the cyanide is bridging the Co to a $\mathrm{Co(CN)_5}$ moiety, as in $\mathrm{(NH_3)_5CoCNCo(CN)_5}$, there is no evidence for trans bond lengthening.[27]

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Studies of Ammineaquocobalt(III) Chemistry. Kinetics and Mechanism of Some Electron-Transfer Reactions of *cis*-Diammineaquocobalt(III) in Acid Perchlorate Solution

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The stoichiometry and kinetics of reduction of *cis*-$\mathrm{Co(NH_3)_2}^{3+}{}_{\mathrm{aq}}$ species by iodide, hydroquinone, tris(*o*-phenanthroline)iron(II), vanadium(II), iron(II), and chromium(II) have been investigated in acidic, 2 M perchlorate media ($\mathrm{HClO_4}$, $\mathrm{NaClO_4}$). The stoichiometries were measured by standard techniques and the kinetics were measured by conventional and stopped-flow spectrophotometry over a range of concentrations and temperatures. The rate law for the reactions with $\mathrm{Cr^{2+}}_{\mathrm{aq}}$ and $\mathrm{Fe^{2+}}_{\mathrm{aq}}$ is given by $-d[\mathrm{Co^{III}}]/dt = d[\mathrm{product}]/dt = (A + B/[\mathrm{H^+}])[\mathrm{Co^{III}}][\mathrm{reductant}]$ whereas the rate law for the other reductants is given by $-(1/S)d[\mathrm{Co^{III}}]/dt = d[\mathrm{product}]/dt = A[\mathrm{Co^{III}}][\mathrm{reductant}]$, where S is the appropriate stoichiometric factor. The values of A for the reactions with $\mathrm{I^-}_{\mathrm{aq}}$, $\mathrm{H_2Q}$, $\mathrm{Fe^{2+}}_{\mathrm{aq}}$, $\mathrm{Fe(}o\mathrm{\text{-}phen)_3}^{2+}{}_{\mathrm{aq}}$, $\mathrm{V^{2+}}_{\mathrm{aq}}$, and $\mathrm{Cr^{2+}}_{\mathrm{aq}}$ are 0.38, 0.028, 11.0, 2.42, 3350, and 151 $\mathrm{M^{-1}\ s^{-1}}$, respectively, at 25 °C. For reduction by $\mathrm{Cr^{2+}}_{\mathrm{aq}}$ and $\mathrm{Fe^{2+}}_{\mathrm{aq}}$, the values of B are 497 and 1.99 $\mathrm{s^{-1}}$, respectively, at 25°. Comparison of the kinetic data with those for reduction of analogous cobalt(III) systems suggests that the reactions of $\mathrm{Co(NH_3)_2}^{3+}{}_{\mathrm{aq}}$ and $\mathrm{Co(NH_3)_2OH^{2+}}_{\mathrm{aq}}$ with $\mathrm{I^-}_{\mathrm{aq}}$, $\mathrm{V^{2+}}_{\mathrm{aq}}$, $\mathrm{Fe(}o\mathrm{\text{-}phen)_3}^{2+}{}_{\mathrm{aq}}$, and $\mathrm{H_2Q}$ are outer sphere, while that of $\mathrm{Co(NH_3)_2OH^{2+}}_{\mathrm{aq}}$ with $\mathrm{Cr^{2+}}_{\mathrm{aq}}$ may be limited by substitution at the chromium(II) center. A value of $\mathcal{E}° \geq 0.91$ V for the standard potential of the $\mathrm{Co(NH_3)_2}^{3+}{}_{\mathrm{aq}}/\mathrm{Co(NH_3)_2}^{2+}{}_{\mathrm{aq}}$ couple is consistent with the experimental data.

