$(\pi\text{-C}_5\text{H}_5)_3(\text{L})_2$, and $\text{M}_3(\pi\text{-C}_5\text{H}_5)_3(\text{O})_2$ (where L represents S, O, or other suitable ligands and M designates Ni or Co) can be isolated. Further preparative work is in progress along this line in order to extend the structural and bonding principles recently proposed[20,34,47] for these metal atom clusters.

Acknowledgments. This research was supported financially by the National Science Foundation (GP-4919). The use of the 3600 and 1604 computers at the University of Wisconsin Computing Center was made possible through partial financial support from NSF and WARF through the University Research Committee. The helpful consultations with both Dr. C. H. Wei of Oak Ridge National Laboratory (Biology Division) and Dr. Heinrich Vahrenkamp are gratefully acknowledged.

Nonbridging Ligand Effects on the Rate of the Vanadium(II) Reduction of Some Cobalt(III) Complexes[1]

Peter R. Guenther and R. G. Linck

Contribution from the Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92037.
Received January 24, 1969

Abstract: The rates of reduction of several Co(III) complexes by V(II) have been measured at 25° in a medium of unit ionic strength. The Co(III) complexes all contain a Cl^- in the first coordination sphere, but the other ligands are varied. This variation leads to measured second-order rate constants between 2 and about 500 M^{-1} sec^{-1}. These rate constants correlate well with the previously reported data on the Fe(II) reduction of the same complexes. What the implications of these linear free energy relationships are is discussed. The mechanism of the fastest of the V(II) reductions must be outer sphere; the mechanism of the slower reactions may be outer sphere also.

Those studying oxidation–reduction reactions of metal ions have always maintained an interest in the reduction of Co(III) complexes—complexes which are inert in the oxidized form but labile in the reduced form. The inertness of these complexes allowed one to vary the bridging group—to change its chemical nature significantly—and hence investigate features of the reactions that depended on the nature of this bridging group.[2] However, the complexity of the functions that a bridging group performs have made interpretation of these features difficult. Recently, renewed interest in the reduction of Co(III) complexes with simple bridging groups has arisen.[3] This interest centers around the effect of a change of nonbridging ligands[4–6] on the rate of reduction of a Co(III) complex. Since the variation in the molecule is at a site removed from the bridging ligand, it might be expected that the effect of nonbridging ligands on the rate would be more easily interpreted than those of bridging ligands.

From the data that have been accumulated on nonbridging ligand effects,[4–8] it is beginning to appear that this presumption might be true. Early evaluations of similarities in relative rates[4a] have recently been extended to encompass linear free energy relationships.[5b,6] Evidence for these relationships is, thus far, relatively fragmentary. In order to extend the number of systems studied and hence to establish that linear free energy relationships are generally to be found, we have investigated the rate of reduction of several Co(III) complexes by V(II).

While this work was in progress, Price and Taube published data that suggested to them that several reductions of Co(III) complexes by V(II) were limited in rate by the rate of water substitution on the V(II) center.[9] More recently, Sutin[10] has summarized the results on a wider variety of V(II) reductions. These two studies establish (1) that, unambiguously, several V(II) reductions proceed by the inner-sphere mechanism and (2) that the upper limit on an inner-sphere reaction of V(II) is about 40 M^{-1} sec^{-1}. However, neither of these studies[9,10] establishes the mechanism of the V(II) reduction of $\text{Co(NH}_3)_5\text{Cl}^{2+}$, a mechanism that has been the subject of much discussion in the literature.[2a,11–13] In addition to our main purpose,

---

[1] This work is taken, in part, from the M.S. dissertation of P. G., University of California, San Diego, 1968.

[2] For recent reviews, see (a) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

[3] We shall use the term "bridging ligand" in the broadest possible sense: that ligand which does serve, or most probably would serve, as the bridging ligand if the reaction proceeds by an inner-sphere path. In practice, for outer-sphere reactions, it is the ligand in the coordination sphere that is not changed in the series of compounds under investigation; for inner-sphere reactions, it is important for the success of linear free energy relationships that this ligand is the bridging ligand.

[4] (a) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965); (b) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[5] (a) C. Bifano and R. G. Linck, *ibid.*, **89**, 3945 (1967); (b) R. G. Linck, *Inorg. Chem.*, 7, 2394 (1968).

[6] R. C. Patel and J. F. Endicott, *J. Am. Chem. Soc.*, **90**, 6364 (1968).

[7] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966); **6**, 2138 (1967); 7, 1659 (1968).

[8] J. M. DeChant and J. B. Hunt, *J. Am. Chem. Soc.*, **89**, 5988 (1967); **90**, 3695 (1968).

