## Conclusions

A comparison of the results for the thermal and the photochemical isomerization of $Co(CN)_4(H_2O)_2^-$ and $Co(CN)_4(OH)_2^{3-}$ proves that two different mechanisms are involved. The thermal trans–cis isomerization is in accordance with an SN1 type mechanism. The data on the photochemical cis–trans isomerization can only be explained by accepting a nondissociative mechanism, in which ligands exchange place without bond breaking.

The photochemical reactions evidence also the specificity of the interaction with light: excitation of a specific axis in the complex results in a preferential subsequent reaction pattern.

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**Registry No.** *cis*-$Co(CN)_4(H_2O)_2^-$, 56403-82-8; *trans*-$Co(CN)_4(H_2O)_2^-$, 56403-83-9; *cis*-$Co(CN)_4(OH)_2^{3-}$, 53797-83-4; *trans*-$Co(CN)_4(OH)_2^{3-}$, 53769-69-0; $Co(CN)_6^{3-}$, 14897-04-2.

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Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

# Kinetics and Mechanisms of Chromium(II)-Catalyzed Nitrosyl Ligand Transfer Reactions

RICHARD L. ROBERTS, DAVID W. CARLYLE, and GARY L. BLACKMER*

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The reaction of nitrosylbis(ethylenediamine)cobalt(III) ion with chromium(II) was studied in an aqueous perchlorate medium. The electron-transfer reaction involving $Co(en)_2(H_2O)NOH^{3+}$ (the dominant species in highly acidic solution) and chromium(II) can be represented by the rate expression

$$\frac{d[Cr(H_2O)_5NO^{2+}]}{dt} = k_{et}Q\frac{[Co(en)_2(H_2O)NOH^{3+}][Cr^{2+}]}{[H^+]}$$

The activation parameters reported for this reaction are in accord with those previously reported for a series of Co(III)–Cr(II) inner-sphere electron-exchange reactions. The cobalt(III) nitrosyl–chromium(II) reaction product, $Cr(H_2O)_5NO^{2+}$, was observed to undergo a further Cr(II)-catalyzed ligand exchange reaction to yield $Cr(H_2O)_6^{3+}$. Mechanisms are proposed for all reactions studied and chloride ion dependencies for both the electron-transfer and aquation reactions are discussed.

## Introduction

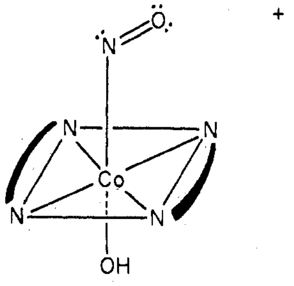
Although the literature contains numerous reports of the synthesis of a variety of metal–nitrosyl complexes,[2–7] only a few[8–15] report data concerning the reactions that these species undergo. Of the reactions that have been reported most include direct oxidations and/or reductions of the nitrosyl ligand itself by various reagents. Armor and Taube[15] have shown that the nitrosyl ligand of nitrosylpentaammineruthenium(III) can be reduced by chromium(II) to yield an amine. Their reaction sequence was shown to generate $Ru(NH_3)_6^{2+}$ and 6 equiv of chromium(III) as products. Armor[9] reported that the reaction of chromium(II) and $Co(NH_3)_5NO^{2+}$ in acidic aqueous chloride media produces $Cr(H_2O)_5NO^{2+}$ and cobalt(II), although he did not report the complete kinetic data for the reaction. Armor and Buchbinder[8] further found that chromium(II) reacts with $Cr(H_2O)_5NO^{2+}$ to yield hydroxylamine and a chromium(III) dimer, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4$. Additional work[9] indicated that the nitrosyl ligand, when coordinated to a transition metal, can undergo a series of successive reduction reactions to yield such species as $NO^-$, $N_2$, $NH_3OH^+$, $N_2H_4$, or $NH_3$.

The study reported here concerns the chromium(II)-catalyzed nitrosyl ligand "transfer" reactions of nitrosylbis(ethylenediamine)cobalt(III) via an oxidation–reduction mechanism.

In the cobalt complex shown in I, the basal position, trans to the NO group, may be occupied by either $H_2O$ or $OH^-$, depending on the pH. The dominant species at high pH is $Co(en)_2(OH)NO^+$. Acidification of this complex results in the formation of the protonated aquo species represented by the equation

$$Co(en)_2(OH)NO^+ + 2H^+ \rightleftharpoons Co(en)_2(H_2O)NOH^{3+}$$

Also, the nitrosyl ligand is bent in this complex (see I) as was



I

found to be the case in similar nitrosyl complexes,[16] thereby allowing a chromium(II) ion the option of attacking the lone pair of electrons on the nitrogen atom or one of the lone pairs of electrons on the oxygen atom. In an inner-sphere redox reaction of this type, either one of the two modes of attack could provide an exclusive pathway to form Cr–NO or Cr–ON products. Alternatively, of course, the reaction could proceed in a parallel manner employing both pathways. This type of reaction sequence was shown to occur in the redox reaction of thiocyanatopentaamminecobalt(III) with chromium(II).[17]

Attack of the chromium(II) at the oxygen atom of a coordinated nitrosyl ligand, in the system currently under investigation, should produce $(H_2O)_5CrON^{2+}$. This product could, of course, undergo linkage isomerization and also yield a different more stable product, the nitrogen bound species.