Introduction

Recent studies of the reduction of $\mathrm{Co(NH_3)_2OH^{2+}}_{\mathrm{aq}}$ by $\mathrm{Br^-}$ [1] and $\mathrm{H_2O_2}_{\mathrm{aq}}$[2] have revealed the existence of a base-catalyzed substitution-controlled mechanism like that found for the corresponding reactions of $\mathrm{CoOH^{2+}}_{\mathrm{aq}}$,[3,4] although great differences exist in the substitutional labilities of these two cobalt(III) species. An examination of the available data for reduction of $\mathrm{CoOH^{2+}}_{\mathrm{aq}}$ by a wide variety of reducing agents (including those of this study) has suggested that reactions of this complex may be grouped on the basis of their rate constants and activation parameters:[4] thus, substitution-controlled reduction reactions of $\mathrm{CoOH^{2+}}_{\mathrm{aq}}$ consistently exhibit higher observed enthalpies and entropies of activation, $\Delta H^{\ddagger}_{\mathrm{obsd}}$, and $\Delta S^{\ddagger}_{\mathrm{obsd}}$, respectively, than do outer-sphere reactions involving the same reactant charge product. In addition, the dependence of the observed free energy of activation, $\Delta G^{\ddagger}_{\mathrm{obsd}}$, on the overall free energy change, ΔG_0, for the outer-sphere reactions of $\mathrm{Co^{3+}}_{\mathrm{aq}}$ and $\mathrm{CoOH^{2+}}_{\mathrm{aq}}$ deviates markedly from theoretical predictions and this has prompted speculation concerning the mechanistic involvement of a high-spin cobalt(III) species.[4]

The existence of substitution-controlled mechanisms for reduction of $\mathrm{CoOH^{2+}}_{\mathrm{aq}}$ and $\mathrm{Co(NH_3)_2OH^{2+}}_{\mathrm{aq}}$ suggests that similar, but energetically different, reactivity barriers exist in the series $\mathrm{Co(NH_3)}_n\mathrm{(H_2O)}_{6-n}{}^{3+}{}_{\mathrm{aq}}$ as n increases from 0 to 6. With a view toward understanding the thermodynamic and kinetic factors which determine the reactivity of these centers, we have investigated the stoichiometry and kinetics of some of the faster reactions of *cis*-diammineaquocobalt(III). In this paper we report on the reduction of *cis*-diammineaquocobalt(III) by iodide, hydroquinone, iron(II), tris(*o*-phenanthroline)iron(II), vanadium(II) and chromium(II) at ionic strength 2.0 M ($\mathrm{HClO_4}$, $\mathrm{NaClO_4}$). The reactions have been studied over a range of temperatures so that the respective activation parameters may be compared with those for the corresponding reactions of aquocobalt(III) complexes.

Experimental Section

Materials. The water used throughout this work was doubly distilled from an all-glass apparatus and deoxygenated before use with a stream of purified nitrogen. Sodium perchlorate stock solutions were prepared by neutralization of perchloric acid with sodium carbonate and contained no detectable chloride ion impurities. The preparation and purification of anhydrous *cis*-diammineaquocobalt(III) perchlorate have been described previously.[1] All air-sensitive chemicals were prepared and stored under a purified nitrogen atmosphere. Stock solutions of iron(II) perchlorate in perchloric acid were prepared by reaction of iron(II) sulfate with the stoichiometric amount of barium perchlorate. The iron(III) content of these solutions was reduced to less than 0.5% by reduction at a platinum electrode for ca. 3 h. Solutions of vanadyl perchlorate in perchloric acid were prepared by addition of a slight excess of barium perchlorate to vanadyl sulfate (Ventron Corp.). Chromium(III) perchlorate solutions in perchloric acid were made from the solid hexahydrate (G. F. Smith Chemical Co.). Vanadium(II) and chromium(II) solutions were prepared from stock $\mathrm{VO^{2+}}_{\mathrm{aq}}$ and $\mathrm{Cr^{III}}_{\mathrm{aq}}$ solutions by reduction with freshly prepared zinc amalgam. Hydroquinone (Will Corp.) was recrystallized from absolute methanol and then sublimed. Fresh solutions were prepared daily in 0.001 M $\mathrm{HClO_4}$ and stored in darkened containers. Stock solutions of sodium iodide were also protected from light and were used within a few days of preparation. Tris(*o*-phenanthroline)iron(II) sulfate solutions were made by dilution of a stock 0.025 M solution (G. F. Smith Chemical Co.). The complex $\mathrm{[Co(NH_3)_5Cl]Cl_2}$ was prepared and purified according to a literature method.[5] Zinc perchlorate solutions were made by dissolving purified zinc metal in perchloric acid. All other chemicals used were of reagent grade.

