met the steady-state criterion by addition of V^{3+} or Cr^{2+}. The predictions were borne out by these computations, the steady-state assumption proved adequate, and a close fit of observed and calculated absorbance readings was obtained.

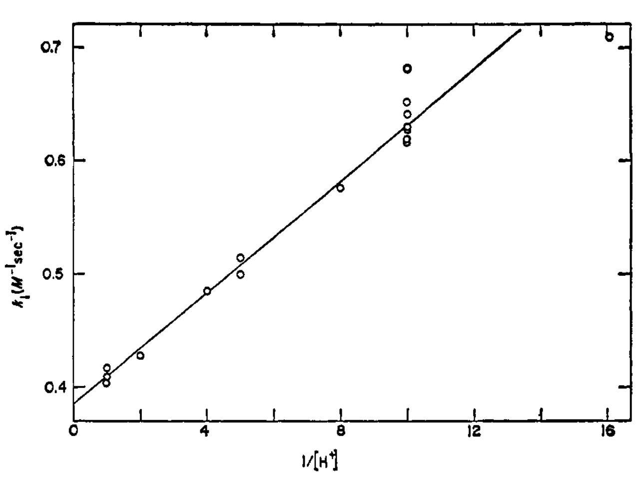

Figure 5. Illustrating the dependence of k_1 upon $[H^+]$ in a plot of k_1 *vs.* $1/[H^+]$.

Effect of $[H^+]$ and Temperature on the Various Rate Constants. In the original study of the reaction of V^{3+} and Cr^{2+} in perchlorate solution,[3] the apparent second-order rate constant k_3 was found to vary with $[H^+]$ according to eq 13. The data obtained here were fit to the same relation, leading to the values q =

$$k_3 = q/(r + [H^+]) \qquad (13)$$

1.09 sec^{-1} and r = 0.12 *M* at 25.0°, μ = 2.5 *M*, compared to q = 0.624 sec^{-1} and r = 0.108 *M* at μ = 0.65 *M*.[3]

A plot of k_1 *vs.* $1/[H^+]$ (see Figure 5) is linear; $k_1 = e + f/[H^+]$, with e = 0.0384 M^{-1} sec^{-1} and f = 0.0025 sec^{-1}. If the interpretation offered above is correct, and the rate terms $k_1[CrCl^{2+}][V^{2+}]$ and $k_2[V^{3+}][Cr^{2+}]\cdot[Cl^-]$ are the reverse of one another, then the principle of microscopic reversibility requires that k_2 have the following dependence upon $[H^+]$: $k_2 = g + h/[H^+]$, with $k_1/k_2 = e/g = f/h$. The observed values of $10^2 \times k_1/k_2$ are: 0.92, 0.94, 0.89, 1.00, and 0.84 at $[H^+]$ = 0.100, 0.133, 0.200, 0.500, and 1.00 *M*; the ratio of rate constants remained satisfactorily constant with varying $[H^+]$. The relatively low precision with which k_2 was evaluated did not permit the proposed relation to be tested very rigorously, but the values of k_2 cited earlier did show a trend of increasing k_2 with decreasing $[H^+]$ that appeared to be outside of experimental uncertainty. The approximate relation is $k_2 = 4.3 + 0.27/[H^+]$.

A few measurements of k_2 were carried out at other temperatures. At 1.00 *M* H^+, values of k_2 are as follows: 5.0°, 0.90; 15.0°, 2.21 M^{-2} sec^{-1}. Since k_2 represents a composite constant, meaningful activation parameters cannot be computed from these data. The value of k_2 is largely the contribution of the hydrogen-ion-independent term g at $[H^+]$ = 1.00 *M*, however, and at least approximate values for the activation parameters of rate constant g can be computed to be $\Delta H^{\ddagger}$ = 13 kcal $mole^{-1}$ and $\Delta S^{\ddagger}$ = −11 cal $mole^{-1}$ deg^{-1}. Considering the low precision with which we were able at present to evaluate k_2, it did not appear useful to carry out a detailed investigation of temperature effects.