We report evidence that indicates the oxidation–reduction reaction of chromium(II) and $Co(en)_2NO^{2+}$ proceeds through an adjacent attack, inner-sphere mechanism, producing $(H_2O)_5CrNO^{2+}$ directly. We also report that the subsequent reaction of $Cr(H_2O)_5NO^{2+}$ with chromium(II) produces $Cr(H_2O)_6{}^{3+}$ *without* the production of hydroxylamine. Chloride ion dependencies on these reactions were also studied.

## Experimental Section

**Materials.** Stock chromium(II) perchlorate solutions were prepared from $Cr(ClO_4)_3{\cdot}6H_2O$ by reduction with amalgamated zinc. The analytical concentrations of Cr(II) in these solutions were determined by conversion to the $CrO_4{}^{2-}$ ion in alkaline peroxide solution. The chromate ion concentrations were determined spectrophotometrically by measuring the absorbances at 372 nm ($\epsilon$ 4826).

The $[Co(en)_2NO](ClO_4)_2$ was prepared and characterized by the method of Feltham and Nyholm.[18]

Sodium perchlorate was prepared by dissolution of sodium carbonate in perchloric acid and recrystallized at least twice from water. The $Na^+$ concentration was determined by adding an aliquot of $NaClO_4$ to a column containing Dowex 50W-X8, 50–100-mesh resin in the acid form. The column was rinsed with doubly distilled water and the hydrogen ions released were titrated with a standard NaOH solution.

Water used in all reagent solutions and in all rate measurement studies was doubly distilled. All other reagents were of the best available grade and were used without further purification.

**Kinetic Experiments.** The oxidation–reduction reactions (and decomposition of the intermediates) were studied spectrophotometrically employing a Cary 17 recording spectrophotometer. Reactions were carried out in cylindrical spectrophotometer cells sealed with rubber serum caps. Reaction solutions were deoxygenated with purified nitrogen. The purging gas was deoxygenated by passage through chromium(II) scrubbing solutions. Cells containing reagent solutions were purged with nitrogen for at least 15 min prior to usage. Solutions were brought to constant temperature by immersing the filled cell in a thermostated water bath for at least 20 min prior to study. Constant temperature was maintained throughout the course of the reaction by the circulation of thermostated water through coils surrounding the cell holder, described in detail elsewhere.[19]

A stopped-flow spectrophotometer was used to study fast reactions where appropriate. Details of the stopped-flow apparatus have been previously described.[20] In the stopped-flow experiments four or five repetitive measurements were made on each set of reaction solutions.

**Product Analysis.** Analyses of the products of the reactions studied were carried out chromatographically and spectrophotometrically. In the former, a Dowex 50W-X8, 100–200-mesh cation-exchange resin column was used while the latter method employed a Cary 17 spectrophotometer using a 5-cm quartz spectrometer cell as the reaction vessel. By running the desired reaction in the spectrometer cell, the progress of the reaction could be monitored, and when the reaction had ceased, as denoted by no further change in the absorption spectrum, the products of the reaction were charged onto the cation-exchange column. Upon careful elution the products could be individually analyzed spectrophotometrically.

The product analysis of the electron-transfer reaction was conducted as follows. A series of experiments at a constant hydrogen ion concentration (0.400 *M*) and a constant ionic strength (1.00 *M*) were done by varying the chromium(II) concentrations in solutions of known cobalt(III) concentration. This was accomplished by adding a predetermined amount of chromium(II) solution to the cobalt(III)–nitrosyl solution. This reaction mixture was allowed to stand undisturbed for 30 min and the visible spectrum was recorded over the range 300–700 nm. The cell was then allowed to stand for an additional 30 min and the spectrum again recorded. This procedure was repeated until no spectral change was observed. The contents of the cell were then charged onto the cation-exchange resin column in the hydrogen form. A 0.5 *M* solution of perchloric acid eluted two bands from the column which were identified as $Co(H_2O)_6{}^{2+}$ and $Cr(H_2O)_5NO^{2+}$. A dark green band was eluted using 3 *M* perchloric acid which was identified as the chromium(III) dimer, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+}$. When chromium(II) was used in excess, a small purple band was also eluted with 1.0 *M* acid which was identified spectrophotometrically as $Cr(H_2O)_6{}^{3+}$.

A similar procedure was used for the analysis of the products of the $Cr(H_2O)_5NO^{2+}$ aquation reaction with excess Cr(II). Again the 0.5 *M* perchloric acid solution eluted a band from the column which was identified as $Co(H_2O)_6{}^{2+}$ and 1.0 *M* acid solution was used to elute a purple band identified as $Cr(H_2O)_6{}^{3+}$. The dark green band eluted with a 3.0 *M* acid solution was again identified as the chromium(III) dimer.

The solutions containing the aquation reaction products were checked for the presence of hydroxylamine as described by Armor and Buchbinder.[8] No hydroxylamine was detected.

**Stoichiometry.** Experiments were conducted to determine the stoichiometry of both the electron transfer and the aquation reactions. These experiments were alternately carried out with cobalt(III) in excess and then with chromium(II) in excess.

