Kinetic Studies of Anion-Assisted Outer-Sphere Electron Transfer Reactions[1]

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Abstract: The rate of reduction of $\mathrm{Co(en)_3^{3+}}$, $\mathrm{Co(NH_3)_6^{3+}}$, and $\mathrm{Co(phen)_3^{3+}}$ by chromium(II) and vanadium(II) and of $\mathrm{Fe^{3+}}$ by $\mathrm{Co(phen)_3^{2+}}$ in the presence of perchlorate, chloride, and thiocyanate ions has been studied at 25°, 0.1 *M* $\mathrm{H^+}$, and [total anion] = 1.0 *M*. At low concentrations of the added anions, the reduction rate is given by $-\mathrm{d[Co(III)]}/\mathrm{d}t = (k_0 + k_x[\mathrm{X^-}])[\mathrm{M(II)}][\mathrm{Co(III)}]$, where k_0 is the rate constant in 1 *M* perchlorate, M is the reducing agent, and $\mathrm{X^-}$ is chloride or thiocyanate. With the possible exception of the reactions involving the $\mathrm{Co(phen)_3^{3+}}$ complex, for which a multistep mechanism in which the electron is transferred into the π-system of the ligand might obtain, the k_0 values are in good agreement with those calculated using the Marcus theory. The k_x/k_0 ratios are found to be 10^1–10^2 times larger than are predicted solely by thermodynamic considerations and are correlated with the orbital symmetries of the electron donor, the electron acceptor, and the added anion. The patterns of the $k_{\mathrm{SCN}}/k_{\mathrm{Cl}}$ ratios for outer-sphere electron transfer reactions are compared with those for inner-sphere reactions, and both are discussed in relation to the reactivity pattern for the ferricytochrome *c* reduction by chromium(II).

One of our main interests in this laboratory is the study of the reactions of cytochrome *c*, a small hemeprotein which is an important member of the mitochondrial respiratory chain.[2,3] During the course of some work on the rate of reduction of ferricytochrome *c* by chromium(II), it was found that the reaction was catalyzed by added anions in the order $\mathrm{Cl^-} < \mathrm{I^-} < \mathrm{N_3^-} \sim \mathrm{SCN^-}$.[2] This reactivity pattern is not characteristic of a mechanism in which the added anion is directly connected to the two metal centers, as occurs, for example, in the iron(II)–iron(III)[4] and chromium(II)–iron(III)[5] reactions, where added chloride ions significantly increase the reaction rate. Moreover, when both the oxidant and the reductant are relatively hard, coordination to nitrogen rather than to sulfur is favored, and azide ion (with a symmetrical $[\mathrm{M{-}NNN{-}M'}]^{4+}$ transition state) is about 10^5 times more effective than thiocyanate (with a $[\mathrm{M{-}NCS{-}M'}]^{4+}$ transition state).[6]

Since the effects of anions on the rate of the chromium(II)–ferricytochrome *c* reaction are not similar to those seen in inner-sphere electron transfer reactions, they were interpreted in terms of an outer-sphere mechanism in which the electron transfer occurs through the exposed edge of the porphyrin ring system of the hemeprotein. To test this hypothesis, it is necessary to compare the observed anion effects with those seen in other outer-sphere reactions. Unfortunately, although some data on anion-assisted outer-sphere reactions have been reported,[7,8] those studies are not sufficiently extensive to permit the formulation of general conclusions.

In order to obtain more information about the effects of anions on the rates of outer-sphere electron transfer reactions, a study of the reductions of $\mathrm{Co(phen)_3^{3+}}$, $\mathrm{Co(en)_3^{3+}}$, and $\mathrm{Co(NH_3)_6^{3+}}$ by $\mathrm{Cr^{2+}}$ and $\mathrm{V^{2+}}$ and the oxidation of $\mathrm{Co(phen)_3^{2+}}$ by $\mathrm{Fe^{3+}}$ in the presence of perchlorate, chloride, thiocyanate, and azide ions was undertaken. The choice of $\mathrm{Co(phen)_3^{3+}}$ was made to complement the previously reported $\mathrm{Fe(phen)_3^{3+}}$–$\mathrm{Fe^{2+}}$ system[8a] and to provide information about the effects of the central metal ion and of a ligand with extensive π-delocalization. The other two oxidants are complexes which have no π-delocalization at all; one of these is chelated and the other is not. Of the reducing agents, a metal which transfers a σ or $\mathrm{e_g}$ electron and two which transfer a π or $\mathrm{t_{2g}}$ electron are included. With this wide variation of the type of oxidant, anion, and reductant, we hoped to be able to reach some general conclusions concerning anion effects.

Experimental Section

Materials. Iron(III) perchlorate was recrystallized from perchloric acid. Chromium(II) perchlorate solutions were prepared by the reduction of chromium(III) perchlorate with amalgamated zinc and were stored under argon. Chromium(II) chloride solutions were prepared by dissolving high purity chromium metal (Varcaloid Chemical Co.) in hydrochloric acid under an argon atmosphere. Solutions of vanadium(II) perchlorate or chloride were made by dissolving vanadium pentoxide in perchloric or hydrochloric acid and reducing the vanadium(V) with amalgamated zinc under argon. Each vanadium(II) solution was used within 5 hr after preparation. Hexaamminecobalt(III) chloride was prepared following the procedure of Bjerrum and McReynolds.[9] The perchlorate salt was made by adding sodium perchlorate to a solution of the chloride complex until a precipitate formed. Tris(ethylenediamine)cobalt(III) chloride was prepared following the procedure of Work and McReynolds.[10] Conversion to the perchlorate salt was accomplished in the same manner as for the hexaammine complex. Tris(1,10-phenanthroline)cobalt(III) chloride was prepared following the procedure of Pfeiffer and Werdelmann.[11] The chloride salt was never isolated; instead, perchloric acid was added to the solution containing the complex until the perchlorate salt precipitated. Lithium and sodium perchlorate were made by the neutralization of lithium and sodium carbonate with perchloric

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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acid. The resulting solutions were boiled to expel carbon dioxide, and the pH was adjusted to 4–5. Sodium chloride, sodium thiocyanate, and sodium azide were used without further purification. Triply distilled water was used throughout.

Analyses. The concentration of the iron(III) stock solution was determined by passing an aliquot through an amalgamated zinc column and titrating the resulting iron(II) with standard cerium(IV) sulfate using ferroin as an indicator. The acid concentration of the iron(III) stock solution was determined by ion exchanging the solution on a Dowex 50W-X2 column in the H^+ form and subtracting the equivalents of iron(III) from the total amount of base necessary to neutralize the eluate. Chromium(II) stock solutions were analyzed for total chromium by allowing them to react with excess peroxydisulfate, boiling to decompose the remaining peroxydisulfate, adding excess standard iron(II), and titrating the nonreacted iron(II) with standard cerium(IV) using ferroin as an indicator. The acid concentration of the chromium(II) solutions was determined in the same manner as for the iron(III) solutions. The concentration of vanadium(II) solutions was taken to be the same as the vanadium(V) starting solution. The acid concentration of these solutions was assumed to be that of the starting solution minus five times the initial vanadium(V) concentration. The spectra of the hexaamminecobalt(III) and tris(ethylenediamine)cobalt(III) complexes closely matched those reported earlier for these compounds.[12] Since the tris(1,10-phenanthroline)cobalt(III) complex is not quite as well characterized, the spectral data will be given; this compound exhibited spectral maxima at 450, 350, and 330 nm with molar absorptivities, based on the compound being the dihydrate $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$,[13] of 99, 3700, and 4680 M^{-1} cm^{-1}, respectively. A cobalt analysis revealed 6.33% Co, while the calculated value is 6.31%.

Kinetic Measurements. Due to the limited solubility of $Co(phen)_3^{2+}$ in perchlorate media and the small differences between the spectra of $Co(phen)_3^{3+}$ and $Co(phen)_3^{2+}$, the kinetics of the $Co(phen)_3^{2+}$–Fe^{3+} reaction were followed by employing a method involving determination of the $Co(phen)_3^{3+}$–Co^{2+} product ratio of competitive oxidation–reduction and aquation reactions using ion-exchange and flame-photometry techniques. A 39-ml solution containing $HClO_4$–$LiClO_4$ and, when necessary, LiCl or NaSCN (total anion concentration 1 *M*) was placed in a 100-ml beaker. The iron(III) solution, usually 0.5 ml of 2×10^{-2} *M* Fe^{3+} in 1 *M* $HClO_4$, was added next. One milliliter of $Co(phen)_3^{2+}$ ($\sim 2 \times 10^{-3}$ *M*, freshly prepared by dissolving 1,10-phenanthroline and $CoCl_2 \cdot 6H_2O$ in a 3.2:1 ratio in 1 *M* sodium chloride) was added with stirring, and the competitive $Co(phen)_3^{2+}$ aquation and iron(III) oxidation reactions were allowed to proceed for 1 min. Nine milliliters of 2×10^{-1} *M* Fe^{3+} in 1 *M* perchloric acid was added, and the resulting solution was eluted on a Dowex 50W-X1, H^+ form ion-exchange column. After this solution had passed through the column, more 1 *M* perchloric acid was added until 100 ml of the eluate was collected. This fraction contained the Co^{2+} produced in the aquation reaction. The column was then washed with 6 *M* perchloric acid until a second 100-ml portion was collected; this fraction contained the $Co(phen)_3^{3+}$ produced in the oxidation-reduction reaction. For every different run, test solutions containing known amounts of Co^{2+} and $Co(phen)_3^{3+}$, first separate and then together, were eluted from the column. In all cases, at least 95% of the Co^{2+} or $Co(phen)_3^{3+}$ was recovered in the proper eluate fraction.

The solutions were analyzed for cobalt content by using a Jarrell-Ash atomic absorption-flame emission spectrophotometer. The absorptions of the samples at 240.7 nm were compared with those of standard Co^{2+} solutions. Blank corrections were made by measuring the absorption of solutions containing all the components except $Co(phen)_3^{2+}$ which had been ion-exchanged and eluted exactly the same way as the cobalt-containing samples. As with the test solutions, the total amount of cobalt recovered in the actual runs was always at least 95% of the original amount of $Co(phen)_3^{2+}$.

