Inner-Sphere and Outer-Sphere Mechanisms in the Reductions of Oxalatocobalt(III) Complexes by Vanadium(II)[1]

Bernard Grossman and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11790. *Received March 30, 1971*

Abstract: The reductions of $Co(en)(C_2O_4)_2^-$ and $Co(C_2O_4)_3^{3-}$ by vanadium(II) have been studied in aqueous solutions of ionic strength 1.0 *M*. For $Co(en)(C_2O_4)_2^-$, the second-order rate constant (25°, $[H^+] = 0.56$ *M*) is $(1.08 \pm 0.04) \times 10^2$ M^{-1} sec^{-1} with $\Delta H^{\ddagger} = 9.3 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -18 \pm 1$ eu. For $Co(C_2O_4)_3^{3-}$, the second-order rate constant (25°, $[H^+] = 1.0$ *M*) is $(2.04 \pm 0.06) \times 10^4$ M^{-1} sec^{-1} with $\Delta H^{\ddagger} = 2.2 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -31.5 \pm 0.8$ eu. Both reactions produce $VC_2O_4^-$ and V^{3+} as primary products, and it is concluded that parallel inner-sphere and outer-sphere mechanisms are operative. The reduction of $Co(en)(C_2O_4)_2^-$ by Fe^{2+} has also been studied. At 25°, $[H^+] = 0.60$ *M*, the second-order rate constant is 3.15×10^{-3} M^{-1} sec^{-1} with $\Delta H^{\ddagger} = 15.7 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -17.5 \pm 1.0$ eu. Comparisons of vanadium(II) and iron(II) reductions of various cobalt(III) complexes are made and interpreted mechanistically.

Oxidation–reduction reactions of vanadium(II), in common with those of chromium(II) and iron(II), fall into the inner-sphere–outer-sphere mechanistic classification.[2] However, in contrast with the inner-sphere reductions by chromium(II) and iron(II) for which electron transfer within the precursor binuclear complex is rate-determining, inner-sphere reductions by vanadium(II) have been understood on the basis of a rate-determining substitution into the coordination sphere of vanadium(II).[2] It has been suggested that redox reactions of vanadium(II) that proceed with rate constants in the range 1–50 M^{-1} sec^{-1} (25°) and activation energies in the range 11–13 kcal/mol are of the inner-sphere type.[2] However, when the rate constants exceed appreciably the upper limit of 50 M^{-1} sec^{-1} and the activation energies fall below 10 kcal/mol, then the outer-sphere mechanism becomes operative.[2] Examples of reactions that conform to this generalization are *cis*-$Co(en)_2(N_3)_2^+ + V^{2+}$,[3] $CrSCN^{2+} + V^{2+}$,[4] $Co(NH_3)_5C_2O_4^+ + V^{2+}$,[5] $FeNCS^{2+} + V^{2+}$,[4] and $FeN_3^{2+} + V^{2+}$.[4] The first three reactions are known to proceed by an inner-sphere mechanism with rate constants 32, 8, and 45 M^{-1} sec^{-1} (25°), respectively. The last two reactions are known to be of the outer-sphere type, and proceed with rate constants 6.6×10^5 and 5.2×10^5 M^{-1} sec^{-1} (25°), respectively. Confirmation of the adequacy of the mechanistic assignment based on the magnitude of the second-order rate constant comes from recent measurements of the rate constant for water exchange between solvent and the aquovanadium(II) ion.[6]

In the present work, we have extended our previous studies[7] of the $Co(NH_3)_4C_2O_4^+$–V^{2+} reaction to the complexes $Co(en)(C_2O_4)_2^-$ and $Co(C_2O_4)_3^{3-}$. Since equilibrium between vanadium(III) and oxalate is achieved relatively slowly,[5] these systems offer an opportunity to establish the mechanism by direct observation of the products. Moreover, we were interested in the possible transition from an inner-sphere to an outer-sphere mechanism as the reactivity of the cobalt(III) center in $Co(NH_3)_4C_2O_4^+$ is increased by successive substitution of the amine ligands by oxalate ligands. The trends in rate constants in systems of known mechanism are of particular importance because recent work[8] on the vanadium(II) reductions of various complexes of the class $Co(en)_2XCl^{n+}$ (X = NH_3, py, Cl^-, H_2O) has led to the suggestion that all these reactions, which proceed with rate constants in the range 1.9–460 M^{-1} sec^{-1} (25°), are mechanistically of the outer-sphere type.