Equilibrium Involving $CrCl^{2+}$ Formation. A value for the stability quotient of $CrCl^{2+}$ at the ionic strength in question was not available. Baltisberger and King[4] and Hale and King[19] had reported values for $Q_1 = [\mathrm{CrCl^{2+}}]/[\mathrm{Cr^{3+}}][\mathrm{Cl^-}]$. Values of Q_1 extrapolated to 25.0° are 0.105, 0.072, 0.094, and 0.32 M^{-1} at $\mu = 0.19$, 0.96, 0.98, and 4.0 M, respectively. We proceeded to evaluate Q_1 at $\mu = 2.50$ M and 25.0°. A total of 21 solutions were studied, 13 of which started with $\mathrm{Cr^{3+}}$ (0.04–0.1 M), $\mathrm{Cl^-}$ (0.05–0.5 M), and the remaining 8 with $\mathrm{CrCl^{2+}}$ (0.1–0.2 M). The latter series also contained added $\mathrm{Cl^-}$ (0.05–0.5 M). The average equilibrium quotient is $Q_1 = 0.058 \pm 0.003$ M^{-1}.

Interpretation and Discussion

Mechanism of the Reaction of $\mathrm{V^{3+}}$ and $\mathrm{Cr^{2+}}$ in Perchlorate Solution. The reaction of $\mathrm{V^{3+}}$ and $\mathrm{Cr^{2+}}$ has been the subject of an earlier study[3] and the object of some discussion in the literature.[20-23] The rate law was originally interpreted[3] in terms of a sequence of consecutive reactions (eq 14 and 15), mechanism A, in which the empirical parameters are $q = k_1k_3/k_2$ and $r = k_3/k_2$. Mechanism B, suggested by Haim,[22] is equally consistent with the observed kinetics; in terms of mechanism B, the values of q and r are $q = k'_1Q_a$ and $r = k'_2/k'_3$.

Mechanism A

$$\mathrm{V^{3+} + Cr^{2+}} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{V(OH)Cr^{4+} + H^+} \tag{14}$$

$$\mathrm{V(OH)Cr^{4+}} \xrightarrow{3} \mathrm{V^{2+} + CrOH^{2+}} \tag{15}$$

$$\mathrm{CrOH^{2+}} \xrightarrow{\mathrm{H^+}} \mathrm{Cr^{3+}}\ \text{(rapid)}$$

Mechanism B

$$\mathrm{V^{3+} + H_2O} \rightleftharpoons \mathrm{VOH^{2+} + H^+}\quad (\text{rapid } Q_a) \tag{16}$$

$$\mathrm{VOH^{2+} + Cr^{2+}} \underset{2'}{\overset{1'}{\rightleftharpoons}} \mathrm{V(OH)Cr^{4+}} \tag{17}$$

$$\mathrm{V(OH)Cr^{4+} + H^+} \xrightarrow{3'} \mathrm{V^{2+} + Cr^{3+} + H_2O} \tag{18}$$

No rigorous method will serve to distinguish these alternatives, but the following indirect argument can be advanced in favor of mechanism B. The reaction involves the intermediate $\mathrm{VOHCr^{4+}}$; provided one accepts that its most probable structure is a $\mathrm{OH^-}$-bridged species, then the mechanism incorporates an inner-sphere transition state. The point in question is whether the intermediate forms from the aquo ions (mechanism A), or from $\mathrm{VOH^{2+}}$ and $\mathrm{Cr^{2+}}$ (mechanism B). The pattern of reactivity established by $\mathrm{Cr^{2+}}$ in its inner-sphere reactions with Co(III), Cu(II), Cr(III), and Fe(III) complexes[24-26] is that hydroxide ion is a favored bridging ligand, as evidenced by the major rate terms which are proportional to $1/[\mathrm{H^+}]$. By way of contrast, the aquo reaction generally dominates for $\mathrm{V^{2+}}$ reactions,[26-28] with but a minor contribution, if any, from the hydroxo reaction. (The latter pattern of reactivity parallels that of outer-sphere reactions; $\mathrm{Cr(bipy)_3{}^{2+}}$ reductions, for example.) Accepting on a provisional basis that the pattern of reactivity toward aquo and hydroxo complexes constitutes evidence concerning mechanism, B is thus the preferred pathway. Conclusions based largely on analogy must be regarded as provisional, however.

Reactions in Chloride Solution. Consider in detail the first step (eq 2) of the mechanism outlined previously. Does the detailed mechanism of the reaction of $\mathrm{V^{2+}}$ and $\mathrm{CrCl^{2+}}$ involve an inner-sphere transition state? The chlorovanadium(III) substitution equilibrium is established rapidly, and hence the question cannot be answered by experiments on the product distribution. Whatever the mechanism of the $\mathrm{V^{2+} + CrCl^{2+}}$ reaction, its reverse, $\mathrm{V^{3+} + Cr^{2+} + Cl^-}$, must proceed by an identical transition state.