The kinetics of the reductions of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ by chromium(II) and vanadium(II) were followed on Cary 14 or Cary 16K recording spectrophotometers. The Cary 16K was used with 1-cm cells for reactions with half-lives of 10 min or longer, while the Cary 14 was used with a 10-cm cell equipped with a fast-stirring device for reactions with half-lives of 20 sec to 10 min, or for complexes with low solubilities in perchlorate media. The concentration of one reactant was always in such excess that the reactions were pseudo first order, and the plots of log $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the absorbances at time *t* and infinity, respectively, were linear for greater than 90% of the reaction.

The kinetics of the reduction of $Co(phen)_3^{3+}$ by vanadium(II) and chromium(II) were followed on a stopped-flow apparatus either of the Dulz-Sutin type[14] or a Durrum Model D110. The former apparatus was also used for the studies of the $Co(phen)_3^{2+}$–Fe^{3+}–N_3^- and $Co(phen)_3^{2+}$–Fe^{3+}–SCN^- systems. With chromium(II) as the reducing agent, the kinetics were independent of the order of mixing; chloride or thiocyanate in either the chromium(II) or cobalt(III) solutions gave the same results. The reaction of Fe^{3+} with N_3^- or Cl^- to form FeN_3^{2+} [15] or $FeCl^{2+}$ [16] is fairly rapid at pH 2, so that the initial fraction of the total azide or chloride in either solution was not a factor in the kinetic measurements. In the one experiment with $FeNCS^{2+}$, conditions were chosen so that the redox reaction was faster than the formation or dissociation of the iron(III) complex;[17] under these conditions, the rate of disappearance of $FeNCS^{2+}$ (at 460 nm) is a measure of the rate of the oxidation–reduction reaction. When vanadium(II) was used as the reducing agent, however, the results did depend on the order of mixing. The rates of formation and dissociation of $VNCS^+$ [18] and $VNCS^{2+}$ [19] are of the same order of magnitude as the oxidation–reduction reaction, and for this reason the thiocyanate was added to the vanadium reactant solution. The concentration of $VNCS^+$ was made high enough so that the oxidation-reduction reaction was completed before any vanadium–thiocyanate equilibrium shift could complicate the analysis of the data. In chloride media, the chloride concentration in both the vanadium(II) and cobalt(III) solutions was kept the same; although no quantitative data were obtained, it will be shown later than the vanadium(II)–chloride equilibrium obtains in about the same time scale as the corresponding thiocyanate equilibrium. With either flow system, kinetic data were treated by a least-squares program which analyzed the results in terms of a first-order kinetic scheme.

Results

I. Iron(III) Oxidations. The kinetic data for the Fe^{3+}–$Co(phen)_3^{2+}$–X^- ($X^- = Cl^-, SCN^-, ClO_4^-$) system are presented in Table I. The rate constants were obtained in the following manner. When $Co(phen)_3^{2+}$ is added to a solution of Fe^{3+} in $HClO_4$, two reactions occur simultaneously

$$Co(phen)_3^{2+} + 3H^+ \xrightarrow{k_{aq}} Co^{2+} + 3Hphen^+ \tag{1}$$

$$Co(phen)_3^{2+} + Fe^{3+} \xrightarrow{k_{ox}} Co(phen)_3^{3+} + Fe^{2+} \tag{2}$$

For this scheme, eq 3 obtains provided that H^+ and

$$\frac{[Co^{2+}]}{[Co(phen)_3^{3+}]} = \frac{k_{aq}}{k_{ox}[Fe(III)]} \tag{3}$$

Fe^{3+} are present in excess. The value of k_{aq} under the conditions used in the kinetic studies, as first measured by Wilkins, *et al.*,[20] and confirmed by us, is 0.174 sec^{-1} and is independent of the acid concentration. The values of k_{ox} in 1 *M* perchlorate calculated from eq 3 are 5.3×10^2 and 1.0×10^3 M^{-1} sec^{-1} at 1.0 and 0.01 *M* H^+, respectively. This variation in the second-order rate constant is small (a twofold increase for a 100-fold decrease in acidity) and is most likely a medium effect;[21] it will be considered to be inconsequential, at least over the range studied.

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Table I. Chloride and Thiocyanate Dependence of the Rate Constants for the Co(phen)$_3{}^{2+}$–Fe^{3+} Reaction[a]

[H$^+$], *M*	[X$^-$], *M*	10^5[Co^{2+}],[b] *M*	10^5[Co^{3+}],[b] *M*	$10k_{ox}\cdot$ [Fe(III)], sec^{-1}
		[X$^-$] = ClO$_4{}^-$		
1.0	1.0	1.07	1.53	2.5[c]
1.0	1.0	0.91	1.23	2.4[c]
1.0	1.0	0.67	1.92	5.0[d]
1.0	1.0	1.19	0.92	1.3
1.0	1.0	1.25	1.02	1.4
1.0	1.0	1.22	1.00	1.4
0.01	1.0	0.99	1.36	2.4
0.01	1.0	0.97	1.40	2.5
0.01	1.0	0.88	1.29	2.5
0.01	1.0	0.87	1.27	2.5
		[X$^-$] = Cl$^-$ [e]		
1.0	0.1	0.69	1.55	3.9
1.0	0.1	0.68	1.50	3.8
1.0	0.1	0.74	1.54	3.6
1.0	0.1	0.67	1.52	3.9
1.0	0.2	0.49	1.52	5.3
1.0	0.2	0.49	1.58	5.6
1.0	0.3	0.44	1.61	6.4
1.0	0.3	0.42	1.56	6.5
		[X$^-$] = SCN$^-$ [f]		
0.01	6.0[g]	0.45	1.48	5.7
0.01	6.0	0.53	1.48	4.9
0.01	6.0	0.48	1.54	5.6
0.01	6.0	0.48	1.50	5.5
0.01	10.0	0.37	1.56	7.3
0.01	10.0	0.41	1.56	6.6
0.01	12.0	0.34	1.67	8.5
0.01	12.0	0.42	1.71	7.2

[a] At 25° and [Fe(III)] = 2.46 × 10^{-4} *M*, except for *c* and *d*. [b] The "background" or blank values have already been subtracted. [c] [Fe(III)] = 4.90 × 10^{-4} *M*. [d] [Fe(III)] = 9.56 × 10^{-4} *M*. [e] ([Cl$^-$] + [ClO$_4{}^-$]) = 1.0 *M*. [f] ([SCN$^-$] + [ClO$_4{}^-$]) = 1.0 *M*. [g] The values here are 10^5[SCN$^-$], *M*.

Table II. Azide Dependence of the Rate Constants for the Co(phen)$_3{}^{2+}$–Fe^{3+} Reaction[a,b]

10^3[Co(II)], *M*	[H$^+$], *M*	[HN$_3$], *M*	k_{obsd}, sec^{-1}
1.32	0.01	0.05	4.1
1.08	0.01	0.05	3.3
1.08	0.01	0.10	3.1
1.08	0.01	0.20	2.9
1.14	0.02	0.06	2.7
1.14	0.02	0.10	2.8
1.14	0.02	0.20	3.0
1.16	0.015	0.10	3.0
1.16	0.01	0.15	3.3
1.16	0.015	0.20	3.2
1.16	0.01	0.20	3.5
1.21	0.01	0.05	2.7
1.21	0.01	0.08	3.3
1.21	0.01	0.25	3.5
1.21	0.01	0.25	3.9

[a] At 25°, 460 nm, and 1.0 *M* Cl$^-$. [b] [Fe(III)] is always ~10% of [Co(II)].

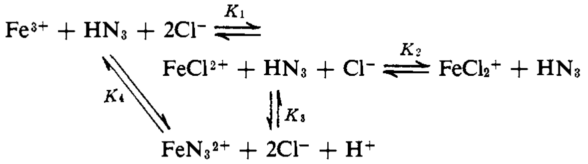
The variation in rate with added chloride or thiocyanate ions is adequately described by eq 3, but now

$$k_{ox} = (k_0 + k_x[X^-])/(1 + K_x[X^-]) \qquad (4)$$

where k_0 is the (second-order) rate constant in the absence of added anions and K_x is the equilibrium constant for the formation of the FeX^{2+} complex (which occurs relatively rapidly under the conditions of these experiments). The values of K_x are 5.2 and 140 M^{-1} when X$^-$ = Cl$^-$ and SCN$^-$, respectively.[17,22] Plots of $k_{ox}(1 + K_x[X^-)]/[Fe(III)]$ *vs.* [X$^-$] were linear with slopes of 2.0 × 10^4 M^{-2} sec^{-1} when X$^-$ = Cl$^-$ and 2.0 × 10^7 M^{-2} sec^{-1} when X$^-$ = SCN$^-$. As a check, one experiment done with the stopped-flow yielded a value of 1.8 × 10^7 M^{-2} sec^{-1} for X$^-$ = SCN$^-$ under the same conditions.

The data for the Fe^{3+}–Co(phen)$_3{}^{2+}$–N$_3{}^-$ system which are presented in Table II require a more complex interpretation. Although the reaction is first order with respect to the cobalt(II) concentration, the second-order rate constant appeared to increase with decreasing cobalt concentration at the lower cobalt concentrations. By observing the reaction at 510 nm (an absorbance maximum of Fe(phen)$_3{}^{2+}$), it was learned that the apparent rate constant increase was the result of interference from the formation of Fe(phen)$_3{}^{2+}$ from the reaction products. As long as the cobalt(II) concentration was greater than 5 × 10^{-4} *M*, however, the primary electron transfer reaction was complete before any appreciable Fe(phen)$_3{}^{2+}$ formation could interfere with the "infinity" absorbance values.