Experimental Section

Materials. Iron(II) perchlorate solutions were prepared by electrolytic reduction of solutions of recrystallized iron(III) perchlorate in perchloric acid. The iron(II) and hydrogen ion concentrations were determined as described previously.[9] 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, and were used immediately after standardization.[7] The preparation of lithium perchlorate solutions and the purification of the argon have been described previously.[10] Distilled water was passed through a Barnstead ion-exchange demineralizer and then was distilled in a Corning Model AG-1b all-glass distilling apparatus. Sodium bis(oxalato)ethylenediaminecobaltate(III) monohydrate was prepared by Dr. Jay Worrell.[11] The observed maxima at 540 and 382 nm with extinction coefficients 109 and 184, respectively, agree reasonably well with literature values.[12] Potassium tris(oxalato)cobaltate(III) sesquihydrate was prepared by a standard procedure.[13]

Kinetic Measurements. The reduction of $Co(en)(C_2O_4)_2^-$ by iron(II) was studied by conventional spectrophotometric methods. The cobalt(III) complex was placed in the spectrophotometric cell and the desired amounts of water, perchloric acid, and lithium perchlorate were added. The cell was placed in the thermostated compartment of a Cary 14 recording spectrophotometer, and, following temperature equilibration, the desired amount of iron(II) solution, previously equilibrated to the same temperature, was added. The absorbance at 540 nm was then recorded as a function of time. The iron(II) was in large excess to ensure pseudo-first-

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

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(13) W. G. Palmer, "Experimental Inorganic Chemistry," University Press, Cambridge, England, 1954, p 550.

order conditions. Pseudo-first-order rate coefficients, k_p, were evaluated from the relation $A_t - A_\infty = (A_0 - A_\infty)e^{-k_pt}$, where A_t, A_0, and A_∞ are the absorbances at times t, 0, and ∞, respectively. The values of A were fitted to the above equation by means of a nonlinear least-squares program,[14] with A_t and t being the dependent and independent variables, respectively, and A_0, A_∞, and k_p were treated as adjustable parameters. Second-order rate constants were calculated from the expression $k = k_p/[Fe^{2+}]$. The reductions of $Co(en)(C_2O_4)_2^-$ and $Co(C_2O_4)_3^{3-}$ by vanadium(II) were studied in the rapid-flow apparatus.[15] The procedure and treatment of the data have been described previously.[10] The wavelengths used were 540 nm for $Co(en)(C_2O_4)_2^-$ and 290 and 280 nm for $Co(C_2O_4)_3^{3-}$

Results

The results of the kinetic measurements of the $Co(C_2O_4)_3^{3-}$–V^{2+} reaction are summarized in Table I.

Table I. Kinetics of the $Co(C_2O_4)_3^{3-}$–V^{2+} Reaction[a]

10^5[Co(III)], M	10^4[V(II)], M	[H^+], M	$10^{-4}k$, M^{-1} sec^{-1} [b]
2.19	2.54	1.00	1.92, 1.92
10.9	12.8	1.00	1.88, 1.95
5.47	13.0	1.00	2.03, 2.16
10.9	25.3	1.00	2.19, 2.09
4.37	4.92	0.85	1.90, 1.96
4.37	4.92	0.70	1.87, 1.85
4.37	4.92	0.70	2.00, 2.03
4.37	5.08	0.50	1.82, 1.83
4.37	5.08	0.50	1.77, 1.75
4.37	7.58	0.30	1.82, 1.80
4.37	7.58	0.30	1.92, 1.97
4.37	5.05	0.10	1.75, 1.71
2.19	2.50	1.00	1.68, 1.72[c]
4.37	5.05	1.00	1.70, 1.89[c]
4.37	5.05	1.00	1.74, 1.86[c]
4.37	5.05	1.00	1.56, 1.50[c]
4.37	5.01	1.00	2.38, 2.32[d]
4.37	5.01	1.00	2.40, 2.27[d]

[a] Ionic strength 1.0 M maintained with $HClO_4$–$LiClO_4$. Measurements at 25° unless specified otherwise. [b] Each entry represents the average of two to four replicate measurements with the same pair of solutions. First and second entries from 280- and 290-nm measurements, respectively. [c] At 15°. [d] At 35°.

At constant hydrogen ion concentration, the second-order rate constants defined by eq 1 are seen to be

$$-d[Co(C_2O_4)_3^{3-}]/dt = k[Co(C_2O_4)_3^{3-}][V^{2+}] \qquad (1)$$

independent of the concentrations of the two reactants[16] and of the wavelength used for the measurements. However, the second-order rate constants decrease with decreasing hydrogen ion concentration. The value of k is approximately 15% higher at [H^+] = 1.0 M as compared to 0.10 M. The significance of this observation is not clear. Two alternate interpretations are plausible. On the one hand, this may be viewed as a chemical effect caused by the operation of two parallel paths, one acid independent (k_0) and one acid dependent (k_1) with $k = k_0 + k_1[H^+]$. On the other hand, the increase in rate with increasing acidity may be viewed as the manifestation of medium effects as lithium ions are replaced by hydrogen ions. We are inclined to favor the latter interpretation. The increase in rate with [H^+] is quite modest and falls well within the range observed for medium effects in other redox reactions.[17] In particular, because of the high negative charge on the cobalt(III) complex, the present system may be quite susceptible to the nature and concentration of the cations in solution,[18] and therefore the *ca.* 15% change in rate observed on replacing 0.90 M H^+ by 0.9 M Li^+ can reasonably be ascribed to a medium effect. Included in Table I are the measured second-order rate constants at [H^+] = 1.0 M and 15 and 35°. Using these values and the values at 25° (average 2.04 × 10^4 M^{-1} sec^{-1}), the activation parameters computed by using the nonlinear least-squares program are: $\Delta H^{\ddagger} = 2.2 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -31.5 \pm 0.8$ eu.