Analytical Procedures. *cis*-Diammineaquocobalt(III) (hereafter referred to as cobalt(III)) and cobalt(II) concentrations were determined spectrophotometrically (ϵ_{537} 48 $\mathrm{M^{-1}\ cm^{-1}}$ [1] and ϵ_{509} 4.84 $\mathrm{M^{-1}\ cm^{-1}}$, [6] respectively). The concentration of cobalt(III) was also checked by adding an aliquot to an excess of standardized iron(II) solution and determining the excess iron(II) by titration with standard chromium(VI) using barium diphenylaminesulfonate as indicator. Concentrations of iron(III) were measured spectrophotometrically

(ϵ_{260} 2880 M^{-1} cm^{-1} [7]). Solutions of sodium perchlorate were standardized gravimetrically after evaporation under vacuum at 105 °C for 12 h. The concentrations of vanadium in various oxidation states were determined spectrophotometrically[8] (ϵ_{400} 0.9 and ϵ_{850} 3.22 M^{-1} cm^{-1} for vanadium(II), ϵ_{400} 8.3 and ϵ_{850} 0.0 M^{-1} cm^{-1} for vanadium(III), and ϵ_{760} 17.2 M^{-1} cm^{-1} for vanadium(IV)). Concentrations of vanadium(II) were also checked by addition of an aliquot to an excess of $Co(NH_3)_5Cl^{2+}{}_{aq}$ and determining the excess cobalt(III) spectrophotometrically at the isosbestic point of the chloro and aquo complexes (ϵ_{506} 45.0 M^{-1} cm^{-1});[8] a spectrophotometric correction for the cobalt(II) product (ϵ_{506} 4.8 M^{-1} cm^{-1}) was made assuming unit stoichiometry (see Results).

The acid concentrations of oxovanadium(IV) perchlorate solutions were determined as follows. An aliquot was charged onto a cation-exchange column in the lithium form and the H^+ ions were eluted using 0.5 M $LiClO_4$. The acid concentration was determined by titration of the eluent with standardized sodium hydroxide. The acid concentration of vanadium(II) solutions was then calculated from the acid concentration of the vanadium(IV) solution by assuming that 2 mol of H^+/mol of V^{IV} is consumed in the reduction. The concentration of zinc perchlorate in the stock solution was calculated from the amount of zinc dissolved in the acid and the acid concentration was calculated from the initial amount of acid added, allowing for consumption of 2 mol of H^+/mol of Zn in the reduction reaction. Iodide was determined gravimetrically as silver iodide. Tris(*o*-phenanthroline)iron(II) was determined spectrophotometrically (ϵ_{510} 11100 M^{-1} cm^{-1}).[9] Concentrations of chromium(II) were determined by addition of an aliquot to an excess of iron(III) and determining the amount of iron(II) produced by titration (see above). The total chromium concentration of solutions was measured by oxidation with alkaline hydrogen peroxide followed by spectrophotometric determination of the chromium(VI) produced (ϵ_{372} 4820 M^{-1} cm^{-1}).[10] Hydroquinone was determined by titration with standard cerium(IV) (ferroin indicator).

Stoichiometric Measurments. Most of the stoichiometry measurements were made by adding a known amount of reductant to a measured excess of the cobalt(III) complex. The remaining complex was then estimated spectrophotometrically with a correction for the absorbance of the products. In other cases the product of the reaction was estimated either by titration or from spectrophotometric measurements. Each reaction stoichiometry is the average of four independent measurements made under constant reaction conditions at ionic strength 2 M and 25 °C.