Since the azide dependence was measured in 1 *M* chloride media, there are several iron(III) species which must be considered. At 0.01 *M* H$^+$, the interconversion of these species is rapid, so that the system may be described by the scheme



$$\begin{tikzcd}
Fe^{3+} + HN_3 + 2Cl^- \arrow[r, shift left, "K_1"] \arrow[dr, shift left] & \arrow[l, shift left] FeCl^{2+} + HN_3 + Cl^- \arrow[r, shift left, "K_2"] \arrow[d, shift right] & \arrow[l, shift left] FeCl_2{}^+ + HN_3 \\
& FeN_3{}^{2+} + 2Cl^- + H^+ \arrow[ul, shift left, "K_4"] \arrow[u, shift right, "K_3"'] &
\end{tikzcd} \qquad (5)$$

The Co(phen)$_3{}^{2+}$ can react with any of the four iron(III) species, so that

$$-\frac{d[Co(II)]}{dt} = (k_0[Fe^{3+}] + k_1[FeCl^{2+}] + k_2[FeCl_2{}^+] + k_3[FeN_3{}^{2+}])[Co(phen)_3{}^{2+}] \qquad (6)$$

The above expression can be rearranged to eq 7 by using the parameters defined in eq 5

$$-\frac{d[Co(II)]}{dt} = \frac{k_0 + k_1K_1[Cl^-] + k_2K_1K_2[Cl^-]^2 + k_3\left[\dfrac{K_1[HN_3]}{K_3[H^+]}\right]}{\beta} \times [Fe(III)][Co(phen)_3{}^{2+}] \qquad (7)$$

where $\beta = 1 + K_1[Cl^-] + K_1K_2[Cl^-]^2 + (K_1[HN_3]/K_3[H^+])$. Since [Co(II)] is in excess and [Cl$^-$] = 1.0 *M*, a plot of (βk_{obsd}/[Co(II)]) *vs.* ($K_1[HN_3]/K_3[H^+]$) should be linear with an intercept of ($k_0 + k_1K_1[Cl^-] + k_2K_1K_2[Cl^-]^2$) and a slope of k_3. Such a plot is shown in Figure 1 using K_1, K_2, and K_3 equal to 5.2, 1.3, and 8.8 M^{-1}, respectively.[22,23] The slope of the line is 3.9 × 10^3 M^{-1} sec^{-1}, which when multiplied by 8.6 × 10^3 M^{-1} (the equilibrium constant for the Fe^{3+} + N$_3{}^-$ $\rightleftharpoons$ FeN$_3{}^{2+}$ reaction) yields a value for the third-

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(22) J. K. Rowley and N. Sutin, *J. Phys. Chem.*, 74, 2043 (1970).

(23) The number was calculated from Fe^{3+} + Cl$^-$ $\rightleftharpoons$ FeCl^{2+}, K = 5.2 (ref 22), and Fe^{3+} + HN$_3$ $\rightleftharpoons$ FeN$_3{}^{2+}$ + H$^+$, K = 0.591 (ref 15).

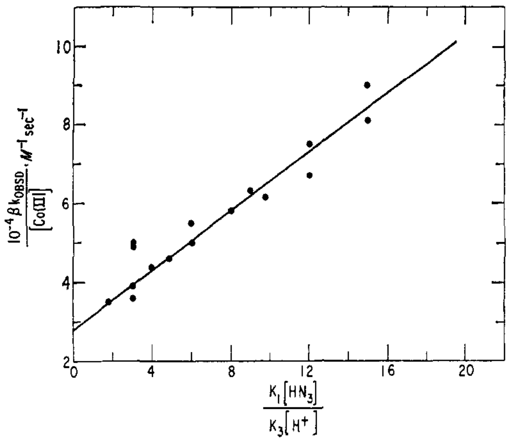

Figure 1. Plot, suggested by eq 7, of $10^{-4}\beta k_{obsd}/[Co(II)]$ *vs.* $K_1[HN_3]/K_3[H^+]$: 25°, $[Cl^-] = 1.0\ M$, 460 nm.

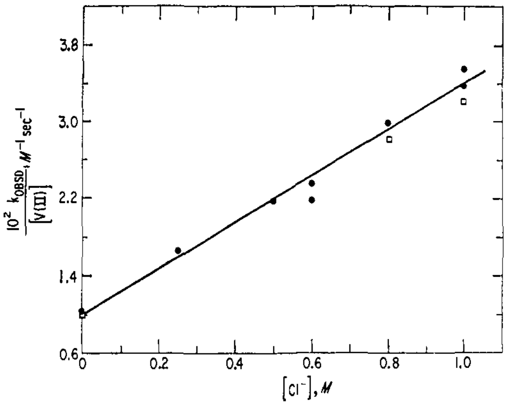

Figure 2. Plot of $10^2k_{obsd}/[V(II)]$ *vs.* $[Cl^-]$ for the V^{2+}–Cl^-–$Co(NH_3)_6^{3+}$ reaction system: 25°, 0.1 M H^+, ($[Cl^-] + [ClO_4^-] = 1.0\ M$), 472 nm, circles are $[V(II)] = 5 \times 10^{-2}\ M$, squares are $[V(II)] = 2 \times 10^{-2}\ M$.

order rate constant of $3.4 \times 10^7\ M^{-2}\ sec^{-1}$. The intercept is $2.8 \times 10^4\ M^{-1}\ sec^{-1}$. The value of k_0 at 0.01 M H^+ is $1.0 \times 10^3\ M^{-1}\ sec^{-1}$, and the value of $k_1K_1[Cl^-]$ ($\equiv k_{Cl}[Cl^-]$) at 1.0 M H^+ and 1.0 M Cl^- is $2.0 \times 10^4\ M^{-1}\ sec^{-1}$. The difference between these numbers and the intercept cannot be unambiguously assigned to the $k_2K_1K_2[Cl^-]^2$ path, however, It must be remembered that there was a variation in the k_0 term with acidity; it is therefore not altogether proper to ascribe the difference between the rates to the $[Cl^-]^2$ path. In the absence of additional data, it may be concluded that the flame photometry–ion-exchange and the stopped-flow experiments yield consistent values for ($k_0 + k_1K_1[Cl^-]$) and that the $k_2K_1K_2[Cl^-]^2$ term is not large.

II. Vanadium(II) Reductions. The results for the V^{2+}–$Co(NH_3)_6^{3+}$–X^- system ($X^- = ClO_4^-$, Cl^-, and SCN^-) are presented in Table III. It can be seen that the reactions are first order with respect to the reagent in excess, and one run was done to show that the reaction was independent of wavelength. The data for the chloride dependence can be treated by eq 4, with $k_{obsd} = k_{ox}[V(II)]$ or $k_{ox}[Co(III)]$, depending upon which reactant is in excess. Rather than repeat several very similar graphs and tables, the data for the representative V^{2+}–$Co(NH_3)_6^{3+}$–Cl^- system are plotted in Figure 2, and hereafter only the results of such plots for the other chloride systems with both chromium(II) and vanadium(II) as the reducing agent will be given. (The one exception will be the V^{2+}–$Co(phen)_3^{3+}$–Cl^- reaction because this reaction exhibits a slightly different behavior.) As shown in Figure 2, the value of k_0 is $1.0 \times 10^{-2}\ M^{-1}\ sec^{-1}$ and k_{Cl} is $2.4 \times 10^{-2}\ M^{-2}\ sec^{-1}$.

Table III. Rate Constants for the V^{2+}–$Co(NH_3)_6^{3+}$–X^- Reaction[a]

$10^2[V(II)]$, M	$[Cl^-]$, M	$10^2[SCN^-]$, M	10^3k_{obsd}, sec^{-1}
5.07, 5.02	1.0		1.8, 1.7[b]
2.01	1.0		0.64
5.02	0.9		1.7
5.02	0.8		1.5
2.02	0.8		0.57
5.04, 5.15	0.6		1.1, 1.2
5.12	0.5		1.1
2.02	0.5		0.45
5.15	0.4		0.96
5.08	0.25		0.82
5.13	0.0		0.53
2.02	0.0		0.21
2.03	1.0	2.0	27[c]
0.541	1.0	2.0	11
2.03	1.0	1.6	19
0.541	1.0	1.6	7.9
2.03	1.0	1.2	12
2.03, 1.98	1.0	1.0	8.3, 8.3,[d] 9.2
2.03, 1.98	1.0	0.6	4.4, 4.2
2.03, 1.98	1.0	0.4	3.5, 2.9

[a] At 25°, 0.1 M H^+, ($[ClO_4^-] + [Cl^-] = 1.0\ M$), $[Co(III)]_0$ ~10% of [V(II)] or $[SCN^-]$, whichever is smaller. Each run is the average of two to five replicate measurements. [b] ($[Cl^-] + [ClO_4^-]$) dependence at 472 nm. [c] ($[Cl^-] + [SCN^-]$) dependence at 300 nm, except for *d*. [d] 468 nm.

It can be seen from the tables that the reaction rate increases with added thiocyanate at a faster rate than would be expected for a strictly first-order dependence, so a term in $[SCN^-]^2$ must be added. Since all vanadium equilibria are established rapidly compared with the electron-transfer reactions

$$-\frac{d[Co(III)]}{dt} = (k_0^*[V^{2+}] + k_1[VNCS^+] + k_2[V(NCS)_2])[Co(III)] \quad (8)$$

This expression can be rearranged to

$$-\frac{d[Co(III)]}{dt} = \left[k_0^* + \frac{k_{SCN}[SCN^-]_0}{(1 + K_{SCN}[V^{2+}])} + \frac{k_{SCN}'[SCN^-]_0^2}{(1 + K_{SCN}[V^{2+}])^2}\right]\left[\frac{[V(II)][Co(III)]}{(1 + K_{SCN}[SCN^-]_f)}\right] \quad (9)$$

where k_0^* is ($k_0 + k_{Cl}$), the rate constant in 1 M chloride, $[SCN^-]_f$ and $[SCN^-]_0$ are the free and total thiocyanate, $[V^{2+}]$ and [V(II)] are the free and total vanadium(II), respectively, and K_{SCN} is the formation constant for the $VNCS^+$ complex. It has been assumed in the derivation that $K_{SCN}K_{SCN}'[SCN^-]_f^2 \ll 1$ (where K_{SCN}' is the formation constant for the $V(NCS)_2$ complex); if one makes a generous estimate of the unknown K_{SCN}' value as being 20% of the known $K_{SCN} = 28\ M^{-1}$,[19] then at the average $[SCN^-]$ used (0.01 M)

$$\frac{[V(NCS)_2]}{[VNCS^+]} = \frac{K_{SCN}'[SCN^-]}{K_{SCN}} = 0.002$$

so that the approximation seems justified.

