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Kinetics of the Reaction of Vanadium(III) and Chromium(II) Ions in Acid Solution. Evidence for a Binuclear Reaction Intermediate[1]

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Received February 15, 1965

The one-equivalent oxidation–reduction reaction of vanadium(III) and chromium(II) ions forms vanadium(II) and chromium(III) ions; the rate is first-order with respect to each metal ion reactant. The rate has been measured from 0.2 to 35.0° over a range of acid concentrations of 0.027–0.500 F $HClO_4$. The rate equation is $-d[V^{3+}]/dt = q[Cr^{2+}][V^{3+}]/(r + [H^+])$, with $q = 0.624$ sec.$^{-1}$ and $r = 0.108$ M at 25.0°. This rate law suggests the mechanism of the reaction involves an intermediate $V(OH)_nCr^{5-n}$ present at a low steady-state concentration, which decomposes to reactant ions or to product ions at a relative rate proportional to $[H^+]$. The structure of the proposed intermediate is discussed from the standpoint of the thermodynamic properties of activation for the two transition states and in terms of the rate at which the intermediate decomposes to products. On the basis of these observations, the hypothesis is made that the intermediate has an inner-sphere structure.

Introduction

This paper reports on a kinetic study of the reaction of vanadium(III) and chromium(II) ions in aqueous acid perchlorate solutions

$$V^{3+} + Cr^{2+} = V^{2+} + Cr^{3+} \qquad (1)$$

Reactions involving chromium(II) ion as a reducing agent for metal ion complexes, including hydrated ions, have received extensive study,[2] although no previous work has been reported on reactions with vanadium ion as oxidizing agent. The question of whether a given oxidation–reduction reaction proceeds *via* an inner- or an outer-sphere transition state has received much attention in reactions of chromium(II) ion and other dipositive metal ions.[3] The present study indicates that this reaction proceeds through a binuclear reaction intermediate which probably has an inner-sphere arrangement.

Experimental

Reagents.—The preparation and purification of chromium(III) perchlorate, the electrolytic preparation of chromium(II) solutions, and the analyses for chromium(II), total chromium, and perchloric acid have been described.[4]

Vanadium(IV) perchlorate solutions were prepared by reaction of equivalent amounts of vanadyl sulfate and barium perchlorate solutions. Vanadium(IV) stock solutions were analyzed by three independent methods: (a) titration with cyclohexanediaminetetraacetic acid in a pyridine buffer in the presence of zinc(II),[5] (b) titration with iron(II) after prior oxidation to vanadium(V) in sulfuric acid solution by cerium(IV), the excess of which was removed by nitrous acid followed by sulfamic acid,[6] and (c) spectrophotometric determination at 4000 Å. using an absorbancy index of 222 M^{-1} cm.$^{-1}$ for the vanadium(V)–peroxide complex after the same oxidation step as in (b). Results of these analyses always agreed to within 0.7%. Vanadium(II) solutions were prepared by reduction of vanadium(IV) perchlorate solutions containing added perchloric acid using amalgamated zinc. Vanadium(III) perchlorate solutions were prepared by reaction of approximately equivalent concentrations of vanadium(II) and (IV), with the former ion in slight excess. Vanadium(II) and (III) solutions in perchloric acid at room temperature were always used for less than 5 and 36 hr., respectively, to minimize any effects due to slow reduction of perchlorate ion.[7] The vanadium(III) content of these stock solutions was computed as the difference of total vanadium and the excess vanadium(II). The latter quantity was determined by reaction of aliquots of the solution with excess $Co(NH_3)_5Cl^{2+}$ in perchloric acid solution under nitrogen; the cobalt(II) produced was analyzed spectrophotometrically as the thiocyanate ion complex in 50% acetone solution. The perchloric acid concentration of vanadium(II) and (III) solutions was computed as the difference of that added and that assuming the vanadium(IV)–zinc and vanadium(II), (IV) reactions each consumes 2 moles of hydrogen ion per mole of vanadium(IV) reacting. The oxygen-sensitive solutions of vanadium(II) and (III) and chromium(II) were stored under nitrogen in screw-cap bottles capped with self-sealing Buna-N rubber disks; aliquots of solution were removed by hypodermic syringe and needle preflushed with purified nitrogen.