The stoichiometries of the reactions with iron(II), vanadium(II), and hydroquinone were measured by spectrophotometric determination of excess cobalt(III) at 537 nm. A correction for the cobalt(II) product (ϵ_{537} 2.7 M^{-1} cm^{-1}) was applied in each case. The following respective concentrations were employed: $[Co^{III}]_0 = 1.0 \times 10^{-3}$ M, $[Fe^{II}]_0 = 3.54 \times 10^{-4}$ M, $[H^+] = 1.0$ M; $[Co^{III}]_0 = 1.41 \times 10^{-3}$ M, $[V(II)]_0 = 7.5 \times 10^{-4}$ M, $[H^+] = 1.0$ M; $[Co^{III}]_0 = 1.52 \times 10^{-3}$ M, $[H_2Q]_0 = 3.38 \times 10^{-4}$ M, $[H^+] = 0.2$ M.

The stoichiometry of the reaction with chromium(II) was measured under the following conditions: $[Co^{III}]_0 = 1.35 \times 10^{-4}$ M, $[Cr^{II}]_0 = 0.83 \times 10^{-4}$ M, at $[H^+] = 0.20$ M. A spectrophotometric correction was applied to account for the chromium(III) product (ϵ_{537} 10.4 M^{-1} cm^{-1}). Iodine produced in the reaction of $Co(NH_3)_2{}^{3+}{}_{aq}$ with iodide was titrated with standard thiosulfate under N_2 (starch indicator). The reaction conditions were $[Co^{III}]_0 = 4.2 \times 10^{-3}$ M, $[I^-]_0 = 8.2 \times 10^{-2}$ M, and $[H^+] = 0.45$ M. The instability toward aquation and reduction by water of the iron(III) product from the reaction of $Co(NH_3)_2{}^{3+}{}_{aq}$ with $(o\text{-phen})_3Fe^{2+}{}_{aq}$ precluded accurate stoichiometric measurements in this system. The identity of the iron(III) product was, however, established by the appearance of a spectral maximum at 590 nm whose intensity decreased with time as expected for $(o\text{-phen})_3Fe^{3+}{}_{aq}$.[11]

Kinetic Measurements. Most of the kinetic measurements were monitored spectrophotometrically in the stopped-flow apparatus previously described.[12] The slower rates were measured in a Beckman DK-1A spectrophotometer equipped with a thermostated cell housing which maintained temperature constant to within ±0.2 °C. The uncertainty in a given experimental temperature for the stopped-flow studies was less than ±0.1 °C. In all cases one of the reactants was present in at least 10-fold excess so that first-order conditions existed throughout the reaction. The reactant in excess was the reductant except in the reaction with tris(*o*-phenanthroline)iron(II). All of the faster reactions ($t_{1/2} < 1$ min) are averages of at least five independent measurements: duplicate measurements usually agreed to within less than ±8%. Most of the measurements were made by following the disappearance of the cobalt(III) complex in the wavelength range 350–600 nm except in the reactions with iodide, where the appearance of the triodide ion was followed at 290–420 nm, and with $(o\text{-phen})_3Fe^{II}$, where the disappearance of the iron(II) complex was monitored at 510 nm. The reactions were studied under the following reaction conditions: $[Co^{III}]_0 = (0.42\text{–}4.0) \times 10^{-3}$ M, $[H^+] = 0.1\text{–}1.99$ M, $[Fe(II)]_0 = (0.53\text{–}7.84) \times 10^{-2}$ M, $[Co^{II}]_0 = (0.94\text{–}9.4) \times 10^{-3}$ M, at 25.0–45.0 °C; $[Co^{III}]_0 = (4.6\text{–}10.6) \times 10^{-4}$ M, $[H^+] = 0.1\text{–}1.96$ M, $[V^{II}]_0 = (2.0\text{–}30) \times 10^{-3}$ M, $[Co^{II}]_0 = 8.3 \times 10^{-3}$ M, $[Zn^{II}]_0 = 10^{-2}$ M, $[V^{III}]_0 = 5.7 \times 10^{-3}$ M, at 3.2–25.0 °C; $[Co^{III}]_0 = (2.5\text{–}5.1) \times 10^{-4}$ M, $[H^+] = 0.2\text{–}2.0$ M, $[Cr^{II}]_0 = (2.3\text{–}23) \times 10^{-3}$ M, $[Zn(II)]_0 = 5.0 \times 10^{-3}$ M, at 3.2–25.0 °C; $[Co^{III}]_0 = (0.18\text{–}4.1) \times 10^{-4}$ M, $[H^+] = 0.05\text{–}1.0$ M, $[I^-]_0 = (2\text{–}30) \times 10^{-3}$ M, at 10.1–30.4 °C; $[Co^{III}]_0 = (8\text{–}11.2) \times 10^{-4}$ M, $[H^+] = 0.08\text{–}2.0$ M, $[H_2Q] = (5.8\text{–}57) \times 10^{-3}$ M, $[Co^{II}]_0 = 7.6 \times 10^{-3}$ M, at 25.3–45.3 °C; $[Co^{III}]_0 = (2\text{–}20) \times 10^{-4}$ M, $[H^+] = 0.05\text{–}1.0$ M, $[Fe(o\text{-phen})_3{}^{2+}]_0 = 10^{-5}$ M, at 15.3–35.3 °C.