A plot of $(k_{obsd}(1 + K_{SCN}[SCN^-]_0)/[V(II)]) - k_0^*][1 + K_{SCN}[V^{2+}]]/[SCN^-]_0$ *vs.* $[SCN^-]_0$ is shown in Figure 3 for the V^{2+}–$Co(NH_3)_6{}^{3+}$–SCN^- system. As with the chloride dependence, this plot is representative of the other V^{2+}– and Cr^{2+}–SCN^- systems (except for the V^{2+}–$Co(phen)_3{}^{3+}$–SCN^- reaction), so that again only the results will be given for the other systems. From Figure 3, it is seen that the intercept, or k_{SCN} value, is 2.4×10^1 M^{-2} sec^{-1}, and the slope at $[V(II)] = 2.0 \times 10^{-2}$ M is 5.0×10^3 M^{-2} sec^{-1}. The slope is $k_{SCN}'/(1 + K_{SCN}[V^{2+}])$, so that k_{SCN}' is 7.8×10^3 M^{-3} sec^{-1}. This value is in good agreement with that obtained at $[V(II)] = 5.0 \times 10^{-3}$ M, namely, 8.4×10^3 M^{-3} sec^{-1}, as shown in the figure.

It would seem to be appropriate at this time to explain why the thiocyanate dependences were done in 1 M chloride instead of 1 M perchlorate media. The early thiocyanate studies were done on the V^{2+}–$Co(en)_3{}^{3+}$–SCN^- system in 1 M perchlorate media. However, it was found that the data had a large scatter and were not reproducible. The cause of the scatter was never precisely determined. One possible cause could have been impurities in the $NaClO_4$ solution, but these impurities would have to be "activated" only by thiocyanate, as the chloride dependence in perchlorate media was very reproducible. Another explanation is that thiocyanate accelerates the rate of the vanadium(II)–perchlorate reaction. Since the reaction of V^{2+} and $Co(en)_3{}^{3+}$ was found to be first order with respect to the reagent in excess over the range of 0.00069–0.048 M in 1 M chloride, the thiocyanate dependence was measured in this medium and the cause of the data scatter in perchlorate media was not investigated further.

The data for the V^{2+}–$Co(phen)_3{}^{3+}$–SCN^- and V^{2+}–$Co(phen)_3{}^{3+}$–Cl^- systems are presented in Tables IV and V, respectively. Because of the rapid rate of these reactions, they will be considered separately from the other systems. When the oxidizing agents were $Co(NH_3)_6{}^{3+}$ or $Co(en)_3{}^{3+}$, the reactions were slow enough so that the equilibrium between the V^{2+} and the V^{3+} produced in the reaction and their corresponding complexes was maintained. With $Co(phen)_3{}^{3+}$ as the oxidizing agent, the reactions $V^{2+} + SCN^-, Cl^- \rightleftharpoons VNCS^+, VCl^+$ and the analogous vanadium(III) reactions occur on the same time scale as the oxidation–reduction reactions, so that several restrictions are imposed. For the thiocyanate dependence shown in Table IV, it was necessary to add the thiocyanate to the vanadium(II) solution before mixing in the flow apparatus. If the thiocyanate was placed in the cobalt(III) solution, the observed rate was more like the one seen without thiocyanate except that the reaction accelerated with time, indicating concurrent $VNCS^+$ complex formation. The kinetics were therefore studied with particular $[VNCS^+]$ at time zero, and the concentration of this species was made high enough so that the reaction was pseudo-first-order and essentially complete before the $VNCS^+$ dissociation reaction[19] could complicate the kinetics. The obvious disadvantage of forcing the reaction to be so rapid was that the range of concentrations studied had to be small; however, in the limited range possible, the kinetics are consistent with a value for the third-order

Table IV. Rate Constants for the V^{2+}–$Co(phen)_3{}^{3+}$–SCN^- Reaction[a]

$10^3[V(II)]$,[b] M	$10^3[SCN^-]$,[b] M	$10^4[VNCS^+]$,[c] M	k_{obsd}, sec^{-1}	$10^{-7}k_{SCN}$, M^{-2} sec^{-1} [d]
0.61	10.0	0.70	145	5.7
1.02	4.0	0.55	137	6.6
1.02	10.0	1.10	216	5.3
2.38	4.0	1.15	285	6.5
3.06	2.0	0.80	225	7.1
3.06	4.0	1.45	376	6.8
1.02	10.0	1.10	101	2.5[e]
2.04	4.0	1.00	82	2.2[e]
2.04	8.0	1.85	154	2.3[e]
3.08	4.0	1.45	137	2.5[e]

[a] At 25°, 0.1 M H^+, 310 nm, and $[Co(III)]_0 \approx 2 \times 10^{-5}$ M (after mixing), 1.0 M Cl^- except for *e*. [b] Before mixing. [c] After mixing. [d] k_{SCN} is $K_{SCN}(k_{obsd} - k_0^*[V^{2+}])/[VNCS^+]$, M^{-2} sec^{-1}, where k_0^* is the rate constant without added thiocyanate. Each run is the average of six to eight replicate runs. [e] In 1 M ClO_4^- media.

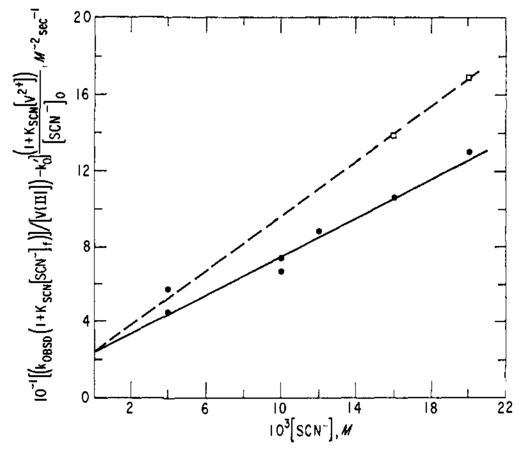

Figure 3. Plot, suggested by eq 9, of $10^{-1}[(k_{obsd}(1 + K_{SCN}[SCN^-]_f)/[V(II)]) - k_0'](1 + K_{SCN}[V^{2+}])/[SCN^-]_0)$ *vs.* $10^3[SCN^-]$ for the V^{2+}–SCN^-–$Co(NH_3)_6{}^{3+}$ system: 25°, 0.1 M H^+, 300 nm 1.0 M Cl^-. Circles are $[V(II)] = 2 \times 10^{-2}$ M; squares are $[V(II)] = 5 \times 10^{-3}$ M.

Table V. Rate Constants for the V^{2+}–$Co(phen)_3{}^{3+}$–Cl^- Reaction[a]

$10^2[V(II)]$, M	$[Cl^-]$, M	$10^{-1}k_{obsd}$, sec^{-1}
2.01	1.0	30[b]
2.03	1.0	28,[c] 29[d]
0.409, 0.411, 0.408	1.0	5.9, 6.2,[d] 6.6[e]
0.391, 0.423	0.9	4.8, 4.7
2.01	0.8	22
0.421	0.8	3.8
0.408	0.75	3.6
2.07	0.6	17
0.404	0.6	3.2
2.06	0.5	14[c]
0.424, 0.419	0.5	3.0, 2.9
2.01	0.4	13
0.406	0.4	2.6
2.03	0.25	11
0.397, 0.412	0.25	1.9, 2.1
2.02	0.1	8.7
0.422, 0.413	0.1	1.7, 1.7
2.05, 2.01	ClO_4^-	7.6, 8.2
0.431, 0.421, 0.440	ClO_4^-	1.7, 1.6, 1.5[e]

[a] At 25°, 0.1 M H^+, $([Cl^-] + [ClO_4^-]) = 1.0$ M, and $[Co(III)]_0 \approx 2 \times 10^{-5}$ M. Each run is the average of six to eight replicate measurements. [b] 310 nm, except *c* and *d*. [c] 350 nm. [d] 390 nm. [e] $[H^+] = 0.45$ M.

Table VI. Rate Constants for Anion-Assisted Outer-Sphere Electron Transfer Reactions[a]

Reactants	k_0, M^{-1} sec^{-1}	k_{Cl}, M^{-2} sec^{-1}	k_{SCN},[d] M^{-2} sec^{-1}	k_{SCN}',[d] M^{-3} sec^{-1}
$Co(phen)_3^{2+}$–Fe^{3+}	5.3×10^{2} [b] 1.0×10^{3} [c]	2.0×10^{4} [b]	2.0×10^{7} [c]	
Cr^{2+}–$Co(NH_3)_6^{3+}$	1.0×10^{-3} 8.8×10^{-5} [e] 7.2×10^{-3} [f]	1.1×10^{-2} 1.2×10^{-2} [e] 6.0×10^{-1} [f]	7.3×10^{-1}	1.4×10^{1}
Cr^{2+}–$Co(en)_3^{3+}$	3.4×10^{-4} $\sim 2 \times 10^{-5}$ [g]	1.5×10^{-3}	3.2×10^{-1}	1.5
Cr^{2+}–$Co(phen)_3^{3+}$	3.0×10^{1}	1.7×10^{2}	2.2×10^{5} 8.0×10^{4} [j] 3.8×10^{4} [k]	
V^{2+}–$Co(NH_3)_6^{3+}$	1.0×10^{-2} 4.4×10^{-3} [h] 3.7×10^{-3} [f]	2.4×10^{-2} 3.5×10^{-2} [h] 2.1×10^{-2} [f]	2.4×10	8.1×10^{3}
V^{2+}–$Co(en)_3^{3+}$	7.2×10^{-4} 2.0×10^{-4} [i]	1.9×10^{-3}	2.4	5.6×10^{2}
V^{2+}–$Co(phen)_3^{3+}$	3.8×10^{3}	6.0×10^{3}	6.3×10^{7} 2.3×10^{7}	

[a] At 25°, ($[ClO_4^-] + [Cl^-] + [SCN^-]$) = 1.0 M, and $[H^+]$ = 0.1 M, unless noted. [b] $[H^+]$ = 1.0 M. [c] $[H^+]$ = 0.01 M. [d] $[SCN^-]$ dependence in 1 M Cl^- unless noted. [e] Reference 8b, $\mu = 0.4$ M, $[H^+]$ = 0.1 M. [f] Reference 7c, $\mu = 2.6$ M, acid concentration not specified. [g] Reference 12, $\mu = 0.4$ M, $[H^+]$ = 0.1 M. [h] Reference 7a, $\mu = 0.4$ M, $[H^+]$ = 0.1 M. [i] Reference 12, $\mu = 1.0$ M, $[H^+]$ = 0.5 M. [j] 0.5 M Cl^- and 0.5 M ClO_4^-. [k] 1.0 M ClO_4^-.