[9] H. J. Price and H. Taube, *ibid.*, 7, 1 (1968).

[10] (a) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968); (b) M. Orhanovic, H. N. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968).

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

[12] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

[13] A. Haim, *ibid.*, 7, 1475 (1968).

our investigations have some relevance to the question of the nature of the transition state in the V(II) reduction of $\mathrm{Co(NH_3)_5Cl^{2+}}$.

Experimental Section

Reagents. All solutions were prepared with deionized water that had been doubly distilled through a quartz apparatus. Molar perchloric acid was prepared by dilution of Baker reagent grade perchloric acid. A lithium perchlorate solution of ionic strength $\mu = 1.0\ M$ and $[\mathrm{H^+}] = 0.151\ M$ was prepared by adding an excess of perchloric acid to Baker reagent grade lithium carbonate, boiling to expel carbon dioxide, and dilution to the proper ionic strength as determined by passing an aliquot through a cation exchange resin and titrating the hydrogen ion released with standard base.

The following Co(III) complexes were those used in previous studies: *cis*-$\mathrm{[Co(en)_2pyCl](ClO_4)_2}$ and *cis*-$\mathrm{[Co(en)_2(3\text{-}Clpy)Cl](ClO_4)_2}$,[5a] $\mathrm{[Co(NH_3)_5Cl](ClO_4)_2}$, *cis*-$\mathrm{[Co(en)_2NH_3Cl]Cl_2}$, *trans*-$\mathrm{[Co(en)_2H_2OCl]SO_4}$, *trans*-$\mathrm{[Co(en)_2Cl_2]ClO_4}$,[14] and $\mathrm{[Co(NH_3)_4H_2OCl]SO_4 \cdot 0.5H_2O}$.[5b, 15]

cis-$\mathrm{[Co(en)_2(C_6H_5CH_2NH_2)Cl](ClO_4)_2}$ was prepared by C. Bifano according to the literature procedure.[16] *Anal.* Calcd for *cis*-$\mathrm{[Co(en)_2(C_6H_5CH_2NH_2)Cl](ClO_4)_2}$: Co, 11.32; N, 13.45; C, 25.38; H, 4.84. Found: Co, 10.85; N, 13.46; C, 25.38; H, 4.62 (ϵ 82.3 at 5270 Å and 101 at 3660 Å). *cis*-$\mathrm{[Co(en)_2Cl_2]Cl \cdot H_2O}$ was prepared by the literature procedure.[17] Spectroscopic analysis agreed with that reported previously.[14]

V(II) perchlorate solutions were prepared by reduction of 0.08 *M* vanadyl perchlorate solutions with zinc amalgam at 0° and were stored until used at −78° in tubes degassed with Cr(II)-scrubbed nitrogen and sealed with sleeve-type rubber stoppers. The vanadyl perchlorate solution was made by addition of a slight excess of barium perchlorate to a vanadyl sulfate solution, followed by filtration. Tests showed that 100% reduction of V(IV) to V(II) was accomplished by zinc amalgam, although when used for kinetic runs, some vanadium was present as V(III).[18]

Total vanadium was determined spectroscopically as the V(V)–peroxide complex at the 4500 Å maximum according to the following procedure.[19, 20] About 0.08 *M* vanadium solution (1.00 ml) was oxidized to V(V) in basic peroxide and then boiled to decompose excess peroxide. The solution was acidified and transferred to a 25-ml volumetric flask; 0.5 ml of 3% $\mathrm{H_2O_2}$ and 1.5 ml of concentrated $\mathrm{H_2SO_4}$ were added, and the solution was diluted to 25 ml. The extinction coefficient used was 281 at 4500 Å. This value was determined from a standard $\mathrm{VO^{2+}}$ solution analyzed by oxidizing the $\mathrm{VO^{2+}}$ to V(V) with permanganate, reducing the excess $\mathrm{MnO_4^-}$ with $\mathrm{NO_2^-}$, and destroying the excess $\mathrm{NO_2^-}$ with urea. The V(V) concentration was determined by titration with standard Fe(II) in 5 *M* $\mathrm{H_2SO_4}$.[21] (Our value at 4000 Å (ϵ 200) is in reasonable agreement with a literature report at this wavelength (ϵ 205).[22])