In all cases the ionic strength of the reaction media was maintained at 2.0 M by addition of sodium perchlorate. Reactant solutions were thermostated at the desired temperature and in the case of the slower reactions were mixed and transferred to the thermostated cell within 60 s of mixing. Absorbance changes were followed for at least 5 half-lives and final absorbances were obtained for each run.

Results

Stoichiometric Measurements. The stoichiometric measurements confirmed that reactions 1–6 occurred under the

$$Co^{III}(NH_3)_{2aq} + Fe^{II}{}_{aq} + 2H^+ \rightarrow Co^{II}{}_{aq} + Fe^{III}{}_{aq} + 2NH_4^+ \quad (1)$$

$$Co^{III}(NH_3)_{2aq} + Cr^{II}{}_{aq} + 2H^+ \rightarrow Co^{II}{}_{aq} + Cr^{III}{}_{aq} + 2NH_4^+ \quad (2)$$

$$2Co^{III}(NH_3)_{2aq} + p\text{-}C_6H_4(OH)_2 + 2H^+ \rightarrow 2Co^{II}{}_{aq} + p\text{-}C_6H_4O_2 + 4NH_4^+ \quad (3)$$

$$Co^{III}(NH_3)_{2aq} + V^{II}{}_{aq} + 2H^+ \rightarrow Co^{II}{}_{aq} + V^{III}{}_{aq} + 2NH_4^+ \quad (4)$$

$$Co^{III}(NH_3)_{2aq} + Fe^{II}(o\text{-phen})_3 + 2H^+ \rightarrow Co^{II}{}_{aq} + Fe^{III}(o\text{-phen})_3 + 2NH_4^+ \quad (5)$$

$$2Co^{III}(NH_3)_{2aq} + 2I^- + 4H^+ \rightarrow 2Co^{II}{}_{aq} + I_2 + 4NH_4^+ \quad (6)$$

conditions used. The maximum experimental uncertainty is ±8% of the reported stoichiometry.

Kinetics. The kinetic data for the reactions are collected in Table I.[13] All of the reaction rates were observed to be first-order in each reactant. The rate law for each reaction is thus eq 7 where Red is the reductant and *S* is the appropriate

$$-\left(\frac{1}{S}\right)\frac{d[Co^{III}(NH_3)_2]}{dt} = \frac{d[\text{product}]}{dt} = k_{obsd}[Co^{III}(NH_3)_2][Red] \quad (7)$$