The mechanisms to be considered are (1) an inner-sphere reaction of $\mathrm{VCl^{2+}}$ and $\mathrm{Cr^{2+}}$, and (2) oxidation of $\mathrm{CrCl^+}$ by $\mathrm{V^{3+}}$. Processes which lead to the same result as the latter (*e.g.*, reduction of an ion pair $\mathrm{V(H_2O)_6{}^{3+}\cdot Cl^-}$ by $\mathrm{Cr^{2+}}$) are indistinguishable and will not be considered as separate mechanisms in the present context. A small concentration of $\mathrm{VCl^{2+}}$ is in rapid equilibrium with $\mathrm{V^{3+}}$ and $\mathrm{Cl^-}$; this does not necessarily implicate $\mathrm{VCl^{2+}}$ as a reactant. Moreover, since the Cr(III) product is $\mathrm{CrCl^{2+}}$, if $\mathrm{VCl^{2+}}$ is a reactant, as in mechanism 1, an inner-sphere mechanism is demanded.

Precedents for both of the mechanisms under consideration are available. Mechanism 1 operates in the reaction of $\mathrm{FeCl^{2+}}$ and $\mathrm{Cr^{2+}}$,[24] and in the chromium(II)–(III) exchange reaction of $\mathrm{CrCl^{2+}}$ and $\mathrm{Cr^{2+}}$.[25,29] Each of these processes is accompanied by a parallel pathway involving $\mathrm{M^{3+} + Cr^{2+} + Cl^-}$, which amounts to mechanism 2. The ability to establish firmly the existence of parallel pathways in those instances, and not in the present case, arises because the Fe(III) and Cr(III) substitution rates are low relative to the rates of oxidation–reduction. The clear-cut distinction is not possible in the present reaction since substitution on V(III) occurs more rapidly than its reduction. The present situation is related to the electron exchange reaction,[30] the rate equation for which has the form $k[\mathrm{Fe^{2+}}][\mathrm{Fe^{3+}}][\mathrm{Cl^-}]$, where a duality of interpretation is also possible. Indirect arguments can be advanced concerning the mechanism, based on comparisons with known cases, as follows.

Actually, the reaction under consideration proceeds along two parallel paths, as shown by the form of the rate expressions for the reaction occurring in the forward and reverse directions, $k_1 = e + f/[\mathrm{H^+}]$ and $k_2 = g + h/[\mathrm{H^+}]$. The detailed configuration of each transition state is a separate question. Consider first the transition state with the composition $(\mathrm{VCrClOH^{3+}})^{\ddagger}$. We infer, first, that $\mathrm{Cl^-}$ is in the primary coordination sphere of chromium in the transition state since the species $\mathrm{CrCl^{2+}}$ is involved. We further conclude that

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[19] C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967).

[20] A. G. Sykes, *Chem. Commun.*, 442 (1965).

[21] J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

[22] A. Haim, *ibid.*, **5**, 2081 (1966).

[23] Sykes[20] used the published data[3] to criticize this equation and proposed instead a three-parameter relation $k_3 = (q + b/[\mathrm{H^+}])/(r + [\mathrm{H^+}])$, the additional term $b/[\mathrm{H^+}]$ being attributed to an expected contribution of a reaction path involving $\mathrm{VOH^{2+}}$ and $\mathrm{Cr^{2+}}$. We have already commented[21] upon Sykes' reinterpretation. Haim[22] has very clearly pointed out a type of ambiguity that remains unresolved from a kinetic study of a reaction whose mechanism consists of a single path with consecutive steps: one cannot learn the order in which the steps occur but only the composition of each activated complex.

[24] G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964).

[25] D. E. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[26] J. H. Espenson, K. Shaw, and O. J. Parker, *ibid.*, **89**, 5730 (1967).

[27] P. Dodel and H. Taube, *Z. Physik. Chem.* (Frankfurt), **44**, 92 (1965).

[28] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

[29] M. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954).

[30] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

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 $h = h'Q_a$.

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

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

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

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

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 $k[CrX^{2+}]\cdot[Cr^{2+}]/[H^+]$. 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).