Since the rate of the $Co(C_2O_4)_3^{3-}$–V^{2+} redox reaction is quite rapid, whereas the rate of equilibration for the vanadium(III) oxalate system (eq 2) is relatively slow,[5] this system offers an opportunity to establish whether an inner-sphere or an outer-sphere mechanism obtains

$$V^{3+} + H_2C_2O_4 \rightleftharpoons VC_2O_4^+ + 2H^+ \qquad (2)$$

by determining the nature of the primary vanadium(III) product. Since much of the necessary information about reaction 2 is not available, the measurements were made on a comparative basis. First, the reaction of 4.38 × 10^{-3} M vanadium(III) with 1.32 × 10^{-2} M $H_2C_2O_4$ in the presence of 0.0158 M vanadium(II) at [H^+] = 0.92 M and 25° was examined at 290 nm. The absorbance was found to increase, with a half-life of 0.36 sec. The value of $\Delta A/[V^{3+}]_0l$, where ΔA is the change in absorbance upon reaction, $[V^{3+}]_0$ is the initial vanadium(III) concentration, and l is the path length of the observation tube of the rapid-flow apparatus, was 261 M^{-1} cm^{-1}. Next, the reaction of 4.38 × 10^{-3} M $Co(C_2O_4)_3^{3-}$ with 0.0201 M vanadium(II) at [H^+] = 0.92 M and 25° was examined at the same wavelength. Under these conditions, first a rapid decrease in absorbance was observed (disappearance of $Co(C_2O_4)_3^{3-}$, ϵ 8 × 10^3, and formation of V^{3+}, ϵ 10), and this was followed by a slower increase in absorbance (equilibration in reaction 2, effective extinction coefficient of the equilibrium mixture 271). The minimum in the absorbance *vs.* time curves occurred at 0.022 sec. The increase in absorbance was associated with a half-life of 0.36 sec and a value of $\Delta A/[Co(III)]_0l$ of 219 M^{-1} cm^{-1}. In this case ΔA was measured as $A_\infty - A_m$, where A_∞ was the absorbance at long times and A_m the absorbance at the minimum. A comparison of the observations for the V^{3+}–$H_2C_2O_4$ reaction and the $Co(C_2O_4)_3^{3-}$–V^{2+} reaction suggests that the latter reaction proceeds *via* the sequence of steps given by eq 3 and 2. On the basis of this sequence, the values of t_{min}, the time for minimum absorbance,[19] and of $\Delta A/$

$$Co(C_2O_4)_3^{3-} + V^{2+} \xrightarrow{H^+} Co^{2+} + 3H_2C_2O_4 + V^{3+} \qquad (3)$$

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(14) Los Alamos Report No. LA 2367, March 4, 1960, and Addenda, Jan 14, 1963.

(15) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

(16) We were particularly interested in the possibility of outer-sphere complex formation between the reactants. This type of interaction would lead to a less than first-order dependence on [V^{2+}] at higher values of [V^{2+}]. Unfortunately, it is not possible to increase [V^{2+}] above the values given in Table I because the reaction becomes too rapid.

(17) D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).

(18) The effect of ionic strength on the analogous system $Co(C_2O_4)_3^{3-} + Fe^{2+}$ has been studied in detail: J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **52**, 210 (1956).

(19) t_m was calculated from the expression $[1/(k_1 + k_2)] \ln [1 + (k_1 - k_2)(\epsilon_1 - \epsilon_2 - \epsilon_3)/k_2(\epsilon_4 - \epsilon_3)]$, where k_1 is the pseudo-first-order constant for reaction 3, k_2 is the pseudo-first-order rate constant for approach to equilibrium in reaction 2, ϵ_1, ϵ_2, and ϵ_3 are the molar absorbances of $Co(C_2O_4)_3^{3-}$ (8.0 × 10^3), Co^{2+} (0.01), and V^{3+} (10), respectively, and ϵ_4 is like the effective molar absorbance of the equilibrium mixture of $VC_2O_4^+$ and V^{3+} under the prevailing condition (ϵ 271).