Lithium perchlorate was recrystallized twice before use, and perchloric acid, reagent grade 72%, was used without further purification. Conductivity water, a double redistillation of laboratory distilled water from alkaline permanganate in a tin-lined still, was used in all reagent purifications and solutions and in all the rate studies reported here.

Kinetic Experiments.—The extent of reaction of vanadium(III) and chromium(II) was followed spectrophotometrically. The sensitivity of vanadium(III) and chromium(II) to oxygen required that all kinetic experiments be conducted under air-free conditions. Cylindrical spectrophotometer cells of path length 5 cm. and volume ~15 ml. were used as reaction vessels. The cells containing the appropriate volumes of perchloric acid and lithium perchlorate were closed with a rubber serum cap wired in place; the solution was purged of dissolved oxygen with nitrogen gas previously purified by passage through a chromium(II) wash solution. The purging nitrogen was introduced by a long hypodermic needle puncturing the serum cap through which a venting needle was also inserted. The reactant ions were introduced through the cap by calibrated hypodermic syringe.

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(1) This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 1660.

(2) (a) H. Taube, *Can. J. Chem.*, **37**, 129 (1958); (b) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958); (c) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961); (d) R. T. M. Fraser, *Rev. Pure Appl. Chem.*, **11**, 64 (1962).

(3) (a) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963); (b) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964); (c) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(4) J. H. Espenson, *ibid.*, **3**, 968 (1964).

(5) J. S. Fritz, J. A. Abbink, and M. E. Payne, *Anal. Chem.*, **33**, 1381 (1961).

(6) H. R. Grady in Part II, Vol. III of "Treatise of Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 227.

(7) W. R. King, Jr., and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

The observed rates were independent of the order of addition of vanadium(III) and chromium(II). The variations of reactant concentrations, hydrogen ion concentration, and temperature were carried out in random order in an effort to minimize any systematic errors. Each hydrogen ion–temperature pair corresponds to at least one new preparation of the reactant ions, required by the inability to store vanadium(II) and (III) perchlorate solutions without reduction of perchlorate ions.

The spectrophotometric measurements were made with a Cary Model 14 recording spectrophotometer. Details of the method of rate measurements and of the thermostating arrangement, in which the cell is immersed in a small water bath in the cell compartment of the spectrophotometer, have been published.[8]

Kinetic Data.—Reaction 1 follows the mixed second-order rate equation

$$-\mathrm{d}[\mathrm{V}^{3+}]/\mathrm{d}t = k[\mathrm{V}^{3+}][\mathrm{Cr}^{2+}] \qquad (2)$$

An apparent second-order rate constant was evaluated in each rate run from the absorbance and time data, which generally were taken to at least 85% reaction. This computation was performed by a nonlinear least-squares program[9] for the IBM 7074 computer to minimize the sum of the squares of the differences of observed and calculated absorbance readings. For comparison with these calculations, rate constants for several kinetic experiments were also computed graphically.[10] No significant differences in the rate constants were noted.

Stoichiometry.—The oxidation potentials in perchloric acid solutions[11] are such that reaction 1 should occur essentially quantitatively. The calculated equilibrium quotient is $\sim 10^3$, and under the most extreme set of concentration conditions studied here, the reverse reaction can occur to <0.2%. Spectral examination in the wave length region 3000–6000 Å. of solutions which had come to equilibrium substantiates this conclusion; equilibrium absorbance readings establish quantitatively that reaction 1 occurs essentially to completion as written. In addition, absorbance readings over these same wave lengths taken during the course of different rate runs indicate no light absorption not accountable for by these reactants and products.