V(II) was determined before each kinetic run by one of the following two spectroscopic methods. (1) Using the standard syringe techniques, 0.30–0.50 ml of the V(II) solution was injected into a degassed solution of excess $\mathrm{[Co(NH_3)_5Cl]Cl_2}$ in molar perchloric acid. After complete reaction, the solution was transferred to a 50-ml volumetric flask; and 25 ml of acetone, 2 ml of concentrated HCl, and 2.5 ml of a 50% weight/volume ammonium thiocyanate solution (1 g/2 ml) were added.[23] The resulting Co(II)–$\mathrm{NCS^-}$ complex was determined at 6230 Å, a maximum in the absorption curve (ϵ 1770 ± 30 as determined from a gravimetrically determined Co(II) solution). The literature value of 1842[22] was obtained with a higher concentration of $\mathrm{NCS^-}$, an observation which we verified. (2) Into a 1-cm cell containing 3.00 ml of a degassed solution of excess $\mathrm{[Co(NH_3)_5Cl](ClO_4)_2}$ in molar perchloric acid was injected 0.15 ml of the V(II) solution. After complete reaction, V(II) was determined from the observed absorption at 5320 Å using the following values for the various extinction coefficients: $\epsilon_{\mathrm{Co(NH_3)_5Cl^{2+}}}$ 49.6, $\epsilon_{\mathrm{V(III)}}$ 3.5,[24, 25] $\epsilon_{\mathrm{Co(II)}}$ 3.8. Agreement between the two methods was within experimental error.

Kinetic Measurements. Measurement of the kinetics of reaction with V(II) for those Co(III) complexes with negligible rates of aquation or isomerization was accomplished in the normal manner. An approximately $10^{-5}\ M$ solution of the Co(III) complex in molar perchlorate was deaerated in a two-necked cell sealed with sleeve-type rubber stoppers by passing Cr(II)-scrubbed nitrogen through the cell. It was then placed in a thermostated (25.0 ± 0.2°) cell compartment of a Cary Model 14 spectrophotometer; and reaction was initiated by injecting 0.03–1.00 ml of a freshly analyzed V(II) solution into the cell, using standard syringe techniques. The change in absorbance with time was observed at an appropriate wavelength between 2300 and 3000 Å.

The increased rates of aquation of *cis*- and *trans*-$\mathrm{Co(en)_2Cl_2^+}$ and isomerization of *cis*- and *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$[26] made special techniques necessary for those systems. For *trans*-$\mathrm{Co(en)_2Cl_2^+}$, it was necesary only to cool the cell while deaerated and to run the kinetics as soon as possible after preparing the solutions. The half-life for aquation of *cis*-$\mathrm{Co(en)_2Cl_2^+}$, however, is less than 1 hr, making the following procedure necessary. An appropriate quantity of *cis*-$\mathrm{[Co(en)_2Cl_2]Cl \cdot H_2O}$ was dissolved in ice-cold water, transferred to small tubes, and frozen at −78°. When about to be used, the solutions were melted and degassed, never allowing the temperature to exceed 2 or 3°. About 0.05 ml of this solution was transferred to the 5-cm cell containing 14 ml of degassed, thermostated perchlorate solution, resulting in a $10^{-5}\ M$ Co(III) solution. The run was then immediately commenced with addition of V(II). In all cases, plots linear to at least three half-lives were obtained by this procedure.

Solutions of *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ were prepared in the way described above for *trans*-$\mathrm{Co(en)_2Cl_2^+}$. In these runs, the absorbance continued to decrease after ten half-lives due to the much slower reaction of *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ with V(II). This drift was extrapolated as a straight line back into the region where the absorbance changed rapidly with time and was used as a base line. (Log $(A_t - A_t')$ was plotted *vs.* time, where A_t' was the value of the absorbance found by extrapolation of the *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ drift.) The assumption that the decrease in absorbance due to *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ was linear with time over the entire reaction of the *trans* isomer is reasonable since the slope of the drift was slight and since good plots of log $(A_t - A_t')$ *vs.* time were obtained. The slopes of these plots, however, were fairly sensitive to how the extrapolation was drawn, and this sensitivity is reflected in the larger scatter in the *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ rate constants. The method used for *cis*-$\mathrm{Co(en)_2Cl_2^+}$ was also used for *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ in a few runs, with A_∞ chosen as the absorbance at ten half-lives. Similar rate constants were obtained, with about the same scatter.

Solutions of *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ were obtained by allowing solutions of *cis*-$\mathrm{Co(en)_2Cl_2^+}$ to aquate at 25° for about 3.5 hr, the time calculated for maximum concentration of *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$.[27] The following percentages were calculated for t = 3.62 hr: 81.2% *cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$, 14.6% *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$, 4.2% *cis*-$\mathrm{Co(en)_2Cl_2^+}$.[28] The concentration of V(II) added to this

---

[14] C. Bifano and R. G. Linck, *Inorg. Chem.*, 7, 908 (1968).

[15] R. G. Linck, *ibid.*, **8**, 1016 (1969).

