

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK, STONY BROOK, NEW YORK 11790**Kinetics and Mechanism of the Reductions of Oxalatotetraamminecobalt(III) by Iron(II), Vanadium(II), and Chromium(II)^{1a}**BY CORDELIA HWANG^{1b} AND ALBERT HAIM

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The reduction of oxalatotetraamminecobalt(III) by iron(II), vanadium(II), or chromium(II) obeys the rate law $-\ln [\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}] = k[\text{M}^{2+}]$, where $\text{M}^{2+} = \text{Fe}^{2+}$, V^{2+} , or Cr^{2+} . At $[\text{ClO}_4^-] = 1.0 M$ and 25° , $k = (4.12 \pm 0.10) \times 10^{-4}$, 45.5 ± 1.5 , and $(2 \pm 1) \times 10^5 M^{-1} \text{sec}^{-1}$ for iron, vanadium, and chromium, respectively. For the iron(II) reduction, $\Delta H^\ddagger = 18.5 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -12.1 \pm 0.6 \text{ eu}$. For the vanadium(II) reduction, $\Delta H^\ddagger = 12.3 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -9.8 \pm 1.6 \text{ eu}$. Various mechanistic details of these and related reactions are discussed.

Introduction

Only in a few cases has it been possible to distinguish between an inner-sphere and an outer-sphere mechanism for reduction by iron(II).^{2,3} One example where the mechanism has been established by identifying the primary iron(III) product relates to the $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ - Fe^{2+} system.³ The "product criterion" of mechanism applied to this rather labile system consisted of detecting the formation and decay of the FeC_2O_4^+ intermediate, the primary iron(III) product of the inner-sphere electron transfer. The criterion is easily applicable to this system because of the slow rate of dissociation of FeC_2O_4^+ .⁴

The present study of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - Fe^{2+} reaction, in the context of our previous work on the iron(II) reductions of tetraamminecobalt(III) complexes,⁵ was started with the hope of finding still another system where the mechanism could be established by identifying the primary iron(III) product. It will be seen below that, because of the slow rate of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - Fe^{2+} reaction, our expectation was not fulfilled. Nevertheless, in view of the interest in systems that feature chelation either by the reductant⁶⁻⁸ or by the oxidant,⁹ some useful comparisons with the results obtained in the $\text{Co}(\text{NH}_3)_3\text{C}_2\text{O}_4\text{H}^{2+}$ - Fe^{2+} system¹⁰ have been made. Moreover, it was of interest to compare the results obtained for the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - Fe^{2+} reaction with those reported⁹ for the related reactions of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ with Cr^{2+} and V^{2+} . For the former reaction, it has been shown that there is quantitative transfer of oxalate from cobalt to chromium, but the reaction was too fast for measurements by conventional techniques.⁹ By using fast-flow techniques, we have been able to obtain an estimate of

the rate constant of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - Cr^{2+} reaction. For the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - V^{2+} reaction, the rate law reported⁹ is $k_0 + k_1[\text{H}^+]$, where $k_0 = 43 M^{-1} \text{sec}^{-1}$ and $k_1 = 22 \text{sec}^{-1}$ at 25° and ionic strength 1.0 M . The background electrolyte consisted of NaClO_4 - HClO_4 mixtures, and in view of the possibility that the k_1 term may be associated with changes in activity coefficients as NaClO_4 is replaced by HClO_4 ,⁶ we have reinvestigated the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^{+}$ - V^{2+} reaction in a LiClO_4 - HClO_4 medium.

Experimental Section

Materials.—Iron(II) perchlorate solutions were prepared by electrolytic reduction of solutions made up by dissolution of recrystallized iron(III) perchlorate in perchloric acid of the desired concentration. When all the iron(III) had been reduced (negative test with thiocyanate), the solution was transferred to a storage bottle and deaerated with purified argon. Vanadium(II) perchlorate solutions were prepared by reduction of solutions of vanadium(V) oxide in perchloric acid with amalgamated zinc under an atmosphere of argon. Since vanadium(II) reduces perchlorate ion, the solutions were used within 8 hr after addition of the zinc. Chromium(II) perchlorate and lithium perchlorate solutions were prepared as described previously.¹¹ Triply distilled water was used to prepare all solutions. The argon was purified by passing it over a BTS catalyst (BASF Colors and Chemicals, Inc.). All other chemicals were reagent grade.

Oxalatotetraamminecobalt(III) sulfate was prepared and recrystallized as described by Schlessinger.¹² Treatment of a solution of the sulfate with a saturated solution of sodium perchlorate yielded the sparingly soluble $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4$. *Anal.* Calcd for $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4$: C, 7.63; H, 3.84; N, 17.82; Co, 18.74. Found: C, 7.76; H, 3.86; N, 17.43; Co, 18.46.