Vanadium(III) and Chromium(II) Dependences.—The second-order rate law, eq. 2, was verified by agreement to such calculations in each rate run and by the constancy of k in runs with varying concentrations. The calculated absorbance values agree with experiment generally to within 0.001 absorbance unit and show no systematic deviations. Concentrations of vanadium(III) and chromium(II) ions were varied at every acid concentration and temperature studied; the most extensive variations, including concentrations of the reaction products, vanadium(II) and chromium(III) ions, were carried out at 25.0° and 0.500 F $\mathrm{HClO_4}$. Table I summarizes results of these experiments. In these kinetic experiments the variation of reactant concentrations causes some variations both in ionic strength and in perchlorate ion concentration. The data in Table I establish the form of the rate equation and also indicate that the reaction is rather insensitive to small changes in medium at the relatively high ionic strength employed in this work. These data exhibit a slight dependence of specific rate upon the ratio $[\mathrm{Cr}^{2+}]/[\mathrm{V}^{3+}]$. This trend barely lies beyond the experimental uncertainties in k and may result, at least in part, from the small variations in ionic strength cited in Table I.

TABLE I

APPARENT SECOND-ORDER RATE CONSTANTS AT VARIOUS CONCENTRATIONS[a]

Conditions: 25.0°, 0.50 F $\mathrm{HClO_4}$, at 5740 Å.

Initial concentrations, M[b]		Obsd. k,
$[\mathrm{V}^{3+}]$	$[\mathrm{Cr}^{2+}]$	M^{-1} sec.$^{-1}$
0.00520	0.0414	0.990
0.00521	0.0204	0.991
0.00556	0.0228	0.964[c]
0.0101	0.0411	1.039
0.0101	0.0206	0.991
0.0101	0.0203	1.052
0.0102	0.0211	1.027[d]
0.0106	0.0211	0.979
0.0105	0.0212	0.971[e]
0.0210	0.0371	0.955[f]
0.0202	0.0103	1.097
0.0204	0.0103	1.102
0.0210	0.0107	1.125
0.0409	0.0104	1.108
0.0206	0.00527	1.090
0.0412	0.00527	1.122

[a] The runs with no added products represent a range of ionic strengths of 0.60–0.81 M and a $[\mathrm{ClO_4}^-]$ range of 0.56–0.74 M, with most experiments near 0.65 M ionic strength and 0.62 M $\mathrm{ClO_4}^-$. ($I = 0.500 + 3[\mathrm{Cr(II)}] + 7.5[\mathrm{V(III)}]$ and $[\mathrm{ClO_4}^-] = 0.500 + 2[\mathrm{Cr(II)}] + 4[\mathrm{V(III)}]$; V(III) solutions contain equivalent concentrations of Zn^{2+}.) [b] A few additional runs under the same conditions gave greatly different results which may be due to substantial air oxidation of Cr^{2+} and/or V^{3+}. These spurious runs are typical of those above—they do not represent concentration extremes. [c] 0.00508 M Cr^{3+}. [d] 0.00957 M Cr^{3+}. [e] 0.0105 M V^{2+}. [f] 0.0107 M V^{2+}.

Although kinetic data result most accurately from experiments with absorbance readings taken at 5740 Å., where the absorbancy index difference of reactants and products is known most precisely (it is a slight function of hydrogen ion concentration and temperature at 5740 Å.), rate runs were also carried out at other wave lengths to learn of the possible presence of extraneous light absorption (due to a reaction intermediate, for example). Table II summarizes results of two series of such kinetic experiments. The demonstrated lack of dependence upon wave length of the apparent rate constant indicates the absence of complexities such as an intermediate which attains high concentration, or appreciable optical interaction of the several metal ions; it also demonstrates the adequacy of the mixed second-order rate equation.

TABLE II

APPARENT SECOND-ORDER RATE CONSTANTS (M^{-1} SEC.$^{-1}$) EVALUATED IN KINETIC EXPERIMENTS AT VARIOUS WAVE LENGTHS

Conditions: 0.115 F $\mathrm{HClO_4}$, 0.385 F $\mathrm{LiClO_4}$, 0.021 M Cr^{2+}, 0.011 M V^{3+} at time zero

Wave length, Å.	0.2°	25.0°
5740	0.344	2.65
5400	0.37	2.4
4600	*a*	*a*
4000	0.364	2.2
3000	...	2.56

[a] The absorbance change in a 5-cm. cell at 4600 Å. amounts to only ~0.08; these data cannot yield an accurate value of k, but they are not inconsistent with the rate constants found at the other wave lengths.