[16] J. C. Bailar, Jr., and L. O. Clapp, *J. Am. Chem. Soc.*, 67, 171 (1945).

[17] J. C. Bailar, Jr., *Inorg. Syn.*, 2, 222 (1946).

[18] This oxidation occurred after thawing and was caused by leakage around the frozen serum caps. This was verified by experiments using long-necked tubes in which the serum cap remained at room temperature.

[19] G. Telep and D. F. Boltz, *Anal. Chem.*, 23, 901 (1951).

[20] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. van Nostrand and Co., Princeton, N. J., 1949, p 453.

[21] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957, p 607.

[22] J. H. Espenson and O. J. Parker, *J. Am. Chem. Soc.*, **90**, 3689 (1968).

[23] R. E. Kitson, *Anal. Chem.*, 22, 664 (1950).

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

[25] G. Gordon and P. H. Tewari, *ibid.*, 70, 200 (1966).

[26] See M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961), for a summary of these rate constants and the stereochemical consequences of the aquation.

[27] This calculation is for the reactions

$$\mathit{cis}\text{-}\mathrm{Co(en)_2Cl_2^+} \xrightarrow{k_1} \mathit{cis}\text{-}\mathrm{Co(en)_2H_2OCl^{2+}}$$

$$\mathit{cis}\text{-}\mathrm{Co(en)_2H_2OCl^{2+}} \underset{k_3}{\overset{k_2}{\rightleftharpoons}} \mathit{trans}\text{-}\mathrm{Co(en)_2H_2OCl^{2+}}$$

Values of the k's were obtained from ref 26.

[28] These percentages do not reproduce the observed spectrum of such a solution if the known extinction coefficients[14] are used. This is probably due to the fact that the rate constants used were measured under drastically different conditions (0.01 *M* $\mathrm{HNO_3}$) from those employed herein. A significant change in the rate of aquation of a related complex as the medium is changed has been reported.[15] Nevertheless, the kinetic plots showed that the percentages did approximate the actual conditions.

Table I. Summary of Kinetic Data for the V(II) Reductions of Some Co(III) Complexes at 25°, Ionic Strength of 1.0 *M* and $[\mathrm{H^+}] = 1.0\ M$

	Co(III) complex	$[\mathrm{Co(III)}]_0 \times 10^5\ M$	$[\mathrm{V(II)}]_0 \times 10^4\ M$	No. of expts	k_2,[a] $M^{-1}\ \mathrm{sec}^{-1}$
A	*cis*-$\mathrm{Co(en)_2NH_3Cl^{2+}}$	2.89–5.92	7.06–23.6	6	1.89 ± 0.06
B	*cis*-$\mathrm{Co(en)_2(C_6H_5CH_2NH_2)Cl^{2+}}$	1.14–3.46	6.83–16.7	4	2.84 ± 0.08
C	$\mathrm{Co(NH_3)_5Cl^{2+}}$	2.01–17.2	6.32–42.2	8	7.58 ± 0.22
D	*cis*-$\mathrm{Co(en)_2H_2OCl^{2+}}$	1.14–3.18	7.88–22.2	12	10.1 ± 0.5
E	*cis*-$\mathrm{Co(en)_2Cl_2^+}$	0.9–1.5	7.75–21.7	10	24.0 ± 1.2
F	*cis*-$\mathrm{Co(en)_2pyCl^{2+}}$	0.58–1.99	3.45–13.5	8	32.4 ± 1.8
G	*cis*-$\mathrm{Co(NH_3)_4H_2OCl^{2+}}$	0.58–4.90	0.88–8.65	6	57.6 ± 5.1
H	*cis*-$\mathrm{Co(en)_2(3\text{-}Clpy)Cl^{2+}}$	0.44–1.24	2.17–12.6	9	58.5 ± 2.0
I	*trans*-$\mathrm{Co(en)_2Cl_2^+}$	0.57–1.18	1.17–5.81	6	128 ± 2
J	*trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$	0.56–1.34	1.22–4.55	8	259 ± 18

[a] Second-order rate constant defined by the rate law (1). Average values and standard deviations are listed.

solution was sufficient to assure that all of the *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ had reacted before the first absorbance point was recorded. No interference due to *cis*-$\mathrm{Co(en)_2Cl_2^+}$ was observed in the good plots obtained.

Results

Stoichiometry. The stoichiometry of the reaction of V(II) with Co(III) complexes is of some concern, for there is the possibility that V(III) might also react with the Co(III) complex. Because we anticipated that this latter reaction would be slow (extensive rearrangement of the primary coordination shell of the V(III) is probably necessary to achieve a transition state compatible with the $\mathrm{VO^{2+}}$ product), only three of the complexes which we studied were absolutely established to react by a 1:1 stoichiometry. It should be observed, however, that the quality of the rate data in all cases establish that any other stoichiometry can occur, at best, to only a slight extent.