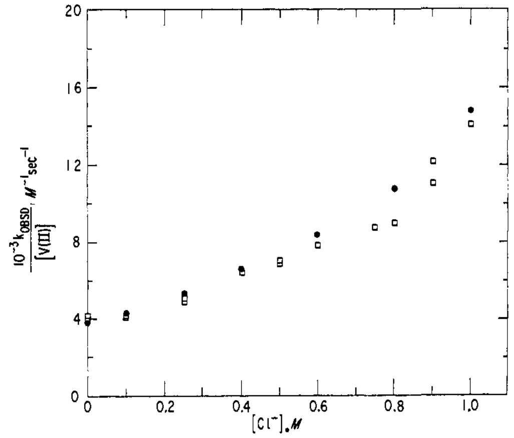

Figure 4. Plot of $10^{-3}k_{obsd}/[V(II)]$ *vs.* $[Cl^-]$ for the V^{2+}–Cl^-–$Co(phen)_3^{3+}$ system: 25°, 0.1 M H^+, ($[Cl^-] + [ClO_4^-]$ = 1.0 M), 310 nm, circles are $[V(II)] = 2 \times 10^{-2}$ M, squares are $[V(II)] = 4 \times 10^{-3}$ M.

rate constant, k_{SCN}, of 6.3×10^{7} M^{-2} sec^{-1} in 1 M chloride and 2.3×10^{7} M^{-2} sec^{-1} in 1 M perchlorate. (The reason that the thiocyanate dependence can be done in 1 M perchlorate for $Co(phen)_3^{3+}$ and not for $Co(en)_3^{3+}$ or $Co(NH_3)_6^{3+}$ is that in the former case the degassed thiocyanate solution is added to the degassed vanadium(II) in 1 M perchlorate just prior to being used on the flow apparatus, so that the time of contact between the SCN^-, ClO_4^-, and V^{2+} is of the order of 10 min and not 10 hr as is the case for some of the $Co(NH_3)_6^{3+}$ or $Co(en)_3^{3+}$ reactions.)

The V^{2+}–$Co(phen)_3^{3+}$–Cl^- system also presented some difficulties. As shown in Table V, the reaction is first order with respect to the excess reagent (vanadium(II)) and is relatively independent of acidity. The reaction is independent of wavelength in the region of 300–400 nm but this independence does not extend to the 240–270-nm region of the spectrum. Blank experiments showed that V^{2+} and Zn^{2+} (present from the reduction of vanadium(V) by amalgamated zinc) react with the phenanthroline liberated from the aquation of the $Co(phen)_3^{2+}$. Since the absorbance changes from these Zn^{2+}– or V^{2+}–phen reactions are large compared with the $Co(phen)_3^{3+}$–$Co(phen)_3^{2+}$ changes in this wavelength region, a small amount of free phenanthroline can cause a severe distortion in the absorbance *vs.* time plots for the oxidation–reduction reaction. However, as long as the kinetics of the latter reaction were studied above 300 nm, no interference from side reactions was observed.

When vanadium(II) in perchlorate was mixed with $Co(phen)_3^{3+}$ in chloride media, the resulting curve of absorbance *vs.* time was not first order, probably because the $V^{2+} + Cl^- \rightleftharpoons VCl^+$ reaction was occurring on the same time scale as the oxidation–reduction reaction. Consequently, the Cl^-–ClO_4^- ratio in both the V^{2+} and $Co(phen)_3^{2+}$ solutions was kept the same in order to minimize any VCl^+ equilibration reactions. The plot of the kinetic data in Figure 4 showed a mixed first- and second-order dependence on chloride, with the intercept or k_0 value of 3.8×10^{3} M^{-1} sec^{-1}. After allowance was made for the VCl^+ equilibrations, the value for the k_{Cl} term was found to be 6.0×10^{3} M^{-2} sec^{-1}; it was not possible to establish a reliable value for the k_{Cl}' term.

III. Chromium(II) Reductions. The data for the Cr^{2+}–$Co(NH_3)_6^{3+}$–X^- and Cr^{2+}–$Co(en)_3^{3+}$–X^- reactions were analyzed in a manner similar to that used for the corresponding vanadium(II) reductions, and the derived rate constants are given in Table VI.

There is one significant difference between the vanadium(II) and chromium(II) reductions of the $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ complexes. The $VNCS^+$ reduction was shown to be independent of the wavelength chosen; this is not true of the $CrNCS^+$ reduction. At 280–320 nm, the region of the absorbance maximum for the formation of the $CrNCS^{2+}$ product, the observed absorbance change *vs.* time was much slower and was not first order with respect to the chromium(II) concentration, while at 470 nm, the reaction was well-behaved. There are at least two possible explanations. The $[CrOCr]^{4+}$ dimer absorbs very strongly in this region,[24] so that a small amount of air

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(24) J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959).

Table VII. Comparison of Theoretical and Observed Rate Constants[a]

Reactants	Exchange rates,[b] M^{-1} sec^{-1}	E^0, V[b,c]	k_{calcd}, M^{-1} sec^{-1}	k_{obsd}, M^{-1} sec^{-1}
$Co(phen)_3^{2+}$–Fe^{3+}	5.0, 4.0	+0.42, +0.74	1.5×10^3	5.3×10^2
Cr^{2+}–$Co(NH_3)_6^{3+}$	$\leq 2 \times 10^{-5}$, $\leq 10^{-9}$	−0.41, +0.1	$\leq 1.6 \times 10^{-3}$	1.0×10^{-3}
Cr^{2+}–$Co(en)_3^{3+}$	$\leq 2 \times 10^{-5}$, 2×10^{-5}	−0.41, −0.240	$\leq 5.1 \times 10^{-4}$	3.4×10^{-4}
Cr^{2+}–$Co(phen)_3^{3+}$	$\leq 2 \times 10^{-5}$, 5.0	−0.41, +0.42	$\leq 1.1 \times 10^4$	3.0×10^1
V^{2+}–$Co(NH_3)_6^{3+}$	1.0×10^{-2}, $\leq 10^{-9}$	−0.255, +0.1	$\leq 2.3 \times 10^{-3}$	1.0×10^{-2}
V^{2+}–$Co(en)_3^{3+}$	1.0×10^{-2}, 2×10^{-5}	−0.255, −0.240	5.8×10^{-4}	7.2×10^{-4}
V^{2+}–$Co(phen)_3^{3+}$	1.0×10^{-2}, 5.0	−0.255, +0.42	2.3×10^4	3.8×10^3
V^{2+}–$Co(bipy)_3^{3+}$	1.0×10^{-2}, 7.0	−0.255, +0.37	7.6×10^3	1.1×10^3 [d]

[a] At 25° and $\mu = 1.0$ *M*, except *d*. [b] The exchange rates and potentials are in the same order as the reactants. [c] Written for both reactants as $M^{3+} + e^- \rightarrow M^{2+}$. [d] $\mu = 2.0$ *M*: R. Davis, M. Green, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1171 (1972).

could result in the unusual absorbance changes observed. In addition, if the product of the oxidation–reduction reaction by the $[SCN^-]^2$ path is a $Cr(NCS)_2^+$ complex, then it would not be unreasonable to expect that the absorbance change at 280–320 nm could be the result of $CrNCS^{2+}$ formation as the product of the $[SCN^-]$ path of the oxidation–reduction reaction and a slower change as the product of $Cr^{2+} + Cr(NCS)_2^+ \rightarrow CrSCN^{2+} + Cr^{2+} + SCN^- \rightarrow CrNCS^{2+} + Cr^{2+} + SCN^-$. Such a multistep reaction could account for the observed kinetic behavior.

The data for the Cr^{2+}–$Co(phen)_3^{3+}$–Cl^- and Cr^{2+}–$Co(phen)_3^{3+}$–SCN^- systems differed from the corresponding V^{2+}–$Co(phen)_3^{3+}$ reactions in that the $Cr^{2+} + X^- \rightleftharpoons CrX^+$ equilibria are established very rapidly and the CrX^{2+} products are very inert, at least on the time scale for the oxidation–reduction reactions. The problem of a Zn^{2+} + phen reaction remained, so the reaction was studied at 300–400 nm, where it was wavelength independent and first order with respect to the chromium(II) concentration. The chromium(II) concentration had to be kept high enough so that the aquation of the $Co(phen)_3^{2+}$ product (0.174 sec^{-1}) would not interfere.