To determine the stoichiometry of the electron-transfer reaction, a weighed amount of the cobalt(III) complex was dissolved in doubly distilled water containing perchloric acid and sodium perchlorate. The cell contents were purged with deoxygenated nitrogen for 15 min. After addition of the cobalt(III) complex the cell was sealed with a rubber serum cap and its contents again purged with deoxygenated nitrogen for an additional 15 min. To this solution was added increasing amounts of the stock chromium(II) solution via syringe. With each addition of chromium(II) the difference spectrum of the reaction products was immediately measured on the Cary 17 spectrophotometer. The reference cell contained a cobalt(III) solution of nine-tenths the concentration of the cobalt(III) solution in the sample cell. The reference cell and the sample cell contained perchloric acid and sodium perchlorate of equal concentrations. The difference spectrum was recorded in the range 700–300 nm with absorption maxima at 448 and 562 nm. Our spectrum corresponded exactly to those reported by Swaddle,[21] Fraser,[12] and Armor and Buchbinder[8] for $Cr(H_2O)_5NO^{2+}$ with the following molar absorptivities: 448 nm, $\epsilon$ 121; 562 nm, $\epsilon$ 28.5. From these values the amount of cobalt consumed in the reaction was calculated using Beer's law.[22]

Another set of experiments was run in an analogous manner to the above using excess chromium(II) with an appropriate amount of chromium(II) in the cell of the reference beam. It should be noted here that the excess chromium(II) reacts with the chromium(II) product to yield yet another reaction product. In order to avoid the problem of competing successive reactions, the experiments were conducted at ice bath temperatures in order to inhibit the slower second reaction.

A calculated amount of the chromium(II) stock solution was added via a syringe to a 5-cm cell containing perchloric acid, sodium perchlorate, and deoxygenated doubly distilled water. To this solution various amounts of the stock cobalt(III) solution were added. The difference spectrum was again recorded. Using the molar absorptivities at 448 and 562 nm,[12] the amount of chromium consumed was calculated from the amount of product formed.

When the $Cr(H_2O)_5NO^{2+}$ was in excess, difference spectroscopy was again used, with the reference cell containing an appropriate amount of $Cr(H_2O)_5NO^{2+}$, to eliminate the large absorptions of the $Cr(H_2O)_5NO^{2+}$ which would interfere with the absorption spectrum of the products. By measuring the absorbance at 580 nm, the amount of $Cr(H_2O)_5NO^{2+}$ consumed in the reaction was calculated from Beer's law and the molar absorptivity of $Cr(H_2O)_6{}^{3+}$.

**Equilibrium Studies.** To elucidate the effect of the hydrogen ion concentration on the cobalt(III) complex and to ensure that acid decomposition of the complex had not taken place, a determination of complex formation was studied by the mole ratio method.[23] In this study, the absorbances were measured at 470 nm as a function of hydrogen ion concentration which varied from $10^{-4}$ to 0.880 *M*.

## Results

**Product Analysis.** The metal ion complexes which were produced by the electron-transfer reaction were the nitrosylpentaaquochromium(III) ion and the cobalt(II) ion

$$Co(en)_2NO^{2+} + Cr^{2+} \rightarrow Co^{2+} + 2en + Cr(H_2O)_5NO^{2+}$$

No other metal ion complexes were detected in the reaction mixture except for unreacted starting material when the reaction was studied with an excess of cobalt(III) complex. When the chromium(II) ion was used in excess and the reaction carried out at ice bath temperatures, the products from elution of the column were identified as the nitrosylpentaaquochromium(III) ion, the cobalt(II) ion, and the chromium(III) dimer, $(H_2O)_4Cr(OH)_2Cr(H_2O)_4{}^{4+}$. In some cases small amounts of the hexaaquochromium(III) ion were found in the product mixture. This was apparently produced from the chromium(II)-catalyzed aquation of the nitrosylpentaaquochromium(III) ion. The chromium(III) dimer was produced from exposure of the excess chromium(II) to oxygen.

When equimolar quantities of the two reactants, $Co(en)_2NO^{2+}$ and $Cr^{2+}$, were mixed together and the reaction was allowed to go to completion, the only detectable metal ion species were the cobalt(II) and the nitrosylpentaaquochromium(III) ion.

The metal ion complexes of the aquation reaction were identified as the hexaaquochromium(III) ion and the chromium dimer. The only other metal ion complex found in the product mixture was the nitrosylpentaaquochromium(III) ion which remained unreacted when used in excess. When the chromium(II) ion was used in excess, a greater amount of the chromium(III) dimer (resulting from elution in air) was produced but no products other than those mentioned were detected. When $Cr(H_2O)_5NO^{2+}$ and $Cr^{2+}$ were mixed in equimolar quantities, the final products of the reaction were the chromium dimer and hexaaquochromium(III).

In experiments containing chloride ions, the products found included small amounts of species in which the chloride ion was a ligand of the metal ion complex. Electron-transfer reactions conducted in the presence of chloride ions yielded such products as chloronitrosyltetraaquochromium(III) ion, $Cr(NO)Cl(H_2O)_4{}^+$, the chloropentaaquochromium(III) ion, $Cr(H_2O)_5Cl^{2+}$, and the above-mentioned products. The chloropentaaquochromium(III) ion probably resulted from chromium(II) attack of the chloronitrosyltetraaquochromium(III) ion at the chloride ion site of the complex. This is substantiated by the fact that when the reaction was studied using an excess of cobalt(III) complex a very small amount of this product was detected, whereas when the chromium(II) ion was used in excess, very little of the chloronitrosylchromium(III) ion was detected and a greater yield of the chloropentaaquochromium(III) resulted.