Analytical Methods.—The iron(II) and hydrogen ion concentrations of the stock iron(II) perchlorate solutions were determined as described previously.⁵ Vanadium(II) concentrations were determined by titration with a standard iron(III) perchlorate solution in the presence of sodium thiocyanate under an argon atmosphere.¹³ The acid concentration of the vanadium(II) stock solutions was determined as follows. An aliquot of the vanadium(II) solution was added to a slight excess of a deoxygenated iron(III) sulfate solution. The resulting solution was added to a column of Dowex 50W-X8 resin in the lithium form. The ions Fe^{2+} , Fe^{3+} , V^{3+} , and H^+ were absorbed on the resin. The hydrogen ions were eluted with 0.5 M lithium perchlorate and then titrated with standard sodium hydroxide. Cobalt and

(1) (a) This work was supported by Grant GP-6528 from the National Science Foundation. (b) Abstracted in part from the M.S. thesis of Cordelia Hwang (née Jong), State University of New York at Stony Brook, March 1969.

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chromium were analyzed as described before.¹¹ Carbon, hydrogen, and nitrogen analyses were performed by Schwarzkopf Microanalytical Laboratories.

Kinetic Measurements.—The reductions of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ by Fe^{2+} and V^{2+} were studied by conventional spectrophotometric methods. The reduction by iron(II) was studied under pseudo-first-order conditions in the presence of a large excess of reductant. The cobalt complex was first dissolved in triply distilled water, and subsequently the desired amounts of perchloric acid and/or lithium perchlorate were added.¹⁴ The desired volume of iron(II) perchlorate solution was added, and then the solution was made up to volume. The solution was transferred to a 10-cm cylindrical cell, which was then covered with a serum cap fitted with two syringe needles. The cell was placed in a constant-temperature bath at the desired temperature, and the solution was deoxygenated by means of a stream of argon. After 20 min, the cell was placed in the thermostated compartment of a Cary 14 recording spectrophotometer, and the absorbance at 510 nm (an absorption maximum for the cobalt(III) complex) was recorded as a function of time. The pseudo-first-order rate constants k_m for each run were evaluated from the relation $D - D_\infty = (D_0 - D_\infty)e^{-k_m t}$, where D , D_0 , and D_∞ are the absorbances at time t , 0, and ∞ , respectively. The values of D were fitted to the above equation by means of a nonlinear least-squares program,¹⁶ with D and t being the dependent and independent variables, respectively, and D_0 , D_∞ , and k_m were treated as adjustable parameters. Second-order rate constants were calculated from the expression $k_t = k_m/[\text{Fe}^{2+}]$.

The reduction by vanadium(II) was carried out under second-order conditions. The procedure was analogous to that used in the iron(II) measurements, except that the solution was made up directly in the spectrophotometric cell. The second-order rate constants k_t were evaluated graphically by plotting the left-hand side of eq 1 vs. time. A_0 and B_0 are initial concentrations of the reactants, A being the limiting reagent.

$$\ln \left[1 + \frac{(B_0 - A_0)(D_0 - D_\infty)}{A_0(D - D_\infty)} \right] = \ln \frac{B_0}{A_0} + (B_0 - A_0)k_t t \quad (1)$$

The chromium(II) reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ is extremely fast, and, therefore, a cursory examination of this system was carried out using the rapid-flow apparatus.¹⁶ Second-order conditions were used and values of k_t were obtained by fitting the observed optical density to the integrated second-order equation with the nonlinear least-squares program.

Results

The results of the kinetic measurements of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{Fe}^{2+}$ reaction at 25.0, 34.8, and 44.6° are summarized in Table I. Excellent pseudo-first-order kinetics were obeyed over 5 half-lives. The values of the second-order rate constants calculated from the relation $k_t = k_m/[\text{Fe}^{2+}]$ are listed in the last column of Table I. It is seen that k_t is independent of $[\text{Co}(\text{III})]$, $[\text{Fe}^{2+}]$, and $[\text{H}^+]$, and we conclude, therefore, that the reaction obeys the mixed second-order rate law

$$-\frac{d[\text{Co}(\text{III})]}{dt} = k_t[\text{Co}(\text{III})][\text{M}^{2+}] \quad (2)$$

where $\text{M}^{2+} = \text{Fe}^{2+}$. From the temperature dependence of k_t , the following activation parameters are calculated: $\Delta H^\ddagger = 18.5 \pm 0.2$ kcal mol⁻¹ and $\Delta S^\ddagger = -12.1 \pm 0.6$ eu.

(14) We found that the rate of solution of $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{ClO}_4$ in perchlorate solutions is exceedingly slow. Therefore, it was imperative to dissolve the complex in water.