Hydrogen Ion and Temperature Dependences.—An extensive series of experiments was performed in which lithium perchlorate replaced perchloric acid ($C_{\mathrm{LiClO_4}} + C_{\mathrm{HClO_4}} = 0.500$) to a minimum of 0.027 F $\mathrm{HClO_4}$. The rate increases on substitution of Li^+ for H^+, although the effect generally becomes much less pro-

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

(9) Computer programs were generously supplied by Drs. R. H. Moore and T. W. Newton; these are based on the report from Los Alamos Scientific Laboratory, LA 2367 + addenda. These programs were adapted for use on the IBM 7074 computer by Mr. J. P. Birk.

(10) The second-order rate constant was evaluated as $(2.303/C_\infty) \times$ slope of $\log (A_\infty + \Delta abC_{\mathrm{min}})/(A_\infty - A)$ *vs.* time; $C_\infty = |[\mathrm{V(III)}_0] - [\mathrm{Cr(II)}]_0|$; C_{min} = lower of the two initial concentrations; Δa = absorbancy index difference, products − reactants; b = optical path length.

(11) (a) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952; (b) E. H. Swift, "A System of Chemical Analysis," Freeman and Co., San Francisco, Calif., 1939, p. 541.

TABLE III

APPARENT SECOND-ORDER RATE CONSTANTS (M^{-1} SEC.$^{-1}$) AT VARIOUS $HClO_4$ CONCENTRATIONS AND TEMPERATURES[a]

Conditions: $HClO_4 + LiClO_4 = 0.50$ F[b]; $[Cr^{2+}]$ and $[V^{3+}]$ each varied 0.005–0.04 M.

$HClO_4$,[c] F	15.0° Obsd.[d] (no. of expts.)	15.0° Calcd.[e]	25.0° Obsd. (no. of expts.)	25.0° Calcd.	35.0° Obsd. (no. of expts.)	35.0° Calcd.
0.027			5.00 ± 0.21 (2)	4.650		
0.040			4.32 ± 0.24 (3)	4.218		
0.115			2.66 ± 0.13 (5)	2.786		
0.155	1.061 ± 0.035 (5)	1.109	2.29 ± 0.09 (8)	2.360	4.12 ± 0.05 (3)	4.209
0.192			2.03 ± 0.02 (2)	2.068		
0.250	0.750 ± 0.020 (3)	0.7571	1.78 ± 0.04 (6)	1.732	3.19 ± 0.04 (3)	3.358
0.269			1.63 ± 0.01 (2)	1.695		
0.365			1.25 ± 0.01 (2)	1.310		
0.500	0.408 ± 0.009 (6)	0.4126	1.040 ± 0.051 (16)	1.019	2.23 ± 0.08 (5)	2.192

[a] An additional result not tabulated above: at 0.2° and 0.115 F $HClO_4$, $k = 0.351 \pm 0.010$ (three experiments), calcd., 0.347. [b] See note a to Table I. [c] Estimated uncertainty in perchloric acid concentration is 0.005 F. [d] The tabulated uncertainty represents the average deviation in the observed rate constant in the number of rate runs cited. [e] From the parameters q and r (eq. 3) with the activation parameters as listed in Table IV.

TABLE IV

SUMMARY OF HYDROGEN ION AND TEMPERATURE DEPENDENCES

Empirical rate parameter[a]	ΔH^*, kcal. mole^{-1}	ΔS^*, cal. mole^{-1} deg.$^{-1}$	Value at 25.0°
	Part A: Fit[b] to $k = q/(r + [H^+])$		
q (k_1k_3/k_{-1})	17.71 ± 0.22	−0.10 ± 0.75	0.624 sec.$^{-1}$
r (k_2/k_{-1})[c]	13.2 ± 1.4	39.7 ± 4.1	0.108 M
k_1 (calcd. q/r)	4.55 ± 1.42	−39.8 ± 4.1	5.76 M^{-1} sec.$^{-1}$
	Part B: Fit[b] to $k = s + t/[H^+]$		
s	15.5 ± 2.5	−6.7 ± 8.3	0.87 M^{-1} sec.$^{-1}$
t	9.3 ± 1.9	−31.2 ± 6.5	0.147 sec.$^{-1}$