Discussion

Table VI presents a summary of the rate constants obtained in this work as well as those reported by others for the same systems. It can be seen that the agreement with data from the other studies is reasonable after allowance is made for the different ionic strengths used. The only point of disagreement with other work is for the V^{2+}–$Co(en)_3^{3+}$ system, where Candlin, Halpern, and Trimm[12] reported a value of 2.0×10^{-4} M^{-1} sec^{-1} at 0.5 *M* H^+ and 1.0 *M* ClO_4^-. For the same reaction at 0.1 *M* H^+ and 1.0 *M* ClO_4^-, we obtain a value of 7.2×10^{-4} M^{-1} sec^{-1}; the reaction is relatively insensitive to the acid concentration, so the difference cannot be rationalized on this basis. The rate constant measured in our experiment was not only reproducible in 1 *M* perchlorate but was also consistent with the runs done at various Cl^-–ClO_4^- ratios (the plot of $k_{\text{obsd}}/[V(II)]$ *vs.* $[Cl^-]$ was a straight line with an intercept of 7.2×10^{-4} M^{-1} sec^{-1}). Also, the rate was independent of whether $Co(en)_3^{3+}$ or V^{2+} was present in tenfold excess. In view of these considerations, we will use 7.2×10^{-4} M^{-1} sec^{-1} as the rate constant for the V^{2+}–$Co(en)_3^{3+}$ reaction.

Comparison of Uncatalyzed Rates with the Marcus Theory. The rate constants measured in 1 *M* perchlorate media can be compared to those predicted by the Marcus theory.[25] The "cross-reaction" relationship is used

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{10}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{11}$$

where k_{12} is the rate constant and K_{12} is the equilibrium constant for a reaction such as

$$Co(en)_3^{3+} + V^{2+} \longrightarrow Co(en)_3^{2+} + V^{3+} \tag{12}$$

k_{11} and k_{22} are the rate constants for the $Co(en)_3^{3+/2+}$ and $V^{3+/2+}$ exchange reactions, and *Z*, the frequency of collisions between two uncharged particles in solution, is 10^{11} M^{-1} sec^{-1}. The theoretical values for the rate constants are compared with the values obtained in this work in Table VII. The comparison for the closely related V^{2+}–$Co(bipy)_3^{3+}$ reaction is also included in this table. From the table, it is evident that the theoretical and observed values are in good agreement; possible exceptions are the $Co(phen)_3^{3+}$ reactions, which tend to proceed more slowly than predicted.

A large difference between the predicted and observed rate constants for a reaction involving cobalt(III) is not unusual. Such differences generally have the observed rate constant slower than the theoretical value, and one explanation which is invoked to account for this is the associated multiplicity change. The cobalt(III) reactants are in low-spin $t_{2g}^6e_g^0$ states while the ground states of the cobalt(II) products (with a few exceptions, such as $Co(terpy)_2^{2+}$) are high-spin $t_{2g}^5e_g^2$. Consequently, electron-transfer reactions such as (12) are accompanied by a change in the spin state of the cobalt from $t_{2g}^6e_g^0$ to $t_{2g}^5e_g^2$. The reactions are thus partially spin forbidden and could be nonadiabatic. Equation 10 assumed that all of the reactions involved are adiabatic; if this is not the case, then the more complete eq 13 may be employed, where the *p* factors are

$$k_{12} = p_{12}[k_{11}k_{22}K_{12}f/p_{11}p_{22}]^{1/2} \tag{13}$$

the adiabaticities of the respective reactions ($p = 1$ for an adiabatic reaction). This expression admittedly has less immediate usefulness than the simpler eq 10 because of the increase in the number of parameters, but the full expression may be the one which is required in practice. Thus it is possible for the cross reaction to be adiabatic while one or both of the exchange reactions are not and *vice versa*. Small *p* factors tend to show up as relatively negative entropies of activation, so information about the magnitudes of the *p* factors

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[25] R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

can be obtained from temperature dependence studies. If the reactions involved have very different activation entropies, then eq 13 should be used. This procedure assumes, of course, that the breakdown of eq 10 is due to nonadiabaticity and not to other factors such as those which are discussed next.

Alternatively, reactions such as (12) could proceed in a number of steps. If the primary cobalt(II) product could be formed in a low-spin $t_{2g}{}^6e_g{}^1$ state, the unfavorable driving force for the formation of this excited cobalt(II) could be responsible for the slowness of the reaction; if the cobalt(III) complex rearranged to a $t_{2g}{}^5e_g{}^1$ state before electron transfer occurred, the promotional energy required to excite the low-spin cobalt(III) complex to the high-spin state could cause the reaction to proceed much slower than predicted. Evidence consistent with a rapid, preequilibrium spin change mechanism has been obtained; the rate of high-spin $\rightleftharpoons$ low-spin equilibration of an iron(II) complex, bis(hydrotris(pyrazolyl)borate)iron(II), has recently been measured by Beattie, Sutin, Turner, and Flynn using a laser temperature-jump apparatus.[26] They have determined that the forward and reverse rate constants are 1-2 × 10^7 sec^{-1} and that the p_{12} adiabaticity factor is about 10^{-5}. This equilibration differs from the cobalt(III) reactions in two respects. A two-electron excitation is involved, which should be less favorable than the one-electron cobalt(II)–cobalt(III) spin changes; also the free energy change and associated reorganization energies are much lower for the iron(II)–iron(III) equilibration (which suggests but does not demand a faster rate constant). These differences notwithstanding, the point to be made is that spin changes in transition metal complexes might not be as slow as was once expected, and that spin multiplicity restrictions *per se* may not markedly slow down the rates of cobalt(II)–cobalt(III) electron-transfer reactions.

The above explanations are not wholly satisfactory in that they do not account for the fact that of all the cobalt(III) complexes studied in this work, only the $Co(phen)_3{}^{3+}$ reactions appear to proceed more slowly than predicted; the spin change just discussed occurs in all the cobalt(III) complexes, even the ones whose experimental and calculated rates agree quite well. An alternative explanation for the slowness of only the $Co(phen)_3{}^{3+}$ reactions can be offered. This explanation, which will be more fully discussed in the next section, involves the formation of a radical ion intermediate in which the initial product of the reaction has the electron in the π-system of the phenanthroline ligand. Since the $Co(en)_3{}^{3+}$ or $Co(NH_3)_6{}^{3+}$ complexes do not have π-systems capable of accepting an electron, this radical mechanism is applicable only to the $Co(phen)_3{}^{3+}$ complex. If this type of mechanism does obtain, then the Marcus theory calculations, which assume a smooth transition from reactants to products, are not valid and cannot be used to predict the reaction rate. A *caveat* should be presented, however. It should be noted that the reaction of Fe^{2+} and $Fe(phen)_3{}^{3+}$, which presumably does not involve a radical ion intermediate because of overlap between the acceptor t_{2g} orbital and the phenanthroline, is also much slower than predicted by the Marcus theory.

Comparison of Anion-Assisted Rate Constants. Table VIII presents the ratios of the third-order anion-assisted rate constants for the thiocyanate and chloride enhancement of the electron-transfer reactions. Since these ratios could in principle be calculated using either second- or third-order rate constants for the anion-assisted reactions, some justification for the latter choice will be offered. First, from a practical point of view, it is more useful to know how the rate will vary with changing $[X^-]$; calculation of the $[MX^+]$ concentration is sometimes neither convenient nor necessarily straightforward, while a rate expression of the form $k_0 + k_x \cdot [X^-]$ presents the rate changes in a very clear manner. Second, calculation of the second-order rate constants requires that the value of the formation constant for the MX^+ or $Co^{3+} \cdot X^-$ complex be known. In the case of the $CrCl^+$, VCl^+, or some $Co^{3+} \cdot X^-$ complexes, this information is not available. Use of the third-order rate constants does not require knowledge of K_x (apart from the small stoichiometric corrections discussed later). Third, use of third-order rate constants allows rate comparison to be made irrespective of the direction of the reaction which is measured. Thus, using third-order rate constants, the value of the ratio k_{SCN}/k_{Cl} is the same if either the Fe^{3+}–$Co(phen)_3{}^{2+}$ or the Fe^{2+}–$Co(phen)_3{}^{3+}$ system is used; this lack of directional dependence is not valid when second-order rate constants are used. Finally, it might also be mentioned that the use of rate ratios with third-order rate constants has a precedent in the case of inner-sphere electron transfer reactions.[27] In terms of the "stability of transition-state" formalism, the ratios calculated in Table VIII represent the value of the transition-state equilibrium quotient, $Q^{\ddagger} = k_{SCN}/k_{Cl}$, for a reaction such as (14)

$$[Co(NH_3)_6 \cdot Cl \cdot V^{4+}]^{\ddagger} + SCN^- \overset{Q^{\ddagger}}{\rightleftharpoons} [Co(NH_3)_6 \cdot SCN \cdot V^{4+}]^{\ddagger} + Cl^- \quad (14)$$

Table VIII. Ratios of Anion-Assisted Electron Transfer Reactions[a]

Reactants	k_{SCN}/k_{Cl}	k_{NNN}/k_{SCN}
Fe^{2+}–FeX^{2+} [b,c]	2.8×10	3.0×10^4
Cr^{2+}–CrX^{2+} [b,d]	3.3×10^{-2}	2.4×10^4
Cr^{2+}–FeX^{2+} [b,e]	9.1×10	5.2×10
Cr^{2+}–$Co(NH_3)_5X^{2+}$ [b,f]	1.3×10^{-2}	5×10^4
$Cr(bipy)_3{}^{2+}$–$Co(NH_3)_5X^{2+}$ [g]	2.7×10	1.3
Fe^{2+}–$Fe(phen)_3{}^{3+}$	4.1×10^3	4.1×10^{-1}
Fe^{2+}–$Co(phen)_3{}^{3+}$	5.4×10^2	1.3
Cr^{2+}–$Co(phen)_3{}^{3+}$	1.3×10^3	
Cr^{2+}–$Co(en)_3{}^{3+}$	2.1×10^2	
Cr^{2+}–$Co(NH_3)_6{}^{3+}$	6.1×10	
V^{2+}–$Co(phen)_3{}^{3+}$	1.0×10^4	
V^{2+}–$Co(en)_3{}^{3+}$	1.3×10^3	
V^{2+}–$Co(NH_3)_6{}^{3+}$	1.0×10^3	

[a] At 25°, $\mu = 1.0$ *M*, unless noted. The comparisons are ratios of third-order rate constants. [b] Inner-sphere reaction. [c] $\mu = 0.55$ *M*, ref 4. [d] Reference 4. [e] References 5 and 6. [f] Rate data from ref 12; equilibria data from T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8**, 1604 (1969), ($\mu = 0.5$ *M*). [g] Rate data from ref 12 ($\mu = 0.1$ *M*), equilibria data from T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8**, 1604 (1969) ($\mu = 0.5$ *M*).