The products of the aquation reaction, when conducted in the presence of chloride ions, included the chloropentaaquochromium(II) ion and a very small amount of dichlorotetraaquochromium(II). The latter two products were present in the greatest quantity when the chromium(II) ion was used in excess.

**Stoichiometry of the Electron Transfer and Aquation Reactions.** A stoichiometric quantity of $Cr(H_2O)_5NO^{2+}$ was produced by the electron-transfer reaction for each mole of limiting reagent when Cr(II) was limiting, when Co(III) was limiting, and when equimolar quantities of Cr(II) and Co(III) were mixed. Thus, a 1:1 stoichiometry for the electron-transfer reaction was established.

In an analogous manner, the amount of the hexaaquochromium(III) ion was used to determine the stoichiometry of the aquation reaction. When the aquation reaction was conducted with either the chromium(II) ion or the nitrosylpentaaquochromium(III) ion in excess, the amount of product was found to be equal to the concentration of the species used as the limiting reagent. In the reaction in which equimolar quantities of the chromium(II) and the nitrosylpentaaquochromium(III) ion were used the amount of the hexaaquochromium(III) ion produced was found to be equal to the amount of either reagent used in the reaction. This establishes the stoichiometry of the aquation reaction as one nitrosylpentaaquochromium(III) ion to one chromium(II) ion.

Table I. Observed Absorbance Measurements for Determination of Complex Formation by the Mole Ratio Method at $2.64 \times 10^{-3}$ $M$ $Co(en)_2NO^{2+}$ and 1.00 $M$ Ionic Strength

| Expt no. | $[H^+]$, $M$ | Mole ratio $H^+$:Co(III) | Obsd absorbance (460 nm) |
|---|---|---|---|
| 1 | 0 | 0 | 2.190 |
| 2 | $2.64 \times 10^{-4}$ | 0.100 | 2.010 |
| 3 | $1.32 \times 10^{-3}$ | 0.500 | 1.590 |
| 4 | $2.64 \times 10^{-3}$ | 1.000 | 1.150 |
| 5 | $3.30 \times 10^{-3}$ | 1.250 | 1.010 |
| 6 | $5.28 \times 10^{-3}$ | 2.000 | 0.601 |
| 7 | $7.92 \times 10^{-3}$ | 3.000 | 0.360 |
| 8 | $1.32 \times 10^{-2}$ | 5.000 | 0.202 |
| 9 | $1.45 \times 10^{-2}$ | 8.20 | 0.203 |
| 10 | $2.64 \times 10^{-2}$ | 10.00 | 0.198 |
| 11 | $2.64 \times 10^{-1}$ | 100.0 | 0.200 |
| 12 | $4.00 \times 10^{-1}$ | 151.0 | 0.201 |
| 13 | $8.80 \times 10^{-1}$ | 333.0 | 0.197 |

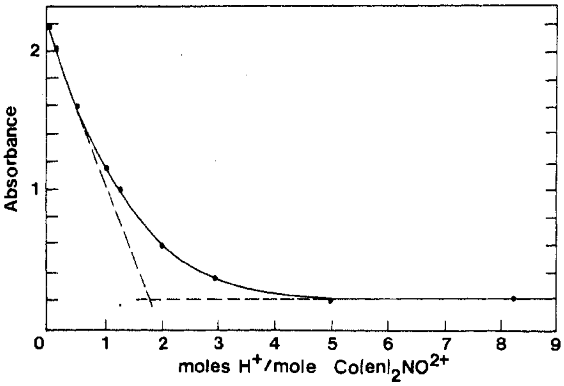


Figure 1. Observed absorbance vs. the mole ratio of hydrogen ions to $Co(en)_2NO^{2+}$ ions.

**Effects of Hydrogen Ions on $Co(en)_2NO^{2+}$.** In the presence of hydrogen ions the cobalt(III)–nitrosyl complex studied herein was previously believed to undergo a reaction of the type shown in eq 1.[24] If such a reaction were to occur, an

$$Co(en)_2NO^{2+} \xrightarrow[H_2O]{H^+} Co(H_2O)_6{}^{2+} + 2en + NO(g) \qquad (1)$$

absorption maximum should be observable at 538 nm [25]which corresponds to $Co(H_2O)_6{}^{2+}$. When $Co(en)_2NO^{2+}$ was treated with perchloric acid in an oxygen-free solution at an ionic strength of 1.00 $M$, no absorptions at this wavelength could be detected. An absorption was detected however at 470 nm. This absorption is slightly shifted from the absorption maximum of the cobalt(III)–nitrosyl complex in an oxygen-free solution at a pH of 7 (460 nm). At neutral pH this complex has a molar absorptivity of 100 $M^{-1}$ cm$^{-1}$ but in strongly acidic solutions the molar absorptivity of the species absorbing at 460 nm drops to only 15.2 $M^{-1}$ cm$^{-1}$.