[a] With the empirical parameters identified with the rate constants in the postulated reaction sequences, eq. 8 and 9. [b] The uncertainties listed are standard deviations. [c] The quantity r is the ratio of two rate constants, and the "activation parameters" are differences of these quantities for two rate constants according to the expression $r = \exp(\Delta S^*/R)\exp(-\Delta H^*/RT)$. At 15.0°, $r = 0.0504$; at 35.0°, $r = 0.224$.

nounced at lower concentrations of hydrogen ion. Table III tabulates the observed apparent second-order rate constants at each hydrogen ion concentration studied and at various temperatures.

The data at each temperature are consistent with an empirical dependence of apparent rate constant upon $[H^+]$ given by the relation

$$k = q/(r + [H^+]) \qquad (3)$$

The data were treated to yield values for the parameters q and r; this computation was performed using a nonlinear least-squares program to find the values of the thermodynamic quantities of activation for both q and r which best reproduce the experimental k values at all hydrogen ion concentrations and temperatures simultaneously.[9] The 74 individual rate constants, the averages of which are presented in Table III, were weighted by estimates of their precision to minimize the sum of the squares of the per cent deviation of observed and calculated values. This procedure allowed objective estimates to be made of the activation parameters. Table IV presents the results of these computations. These activation parameters recalculate the observed rate constants with an average deviation of 2.5% and a maximum deviation of 7.0% (these calculated values are listed in Table III).

Kinetic data of limited precision taken over a limited range of $[H^+]$ and temperature may fit, within experimental uncertainties, more than one empirical relation. Many oxidation–reduction reactions between metal ions in solution exhibit dependences upon hydrogen ion concentration of the form

$$k = s + t/[H^+] \qquad (4)$$

Although this equation causes d log k/d log $[H^+]$ to decrease with increasing $[H^+]$, whereas eq. 3 causes it to increase, the experimental uncertainties may not allow a definitive distinction to be made. The kinetic data in Table III were fit to eq. 4 using the computer program. As the results given in Table IV substantiate, the fit is quite poor. Observed and calculated rate constants exhibit an average deviation of 17.5% and a maximum deviation of 26.5%; of the 16 entries in Table III for the average k, 10 of the calculated rate constants differ by more than 10%, and only 3 values agree to within 5%. Figure 1 shows the experimental rate constant as a function of $[H^+]$ at 25.0°, the temperature of maximum $[H^+]$ variation. The curves in the figure are those calculated from eq. 3 and 4. The poor fit generated by eq. 4 lies substantially beyond experimental errors and will be discarded for this reason.

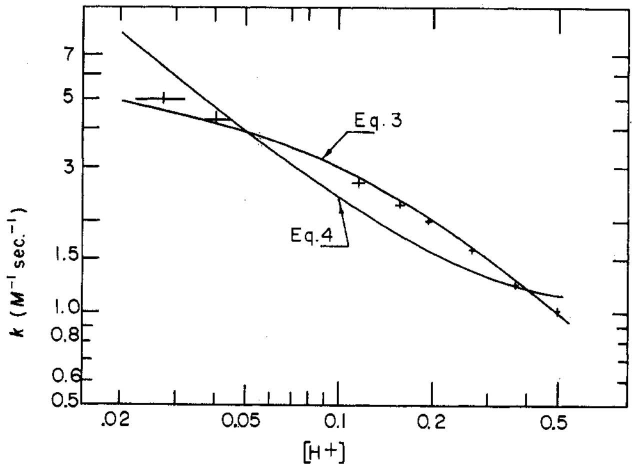

Figure 1.