$[\mathrm{Co(III)}]_0 l$[20] are 0.020 sec and 245 M^{-1} cm^{-1}, respectively. The reasonable agreement between the measured and the calculated values is noteworthy, and it is concluded that the proposed scheme (eq 3 and 2) is basically correct. However, the measured value of $\Delta A/[\mathrm{Co(III)}]_0 l$ is somewhat smaller than the calculated value. If it is assumed that the discrepancy is caused by a parallel inner-sphere reaction (eq 4) that produces $VC_2O_4^+$ as the primary vanadium(III) product, then

$$\mathrm{Co(C_2H_4)_3}^{3-} + \mathrm{V}^{2+} \xrightarrow{\mathrm{H}^+} \mathrm{Co}^{2+} + 2\mathrm{H_2C_2O_4} + \mathrm{VC_2O_4}^+ \quad (4)$$

it can be shown that the value of $\Delta A/[\mathrm{Co(III)}]_0 l$ is given by

$$\frac{\Delta A}{[\mathrm{Co(III)}]_0 l} = \frac{k_1 k_2 f_{\mathrm{IS}}(\epsilon_4 - \epsilon_3)}{(k_1 - k_2)k_\mathrm{f}} \times [\exp(-k_1 t_\mathrm{m}) - \exp(-k_2 t_\mathrm{m})] - (\epsilon_1 - \epsilon_2 - \epsilon_3)\exp(-k_1 t_\mathrm{m}) - \frac{(\epsilon_4 - \epsilon_3)}{(k_1 - k_2)}[k_2 \exp(-k_1 t_\mathrm{m}) - k_1 \exp(-k_2 t_\mathrm{m})]$$

where f_{IS} is the fraction of the $\mathrm{Co(C_2O_4)_3}^{3-}$–$\mathrm{V}^{2+}$ reaction that proceeds *via* an inner-sphere mechanism and k_f is the pseudo-first-order rate coefficient for the forward reaction in eq 2. Using the values $\Delta A/[\mathrm{Co(III)}]_0 l = 219$, $k_1 = 320$ sec^{-1}, $k_2 = 1.93$ sec^{-1}, ϵ_1 8.0 × 10^3, ϵ_2 0.01, ϵ_3 10, ϵ_4 271, and t_m 0.022 sec, it is calculated that $f_{\mathrm{IS}}/k_\mathrm{f} = 0.054$. Using the equilibrium quotient of ~100[21] for reaction 2 and the measured value of k_2 (1.93 sec^{-1}) under the experimental conditions, $k_\mathrm{f} = 1.1$ sec^{-1}, and therefore $f_{\mathrm{IS}} = 0.06$. It is concluded that the overall $\mathrm{Co(C_2O_4)_3}^{3-}$–$\mathrm{V}^{2+}$ reaction proceeds *via* parallel outer- (94%) and inner-sphere (6%) paths.

The results obtained in the study of the $\mathrm{Co(en)(C_2O_4)_2}^{-}$–$\mathrm{V}^{2+}$ reaction are summarized in Table II. It was assumed, rather than proved, that the reaction is first order in cobalt(III) and first order in vanadium(II), and the calculated second-order rate constants are listed in column 4 of Table II. As was the case for the $\mathrm{Co(C_2O_4)_3}^{3-}$–$\mathrm{V}^{2+}$ reaction, there is a modest increase in rate with increasing [H$^+$] (compare entries 3 and 4 with 5 and 6). Again the increase in rate is ascribed to a medium effect rather than a chemical effect. The activation parameters calculated from the measurements at [H$^+$] = 0.56 M are: $\Delta H^\ddagger = 9.3 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -18 \pm 1$ eu.

Table II. Kinetics of the $\mathrm{Co(en)(C_2O_4)_2}^{-}$–$\mathrm{V}^{2+}$ Reaction[a]

10^4[Co(III)], M	10^2[V(II)], M	Temp, °C	k, M^{-1} sec^{-1} [b]
2.45	2.01	15	68 ± 4
2.53	2.01	15	61 ± 3
2.50	1.01	25	104 ± 4
2.48	2.01	25	112 ± 4
22.0	1.00	25	123 ± 6[c]
4.03	2.02	25	116 ± 3[d]
2.53	2.01	35	187 ± 7
5.00	2.01	35	194 ± 3

[a] Unless specified otherwise, ionic strength = 1.0 M maintained with $HClO_4$–$LiClO_4$; [H$^+$] = 0.56 M. [b] Each entry is the average of four replicate measurements with the same pair of solutions. [c] In the presence of 2.20 × 10^{-3} M added $H_2C_2O_4$; [H$^+$] = 1.0 M. [d] At [H$^+$] = 1.0 M.