stoichiometric factor ($S = 2$ for reactions 3 and 6 and 1 for the other reactions). The observed second-order rate constants k_{obsd} were found to be independent of the initial cobalt(III) concentration and the monitoring wavelength except in reaction 5, where only one monitoring wavelength (510 nm) was used and the cobalt(III) complex was present in excess. In this case the observed second-order rate constant is the sum of the rate constant for oxidation and aquation of $Fe(phen)_3{}^{2+}{}_{aq}$. Thus, a plot of k_{obsd} vs. $[Co^{III}]_0$ was linear with an intercept at $[Co^{III}]_0 = 0$. The value of the intercept observed at the three experimental temperatures was in very good agreement with independent measurements of the aquation rate of $Fe(o\text{-phen})_3{}^{2+}{}_{aq}$ under the same reaction conditions and with data reported in the literature.[14] The value of k_{obsd} was found to be slightly dependent on the acid concentration (k_{obsd} = 2.36, 2.54, 2.42, and 2.72 M^{-1} s^{-1} at acid concentrations of 1.0, 0.5, 0.1, and 0.05 M, respectively at 25.0 °C). Since the rate of aquation of $Fe(phen)_3{}^{2+}{}_{aq}$ is acid independent in the range 0.005–0.5 M H_2SO_4,[14] these variations may be due to changes in the electrode potential of the $Fe(o\text{-phen})_3{}^{2+}{}_{aq}$–Fe(*o*-

Table II. Kinetic Data for Some Oxidation Reactions of $Co(NH_3)_2{}^{3+}{}_{aq}$ Species in Aqueous Perchlorate Media at Ionic Strength 2.0 M

Reductant	$k_o{}^a$	$k_1K_h{}^b$	$\Delta H^{\ddagger}{}_o{}^c$	$\Delta S^{\ddagger}{}_o{}^d$	$\Delta H^{\ddagger}{}_o{}^{c,e}$	$\Delta S^{\ddagger}{}_o{}^{d,e}$	Ref
Br^-	$(6.0 \pm 0.2) \times 10^{-5\,f}$	$(1.7 \pm 0.2) \times 10^{-4\,f}$	8 ± 3	−46 ± 10	29 ± 1	21 ± 4	1
H_2O_2		$(0.7 \pm 0.1) \times 10^{-4\,g}$			28 ± 1	16 ± 2	2
I^-	0.38 ± 0.01		23.6 ± 0.8	22 ± 3			*h*
H_2O	0.0285 ± 0.0005		19.1 ± 0.3	4 ± 1			*h*
$Fe(o\text{-phen})_2{}^{2+}{}_{aq}{}^i$	2.42 ± 0.04		14.5 ± 0.3	−6 ± 1			*h*
$Fe^{2+}{}_{aq}$	11.0 ± 0.2	1.99 ± 0.06	6.5 ± 0.4	−30 ± 1	16.3 ± 0.5	0 ± 2	*h*
$V^{2+}{}_{aq}$	3350 ± 60		5.1 ± 0.2	−23 ± 1			*h*
$Cr^{2+}{}_{aq}$	151 ± 3	497 ± 5	4.4 ± 1.2	−31 ± 4	13.8 ± 0.6	2 ± 2	*h*

[a] Units are M^{-1} s^{-1}, at 25.0 °C (errors quoted are one standard deviation). [b] Units are s^{-1}, at 25.0 °C. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1}. [e] Values are for the product k_1K_h. [f] Data refers to 28.0 °C. [g] Data at 28.5 °C. [h] This work. [i] Data have been corrected for aquation and refer to 0.1 M acid (see text).