Interpretation and Discussion

Mechanism.—Kinetic salt effects may prevent unequivocal interpretation of concentration dependences in terms of true rate laws from which inferences concerning reaction mechanism can be drawn. The extent of the disagreement of these kinetic data with eq. 4 appears to lie substantially beyond that reasonably attributable to medium effects arising from replacement of H^+ by Li^+ with other concentrations held constant. Newton and Baker[12] have discussed this situation with regard to hydrogen ion dependences of oxidation–reduction reactions between metal ions in solution. As they point out, only rarely is the rate dependence upon hydrogen ion concentration not a sum of terms, each involving $[H^+]$ raised to a small positive or negative integral power or zero (*i.e.*, eq. 4 in the present instance). The present reaction seems to constitute an exception, since the two-parameter eq. 4 cannot fit satisfactorily the kinetic data.

The acid ionization of one metal ion followed by a reaction of the hydroxo complex with the other metal ion is shown in the sequence

$$V^{3+} = VOH^{2+} + H^+ \text{ (rapid, } Q_a) \qquad (5)$$

$$VOH^{2+} + Cr^{2+} \longrightarrow (e.g., V^{2+} + CrOH^{2+}) \text{ (rate-determining, } k_h) \qquad (6)$$
$$(CrOH^{2+} + H^+ = Cr^{3+} + H_2O) \quad \text{(rapid)}$$

The rate equation derived from this mechanism is

$$-d[V(III)]/dt = k_hQ_a[Cr^{2+}][V(III)]/(Q_a + [H^+]) \qquad (7)$$

in which [V(III)] is the instantaneous formal concentration of vanadium(III). This equation resembles eq. 3 if [V(III)] is replaced by $[V^{3+}]$, which is a good approximation at all but the lower hydrogen ion concentration, at which up to ~7% of the vanadium(III) exists as VOH^{2+}. The value of the empirical r, identified as Q_A in the reaction sequence under consideration, has the value 0.108 M at 25.0°, whereas the accepted value for Q_A is 0.002 M; this mechanism does not satisfactorily account for these results, because of this disagreement. (The high concentrations of VOH^{2+} which would result were the acid ionization constant of vanadium(III) equal to 0.1 M were not present, as shown spectrophotometrically.)

A mechanism[13] is proposed here involving an unstable reaction intermediate with the property that its conversion back to reactant ions and its reaction to products, or species rapidly converted to products, differ in the number of hydrogen ions required. The mechanism

$$V^{3+} + Cr^{2+} + nH_2O \underset{-1}{\overset{1}{\rightleftarrows}} V(OH)_nCr^{5-n} + nH^+ \qquad (8)$$

$$V(OH)_nCr^{5-n} + (n - 1)H^+ \xrightarrow{2} (e.g., V^{2+} + CrOH^{2+}) \qquad (9)$$
$$(CrOH^{2+} + H^+ = Cr^{3+} + H_2O, \text{ rapid})$$

with the usual steady-state approximation for the intermediate $V(OH)_nCr^{5-n}$ leads to the relation

$$k = [Cr^{2+}]^{-1}[V^{3+}]^{-1}(-d[V^{3+}]/dt) = (k_1k_2/k_{-1})/((k_2/k_{-1}) + [H^+]) \qquad (10)$$

Comparison of this equation to the empirical relation, eq. 3, allows identification of the empirical q as k_1k_2/k_{-1} and r as k_2/k_{-1}.

The postulated intermediate written in the simple form $VOCr^{3+}$ (*i.e.*, $n = 2$) is not unlike similar ions of established existence. The kinetically inert species $CrOCr^{4+}$ [14] and $NpO_2 \cdot Cr^{4+}$ [15] have been isolated and analyzed; $UO_2 \cdot Cr^{4+}$ [16] and VOV^{4+} [17] have been identified spectrally, and their rates of decomposition studied; $UO \cdot PuO_2^{4+}$ [18] and $PuO_2 \cdot Fe^{4+}$ [12] are intermediates present at steady-state concentrations for which there exists kinetic evidence based upon hydrogen ion dependences as in the present study.