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TABLE I
KINETICS OF THE $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{Fe}^{2+}$ REACTION^a

$10^4[\text{Co}(\text{III})], M$	$[\text{Fe}^{2+}], M$	$[\text{H}^+], M$	Temp, °C	$10^4 k_t, M^{-1} \text{sec}^{-1}$
11.7	0.095	0.500	25	4.22
6.92, 7.22	0.150	0.501	25	4.04, 4.01
12.7	0.190	0.308	25	4.19
5.95	0.190	0.500	25	4.24
12.7	0.190	0.596	25	4.25
12.8	0.190	0.776	25	4.37
6.30, 6.40	0.285	0.495	25	4.16, 4.01
1.80, 11.3	0.285	0.496	25	4.22, 4.04
			25	Av 4.16 ± 0.10
12.6	0.095	0.500	34.8	11.7
13.7	0.150	0.244	34.8	11.0
12.9, 13.5	0.150	0.499	34.8	11.2, 11.2
13.7	0.150	0.756	34.8	11.4
12.7	0.200	0.499	34.8	11.0
13.0	0.275	0.500	34.8	10.9
			34.8	Av 11.2 ± 0.3
18.9	0.095	0.501	44.6	30.0
20.5	0.150	0.243	44.6	29.4
19.8, 20.3	0.150	0.499	44.6	29.6, 29.4
22.4	0.150	0.758	44.6	30.0
18.0	0.200	0.499	44.6	29.7
17.8	0.275	0.502	44.6	28.3
			44.6	Av 29.5 ± 0.7

^a $[\text{ClO}_4^-] = 1.06 M$ maintained with $\text{HClO}_4\text{-LiClO}_4$.

TABLE II
KINETICS OF THE $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{V}^{2+}$ REACTION^a

$10^4[\text{Co}(\text{III})], M$	$10^4[\text{V}^{2+}], M$	$[\text{H}^+], M$	Temp, °C	$k_t, M^{-1} \text{sec}^{-1}$
9.86	7.66	1.09	25.0	46.1 ^b
9.86	7.92	1.09	25.0	45.8 ^{b,c}
14.76	7.73	0.99	25.0	46.5
9.84	7.76	0.497	25.0	45.8
9.84	7.37	0.200	25.0	42.8 ^d
			25.0	Av 45.4 ± 1.4
10.1	7.97	0.995	17.2	25.5
10.1	7.90	0.500	17.2	24.8
10.1	7.95	0.200	17.2	26.2 ^d
10.1	6.09	0.200	17.2	25.8 ^e
			17.2	Av 25.6 ± 0.5
10.1	8.17	0.995	10.5	14.1
10.1	8.17	0.499	10.5	14.1
10.1	8.17	0.203	10.5	13.9 ^d
			10.5	Av 14.0 ± 0.1

^a $[\text{ClO}_4^-] = 1.00 M$ maintained with $\text{HClO}_4\text{-LiClO}_4$. ^b $[\text{ClO}_4^-] = 1.095 M$. ^c With 0.023 M NaCl added. ^d Calculated from initial slopes. ^e With $7.3 \times 10^{-3} M$ $\text{Na}_2\text{C}_2\text{O}_4$ added.

The results of the kinetic measurements of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{V}^{2+}$ reaction are presented in Table II. Some comments must be made regarding the procedure used to calculate the rate constants listed in column 5. At the higher acidities used ($\geq 0.50 M$), plots of the left-hand side of eq 1 vs. time were linear, as required for a mixed second-order rate law given by eq 2 ($\text{M}^{2+} = \text{V}^{2+}$). For the linear plots (see Figure 1), the second-order rate constants were calculated from the slopes using the expression $k_t = \text{slope}/([\text{Co}(\text{III})]_0 - [\text{V}^{2+}]_0)$. For the experiments carried out at $[\text{H}^+] = 0.20 M$, the plots exhibited curvature after about 60% of the vanadium(II) had been oxidized. In these cases (see Figure 2), the rate constants were obtained from the initial slopes. The justification for using this procedure

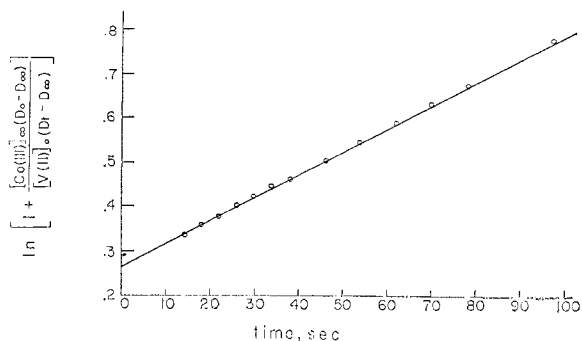


Figure 1.—Second-order plot for the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{V}^{2+}$ reaction at 17.2° . $[\text{Co}(\text{III})]_0 = 1.01 \times 10^{-3} M$, $[\text{V}^{2+}]_0 = 7.97 \times 10^{-4} M$, $[\text{H}^+] = 0.995 M$, and $[\text{ClO}_4^-] = 1.00 M$.