In addition to providing the rate constant for the $\mathrm{Co(en)(C_2O_4)_2}^{-}$–$\mathrm{V}^{2+}$ reaction, the fifth and sixth experiments in Table II provided information about the nature and yields of the primary vanadium(III) products. For the fifth experiment, transmittance *vs.* time measurements were also performed at 290 nm. Plots of log ($A_t - A_\infty$) *vs.* time were linear for at least three half-lives and yielded a second-order rate constant of 124 ± 3. Calculations of log ($A_t - A_\infty$) *vs.* time at 290 nm were carried out under the following assumptions: (a) that $VC_2O_4^+$ was produced in 100% yield and then dissociated to produce the equilibrium mixture of $VC_2O_4^+$ and V^{3+} appropriate to the experimental conditions used; (b) that V^{3+} was produced and then associated with $H_2C_2O_4$ to produce the equilibrium mixture of V^{3+} and $VC_2O_4^+$. Under either of these assumptions curved log ($A_t - A_\infty$) *vs.* time plots were obtained, and the initial slopes yielded second-order rate constants in the range of 80–100 M^{-1} sec^{-1}. Since the experimental log ($A_t - A_\infty$) *vs.* time plots at 290 nm were linear and yielded second-order rate constants in excellent agreement with those measured at 540 nm, it is concluded that both $VC_2O_4^+$ and V^{3+} are produced in the redox reaction in quantities approximately equal to the equilibrium values appropriate to the experimental conditions used. Using the equilibrium quotient of ~100[21] for reaction 2 and the concentrations of V(III), $H_2C_2O_4$, and H$^+$ used in the experiment, it is calculated that the ratio [$VC_2O_4^+$]/[V^{3+}] at equilibrium is 0.57, and therefore it is concluded that the $\mathrm{Co(en)(C_2O_4)_2}^{-}$–$\mathrm{V}^{2+}$ reaction yields approximately 36% $VC_2O_4^+$ and 64% V^{3+}. A more accurate determination of the yields of $VC_2O_4^+$ and V^{3+} was carried out by measuring the changes in transmittance as a function of time at 290 nm under conditions where the $VC_2O_4^+$–V^{3+} equilibrium favors dissociation of $VC_2O_4^+$. This is the sixth experiment listed in Table II for which it is calculated that the ratio [$VC_2O_4^+$]/[V^{3+}] at equilibrium is 0.08. Under the conditions used, the rate of the Co(III)–V(II) reaction is faster than the rate of dissociation of $VC_2O_4^+$, and therefore the log ($A_t - A_\infty$) *vs.* time plots consisted of two exponential decays, the second (and slower) decay corresponding to the dissociation of the $VC_2O_4^+$ formed in the first reaction. By extrapolating the second exponential to time 0, it can be shown[22] that f_{IS}, the fraction of reaction that proceeds *via* the inner-sphere mechanism and produces $VC_2O_4^+$, is given by

$$f_{\mathrm{IS}} = [m/(\epsilon_5 - \epsilon_3)][1 - (k_4/k_3)] + k_\mathrm{f}'/k_4$$

where m is the intercept obtained by extrapolating the second exponential in the log $\{(A_t - A_\infty)/[\mathrm{Co(III)}]_0 l\}$ *vs.* time plots to time 0.[22] Using the values $m = 285$, ϵ_3 10, ϵ_5 5 × 10^2, $k_3 = 2.34$ sec^{-1}, $k_4 = 0.65$ sec^{-1}, and

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(20) $A_\mathrm{m}/[\mathrm{Co(III)}]_0 l$ was calculated from the expression $(\epsilon_4 + \epsilon_2) + (\epsilon_1 - \epsilon_2 - \epsilon_3)\exp(-k_1 t_\mathrm{m}) + (\epsilon_4 - \epsilon_3)/(k_1 - k_2)[k_2 \exp(-k_1 t_\mathrm{m}) - k_1 \cdot \exp(-k_2 t_\mathrm{m})]$.

(21) C. Hwang, unpublished observations.

(22) The dependence of $(A_t - A_\infty)/[\mathrm{Co(III)}]_0 l$ is given by $(A_t - A_\infty)/[\mathrm{Co(III)}]_0 l = (\epsilon_5 + \epsilon_6 - \epsilon_2 - \epsilon_3)\exp(-k_3 t) + (\epsilon_7 - \epsilon_3)[k_\mathrm{f}'/(k_3 - k_4)\exp(-k_3 t) + k_3 f_{\mathrm{IS}}/(k_3 - k_4)[\exp(-k_4 t) - \exp(-k_3 t)] - k_3 k_\mathrm{f}'/k_4(k_3 - k_4)\exp(-k_4 t)]$, where ϵ_5, ϵ_6, and ϵ_7 are the molar absorbances of $\mathrm{Co(en)(C_2O_4)_2}^{-}$, V^{2+}, and $VC_2O_4^+$, respectively, k_3 is the pseudo-first-order rate coefficient for reaction 5, k_4 is the pseudo-first-order rate coefficient for approach to equilibrium in reaction 2, and k_f' is the pseudo-first-order rate coefficient for the forward reaction in eq 2. At long times, $(A_t - A_\infty)/[\mathrm{Co(III)}]_0 l = (\epsilon_7 - \epsilon_3)(k_3 k_4 f_{\mathrm{IS}} - k_3 k_\mathrm{f}')/(k_3 - k_4)k_4 \exp(-k_4 t)$. Extrapolation to time 0 yields the desired relation.