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(26) J. K. Beattie, N. Sutin, D. Turner, and G. Flynn, *J. Amer. Chem. Soc.*, **95**, 2052 (1973).

(27) (a) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968); (b) H. Taube and H. Meyers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954); (c) H. Taube, "Electron Transfer Processes in Solution," Academic Press, New York, N. Y., 1970, p 51ff.

The use of third-order rate constants does have one drawback in that this does not by itself reveal how the added anion is brought into the transition state for the reaction. It is possible for the anion to be either in the inner-coordination sphere of the reducing agent (for example, $VNCS^+$ or $CrCl^+$) or to be part of an ion-pair complex of the oxidizing agent ($Co(NH_3)_6{}^{3+}\cdot SCN^-$). However, direct evidence that the added anion is complexed with the reducing agent was obtained for some of the vanadium(II) reactions studied in this work. When the vanadium(II) in perchlorate media was allowed to react with $Co(phen)_3{}^{3+}$ in chloride or thiocyanate media using the stopped-flow apparatus, the reaction rate was much slower than when chloride or thiocyanate was mixed with the vanadium(II) prior to the reaction. Formation of an ion pair is essentially diffusion controlled; the slowness of the oxidation–reduction reaction means that $VNCS^+$ or VCl^+ must be formed beforehand in order for the anion-assisted rate to be seen. Although no such direct proof can be offered for the chromium(II) or iron(III) reactions, it will be assumed that they are analogous.

There remains one more point which must be mentioned before the detailed comparison of rate constants is made. In the treatment of the data using eq 9, it was assumed that ion pairing of the cobalt(III) did not occur to any appreciable extent. To allow for ion pairing, two terms should be modified. The term $(1 + K_{SCN}\cdot[V^{2+}])$ should be expanded to $(1 + K_{SCN}[V^{2+}] + K_{IP}\cdot[Co^{3+}])$, where K_{IP} is the association constant between thiocyanate and the cobalt(III) complex and $[Co^{3+}]$ is the amount of free cobalt(III) complex in solution. Since vanadium(II) (or chromium(II)) was usually the reagent in excess and K_{SCN} should be larger than K_{IP}, the additional term is relatively small and cannot significantly affect the results; the same is not necessarily true of the second correction factor. In eq 9, the concentration of the free cobalt complex was assumed to be the same as the total cobalt(III), *i.e.*, $[Co^{3+}] = [Co(III)]$. The more rigorous derivation has $[Co(III)] = [Co^{3+}] + [Co^{3+}\cdot SCN^-] + [Co^{3+}\cdot Cl^-]$, and thus $[Co^{3+}]$ is equal to $[Co(III)]/(1 + K_{IP}[SCN^-]_f + K_{IP}{}^*[Cl^-]_f)$, where $[SCN^-]_f$ and $[Cl^-]_f$ are the free thiocyanate and chloride in solution and $K_{IP}{}^*$ is the association constant between the cobalt(III) complex and chloride.

It is unfortunate that precise values of outer-sphere association constants are not available, and the subject is still controversial. Evans and Nancollas[28] obtained values of 91 and 51 M^{-1} for the association constants of $Co(NH_3)_6{}^{3+}$ with chloride and bromide, respectively, at $\mu = 0.05\ M$. King, Espenson, and Visco[29] found that the values for these same pairs at $\mu = 0.9\ M$ were less than 0.2 M^{-1}, and they stated that the values at $\mu = 0.05\ M$ should not be greater than 5 M^{-1}. Haim and Taube[30] have measured a value of 4.5 M^{-1} for the outer sphere association constant of $Co(NH_3)_5H_2O^{3+}$ with thiocyanate at $\mu = 0.5\ M$; Langford and Muir[31] obtained a value of 0.4 M^{-1} for the same pair and 3.1 M^{-1} for the $Co(NH_3)_5H_2O^{3+}$–Cl^- pair at $\mu = 1.00\ M$. Not only are the experimental results in disagreement but some experimental evidence has been presented which is inconsistent with the simple model from which these constants may be calculated. The theory of Bjerrum[32] assumes that the association constant varies inversely as the radii of the ions involved, but in a recent paper Stengle and Langford[33] found that the amount of chloride association is greater with $Co(pn)_3{}^{3+}$ than with $Co(en)_3{}^{3+}$. They state that large organic groups reduce solvation by water and allow anions to more easily enter the outer-coordination sphere of the cobalt(III) complex.

The point of the above discussion is that since precise values for the outer-sphere association constants of the cobalt(III) complexes studied in this work are not known, any attempt to correct for their existence is merely a *gedanken* calculation. The rate ratios will be discussed and compared on the assumption that these values are small ($K_{IP} \sim 0.01$–$0.2\ M^{-1}$); if later experimental work reveals that this assumption is not justified, the conclusions reached here will have to be modified.

With the preceding reservations in mind, the results shown in Table VIII can be examined. This type of comparison has been used before in discussing types of reaction mechanisms. The most striking feature of the table is that, for a given reducing agent, the k_{SCN}/k_{Cl} ratios are not constant as the oxidizing agent is varied. This is not in accord with purely thermodynamic considerations, which predict a constant ratio of $k_{SCN}/k_{Cl} = \sqrt{K_{SCN}K_{SCN}'''/K_{Cl}K_{Cl}'''}$ for the different oxidizing agents, where K_x and K_x''' are the formation constants for the MX^+ and MX^{2+} complexes, respectively. Since $K_{Cl}\ K_{Cl}'''$ data are not available, no quantitative estimates for this ratio can be made; however, it may be concluded that while these and other rate ratios[7a,d] tend to lie in the order expected on the basis of thermodynamic considerations, variations in the driving forces for the reaction are not the only factors determining the anion-assisted rates.

The explanation which is offered to explain the patterns of the rate ratios is essentially a symmetry argument. This type of argument is not new, as Stritar and Taube[34] have previously explained reactivity patterns in inner-sphere reactions on the basis of symmetry considerations; our argument is an extension of theirs. In essence, the argument consists of considering the symmetry of the orbitals through which the electron is transferred; overlap between orbitals of the same symmetry facilitates the electron transfer process by providing a relatively favorable "path." Vanadium(II) loses a t_{2g} or π electron when it is oxidized, while chromium(II) loses an e_g or σ electron. Thiocyanate is considered to be a good π-bridging ligand, while chloride is a σ-bonding ligand. Thus, k_x/k_0 should be larger for $VNCS^+/V^{2+}$ than for $CrNCS^+/Cr^{2+}$, while it should be larger for $CrCl^+/Cr^{2+}$ than for VCl^+/V^{2+}. These predictions are borne out by the experimental results. The $CrCl^+/Cr^{2+}$ ratios are 4–11 M^{-1}, while the VCl^+/V^{2+} ratios are 1–2 M^{-1}. For $VNCS^+/V^{2+}$, the values are 0.2–$2 \times 10^4\ M^{-1}$, as compared with the $CrNCS^+/Cr^{2+}$ ratios of 0.7–$7 \times 10^3\ M^{-1}$.

The more interesting effect is seen with the oxidizing

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[28] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

[29] E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[30] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

[31] C. H. Langford and W. R. Muir, *J. Amer. Chem. Soc.*, **89**, 3141 (1967).

[32] N. Bjerrum, *Kgl. Dan. Vidensk. Selsk.*, 7, No. 9 (1926).

[33] T. R. Stengle and C. H. Langford, *J. Phys. Chem.*, **69**, 3299 (1965).

[34] J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

agent. The electron accepted by all the cobalt(III) complexes ultimately occupies an e_g or σ orbital. However, there is some question as to whether the initial product of the electron transfer in the $Co(phen)_3{}^{3+}$ reactions is not a radical ion intermediate. Waltz and Pearson[35] have found that the reaction of $Co(bipy)_3{}^{3+}$ with e^-_{aq} yields an excited state $Co(bipy)_3{}^{2+}$ species which then decays to the ground state. Their findings were confirmed by Baxendale and Fiti,[36] who also reported evidence for radical ion intermediates in the reactions of $Ru(bipy)_3{}^{2+}$ and $Co(terpy)_2{}^{3+}$ with e^-_{aq}. Since phenanthroline and bipyridine behave similarly as ligands, it is possible that the $Co(phen)_3{}^{3+}$ reactions have as their initial products excited $Co(phen)_3{}^{2+}$ molecules where the electron is in the π system of the phenanthroline rings. On the other hand, the $Co(en)_3{}^{3+}$ and $Co(NH_3)_6{}^{3+}$ complexes do not have ligands with orbitals that possess π character, and the added electron therefore goes into an orbital possessing σ character. (It must be stated that it is possible for the reduction by e^-_{aq} to be the only reduction which is sufficiently exothermic to produce the radical ion intermediates; if this is true, the argument presented here is not valid.)