Net Activation Processes.—Effective use has been made of the concept[12,19] of the net activation process—the net reactions for formation of each transition state from the dominant forms of the reactant ions. Expressed in these terms the two relevant processes in the present study are

$$V^{3+} + Cr^{2+} = [VCr^{5+}]^*; \quad \text{effective } k \text{ is } k_1 \qquad (11)$$

$$V^{3+} + Cr^{2+} + H_2O = [VOHCr^{4+}]^* + H^+; \quad \text{effective } k \text{ is } k_1k_2/k_{-1} \qquad (12)$$

If the ionic entropies of V^{3+} and Cr^{2+} are assumed to be −65 and −23 e.u., respectively, the calculated values of S^*, the entropies of the transition states, are −128 for $[VCr^{5+}]^*$ and −88 for $[VOHCr^{4+}]^*$. Combination of the two activation processes yields data on the hypothetical "acid dissociation" of the activated complex

$$[VCr^{5+}]^* = [VOHCr^{4+}]^* + H^+ \qquad (13)$$

For this hypothetical reaction, the following thermodynamic data are calculated from the activation parameters in Table IV: $\Delta H = +13.2 \pm 1.6$ kcal. mole^{-1}, $\Delta S = +39.7 \pm 4.9$ e.u., and $\Delta G = +1.4$ kcal. mole^{-1} at 25°. In his correlation of such thermodynamic properties, Newton[20] has noted that several hypothetical "acid dissociation" reactions of activated complexes have positive ΔH and ΔS values, similar to those found in the acid dissociation of aquo metal ions. One such instance noted by Newton is the pair of inner-sphere activated complexes $Cr(H_2O)Co(NH_3)_5^{3+}$ and $Cr(OH)Co(NH_3)_5^{2+}$, suggesting that processes such as eq. 13 involve the same sort of relatively minor structural changes as does the acid dissociation of an aquo metal ion.

Inner- and Outer-Sphere Transition States.—Dulz and Sutin[21] have predicted the rate of the vanadium(III)–chromium(II) oxidation–reduction reaction on the assumption that electron transfer proceeds *via* an outer-sphere mechanism. This calculation, based on the theories of Marcus,[22] uses the rates of the individual metal(II)–(III) exchange rates and the equilibrium

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[12] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

[13] The author is very grateful to Dr. T. W. Newton for the suggestion of his reaction mechanism.

[14] (a) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959); (b) R. E. Connick and Sr. M. G. Thompson, 148th National Meeting of the American Chemical Society, Sept. 1964, Inorganic Division, papers 23, 24.

[15] J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

[16] T. W. Newton and F. B. Baker, *ibid.*, **1**, 368 (1962).

[17] T. W. Newton and F. B. Baker, *ibid.*, **3**, 569 (1964).

[18] T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

[19] T. W. Newton and S. W. Rabideau, *ibid.*, **63**, 365 (1959).

[20] T. W. Newton, personal communication.

[21] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[22] R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

constant for the net reaction; it predicts a specific rate at 25° of 10^{-2} M^{-1} sec.$^{-1}$. Although the observed rate is ~60 times higher, this may be due to the present suggested mechanism for electron transfer, which is entirely different from the outer-sphere process assumed in the theory. The present study does not provide a check on any of the premises of the Marcus theory. Since the outer-sphere path has a predicted rate lower than that observed, it also does not refute the theory in any way.

Acknowledgment.—The author wishes to acknowledge the helpful suggestions of Dr. T. W. Newton and Prof. E. L. King during the course of these studies.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics of the Reduction of Halopentaamminecobalt(III) Complexes by Iron(II) and Vanadium(II)

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Received December 28, 1964

The rates at which the complex ions $(NH_3)_5CoF^{2+}$, $(NH_3)_5CoCl^{2+}$, and $(NH_3)_5CoBr^{2+}$ react with Fe^{2+} are strictly first order in each of the reactants. At 25.5° and $\mu = 1.7$, the corresponding specific rates k_0 are 76×10^{-4}, 16×10^{-4}, and 9.2×10^{-4} M^{-1} sec.$^{-1}$. The respective values of ΔH^* are 13.4, 14.5, and 15.6 kcal. mole^{-1} and of ΔS^* are -23, -23, and -20 e.u. The reactions are accelerated by free halide in solution and this acceleration can be expressed by the rate term $k_1(Fe^{2+})\cdot(\text{complex}^{2+})(X^-)$. With $(NH_3)_5CoF^{2+}$ as reactant $k_1 = 3.5 \pm 1 \times 10^{-3}$, $2.1 \pm 0.2 \times 10^{-2}$, and 13 ± 2 M^{-2} sec.$^{-1}$ for $X^- = Br^-$, Cl^-, and F^-, respectively; with $(NH_3)_5CoBr^{2+}$, $k_1 \leq 1 \times 10^{-3}$ M^{-2} sec.$^{-2}$ for $X^- = Cl^-$ and 4 ± 1 M^{-2} sec.$^{-1}$ for $X^- = F^-$ (temperature $25.8 \pm 0.2°$, $\mu = 1.7$ except for $X^- = F^-$; here the temperature was $25.1 \pm 0.1°$, $\mu = 2.0$).