The 1:1 stoichiometry was shown by verifying the observed spectral change for the reaction of V(II) with excess Co(III), using known extinction coefficients for reactants and products. This experiment was made for two of the more reactive Co(III) complexes, for which any interference from a possible V(III) reduction would be expected to be greatest. For an experiment with *cis*-$\mathrm{Co(en)_2(3\text{-}Clpy)Cl^{2+}}$ at 5180 Å, the calculated and observed amounts of Co(III) destroyed were 0.0344 and 0.0330 mmol, respectively. For an experiment with *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$ at 5840 Å, the amounts were 0.0414 mmol calculated and 0.0429 mmol observed. In addition, the analytical technique for determination of V(II) establishes a 1:1 stoichiometry for $\mathrm{Co(NH_3)_5Cl^{2+}}$.

Rate Constants. In all kinetic experiments, the initial V(II) concentration exceeded that of the Co(III) complex by a factor of at least 20; all kinetic runs were thus under pseudo-first-order conditions. Plots of log $(A_t - A_\infty)$ where A_t and A_∞ are the absorbance values at time t and at the end of the reaction, respectively, were linear to at least three and in most cases to four or five half-lives. A_∞ was almost always reached at ten half-lives. (See the Experimental Section for details on *trans*-$\mathrm{Co(en)_2H_2OCl^{2+}}$.) Pseudo-first-order rate constants were calculated from the slopes of these straight line plots. Second-order rate constants were then obtained by dividing the pseudo-first-order rate constants by the initial V(II) concentrations. No dependence of the second-order rate constants on the V(II) concentration, usually varied over a two- to threefold range, was observed, thereby proving the second-order rate law

$$\frac{-\mathrm{d}[\mathrm{Co(III)}]}{\mathrm{d}t} = k_2[\mathrm{V(II)}][\mathrm{Co(III)}] \qquad (1)$$

Table I summarizes the rate constants measured in 1.0 *N* $\mathrm{HClO_4}$.

Included in this table is the measurement of the rate of reduction of the species $\mathrm{Co(NH_3)_4H_2OCl^{2+}}$. It has been previously established that this complex exists in 1.0 *N* $\mathrm{HClO_4}$ as a mixture of the *cis* and *trans* isomers, the former predominating.[15] On the basis of the magnitude of the observed spectral change, we conclude that the complex being measured is the *cis* isomer. Extrapolation of the normal $A_t - A_\infty$ plot to zero time results in a value of A_0 less than that calculated by addition of the absorptivities of V(II) and the initial absorbance of the Co(III) complexes. As previously discussed[5b] (with Fe(II) as the reductant) this rapid absorbance change is caused by rapid reduction of *trans*-$\mathrm{Co(NH_3)_4H_2OCl^{2+}}$. In several experiments, the initial [V(II)] was lowered below the usual 20-fold excess in order to attempt to measure the rate of this rapid reduction. We extrapolated the slow reaction to short times, and plotted the difference between the observed absorbance and the extrapolated *vs.* time. The calculated rate constant for V(II) concentrations ranging from 2.8 to 8.8 × 10^{-5} *M* was about 460 $M^{-1}\ \mathrm{sec}^{-1}$ at 25° in 1 *N* $\mathrm{HClO_4}$. Because the absorbance changes used to obtain this value were less 0.1 absorbance unit, the value must be considered provisional. The approximate rate constant is compatible with the failure to observe very rapid change in the other experiments with $\mathrm{Co(NH_3)_4H_2OCl^{2+}}$.

In Table II, values of the rate constant measured at a lower $[\mathrm{H^+}]$ are reported. Although these latter data do

Table II. Summary of Kinetic Data for the V(II) Reductions of Some Co(III) Complexes at 25°, Ionic Strength of 1.0 *M* and $[\mathrm{H^+}] = 0.15\ M$

Co(III) complex	$[\mathrm{Co(III)}]_\mathrm{i} \times 10^5\ M$	$[\mathrm{V(II)}]_\mathrm{i} \times 10^4\ M$	No. of expts	k_2,[a] $M^{-1}\ \mathrm{sec}^{-1}$
cis-$\mathrm{Co(en)_2NH_3Cl^{2+}}$	3.5	6.02–21.6	3	2.06, 0.17
cis-$\mathrm{Co(en)_2OH_2Cl^{2+}}$	2.68	20.1–25.5	2	11.1, 0.4
cis-$\mathrm{Co(en)_2Cl_2^+}$	1.5	11.0–16.4	2	22.3, 0.0
cis-$\mathrm{Co(en)_2pyCl^{2+}}$	1.31	8.59	1	34.6
cis-$\mathrm{Co(en)_2(3\text{-}Clpy)Cl^{2+}}$	1.24	4.88	1	60.6
trans-$\mathrm{Co(en)_2OH_2Cl^{2+}}$	1.44	2.84–4.05	2	231, 8

[a] Second-order rate constants defined by the rate law (1). Average values and range are listed where appropriate.