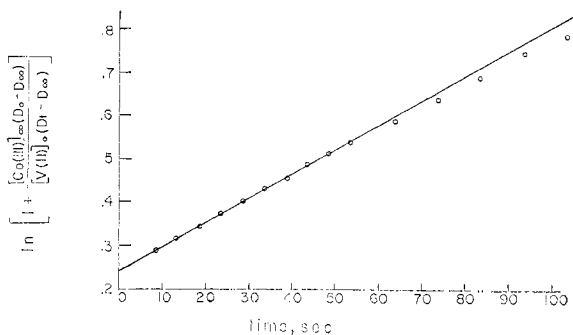
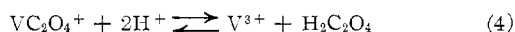


Figure 2.—Second-order plot for the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{V}^{2+}$ reaction at 17.2° . $[\text{Co}(\text{III})]_0 = 1.01 \times 10^{-3} M$, $[\text{V}^{2+}]_0 = 7.95 \times 10^{-4} M$, $[\text{H}^+] = 0.200 M$, and $[\text{ClO}_4^-] = 1.00 M$.

is based on the following considerations. Equation 1 is derived from the standard integrated form of eq 2 and the relation between absorbances and concentrations

$$\frac{D_0 - D_\infty}{D - D_\infty} = \frac{B_0 - B_\infty}{B - B_\infty} \quad (3)$$

Equation 3 is not obeyed exactly in the present system because: (1) the vanadium(III) product consists of an equilibrium mixture of V^{3+} and VC_2O_4^+



(2) the two vanadium (III) species have different molar absorbances at the wavelength of observation, and (3) the ratio $[\text{VC}_2\text{O}_4^+]/[\text{V}^{3+}]$ increases as the reaction proceeds. At high acidities ($\geq 0.5 M$), the equilibrium represented in eq 4 is shifted to the right, and the concentration of VC_2O_4^+ is quite small. Under these circumstances, eq 3 is obeyed, and the plots of eq 1 are linear. At lower acidities ($0.2 M$), the equilibrium given by eq 4 is shifted to the left, and the contribution of the VC_2O_4^+ species becomes significant. Under these circumstances, eq 3 is not obeyed exactly, and therefore curvatures in the plots are observed. Evidence that the deviations from linearity at low acidity were caused by shifts in the equilibrium given by eq 4 was obtained by carrying out runs at low acidity in the presence of added $\text{H}_2\text{C}_2\text{O}_4$. Under these circumstances, the ratio $[\text{VC}_2\text{O}_4^+]/[\text{V}^{3+}]$ remains constant throughout the reaction, eq 1 is obeyed, and the second-order plots are linear. Furthermore, these linear plots yield rate constants in good agreement with those obtained from

initial slope measurements. We conclude, therefore, that the procedure adopted gives an adequate measurement of the rate constants.

It is seen that the second-order rate constants listed in column 5 of Table II are independent of acidity, and we conclude that the vanadium(II) system conforms to the rate law given by eq 2 ($\text{M}^{2+} = \text{V}^{2+}$). Since V^{2+} reduces ClO_4^- to Cl^- , one experiment was carried out in the presence of added Cl^- (second entry in Table II), and it is seen that small concentrations of Cl^- do not affect the reaction rate. From the temperature dependence of k_t , we calculate the activation parameters: $\Delta H^\ddagger = 12.3 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -9.8 \pm 1.6 \text{ eu}$.

A thorough study of the chromium(II) reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ could not be carried out because of the speed of the reaction and the small changes in absorbance upon reaction. The results of several stop-flow runs in the concentration ranges $[\text{Co}(\text{III})] = (3.5-10) \times 10^{-4} M$, $[\text{Cr}^{2+}] = (2.5-5.0) \times 10^{-4} M$, and $[\text{H}^+] = 1.0 M$ yielded a value of $(2 \pm 1) \times 10^5 M^{-1} \text{ sec}^{-1}$ at 25° for the second-order rate constant defined by eq 2 ($\text{M}^{2+} = \text{Cr}^{2+}$). The stoichiometry of the reaction was determined by allowing $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ to react with a slight excess of Cr^{2+} in $0.1 M \text{ HClO}_4$ and then recovering the CrC_2O_4^+ formed by ion-exchange techniques. The ion-exchange behavior and spectrum⁴ of the oxalatochromium(III) complex recovered show clearly that oxalate is acting as a bidentate ligand. The yield of CrC_2O_4^+ was $97.0 \pm 1.6\%$ (average of two experiments), in excellent agreement with the previously reported value of 99% .⁹

Discussion

The rate law for the reduction of oxalatotetraamminecobalt(III) by iron(II) or vanadium(II) conforms closely to eq 2 ($\text{M}^{2+} = \text{Fe}^{2+}$ or V^{2+}). The validity of

$$-\frac{d[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+]}{dt} = k_t[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+][\text{M}^{2+}] \quad (2)$$