Since no cobalt(II) could be detected, the effect of hydrogen ions on the cobalt(III) complex was investigated. Using the mole ratio method for the determination of complex formation in solution a new complex was detected for this system and the stoichiometry and the value of the formation constant for this new complex was determined. Table I lists the observed absorbance measurements as a function of the mole ratio of hydrogen ions to the cobalt(III)–nitrosyl complex. A graph of the observed absorption vs. the mole ratio of hydrogen ions to $Co(en)_2NO^{2+}$ ions for the data in Table I is shown in Figure 1. From the intersection of a line tangent to the initial part

**Table II.** Rate Constants for the Electron-Transfer Reaction at 1.00 *M* Ionic Strength, at 2.50 × $10^{-3}$ *M* Cobalt(III), and at 25°

| Expt no. | $[H^+]$, *M* | $10^2[Cr^{2+}]$, *M* | $k_{obsd}$, $sec^{-1}$ |
|---|---|---|---|
| 13 | 0.400 | 2.50 | 0.465 |
| 14 | 0.400 | 3.25 | 0.642 |
| 15 | 0.400 | 3.75 | 0.679 |
| 16 | 0.400 | 5.00 | 0.945 |
| 17 | 0.088 | 2.50 | 3.280 |
| 18 | 0.300 | 2.50 | 0.495 |
| 19 | 0.600 | 2.50 | 0.398 |
| 20 | 0.880 | 2.50 | 0.379 |
| 21 | 0.400 | 2.50[a] | 0.752 |
| 22 | 0.400 | 2.50[b] | 0.988 |

[a] Run at 30°C. [b] Run at 35°C.

**Table III.** Rate Constants for the Aquation Reaction at Ionic Strength 1.00 *M*, at 2.50 × $10^{-3}$ *M* Chromium(III), and at 25°

| Expt no. | $10[H^+]$, *M* | $10^2[Cr^{2+}]$, *M* | $10^2k_{obsd}$, $sec^{-1}$ |
|---|---|---|---|
| 23 | 4.00 | 2.50 | 1.30 |
| 24 | 4.00 | 3.25 | 1.66 |
| 25 | 4.00 | 3.50 | 1.80 |
| 26 | 4.00 | 3.75 | 2.40 |
| 27 | 4.00 | 5.00 | 2.96 |
| 28 | 0.88 | 2.50 | 1.22 |
| 29 | 2.00 | 2.50 | 1.17 |
| 30 | 3.00 | 2.50 | 1.27 |
| 31 | 6.00 | 2.50 | 1.13 |
| 32 | 8.80 | 2.50 | 1.03 |
| 33 | 4.00 | 2.50[a] | 1.45 |
| 34 | 4.00 | 2.50[b] | 1.56 |

[a] Run at 30°C. [b] Run at 35°C.

of the curve and a line tangent to the final part of the curve the stoichiometry of the complex formed in solution was determined. For this system the intersection of the two lines is at approximately 2 mol of hydrogen ions per mole of $Co(en)_2NO^{2+}$.

The formation constant for this new complex, $Co(en)_2(H_2O)NOH^{3+}$, was calculated by a method described by Ayres.[26] It is described by eq 2 and has a value of 554 ± 20

$$K_f = \frac{[Co(en)_2(H_2O)NOH^{3+}]}{[Co(en)_2(OH)NO^+][H^+]^2} \qquad (2)$$

$M^{-2}$. The dissociation constant for this complex is the reciprocal of the formation constant. The dissociation constant therefore has a value of (1.81 ± 0.05) × $10^{-3}$ $M^2$.

An acid–base titration of the Co(III) complex was conducted in order to prove that decomposition of the complex did not occur upon protonation. Upon the addition of base, the $Co(en)_2(H_2O)NOH^{3+}$ species becomes deprotonated and the reaction is found to be completely reversible.

**Kinetics of the Electron-Transfer Reaction.** A summary of the data showing the experimentally measured rate constants for the electron-transfer reaction involving $Co(en)_2(H_2O)NOH^{3+}$ and chromium(II) at various temperatures and acidities is given in Table II. In these experiments the concentration of the cobalt(III) complex was held constant at 2.50 × $10^{-3}$ *M* at an ionic strength of 1.00 *M*. At the conditions specified in Table II a pseudo-first-order rate constant was obtained for each experiment. The value of the observed rate constant was obtained from Guggenheim plots of the data recorded on the oscilloscope trace.

Experiments 13–16 of Table II establish the first-order chromium(II) dependence of the reaction rate.

The rate constants for these reactions were obtained by fitting these data to a straight line using a least-squares program on an IBM Corp. Model 370 computer. The intercept yielded a small but nonzero value (within error limits) which may indicate that the reaction between cobalt(III) and chromium(II) is preceded by a prior reaction or reactions or that a medium effect exists.

An examination of the observed rate constants for experiments 13 and 17–20 reveals an inverse hydrogen ion dependence upon the rate of the reaction. The order of the inverse hydrogen ion dependence on the reaction rate is established from a plot of log $k_{obsd}$ vs. log $[H^+]$. The slope of the line is −0.971 ± 0.21. This indicates that the rate of the reaction is dependent upon the inverse hydrogen ion concentration to the first power.