$k_f'/k_4 = 0.08$, the calculation yielded the value $f_{IS} = 0.50$, and it is concluded that the $Co(en)(C_2O_4)_2^{-}$–V^{2+} reaction proceeds *via* parallel inner- and outer-sphere paths as shown in the scheme of eq 5.

$$Co(en)(C_2O_4)_2^{-} + V^{2+} \left\{ \begin{array}{ll} \xrightarrow{50\%} Co^{2+} + VC_2O_4^{+} & \text{inner sphere} \\ \xrightarrow[50\%]{} Co^{2+} + V^{3+} & \textit{outer sphere} \end{array} \right. \qquad (5)$$

The results obtained in the study of the $Co(en)(C_2O_4)_2^{-}$–Fe^{2+} reaction are summarized in Table III.

Table III. Kinetics of the $Co(en)(C_2O_4)_2^{-}$–Fe^{2+} Reaction[a]

10^4[Co(III)], M	10^2[Fe(II)], M	Temp, °C	10^3k, M^{-1} sec^{-1}
5.00	1.00	35	6.96
5.00	9.26	35	7.26
6.62	9.26	35	7.40
10.1	9.26	35	7.46
5.33	3.71	35	6.33[b]
5.00	5.56	35	6.80[c]
6.24	9.26	25	3.15
6.66	9.26	25	3.15
5.48	9.26	45	17.2
5.53	9.26	45	16.7

[a] Ionic strength 1.0 M maintained with $HClO_4$-$LiClO_4$; $[H^+] = 0.60$ M unless specified otherwise. [b] $[H^+] = 0.189$ M. [c] $[H^+] = 0.284$ M.

In the limited concentration range studied, the reaction obeys mixed second-order kinetics. The second-order coefficient is seen to be dependent on hydrogen ion concentration (*cf.* entries 1–6 of Table II), but, as was the case in the $Co(C_2O_4)_3^{3-}$–V^{2+} reaction, the change in rate with $[H^+]$ is likely to be a medium effect. The activation parameters calculated from the measurements at 0.60 M hydrogen ion concentration are $\Delta H^{\ddagger} = 15.7 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -17.5 \pm 1.0$ eu.

Discussion

The results obtained in the present work conform, as far as the major features are concerned, to the generalizations about vanadium(II) reductions mentioned in the introduction. The very rapid reduction of $Co(C_2O_4)_3^{3-}$, $k = 2.1 \times 10^4$ M^{-1} sec^{-1} at 25° with $\Delta H^{\ddagger} = 2.2$ kcal/mol, proceeds predominantly by an outer-sphere mechanism. For the slower reduction of $Co(en)(C_2O_4)_2^{-}$, $k = 1.1 \times 10^2$ M^{-1} sec^{-1} at 25° with $\Delta H^{\ddagger} = 9.3$ kcal/mol, an inner-sphere path is important in bringing about the redox reaction. However, for both systems, the detailed examination of the primary vanadium(III) products shows that parallel inner-sphere and outer-sphere mechanisms are operative, the distribution between paths varying considerably for $Co(en)(C_2O_4)_2^{-}$ and $Co(C_2O_4)_3^{3-}$. An entirely similar situation has been previously demonstrated for the VO^{2+}–V^{2+} reaction.[23] The proposed kinetic scheme is described by eq 6–10 (L = en or $C_2O_4^{2-}$). It is assumed that an ion pair or outer-sphere complex is formed rapidly from the cobalt(III) complex and vanadium(II) (eq 6). The ion pair can proceed forward according to one of two possible reactions: (a) a slow outer-sphere electron-transfer process (eq 7) producing V^{3+} (eq 9) as the primary vanadium(III) mononuclear product, and (b) a slow inner-sphere substitution into the coordination sphere of vanadium(II) (eq 8) to produce the precursor binuclear complex $CoL(C_2O_4)_2V^{(2-n)+}$. This slow complex formation is followed by rapid electron transfer within the binuclear complex and dissociation to cobalt(II) and $VC_2O_4^{+}$ (eq 10). According to this mechanism, the observed second-order rate coefficients are given by eq 11. Under the

$$CoL(C_2O_4)_2^{n-} + V^{2+} \rightleftarrows CoL(C_2O_4)_2^{n-}\cdot V^{2+} \quad \text{rapid, } Q \qquad (6)$$

$$CoL(C_2O_4)_2^{n-}\cdot V^{2+} \longrightarrow CoL(C_2O_4)_2^{(n+1)-}\cdot V^{3+} \quad \text{slow, } k_{OS} \qquad (7)$$

$$CoL(C_2O_4)_2^{n-}\cdot V^{2+} \longrightarrow CoL(C_2O_4)_2V^{(2-n)+} \quad \text{slow, } k_{IS} \qquad (8)$$