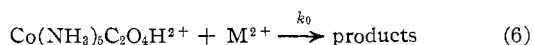
eq 2 could not be established with certainty for the reduction by chromium(II). However, the limited data obtained are consistent with the equation, and we conclude that the three reducing agents react with the cobalt(III) complex according to a simple mixed second-order rate law. It is noteworthy that the second-order rate constants k_t are independent of the hydrogen ion concentration in the range $[\text{H}^+] = 0.200-1.00 M$. Our observations on the vanadium(II) reaction are in disagreement with those reported earlier for the same reaction.⁹ At 23° and $1.00 M$ ionic strength, the observed second-order rate constants k were 43, 51, and $55 M^{-1} \text{ sec}^{-1}$, respectively, and it was concluded that k depended on $[\text{H}^+]$ according to the relation $k = k_0 + k_1[\text{H}^+]$.⁹ Although the magnitudes of the observed second-order rate constants reported previously do not differ substantially from those measured in the present work, a major discrepancy exists between the two sets of data regarding the possible dependence of the rate on acidity. It must be noted, however, that

in the earlier work the ionic strength was maintained with sodium perchlorate-perchloric acid mixtures, whereas lithium perchlorate-perchloric acid mixtures were used in the present work. . . Therefore, the discrepancy can be ascribed, at least in part, to the use of different background electrolytes in the two sets of measurements. However, even after correction for the difference in the ionic media, the disparity appears to remain. Extrapolation of the previously published data to 25° and $[\text{HClO}_4] = 1.00 M$ yields a second-order rate constant of $65 M^{-1} \text{sec}^{-1}$, a value considerably larger than our measured value of 45.3 under the same conditions. We do not have an entirely satisfactory explanation for this disagreement. However, it must be noted that no mention was made in the earlier work of the difficulties caused by the change in the ratio $[\text{VC}_2\text{O}_4^+]/[\text{V}^{3+}]$ as the reaction proceeds. Moreover, the earlier work was carried out at higher reactant concentrations than those used in the present work, and we estimate, from the rates and concentrations reported,⁹ that only the last 25–35% of the reaction was followed in the earlier work. On the basis of these considerations, and because $\text{LiClO}_4\text{--HClO}_4$ mixtures provide a "better" background electrolyte than $\text{NaClO}_4\text{--HClO}_4$ mixtures, we are inclined to believe that our results are more reliable, and we conclude that the rate of the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+ + \text{V}^{2+}$ reaction is acid independent.

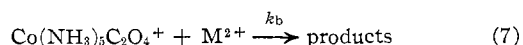
Our results regarding the acid independence of the rates of reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ can be compared with the results obtained for the corresponding reductions of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$. In the case of vanadium(II) and chromium(II), the observed second-order rate constants k_p vary with acidity according to eq 5³. For

$$k_p = k_0 + k_{-1}/[\text{H}^+] \quad (5)$$

iron(II) the inverse acid path was dominant, and the k_0 path was not observed.¹⁰ The contrasting behavior between the pentaammine and tetraammine systems is readily understood when it is recognized that, in the range of hydrogen ion concentrations studied, the dominant form of the pentaammine complex is the protonated form and that the acid dissociation equilibrium $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+} \rightleftharpoons \text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+ + \text{H}^+$ is rapidly established. The acid dissociation quotient Q is $8.8 \times 10^{-3} M$ at 25° and ionic strength 1.0 M .¹⁷ The acid dependence of the rates of reduction of the pentaammine complex simply indicates the occurrence of two parallel pathways. The acid-independent term corresponds to the reaction of the protonated complex *via* eq 6, whereas the inverse acid term corresponds to

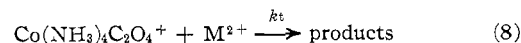


the reaction of the nonprotonated complex *via* eq 7

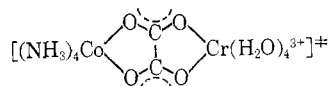


with a second-order rate constant $k_b = k_{-1}/Q$. For the tetraamminecobalt(III) complex, where the oxalate acts as a bidentate ligand, protonation of the ligand does not obtain in the range of hydrogen ion concentra-

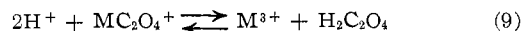
tions studied,¹⁸ and therefore it is not surprising that the second-order rate constants k_t for reaction *via* eq 8 are acid independent.