The rate law for the reaction can now be written as shown in eq 3. In order to obtain the value of the rate constant *k*′

$$\frac{d[Cr(H_2O)_5NO^{2+}]}{dt} = k' \frac{[Co(en)_2(H_2O)NOH^{3+}][Cr^{2+}]}{[H^+]} \qquad (3)$$

a graph of $k_{obsd}[H^+]$ vs. $[Cr^{2+}]$ was made. This graph had a slope of 7.49 ± 0.63 $sec^{-1}$ and an intercept of 0.00172 ± 0.00014 *M* $sec^{-1}$. This intercept can be attributed to a medium effect possibly arising from subtle ionic strength differences caused by the exchange of $NaClO_4$ and perchloric acid in the solvent system. The value *Q* will be used to represent a prior dissociation step involving the removal of a proton from the complex $Co(en)_2(H_2O)NOH^{3+}$. Such a reaction could give rise to the inverse first-order hydrogen ion dependence observed. It seems probable that the slope of the line in the above plot is $k_{et}Q$. Dividing the value of the slope by the independently determined value for *Q*, vide supra, the value of $k_{et}$, the electron-transfer rate constant, is found to be (4.35 ± 0.39) × $10^3$ $M^{-1}$ $sec^{-1}$. The complete rate expression now becomes that shown in eq 4.

$$\frac{d[Cr(H_2O)_5NO^{2+}}{dt} = k_{et}Q \frac{[Co(en)_2(H_2O)NOH^{3+}][Cr^{2+}]}{[H^+]} \qquad (4)$$

From the data given in Table II, for experiments 13, 21, and 22, the activation parameters of the electron transfer were calculated. These calculations were made using the Eyring equation of absolute rate theory[27] as shown in eq 5. The value

$$-\Delta S^* + \frac{\Delta H^*}{T} = -R \ln \frac{k_r h}{\kappa T a} \qquad (5)$$

$k_r$ is the rate constant for the reaction being studied. This value is equivalent to $k_{et}$ for the electron-transfer reaction. For each experiment this value was obtained by dividing the observed rate constant by $Q[Cr^{2+}]$ and multiplying by $[H^+]$.

**Kinetics of the Aquation Reaction.** In the presence of excess chromium(II) ions the product of the electron-transfer reaction, $Cr(H_2O)_5NO^{2+}$, undergoes yet another reaction to yield the hexaaquochromium(III) ion, $Cr(H_2O)_6{}^{3+}$, as the final product. The experimental data (see Table III) are in accord with the rate law in eq 6 with $k_{aq}$ = 0.564 ± 0.053 $M^{-1}$ $sec^{-1}$.

$$\frac{d[Cr(H_2O)_5NO^{2+}]}{dt} = k_{aq}[Cr(H_2O)_5NO^{2+}][Cr^{2+}] \qquad (6)$$

The data obtained from experiments 23, 33, and 34 provided values for the activation parameters: $\Delta H^*$ = 2.96 ± 0.41 kcal/mol and $\Delta S^*$ = −49.9 eu. The standard deviation estimated by least-squares calculations was 1.3 eu.

**Effects of Chloride Ions upon the Rates of the Electron-Transfer and Aquation Reactions.** The effects of a coordinating anion upon the rates of the electron transfer and the aquation reactions were studied. The chloride ion was chosen for this study because chloride ions have been shown to affect the rate of reactions similarly to those studied in this work.[12] Experimentally measured rate constants for the electron transfer and the aquation reactions in the presence of varying amounts of the chloride ion are given in Table IV. The first four experiments, 35–38, correspond to the chloride ion dependence of the electron-transfer reaction. The electron-transfer reaction

**Table IV.** Effect of Chloride Ion on Electron Transfer and Aquation Reaction Rates at 1.00 *M* Ionic Strength, at 0.400 *M* $HClO_4$, and at 25°

| Expt no. | $10[Cl^-]$, *M* | $10^2$ $[Cr^{2+}]$, *M* | $10^3[Co(en)_2(H_2O)NOH^{3+}]$, *M* | $10^3[Cr(H_2O)_5NO^{2+}]$, *M* | $k_{obsd}$, $sec^{-1}$ |
|---|---|---|---|---|---|
| 35 | 0.250 | 2.50 | 2.50 | | 0.566 |
| 36 | 0.750 | 2.50 | 2.50 | | 0.550 |
| 37 | 1.130 | 2.50 | 2.50 | | 0.430 |
| 38 | 1.130 | 3.25 | 2.50 | | 0.386 |
| 39 | 0.375 | 1.25 | | 2.50 | 0.00256 |
| 40 | 0.750 | 2.50 | | 2.50 | 0.00816 |
| 41 | 1.130 | 2.50 | | 2.50 | 0.01500 |
| 42 | 1.130 | 3.75 | | 2.50 | 0.01720 |
| 43 | 1.500 | 5.00 | | 2.50 | 0.03150 |

is seen to be about 22% faster in the presence of the chloride ion than in its absence. When the concentration of the chloride ion becomes greater than 3 times the chromium(II) ion concentration, the observed rate of the electron-transfer reaction decreases (see experiments 37 and 38 of Table IV). This decrease can be attributed to the formation of increasingly greater amounts of species having a chloride ion in the coordination sphere. Since the observed rate constants described for this reaction were measured by monitoring the rate of appearance of $Cr(H_2O)_5NO^{2+}$ (the chloride ion containing species do not absorb at the same wavelength) the pseudo-first-order rate constants should appear to be low.