Table III. The Rates of Reductions of Some Co(III) Complexes

Complex	Reductant		
	Fe(II)[b]	V(II)[g]	$Ru(NH_3)_6^{2+}$ [h]
	k, M^{-1} sec^{-1}		
cis-$Co(en)_2NH_3Cl^{2+}$	1.8×10^{-5}	1.9	1.2×10^1
cis-$Co(en)_2(NH_2CH_2C_6H_5)Cl^{2+}$	3.5×10^{-5} [c]	2.8	3.7×10^1
$Co(NH_3)_5Cl^{2+}$	1.35×10^{-3} [d]	7.6	2.3×10^2 [i]
cis-$Co(en)_2H_2OCl^{2+}$	4.6×10^{-4}	10	2.31×10^2
cis-$Co(en)_2Cl_2^{+}$[a]	8×10^{-4}	12	4×10^2 [i]
cis-$Co(en)_2pyCl^{2+}$	7.9×10^{-4} [e]	32	6.6×10^2
cis-$Co(NH_3)_4H_2OCl^{2+}$	3.5×10^{-2} [f]	58	
cis-$Co(en)_2(3\text{-}Clpy)Cl^{2+}$	2×10^{-3} [e]	58.5	
trans-$Co(en)_2Cl_2^{+}$[a]	1.6×10^{-2}	64	4×10^3 [i]
trans-$Co(en)_2H_2OCl^{2+}$	2.4×10^{-1}	2.60×10^2	$>10^5$
trans-$Co(NH_3)_4H_2OCl^{2+}$	~ 10[f]	$\sim 4.6 \times 10^2$	

[a] Corrected for a symmetry factor of 2. [b] From ref 4a except where noted. $T = 25°$ and $\Sigma[ClO_4^-] = 1.0\ M$. [c] C. Bifano and R. G. Linck, unpublished observation. [d] Reference 12. [e] Reference 5a. [f] Reference 5b. [g] This work. $T = 25°$ and $\Sigma[ClO_4^-] = 1.0\ M$. [h] Reference 6 except where noted. $T = 20°$ and ionic strength $= 0.1\ M$ (NaCl). [i] Reference 33 quotes values at 25°. These numbers are approximated as the appropriate value at 20°.

not, in themselves, constitute proof of the lack of a dependency on $[H^+]$, it is clear that the reduction in $[H^+]$ by a factor of 7 causes little, if any, effect on the rate constant. Hence the overwhelming contribution to the rate must be due to a hydrogen ion independent path.

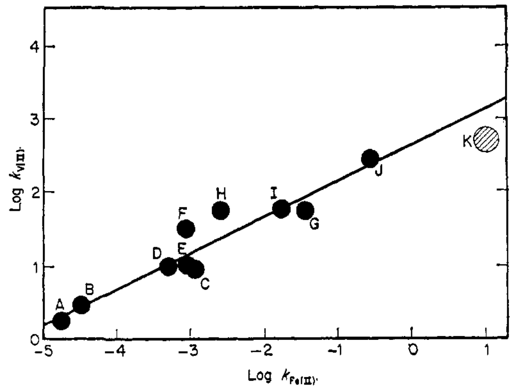

Figure 1. Log $k_{V(II)}$ *vs.* log $k_{Fe(II)}$ for a series of Co(III)–Cl⁻ complexes. The designations are from Table I. The point marked K is the estimated value for *trans*-$Co(NH_3)_4H_2OCl^{2+}$. The values for points E and I have been corrected for symmetry factors. The line is the least-squares fit with the point for *trans*-$Co(NH_3)_4H_2OCl^{2+}$ excluded from the calculation.

A few experiments testing the effects of added chloride and sulfate ions also were made. Slightly different rate constants were obtained from $Co(NH_3)_5Cl^{2+}$ in 1.4×10^{-2} M of added chloride or sulfate, but any catalysis significant in the rate experiments (where Cl^- and HSO_4^- were, if present, in much lower concentration) was ruled out. Catalytic effects derived from the zinc amalgam or due to the slight concentration of Ba(II) present in the V(II) solutions were found to be unimportant; there was an absence of any observable dependence of the second-order rate constants on the vandium concentration. In addition, identical rate constants were obtained using solutions of V(II) stored with zinc amalgam.