The second-order rate law given by eq 2 demonstrates that the rate-determining steps involve the reaction of one $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ with one M^{2+} ($\text{M} = \text{Cr}, \text{V}, \text{Fe}$) but does not serve to distinguish between an inner-sphere and an outer-sphere mechanism. For the reduction by chromium(II), the quantitative formation of $\text{Cr}(\text{OH}_2)_4\text{C}_2\text{O}_4^+$ provides conclusive evidence for an inner-sphere mechanism. Although oxalate acts as a bidentate ligand in the chromium(III) product, we cannot conclude that chelation by chromium(II) obtains in the transition state, because the rate of ring closure of monodentate oxalate bound to chromium(III) is not known. However, since the rate of ring closure for $\text{Cr}(\text{OH}_2)_5(\text{CO}_2\text{CH}_2\text{CO}_2\text{H})^{2+}$ is very slow,⁷ it seems reasonable to assume that the chelated product $\text{Cr}(\text{OH}_2)_4\text{C}_2\text{O}_4^+$ is the primary product of the reaction, rather than the result of ring closure subsequent to electron transfer. We suggest, therefore, that the transition state has the symmetrical structure



Under the conditions used for the kinetic studies of reductions by vanadium(II) and iron(II), the product criterion of mechanism cannot be used. The rates of equilibration for the reactions



where $\text{M} = \text{V}$ or Fe are very rapid compared to the rates of the redox reactions, and therefore the primary reaction products cannot be identified.¹⁹ In the absence of direct evidence to distinguish between an inner-sphere and an outer-sphere mechanism, indirect criteria must be invoked. Consider first the reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ by vanadium(II). Second-order rate constants and activation energies for the reactions of vanadium(II) with SCN^- ,²⁰ CrSCN^{2+} ,^{21,22} VO^{2+} ,²³ *cis*- $\text{Co}(\text{en})_2(\text{N}_3)_2^+$,²⁴ $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$,²⁵ and $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ ($\text{X} = \text{oxalate}, \text{binoxalate}, \text{glyoxalate}, \text{pyruvate}, \text{and oxamate}$)⁶ lie in the very narrow range $1\text{--}45 M^{-1} \text{sec}^{-1}$ and $11\text{--}13 \text{ kcal/mol}$, respectively. Because an inner-sphere mechanism necessarily involves substitution into the coordination sphere of vanadium(II) and definitive evidence for an inner-sphere mechanism has

(18) S. F. Ting, H. Kelm, and G. M. Harris, *ibid.*, **5**, 696 (1966).

(19) At sufficiently high concentration of vanadium(II), the rate of electron transfer becomes comparable to the rate of equilibration for reaction 4.⁹ Preliminary measurements at 25°, $[\text{ClO}_4^-] = 1.0 M$, $[\text{H}^+] = 0.50 M$, and $[\text{V}^{2+}] = 0.04 M$ provide some evidence for the primary production of VC_2O_4^+ . However, a complete analysis of the data is precluded because rate and equilibrium constants for reaction 4 are not available.

(20) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

(21) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967).

(22) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(23) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964).

(24) J. H. Espenson, *J. Amer. Chem. Soc.*, **89**, 1276 (1967).

(25) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).

(17) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

been obtained for the reductions of CrSCN^{2+} , *cis*- $\text{Co}(\text{en})_2(\text{N}_3)_2^+$, and $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ by vanadium(II), it has been suggested that the insensitivity of the rate constants and enthalpies²² of activation to the nature of the oxidant is the manifestation of a common rate-determining step in these reactions, namely, substitution into the first coordination sphere of vanadium(II). If this appealing generalization is accepted, then a rate constant in the range $1\text{--}45\text{ M}^{-1}\text{ sec}^{-1}$ together with an enthalpy of activation of $12 \pm 1\text{ kcal/mol}$ may be taken as diagnostic of an inner-sphere mechanism for vanadium(II) reactions. The values recorded in the present work for the vanadium(II) reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ ($k = 45.3\text{ M}^{-1}\text{ sec}^{-1}$, $\Delta H^\ddagger = 12.3\text{ kcal/mol}$) clearly place this reaction in the inner-sphere category.

For the iron(II) reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$, we cannot invoke an indirect criterion similar to that for vanadium(II). Substitution into the coordination sphere of iron(II) is extremely rapid, and electron transfer is rate determining. Reasoning by analogy, since direct evidence for an inner-sphere mechanism has been presented for the analogous $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}\text{--Fe}^{2+}$ reaction,³ it is tempting to conclude that the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+\text{--Fe}^{2+}$ reaction also proceeds *via* a bridged activated complex. Admittedly, the argument is unsatisfactory, but in view of the tendency of iron(II) to react by an inner-sphere mechanism whenever a potentially bridging ligand is present in the coordination sphere of the oxidant, it seems reasonable to assume an inner-sphere mechanism for the present reaction as well.