The chloride ion was found to have a much greater effect on the aquation reaction than for the electron-transfer reaction. Experiments 39–43 of Table IV give the observed rate constants for the chloride ion dependent aquation rate of $Cr(H_2O)_5NO^{2+}$. The chloride ion and the chromium(II) ion are both found to exhibit first-order dependence. This first-order dependence can be recognized by the fact that a doubling of the concentration of either species while holding the concentration of the other species constant causes a doubling of the rate constant. This establishes the rate law shown in eq 7. The value of the rate constant for this reaction is derived

$$-\frac{d[Cr(H_2O)_5NO^{2+}]}{dt} = k_{Cl^-}[Cr^{2+}][Cr(H_2O)_5NO^{2+}][Cl^-] \qquad (7)$$

from a graph of $k_{obsd}$ vs. $[Cr^{2+}][Cl^-]$. The slope gives the value of $k_{Cl^-}$ as 4.13 ± 0.16 $M^{-2}$ $sec^{-1}$.

## Discussion

**Effects of Hydrogen Ions on $Co(en)_2NO^{2+}$.** The reaction of the nitrosylbis(ethylenediamine)cobalt(III) ion with hydrogen ions produces a species which shall be referred to by the formula $Co(en)_2(H_2O)NOH^{3+}$. This species has a dissociation constant, for the reaction shown in eq 8, of $1.81 \times 10^{-3}$ $M^2$. This value is qualitatively verified by the back-titration experiment. Using the above value for the dissociation constant for the complex, the ratio of the diprotonated complex to the nonprotonated complex is calculated to be 88.4:1. This means that in a 0.4 *M* perchloric acid solution the complex present is $Co(en)_2(H_2O)NOH^{3+}$. Therefore, the dominant species studied in the reactions involving the cobalt(III) complex must be $Co(en)_2(H_2O)NOH^{3+}$.

$$Co(en)_2(H_2O)NOH^{3+} \rightarrow 2H^+ + Co(en)_2(OH)NO^+ \qquad (8)$$

This formula does not indicate the position of attachment of the protons to the cobalt(III) complex. It has been shown[28] that this complex is protonated at the oxygen atom of the nitrosyl ligand in "superacid". In an analogous manner one of the protons is probably on the oxygen atom of the nitrosyl ligand in perchloric acid media. The cobalt(III) complex now has a water molecule in the position trans to the nitrosyl ligand. A water molecule coordinated to transition metal ion has a p*K* value of approximately 4.[29] At low hydrogen ion concentrations, as used in experiments 1 and 2 of Table I, the coordinated water molecule probably exists in the hydroxo form. At higher hydrogen ion concentrations, this hydroxo ligand acquires a proton and is converted to an aquo ligand. The actual formula for the diprotonated cobalt(III) complex is probably $Co(en)_2(H_2O)NOH^{3+}$.

**Mechanism of the Electron-Transfer Reaction.** The empirical rate law given in eq 4, for the electron-transfer reaction involving $Co(en)_2(H_2O)NOH^{3+}$ and chromium(II) is consistent with the following mechanisms: A (reactions 9–11), B (reactions 12–15), and C (reactions 16–19). All of these mechanisms are also consistent with the observed stoichiometry and products of the electron-transfer reaction.

mechanism A

$$Co(en)_2(H_2O)NOH^{3+} \overset{Q}{\rightleftarrows} Co(en)_2(H_2O)NO^{2+} + H^+ \qquad (9)$$

$$Co(en)_2(H_2O)NO^{2+} + Cr^{2+} \xrightarrow{k} (H_2O)_5CrNO^{2+} + Co(en)_2(H_2O)_2{}^{2+} \qquad (10)$$

$$Co(en)_2(H_2O)_2{}^{2+} \xrightarrow{fast} Co(H_2O)_6{}^{2+} + 2en \qquad (11)$$

mechanism B

$$Co(en)_2(H_2O)NOH^{3+} \overset{Q}{\rightleftarrows} Co(en)_2(OH)NOH^{2+} + H^+ \qquad (12)$$

$$Co(en)_2(OH)NOH^{2+} + Cr^{2+} \xrightarrow{k} (H_2O)_5CrNOH^{3+} + Co(en)_2(OH)(H_2O)^+ \qquad (13)$$

$$(H_2O)_5CrNOH^{3+} \xrightarrow{fast} (H_2O)_5CrNO^{2+} + H^+ \qquad (14)$$

$$Co(en)_2(OH)(H_2O)^+ + H^+ \xrightarrow{fast} Co(H_2O)_6{}^{2+} + 2en \qquad (15)$$

mechanism C

$$Co(en)_2(H_2O)NOH^{3+} \overset{Q}{\rightleftarrows} Co(en)_2(H_2O)NO^{2+} + H^+ \qquad (16)$$

$$Co(en)_2(H_2O)NO^{2+} + Cr^{2+} \xrightarrow{fast} (H_2O)_5CrON^{2+} + Co(en)_2(H_2O)_2{}^{2+} \qquad (17)$$

$$(H_2O)_5CrON^{2+} \xrightarrow{k} (H_2O)_5CrNO^{2+} \qquad (18)$$

$$Co(en)_2(H_2O)_2{}^{2+} \xrightarrow{fast} Co(H_2O)_6{}^{2+} + 2en \qquad (19)$$