Where comparisons with literature values are possible, our results, in general, agree with earlier experiments. A value of $k_2 = 5\ M^{-1}$ sec^{-1} in 1.0 M $NaClO_4$–$HClO_4$ mixture is reported by Candlin, Halpern, and Trimm[11] for $Co(NH_3)_5Cl^{2+}$; a value of 5.6 M^{-1} sec^{-1} at 22.5° and $\mu = 0.52\ M$ has also been reported.[29] The literature values for the rate of reduction of *cis*-$Co(en)_2NH_3Cl^{2+}$ are 1.25 and 0.68 M^{-1} sec^{-1} at 29 and 19°, respectively.[30] In view of the limited amount of experimental data reported in the earlier work and the precautions taken here to ensure knowledge of the [V(II)], we believe our value of 1.89 M^{-1} sec^{-1} is more nearly correct.[31]

Discussion

Our aim in measuring the rate of reduction of various Co(III)–Cl systems by V(II) was to determine if these complexes exhibit the same relative rates with V(II) as the reductant as they do with Fe(II) as the reductant.[4a,5b] A summary of the relevant data is given in Table III. It is clear from these data that the relative order of reduction is independent of reducing agent, but that the sensitivity to a change in nonbridging ligands is not as great for V(II) or $Ru(NH_3)_6^{2+}$ as it is for Fe(II). The data exhibit a linear free energy correlation.

Figure 1 demonstrates the linear free energy relationship between V(II) and Fe(II) as reductants for Co(III)–Cl systems. The equation expressing this relationship is

$$\log k_{V(II)} = 0.49 \log k_{Fe(II)} + 2.68 \qquad (2)$$

with a correlation coefficient of 0.94.

That there is a correlation between reductants whose mechanisms presumably differ—Fe(II) and $Ru(NH_3)_6^{2+}$, inner sphere[32] and outer sphere,[33] respectively[34]—is, at first thought, surprising. Our approach is to treat

$$\underset{\text{I}}{\text{X-Co-Cl-M}} \qquad \underset{\text{II}}{\text{X-Co-Cl, H}_3\text{N-M}'}$$

the nonbridging ligand effects in these two types of

---

(29) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).

(30) R. T. M. Fraser, *Proc. Chem. Soc.*, 262 (1963).

(31) Others have also questioned data reported in ref 30. See D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

(32) See especially, A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 5343 (1966), and references therein and ref 14.

(33) J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964), and ref 6.

(34) These data fit the equation

$$\log k_{Ru(NH_3)_6^{2+}} = 0.83 \log k_{Fe(II)} + 5.09$$

with a correlation coefficient of 0.97.

transition states (I and II) as being perturbations by the change in X on $\Delta F^{\ddagger}$. Notwithstanding the model used to explain the effect of a change in X on $\Delta F^{\ddagger}$,[4,5,8] the linear free energy relationship, in this view, is really not too surprising: as long as the metal centers do not interact too strongly, the result of a change of X in I and II, a change which has a certain effect on the energy levels of the Co(III) center, should cause parallel changes in the energies of I and II.

On this basis, we feel the comparison of the rates of reduction of these Co(III) complexes by V(II) and Fe(II)—the two systems in which the number of data points measured under comparable conditions of temperature and ionic medium are greatest—can be meaningfully made regardless of mechanism.[35]

The quantity of most interest for our purposes is the sensitivitiy to a change in nonbridging ligands, the slope of the log–log plots. Both the V(II) and $Ru(NH_3)_6{}^{2+}$ reductions are less sensitive to these changes than are the Fe(II) reductions. It would appear on this basis that the net driving force of the reaction is of some pertinence in determining the magnitude of the sensitivity. In the argument that follows, we prefer to use the language introduced by Hush,[36] rather than that of Marcus.[37] In that our discussion is qualitative, and in that the two treatments can be made equivalent,[37,38] we feel this approach is not unwarranted.