$$CoL(C_2O_4)_2^{(n+1)-}\cdot V^{3} \longrightarrow Co^{2+} + L + 2C_2O_4^{2-} + V^{3+} \quad \text{rapid} \qquad (9)$$

$$CoL(C_2O_4)_2V^{(2-n)+} \longrightarrow Co^{2+} + L + C_2O_4^{2-} + VC_2O_4^{+} \quad \text{rapid} \qquad (10)$$

$$k = (k_{IS} + k_{OS})Q/(1 + Q[V^{2+}]) \qquad (11)$$

experimental conditions employed, $Q[V^{2+}] \ll 1$. Therefore, the observed second-order coefficients are $(k_{IS} + k_{OS})Q$, and separate values for Q and for $k_{IS} + k_{OS}$ could not be obtained from the kinetic measurements. However, according to the proposed mechanism, $k_{IS}/k_{OS} = [VC_2O_4^{+}]/[V^{3+}]$, the ratio of the primary mononuclear vanadium(III) products. Therefore, from the stoichiometric measurements it is possible to calculate k_{IS}/k_{OS} values of 1.0 and 0.064 for $Co(en)(C_2O_4)_2^{-}$ and $Co(C_2O_4)_3^{3-}$, respectively.[24] Expressing the inner-sphere and outer-sphere paths in terms of the second-order rate coefficients Qk_{IS} and Qk_{OS}, respectively, we calculate (25°), for $Co(en)(C_2O_4)_2^{-}$, $Qk_{IS} = 55$ M^{-1} sec^{-1} and $Qk_{OS} = 55$ M^{-1} sec^{-1} and for $Co(C_2O_4)_3^{3-}$, $Qk_{IS} = 1.3 \times 10^3$ M^{-1} sec^{-1} and $Qk_{OS} = 2.0 \times 10^4$ M^{-1} sec^{-1}.

A summary of rate constants (corrected for statistical factors where appropriate) and activation parameters for the vanadium(II) reductions of cobalt(II) oxalate complexes is given in Table IV. It is seen that the statistically corrected value of Qk_{IS} for $Co(en)(C_2O_4)_2^{-}$ falls nicely in the range of rates of the other vanadium(II) inner-sphere redox reactions. The enthalpy of activation for the $Co(en)(C_2O_4)_2^{-}$ reaction (9.3 kcal/mol) is somewhat smaller than the value characteristic of inner-sphere reactions (12 ± 1 kcal/mol). However, since the measured enthalpy of activation includes the contribution of the outer-sphere path, the lower value is reasonable.[25] In this context, it is noteworthy that the enthalpy of activation for the $Co(C_2O_4)_3^{3-}$–V^{2+} reaction, which proceeds predominantly by an outer-sphere path, is only 2.2 kcal/mol. The statistically corrected value of Qk_{IS} (420 M^{-1} sec^{-1}) for $Co(C_2O_4)_3^{3-}$ is somewhat higher than the values for the other inner-sphere reactions. However, values in the range 112–278 M^{-1} sec^{-1} (25°, ionic strength 1.0 M) have been reported for other trinegative ions,[26] and when Qk_{IS} for $Co(C_2O_4)_3^{3-}$ is corrected for an additional statistical factor of 2,[27] then the resulting figure of 210 M^{-1} sec^{-1} falls well within the range for the trinegative ions.

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(23) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

(24) The corresponding value in the VO^{2+}–V^{2+} reaction[23] is 1.85.

(25) R. S. Taylor, R. N. F. Thorneley, and A. G. Sykes, *J. Chem. Soc. A*, 856 (1970).

(26) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 3093 (1969).

(27) The statistical corrections in Table IV yield rate constants per oxalate ligand. However, in comparing $Co(CN)_5X^{3-}$ with $Co(C_2O_4)_3^{3-}$, the rate constant per oxalate ligand must be divided by 2 in order to obtain the rate constant per donor oxygen atom. Note that X^- and not CN^- is the entering ligand in the $Co(CN)_5X^{3-}$–V^{2+} reactions.[26]

Table IV. Second-Order Rate Constants and Activation Parameters for V^{2+} and Fe^{2+} Reductions of Cobalt(III) Complexes[a]

	V^{2+} reductant			Fe^{2+} reductant			
Complex	k	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref
$Co(NH_3)_5C_2O_4H^{2+}$	12[b]	12.2	−13				c
$Co(NH_3)_5C_2O_4^+$	45[b]			4.3×10^{-1}			c, d
$Co(NH_3)_4C_2O_4^+$	45	12.3	−9.8	4.16×10^{-4}	18.5	−12.1	e
$Co(en)(C_2O_4)_2^-$	28[b,f]	9.3	−18	1.6×10^{-3}[f]	15.7	−17.5	g
$Co(en)(C_2O_4)_2^-$	55[h]						
$Co(C_2O_4)_3^{3-}$	420[b,i]	2.2	−31.5	11[b,i]			g, j
$Co(C_2O_4)_3^{3-}$	2.0×10^4[h]						