In Table III we present a summary of the kinetic

TABLE III
RATE CONSTANTS FOR THE REDUCTIONS OF
OXALATOCOBALT(III) COMPLEXES^a

Oxidant	Reductant		
	Cr^{2+}	V^{2+}	Fe^{2+}
$\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$	1.0×10^2 ^b	12.5	$\leq 5 \times 10^{-4}$ ^{c,d}
$\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$	4.6×10^4 ^b	45 ^b	0.43 ^{e,f}
$\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$	$\sim 2 \times 10^5$ ^f	45 ^f	4.16×10^{-4} ^f

^a In $\text{M}^{-1}\text{ sec}^{-1}$ at 25° . ^b Reference 8; $\mu = 1.0\text{ M}$. ^c $\mu = 0.52\text{ M}$. ^d Estimated from data of ref 10; see text. ^e Calculated from data of ref 10 and 17; see text. ^f Present work; $[\text{ClO}_4^-] = 1.0\text{ M}$.

data for the reductions of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$, and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ by V^{2+} , Fe^{2+} , and Cr^{2+} . The rate constant k_b for the $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+\text{--Fe}^{2+}$ reaction was calculated from the rate coefficient $k_{-1} = 3.8 \times 10^{-3}\text{ sec}^{-1}$ corresponding to the rate term $k_{-1}[\text{Co(III)}][\text{Fe(II)}]/[\text{H}^+]^{10}$ and the acid dissociation quotient $Q = 8.8 \times 10^{-3}\text{ M}$ of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$.¹⁷ Since $k_b = k_{-1}/Q$, we calculate $k_b = 0.43\text{ M}^{-1}\text{ sec}^{-1}$. As already mentioned, the rate term $k_0[\text{Co(III)}]\cdot[\text{Fe}^{2+}]$, which corresponds to the $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}\text{--Fe}^{2+}$ reaction, could not be detected. Assuming that at the highest hydrogen ion concentration used, a 5% contribution of the k_0 path would be unnoticed, we calculate an upper limit of $5 \times 10^{-4}\text{ M}^{-1}\text{ sec}^{-1}$ for the value of k_0 .

There are three noteworthy features in the data of Table III. First, reductions by vanadium(II) cover a narrow reactivity range (factor of 3.6), whereas reductions by iron(II) and chromium(II) cover a somewhat broader range (factors of $\sim 10^3$ and 2×10^3 , respectively). Second, removal of the proton from $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$ results in a modest increase in reduction rate by vanadium(II) (factor of 3.6) but in a substantial increase for iron(II) and chromium(II) (factors of ≥ 800 and 460, respectively). Third, the ratios of the rate constant for reduction of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ to the rate constant for reduction of $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ have values of ~ 0.2 , 1.0, and $\sim 10^3$ for chromium(II), vanadium(II), and iron(II), respectively. Some but not all of the noted trends may be rationalized on the basis of the detailed mechanisms of the reactions.

The limited range of rate constants for the reductions by vanadium(II) is easily understood as indicative of the common rate-determining substitution step discussed earlier. The small variation observed can reasonably be ascribed to electrostatic effects, the dipositive complex reacting somewhat more slowly than the monopositive complexes. Moreover, since the basicities (and presumably the nucleophilicities) of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ differ by at least 3 orders of magnitude¹⁸ whereas the rates of reduction are identical, we conclude that the rate of substitution on vanadium(II) is governed principally by the loss of water and that there is little or no assistance by the incoming group.

The increased reactivity toward chromium(II) and iron(II) displayed by $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ as compared to $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{H}^{2+}$ can be ascribed to the different basicities of the two oxalate complexes. The more basic $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ would form a more stable binuclear precursor complex $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4\text{M}^{3+}$ ($\text{M} = \text{Cr}, \text{Fe}$), and, other factors being equal, an increased reaction rate would result. Applying this argument to the $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ complexes, since the tetraammine complex is less basic than the pentaammine complex, we would predict a decrease in rate in going from $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ to $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$. Indeed, with iron(II) as the reductant, $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ is *ca.* 10^3 times less reactive than $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$. However, with chromium(II) as the reductant, the tetraammine complex reacts *ca.* 4 times faster than the pentaammine complex. One possible explanation for the difference in discrimination displayed by iron(II) and chromium(II) in their reactions with $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+$ and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ is that the iron(II) reactions proceed by the resonance-exchange mechanism, whereas the reactions of chromium(II) proceed by the radical ion mechanism.²⁶ The similarity in rates for the $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^+\text{--Cr}^{2+}$ and $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+\text{--Cr}^{2+}$ reactions suggests a common rate-determining step, namely, the reduction of the bound oxalate to its radical ion. Some support for this suggestion comes from the reported reduction of oxalate

(26) P. George and J. S. Griffith, "The Enzymes," Vol. 1, Academic Press, New York, N. Y., 1959, Chapter 8.

ion by chromium(II),²⁷ but additional considerations are in order.

Based on the assumption that the formation of the radical ion intermediate is the rate-determining step and a function solely of ligand and reductant, a proposed criterion to recognize the operation of the radical ion mechanism calls for a comparison of the rate constants for the amine-cobalt(III) complex and the corresponding aquochromium(III) complex.²⁸ A small ratio of cobalt(III) to chromium(III) rates is considered indicative of the importance of the transfer of the electron to the ligand (radical ion mechanism), whereas a large ratio is taken to indicate electron transfer to the metal ion center (resonance exchange mechanism). The reported rate constant for the chromium(II) reduction of $\text{Cr}(\text{OH})_2\text{C}_2\text{O}_4^+$ is $0.13 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° ,²⁹ and therefore the ratio $k_{\text{Co}}/k_{\text{Cr}}$ is $\sim 2 \times 10^6$. On the basis of the proposed criterion, this very high ratio

(27) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).