The cause of a difference in sensitivity to a change in nonbridging ligands presumably lies in the nature of the two transition states. The immediate presumption would then be that the difference in the transition states accounting for the different sensitivity of Fe(II) compared to V(II) and $Ru(NH_3)_6{}^{2+}$ is that the former is inner sphere whereas the latter are outer sphere. We find fault with this argument on two counts. Firstly, if similar log–log plots are made for reactions generally conceded to be outer sphere in nature, the Mn(III) and Ce(IV) oxidations of ferrous complexes of variously substituted 1,10-phenanthrolines,[39,40] sensitivities are found that differ from unity.[41] Hence, since these outer-sphere reactions differ in sensitivity, how can we, with certainty, blame a difference in sensitivity exclusively on a change from outer-sphere to inner-sphere mechanism? Secondly, the sensitivity to a change in nonbridging ligands will be at least equal, or perhaps greater, for an outer-sphere reaction than for an inner-sphere reaction, all other factors being constant. We base this argument on a report concerning oxygen isotope effects on the reduction of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5OH^{2+}$ by a variety of reducing agents,[42] in which it is found that there is a difference in isotope effects, and hence the importance of stretching the bridging ligand in the transition states, between inner-sphere and outer-sphere mechanisms. If similar factors are at work with chloride bridges, the inner-sphere transition state will be characterized by a longer Co–Cl bond; this will produce a major effect on the orbital energies and cause the rate enhancing ability of the nonbridging ligands to be of less relative importance. On this basis, if the sensitivity to a change in nonbridging ligand on the V(II) reduction of $Co(III)–Cl^-$ complexes compared to the Fe(II) reductions were due exclusively to a difference in mechanism—outer sphere *vs.* inner sphere—we would expect the sensitivity, as expressed by the coefficient of $\log k_{Fe(II)}$ in eq 2 to be equal to or greater than 1.0. Our finding of 0.49 as the sensitivity argues against this prediction.

The cause of the lower sensitivity in the V(II) reductions seems most readily explainable on the basis of the net driving force of the reaction. As this increases, the transition state resembles reactants more than products, and hence the electron to be transferred is described by a wave function whose contribution from the reductant orbital is greater than from the oxidant orbital. As the latter orbital is the one influenced directly by the change in nonbridging ligands, the effect of that change will be diminished in a system with large negative free energy change. The relative sensitivity to a change in nonbridging ligand, Fe(II) > $Ru(NH_3)_6{}^{2+}$ > V(II) fits this argument satisfactorily.[43] It is interesting to note that the values of the intercepts in eq 2 and the corresponding equations for other reactants do not vary smoothly with net free energy change, presumably because the self-exchange rate constant is included in this term.[2a,37]

It is of some interest to note that a number of the reactions studied during the course of this work are fast enough to ensure that they must be outer sphere in nature.[10] *trans*-$Co(NH_3)_4H_2OCl^{2+}$, *trans*-$Co(en)_2H_2OCl^{2+}$, and *trans*-$Co(en)_2Cl_2{}^+$ belong in this grouping, and *cis*-$Co(NH_3)_4H_2OCl^{2+}$ and *cis*-$Co(en)_2(3\text{-Clpy})Cl^{2+}$ may be outer sphere since their rate constants are slightly greater than 40 M^{-1} sec^{-1}, the value Sutin[10a] assigns as the upper limit for V(II) inner-sphere reactions. It is pertinent to note that there is no change in the sensitivity of the V(II) reductions as the "break point" of 40 M^{-1} sec^{-1} is passed, especially if the approximate data point for *trans*-$Co(NH_3)_4H_2OCl^{2+}$ is considered. That is, the rate constant for the V(II) reduction relative to that of the Fe(II) reduction changes in a consistent fashion as the nonbridging ligand is varied so as to ensure that the more rapid reactions are outer sphere in nature. This result tends to make us view the mechanism of the V(II) reduction of all the Co(III)–Cl complexes studied herein as outer sphere in nature. This interpretation cannot be assumed to be rigorous until demonstration of a system with known mechanism change exhibits a change in sensitivity as the break point is passed. In a search for such a system, an investigation of the V(II) reduction of Co(III) complexes with azide ion bridges is currently in progress.

Acknowledgment. This research was supported by the U. S. Public Health Service under Grant GM-14830. We are grateful for this support.

---

(35) A similar argument has previously been made. See ref 6.

(36) N. S. Hush, *Trans. Faraday Soc.*, 57, 557 (1961).

(37) R. A. Marcus, *Ann. Rev. Phys. Chem.*, 15, 155 (1964).

(38) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron-Transfer," The Ronald Press Co., New York, N. Y., 1966, p 130.

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

(40) H. Diebler and N. Sutin, *J. Phys. Chem.*, 68, 174 (1964).

(41) This is a restatement of the previously observed failure of these reactions to fit the predicted Marcus equation

$$\log k_{12} = 0.5 \log K_{12} + (\text{constant})$$

with a slope of exactly 0.5.[39,40]

(42) H. Diebler, P. H. Dodel, and H. Taube, *Inorg. Chem.*, 5, 1688 (1966).

(43) So do the data reported in ref 39 and 40. There the sensitivity decreases: $Mn(H_2P_2O_7)_3{}^{3-}$ > Ce(IV) > Mn(III).