If it is accepted that the lowest unoccupied molecular orbital of $Co(phen)_3{}^{3+}$ is one which has π symmetry and is ligand in character, it becomes possible to account for the general reactivity patterns in Table VI. With respect to chromium(II) and vanadium(II) reactions, the k_{SCN}/k_{Cl} ratio increases in the order $Co(NH_3)_6{}^{3+} < Co(en)_3{}^{3+} < Co(phen)_3{}^{3+}$. As stated before, purely thermodynamic considerations would result in a constant ratio; charge considerations would result in the reverse order, as the SCN^- would be more effective than Cl^- at lowering the charge repulsion between the reducing agent and the cobalt(III) complex. (This effect would be greatest for the smaller $Co(NH_3)_6{}^{3+}$ and less for the larger $Co(en)_3{}^{3+}$ and $Co(phen)_3{}^{3+}$ ions.) This pattern can be explained by noting from Table VI that the maximum thiocyanate rate enhancement occurred with the V^{2+}–SCN^-–$Co(phen)_3{}^{3+}$ reaction; this system can be classified as a $\pi \rightarrow \pi \rightarrow \pi$ system. To be more rigorous, if the transfer from the phenanthroline to the cobalt is considered, the system is $\pi \rightarrow \pi \rightarrow \pi \rightarrow \sigma$. (This last distinction is made to differentiate between this reaction and the unmeasured but likely extremely rapid $VNCS^+$–$Fe(phen)_3{}^{3+}$ reaction, in which the electron travels on a super-π-way from reductant to oxidant.) While chloride effects are not as large, the maximum rate enhancement occurs with $CrCl^+$–$Co(NH_3)_6{}^{3+}$, which is $\sigma \rightarrow \sigma \rightarrow \sigma$. The net result of the opposing symmetry trends (thiocyanate favoring $Co(phen)_3{}^{3+} > Co(en)_3{}^{3+} > Co(NH_3)_6{}^{3+}$ and chloride favoring $Co(NH_3)_6{}^{3+} > Co(en)_3{}^{3+} > Co(phen)_3{}^{3+}$) is the rate ratios shown in Table VIII.

Extending the comparisons to include the iron(II) reactions, it is evident that the symmetry argument still holds. The totally symmetric Fe^{2+}–$Fe(phen)_3{}^{3+}$ system has a larger k_{SCN}/k_{Cl} ratio than the nonsymmetric Fe^{2+}–$Co(phen)_3{}^{3+}$ system. It is perhaps surprising that the actual numbers for these systems are less than those observed for the V^{2+}–$Co(phen)_3{}^{3+}$ reaction; it might be expected that the latter number be less than the symmetric Fe^{2+}–$Fe(phen)_3{}^{3+}$ number and be about the same as for the Fe^{2+}–$Co(phen)_3{}^{3+}$ (both V^{2+} and Fe^{2+} are π donors). If one compares the k_{SCN}/k_0 ratios, the thiocyanate rate enhancement relative to the rate in 1 M perchlorate, the values are Fe^{2+}–$Fe(phen)_3{}^{3+}$, $5.8 \times 10^4\ M^{-1}$; Fe^{2+}–$Co(phen)_3{}^{3+}$, $2.0 \times 10^4\ M^{-1}$; and V^{2+}–$Co(phen)_3{}^{3+}$, $1.6 \times 10^4\ M^{-1}$. These values are quite consistent with the symmetry arguments, so the low value for the iron system must result from higher k_{Cl} values. These higher k_{Cl} values are almost certainly due to the stability of the iron–chloride bond in the transition state. To illustrate this point, it can be shown that the stability constants of $FeNCS^{2+}$, $CrNCS^{2+}$, and $VNCS^{2+}$ are all about the same magnitude ($\sim$150 M^{-1}), while the stability constant of $FeCl^{2+}$ (5.2 M^{-1}) is much larger than that of either $CrCl^{2+}$ ($\sim$0.1 M^{-1}) or VCl^{2+} (probably $<$0.1 M^{-1}). The lesson to be learned here is that the symmetry arguments hold for all reducing agents, but caution must be exercised when comparing the absolute values of the ratios obtained for different reducing agents.

Another explanation for the reactivity patterns can be offered which is not wholly independent of the symmetry argument. The electron transfer reactions proceed *via* precursor complexes. Provided all other factors are equal, reactions proceeding *via* more stable precursor complexes will feature more rapid rates. A relatively stable precursor complex is postulated to exist for the $Co(phen)_3{}^{2+,3+}$ reactions involving thiocyanate ion;[8a] it is formed by a nucleophilic attack of the sulfur of the thiocyanate on ring carbons of the phenanthroline bearing a partial positive charge or by interaction of the π orbitals of the thiocyanate with the π orbitals of the phenanthroline ring. Since blocking groups on the ring carbons have little effect on the reaction rate, the latter mode of precursor complex formation is preferred. By forming this type of precursor complex, a substantial rate enhancement for the thiocyanate-assisted reactions with $Co(phen)_3{}^{3+,2+}$ is predicted.

It should be stated that the explanations of reactivity patterns on the basis of symmetry arguments or precursor complexes is somewhat in opposition to ideas given in a previous study. Doyle and Sykes[7b] found that k_x/k_0 ratios for V^{2+}–$(NH_3)_5CoNH_2Co(NH_3)_5{}^{5+}$ were almost the same as for V^{2+}–$Co(NH_3)_6{}^{3+}$. Their conclusion was that the added anion played only a minor role in the reaction, and they felt that the anion was probably in the coordination sphere of the vanadium(II) but at a site remote from the cobalt(III) complex. The scheme which we propose requires that the anion be coordinated to the reducing agent (when it is chromium(II) or vanadium(II)) and be *between* the two metal centers, where it is in the outer-coordination sphere of the oxidizing agent or (in the case of phenanthroline) in between the ligands of the oxidizing agent. We prefer our scheme for several reasons. It is much more favorable electrostatically to have the anion between the positively charged metals, particularly in the reaction of the +2 vanadium and the +5 cobalt dimer. Also, the argument of Doyle and Sykes would predict a constant k_{SCN}/k_{Cl} ratio for the same reducing agent and anion as the oxidizing agent is varied, which is contrary to the experimental results shown here. Our scheme could account for their results if one makes the reasonable assumption that the symmetry of the ac-

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(35) W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, 73, 1941 (1969).

(36) J. H. Baxendale and M. Fiti, *J. Chem. Soc., Dalton Trans.*, 1995 (1972).

ceptor orbitals of $Co(NH_3)_6^{3+}$ and $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$ are similar.

Comparison of Inner- and Outer-Sphere Ratios. Now that a reasonable explanation for the reactivity patterns with added anions in outer-sphere electron transfer reactions has been offered, a comparison between outer- and inner-sphere patterns can be made. It can be seen from Table VIII that the inner-sphere patterns differ from the outer-sphere ones in that, for the most part, $k_{\mathrm{NNN}}/k_{\mathrm{SCN}}$ is large for the former reactions and $k_{\mathrm{SCN}/\mathrm{Cl}}$ is small or less than unity. With regard to the first observation, if both oxidant and reductant are hard and favor coordination to nitrogen rather than to sulfur, the inner-sphere path utilizing azide (with a symmetrical $[\mathrm{MNNNM'}]^{4+}$ transition state) is much favored over one using thiocyanate (which requires that one metal be coordinated to sulfur in the transition state $[\mathrm{MNCSM'}]^{4+}$). On the other hand, thiocyanate and azide behave similarly in outer-sphere reactions because both ligands are bound to the reducing agent through the nitrogen atom and utilize their π systems. The lack of formation of a thermodynamically unfavorable sulfur bond and the similarity of the π systems results in an almost equal rate enhancement for these two ligands in outer-sphere reactions. The second observation is explained in part by the decrease in k_{SCN} because of unfavorable sulfur bonding to a metal as explained above. The ratio may be made even smaller because the value of k_{Cl} in inner-sphere reactions may be higher than for outer-sphere reactions. It can be easily seen that a direct σ bond of chloride to two metals with σ symmetries, as might occur in inner-sphere reactions, would result in a higher rate enhancement than would be the case if the chloride were σ bonded to one metal and had only a remote association with the other (outer-sphere reaction). The magnitude of the chloride enhancement will be less for the reactions which are not totally symmetric (σ–σ–σ); however, the conclusion that chloride is more effective when directly bonded to the metal should apply in all cases, and the larger k_{Cl} term results in a lower $k_{\mathrm{SCN}}/k_{\mathrm{Cl}}$ ratio for inner-sphere reaction. These symmetry effects apply not only to the stability of the precursor complex but also of course to the probability of electron transfer within the precursor complex.

In this context, it is interesting to examine the k_x/k_0 ratios seen for the reduction of ferricytochrome *c* by chromium(II). On the basis of equal rate enhancement by thiocyanate and azide (k_{SCN} is $3.7 \times 10^5\ M^{-2}\ \mathrm{sec}^{-1}$ and k_{NNN} is $4.1 \times 10^5\ M^{-2}\ \mathrm{sec}^{-1}$ at 25°, pH 6.1, and $\mu = 1.0\ M$), it was predicted that these reactions were outer sphere.[37] Later work has shown that this indeed was the case, as the anion-assisted reactions were faster than the rupture of the iron–methionine-80 sulfur bond which was required for the anion to enter the inner-coordination sphere of the iron.[2,3] The k_x/k_{Cl} ratios for both thiocyanate and azide were estimated to be greater than 10^3; for the other chromium(II) reductions shown in Table VIII, only the $Co(phen)_3^{3+}$ reaction, which could proceed through the π ligand system, has a ratio of greater than 10^3. It is not possible, however, to claim that the chromium(II)–ferricytochrome *c* reaction proceeds through the heme ring system; the validity of comparing rate ratios at widely different pH regions and the unknown magnitude of the ion-pairing terms make such a ratio comparison not unambiguous.[38] It can be concluded now that effects of added anions can be used to differentiate between inner- and outer-sphere mechanisms, and that there at least remains the potential to use these effects to ascertain the detailed pathway for the electron transfer process in complex systems.

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[37] N. Sutin, *Chem. Brit.*, **8**, 148 (1972).

[38] Work in progress in our laboratory indicates that $k_{\mathrm{SCN}}/k_{\mathrm{Cl}} \geq 10^3$ for the reaction of chromium(II) with ferricytochrome *c* at 25°, 0.1 M H^+, and $\mu = 1.0\ M$. This system is complicated by an acid-dependent path for the k_{Cl} term and a pH-dependent equilibrium between at least two forms of the ferricytochrome *c*.