(28) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

(29) T. Spinner and G. M. Harris, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, INOR 36.

would place the $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+-\text{Cr}^{2+}$ reaction in the resonance-exchange mechanism category. However, it must be noted that the applicability of the proposed criterion to the detection of the radical ion mechanism has been tested in only one case.²⁸ Moreover, the criterion may not be applicable to oxalate ion as a bridging ligand. Since oxalate ion is easily oxidized,³⁰ some contribution of a structure where the oxalate group has relinquished an electron to the oxidizing center would be considerably more important for $\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4^+$ than for $\text{Cr}(\text{OH})_2\text{C}_2\text{O}_4^+$, and this factor may account for the large $k_{\text{Co}}/k_{\text{Cr}}$ ratio. If this argument is accepted, the suggestion that the chromium(II) reductions proceed by the radical ion mechanism must still be considered as tentative.³¹ As repeatedly emphasized, conclusions based solely on reactivity patterns and rate comparisons may be unreliable.

(30) For the spontaneous oxidation of oxalate bound to cobalt(III), see J. Aggett and A. L. Odell, *J. Chem. Soc., A*, 1415 (1968).

(31) Our suggestion of a radical ion mechanism would appear, at first glance, to contradict the conclusions reached previously⁸ regarding the reactions of Cr^{2+} with $\text{Co}(\text{NH}_3)_4\text{CO}_2\text{COX}^{2+}$ ($\text{X} = \text{O}, \text{OH}, \text{CH}_3, \text{NH}_2, \text{C}(\text{CH}_3)_3$). However, it must be noted that Price and Taube⁸ concluded that not all of their observations could be accommodated by the radical ion mechanism.

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Cobalt(II) Complexes of the Quadridentate Macrocyclic 2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene¹

BY KENNETH M. LONG² AND DARYLE H. BUSCH

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A series of cobalt(II) complexes of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, CR, have been prepared; all are low spin in electronic configuration. The electronic spectra have been interpreted with the aid of an energy level diagram for trigonal-bipyramidal, low-spin cobalt(II), d^7 . Pentacoordination is supported by conductance measurements in several solvents. The low magnetic susceptibilities of the solids $\text{Co}(\text{CR})\text{BrX}$ ($\text{X}^- = \text{ClO}_4^-, \text{PF}_6^-, \text{B}(\text{C}_6\text{H}_5)_4^-$) indicate a cobalt-cobalt interaction in these compounds.

Introduction

Although nickel(II) derivatives of the newer synthetic macrocycles dominated initial studies,³ recently a number of cobalt complexes have been reported.⁴⁻¹³ Most of these have been cobalt(III) derivatives with *meso*- and *dl*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-

azacyclotetradecane (7,14-CTH),^{4,5} with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene (1,7-CT),⁶ with 1,4,8,11-tetraazacyclotetradecane (cyclam),⁷ with 1,4,7,10-tetraazacyclododecane (cyclen),⁸ and with *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CRH).⁹ However, some cobalt(II) derivatives have been reported with the macrocycles 1,7-CT,¹⁰ *meso*-7,14-CTH,¹¹ and 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-diene (1,4-CT).¹² The *meso*-7,14-CTH complexes are generally low spin with normal Curie-Weiss behavior.¹¹

The present work was undertaken as part of a general program concerned with investigation of the characteristics of macrocyclic cobalt(II) complexes. The ligand studied, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR, structure I), was first known in its copper(II)¹³ and

(1) Based in part on the Ph.D. thesis of K. M. L., The Ohio State University, 1967.

(2) National Institutes of Health Predoctoral Fellow, 1965-1967.

(3) D. H. Busch, *Helv. Chim. Acta*, Fasciculus extraordinarius Alfred Werner, 174 (1967).

(4) P. O. Whimp and N. F. Curtis, *J. Chem. Soc., A*, 867 (1966).

(5) P. O. Whimp and N. F. Curtis, *ibid.*, **A**, 1827 (1966).

(6) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).

(7) B. Bosnich, C. K. Poon, and M. L. Tobe, *ibid.*, **4**, 1102 (1965).

(8) J. P. Collman and P. W. Schneider, *ibid.*, **5**, 1380 (1966).

(9) E. Ochiai and D. H. Busch, *ibid.*, **8**, 1474 (1969).

(10) N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.*, **88**, 5468 (1966).

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(12) J. L. Love and H. K. J. Powell, *Inorg. Nucl. Chem. Letters*, **3**, 113 (1967).

(13) R. L. Rich and G. L. Stucky, *ibid.*, **1**, 85 (1965).