This paper presents the results of kinetic studies on the reduction of complexes of the type $[(NH_3)_5CoX]^{2+}$, where X = F, Cl, or Br, by Fe^{2+}(aq) and V^{2+}(aq). The investigation was started originally as part of a somewhat wider program, aimed especially at getting more information on the nature of the activated complex in such electron-transfer reactions by indirect means based on rate comparisons.[1] The investigation was discontinued, however, after the manuscript of a paper now published by Candlin, Halpern, and Trimm[2a] became available dealing with much the same subject and in closely related systems. Our results, however, do seem worth reporting because they are new[2b] and do contribute to the knowledge in this field.

Experimental

Materials.—The Co(III) complexes were used in the form of their perchlorates, $[(NH_3)_5CoCl](ClO_4)_2$ and $[(NH_3)_5CoBr](ClO_4)_2$, which were prepared according to published procedures.[3]

Fluoropentaamminecobalt(III) perchlorate was precipitated from a solution of $[(NH_3)_5CoF](NO_3)_2$, which had been prepared according to a description by Basolo and Murmann.[4] A concentrated solution of sodium perchlorate was used for the precipitation (perchloric acid in high concentration catalyzes the aquation of the complex). The purity of the complex compounds was checked spectrophotometrically. Ferrous perchlorate was obtained from the G. F. Smith Chemical Co. and purified by recrystallization from $HClO_4$. A stock solution of the compound was kept in the dark under nitrogen and standardized from time to time by titration with cerium(IV) sulfate using ferroin as indicator. A solution of V^{2+} was prepared by reduction of a suspension of V_2O_5 (Baker Analyzed Reagent) in $HClO_4$ solution with amalgamated zinc. The V^{2+} solution was standardized spectrophotometrically, using its reduction capacity on a $[(NH_3)_5CoCl]^{2+}$ solution of defined concentration. Sodium perchlorate, which was used to adjust the ionic strength, was prepared from sodium carbonate and perchloric acid.

Chemicals other than the ones mentioned are of the best quality commercially available and were used without further purification.

The reagent solutions were prepared with twice-distilled water.

Procedure.—Great care was exercised to exclude air from the deoxygenated reactant solutions during the mixing procedure and the reaction.

The oxidation–reduction reaction was followed spectrophotometrically, using the absorption maximum of the Co(III) complexes in the visible range for observation. The measurements were carried out with a Cary Model 14 spectrophotometer, the cell compartment of which was thermostated to an accuracy of ±0.1–0.2°. In general a cell of 5-cm. path length was used for the studies. The reductions by Fe^{2+} are slow enough so that large concentrations of this reagent can be used. The reactions were run with (Fe^{2+}) in the range 0.15 to 0.6 M and (Co(III)) about 3×10^{-3} M, thus providing pseudo-first-order kinetic conditions.

Results and Discussion

Reduction by V^{2+}.—The reactions between V^{2+} and the Co(III) complexes were found to be first order in both reactants. The rate law can then be represented as

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[1] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

[2] (a) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964). (b) This is strictly true only of the experiments on the halide-assisted reaction. Concurrently with this work, Dr. J. Espenson of Iowa State University measured the rates of reaction of Fe^{+2} with halopentaamminecobalt(III) complexes. His rates at $\mu = 1.00$ and 25° are about 15% smaller than ours at $\mu = 1.7$. See *Inorg. Chem.*, **4**, 121 (1965).

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

[4] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 172 (1953).