[a] Rate constants in M^{-1} sec^{-1} at 25° and ionic strength 1.0 M. Activation energies and entropies in kcal/mol and eu, respectively. [b] Inner-sphere path. [c] Reference 5. [d] J. Espenson, *Inorg. Chem.*, **4**, 121 (1965). [e] Reference 7. [f] Corrected for statistical factor of 2. [g] This work. [h] Outer-sphere path. [i] Corrected for statistical factor of 3. [j] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

It is instructive to compare the vanadium(II) reductions of oxalatocobalt(III) complexes with the corresponding reductions by iron(II). These results are summarized in Table IV and in Figure 1, where log k_V is plotted against log k_{Fe}.[28] It will be seen that in going through the series $Co(NH_3)_4C_2O_4^+$, $Co(en)(C_2O_4)_2^-$, and $Co(NH_3)_5C_2O_4^+$ the rate constants for reaction with V^{2+} are practically invariant, whereas the rate constants for reaction with Fe^{2+} cover a range of *ca.* 10^3. In going from $Co(NH_3)_5C_2O_4^+$ to $Co(C_2O_4)_3^{3-}$, toe rate of vanadium(II) reduction increases by a factor of *ca.* 4×10^2, whereas the increase is *ca.* 25 for iron(II). The differences in sensitivity to changes in the coordination sphere of cobalt(III) displayed by vanadium(II) and iron(II) reductions can be readily understood on the basis of the mechanisms. The reactions of $Co(NH_3)_5C_2O_4^+$, $Co(NH_3)_4C_2O_4^+$, and $Co(en)(C_2O_4)_2^-$ with vanadium(II) are predominantly substitution-controlled, inner-sphere reactions and, consequently, are quite insensitive to nonbridging ligand effects.[29] Therefore, in the series under consideration the rate constants barely change. In contrast, the corresponding reactions with iron(II) are electron-transfer-controlled, inner-sphere reactions,[7,30] with rate constants that vary considerably with the nature of the nonbridging ligands.[9] This accounts for the horizontal portion of the log k_V *vs.* log k_{Fe} plot. Now, in going from $Co(NH_3)_5C_2O_4^+$ to $Co(C_2O_4)_3^{3-}$, the vanadium(II) reaction undergoes a change in mechanism, from inner sphere to outer sphere, and an abrupt increase in rate obtains. In contrast, the iron(II) reduction of $Co(C_2O_4)_3^{3-}$ is still inner sphere, and the rate continues to increase gradually. This explains why point 4 in Figure 1 is off the horizontal line.

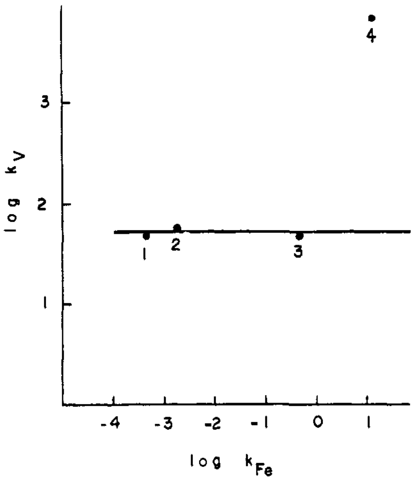

Figure 1. Plot of log k_V *vs.* log k_{Fe} for the reductions of oxalatocobalt(III) complexes: 1, $Co(NH_3)_4C_2O_4^+$; 2, $Co(en)(C_2O_4)_2^-$; 3, $Co(NH_3)_5C_2O_4^+$; 4, $Co(C_2O_4)_3^{3-}$.

It is noteworthy that the present finding of a break in the log k_V *vs.* log k_{Fe} plot when the vanadium(II) reactions change from an inner-sphere to an outer-sphere mechanism contrasts with the finding of a linear free energy relation for the vanadium(II) and iron(II) reductions of a series of chlorocobalt(III) complexes.[8] On the basis of such linear relation, and after recognizing that some of the vanadium(II) reactions were sufficiently fast to ensure the operation of an outer-sphere mechanism, Guenther and Linck suggested that all of the chlorocobalt(III) complexes that they studied reacted *via* an outer-sphere mechanism, but cautioned that their interpretation was dependent on the finding of a system which displayed a change in sensitivity to nonbridging ligands as the mechanism changed from inner sphere to outer sphere. The present results prove that such a change in sensitivity occurs, and consequently they reinforce the conclusion[8] that the vanadium(II) reductions of chlorocobalt(III) complexes proceed by an outer-sphere mechanism.

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[28] The values used in the plots are the measured second-order rate constants divided by the number of oxalate ligands in the cobalt(III) complex.

[29] T. J. Przystas and A. Haim, manuscript in preparation.

[30] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).