Mechanism C unlike the other two mechanisms involves a fast electron-transfer reaction followed by a slower isomerization reaction. This mechanism can be eliminated from further consideration for two reasons. First, no such reaction was observed on the stopped-flow apparatus at scanning speeds of the oscilloscope up to 1 × $10^{-6}$ sec/cm. The rate constant for the reaction at a rate which could not be at least partially observed at this scanning rate would have to be greater than or equal to 2 × $10^{10}$ $M^{-1}$ $sec^{-1}$.[30] Furthermore, a reaction of two 2+-charged species is highly unlikely to occur near the diffusion-controlled limit of 1 × $10^{11}$ $sec^{-1}$. The second reason for eliminating this mechanism is that the isomerization reaction is very unlikely to have a rate constant near the value of 4.35 × $10^3$ $M^{-1}$ $sec^{-1}$ (the electron-transfer rate constant for this reaction). One of the fastest isomerization reactions that has been reported is for the isomerization of the chromium(III) isocyanide complex[31] which has a rate constant of 0.569 $M^{-1}$ $sec^{-1}$. These data therefore seem logically to exclude this mechanism.

The remaining two mechanisms, A and B, differ only in the site of the removal of the proton from the cobalt(III) complex in the equilibrium reaction which precedes the electron-transfer step. Either mechanism could adequately account for all of the known facts about the reaction. Therefore, either or both mechanisms are possible.

The activation parameters for these reactions are similar to those reported for a series of cobalt(III)–chromium(II) inner-sphere-electron transfer reactions.[32]

**Mechanism of the Aquation Reaction.** A mechanism which is consistent with the stoichiometry, the empirical rate law shown in eq 6 and the products of the reaction of $Cr(H_2O)_5NO^{2+}$ and chromium(II) is shown in eq 20 and 21.

$$Cr(H_2O)_5NO^{2+} + Cr^{2+} \xrightarrow{k} (H_2O)_5CrON^{2+} + Cr^{2+} \qquad (20)$$

$$(H_2O)_5CrON^{2+} + H_2O \xrightarrow{\text{fast}} Cr(H_2O)_6{}^{3+} + NO^- \qquad (21)$$

Other mechanisms which could be suggested from the rate law or the stoichiometry do not give the observed products and those suggested by the products are not consistent with the rate law. It should be pointed out, however, that any fast step(s) occurring after eq 20, which yield the proper stoichiometry, could be as consistent as eq 21.

The above mechanism suggests that the chromium(II) must attack the oxygen atom of the nitrosyl ligand which is coordinated to the chromium(III) ion. This attack produces the isonitrosylchromium(III) ion. This complex can either isomerize or aquate. If it isomerizes, a molecule of the reactant is produced. If it aquates, a molecule of the product is produced. Since the isomerization step in the reaction sequence was not observed, such a ligand rearrangement must occur at a slower rate than the aquation reaction. This suggests that the chromium(II) ion could form a molecule of the reactant by two independent means (attack on the nitrogen atom or isomerization after attack at the oxygen atom) while the product is dependent upon attack of the chromium(II) ion at the oxygen atom of the nitrosyl ligand.

The activation parameters for this reaction are a function not only of the number of reactions which occur but also of how frequently these reactions lead to the generation of a product molecule. The greater the number of reactions which occur that do not lead to products, the smaller the value of the transmission coefficient.[27] The actual value of the entropy of activation, $\Delta S^*$, cannot be definitely assigned until the number of reactions which occur in order to form one molecule of product is determined.

**Effects of Chloride Ions on the Electron-Transfer and Aquation Reactions.** The chloride ion was found to accelerate the rate of both the electron transfer and the aquation reactions. Similar phenomena have been found for many similar reactions.[33] Although the electron-transfer reaction was accelerated by about 22% of the rate where chloride was absent, it does not correspond to a first-order dependence on the chloride ion concentration. In the presence of the chloride ions, a small shift in the absorption band of the $Co(en)_2(H_2O)NO^{2+}$ was observed (at about 452 nm) which represents approximately an 8-nm shift of the absorption band of the $Co(en)_2(H_2O)NOH^{3+}$ species. This shift probably represents a chloride ion entering the basal position of the complex which is normally occupied by the water molecule (see I). The chloride ion could add electron density to the nitrogen atom and thus increase the rate of the reaction by providing a better site for the chromium(II) ion to attack.

A mechanism suggesting the role played by the chloride ion in the aquation sequence is shown below. A plot of $k_{obsd}$ vs. $[Cl^-]$ is linear with an intercept equal to the rate constant found in the absence of chloride. Thus the following mechanism of eq 22–24, consistent with our data, seems

$$Cr^{2+} + Cl^- \overset{K}{\rightleftharpoons} CrCl^+ \qquad (22)$$

$$CrCl^+ + CrNO^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ClCrON^+ + Cr^{2+} \rightarrow \text{product} \qquad (23)$$

$$Cr^{2+} + CrNO^{2+} \xrightarrow{k_3} Cr^{2+} + CrON^{2+} \qquad (24)$$

possible.

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**Registry No.** $Co(en)_2(H_2O)NOH^{3+}$, 56282-11-2; $Cr^{2+}$, 22541-79-3; $(H_2O)_5CrNO^{2+}$, 14951-34-9; $Cl^-$, 16887-00-6.

## References and Notes

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