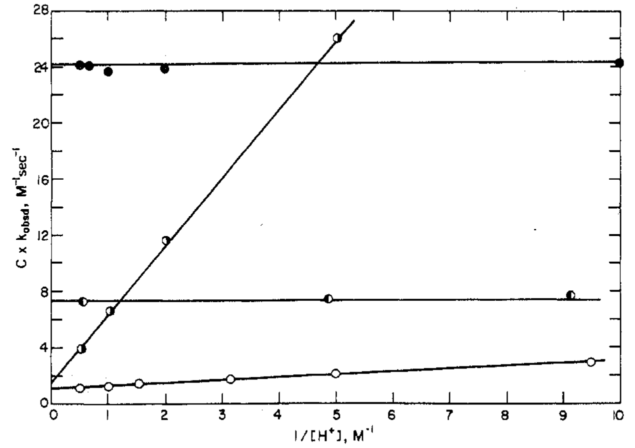

Figure 1. Examples of plots of k_{obsd} vs. $1/[H^+]$ at 25.0 °C and ionic strength 2.0 M. The reductants are as follows: ○, $Fe^{2+}{}_{aq}$ ($C = 10^{-1}$); ◑, $Cr^{2+}{}_{aq}$ ($C = 10^{-2}$); ◐, $I^-{}_{aq}$ ($C = 20$); ●, H_2Q ($C = 10^2$).

phen)$_3{}^{3+}{}_{aq}$ couple with varying acidity[15] and also to the presence of protonated forms of Fe(o-phen)$_3{}^{2+}{}_{aq}$[16] at high acidity; they are almost certainly not due to an acid dependence for the redox reaction of interest. However, we have chosen to report values of k_{obsd} and its activation parameters only at $[H^+] = 0.1$ M and ionic strength 2 M. The rates of reactions 1–4 were unaffected by addition of cobalt(II) and for reactions 2 and 4 (where zinc(II) ions are present in reactant solutions) further addition of zinc(II) had no measurable kinetic effect. Addition of vanadium(III) in reaction 4 also had no effect on the observed rate constant under fixed experimental conditions.

The second-order rate constants k_{obsd} were found to be acid concentration independent under the stated conditions except in the reactions with iron(II) and chromium(II), where

$$k_{obsd} = A + B/[H^+] \tag{8}$$

and A and B are empirical parameters with units of M^{-1} s^{-1} and s^{-1}, respectively. Examples of plots of k_{obsd} vs. $1/[H^+]$ at 25.0 °C are given in Figure 1 for reactions with iron(II), chromium(II), hydroquinone, and iodide.

The mechanism shown by eq 9–11 is consistent with the

$$Co^{3+}{}_{aq} \overset{\text{fast}}{\rightleftharpoons} CoOH^{2+}{}_{aq} + H^+ \quad K_h \tag{9}$$

$$Co^{3+}{}_{aq} + Red \xrightarrow{k_0} Co^{2+}{}_{aq} + Ox \tag{10}$$

$$CoOH^{2+}{}_{aq} + Red \xrightarrow{k_1} Co^{2+} + Ox \tag{11}$$

observed rate law for the one-electron reactions 1, 2, 4, and 5. Steps 10 and 11 are rate determining and Red and Ox are the initial and final forms of the reductants, respectively. The observed rate law (eq 8) is predicted by this mechanism if $K_h/[H^+] << 1$, where K_h is the acid dissociation constant of $Co(NH_3)_2{}^{3+}$ (abbreviated as Co^{3+} for clarity in eq 9–11).

Table III. Activation Parameters for Reactions of Aquocobalt(III) Species in Acidic Perchlorate Media

	$\Delta H^{\ddagger}{}_o{}^a$		$\Delta S^{\ddagger}{}_o{}^b$		
Reductant	$Co^{3+}{}_{aq}$	$Co(NH_3)_2{}^{3+}{}_{aq}$	$Co^{3+}{}_{aq}$	$Co(NH_3)_2{}^{3+}{}_{aq}$	Ref
$Fe^{2+}{}_{aq}$	9.1	6.5	−21	−30	*c*
$Cr^{2+}{}_{aq}$	9.5	4.4	−8	−31	*d*
$I^-{}_{aq}$	19.4	23.6	25	22	*c*
H_2Q_{aq}	18.2	19.1	18	4	*c*
$V^{2+}{}_{aq}$		5.1		−23	*c*

[a] Units are kcal mol^{-1}. [b] Units are cal deg^{-1} mol^{-1}, at 25.0 °C. [c] Data from this work (ionic strength 2 M) and ref 3 (ionic strength 3 M). [d] Data from this work and ref 17 (ionic strength 3 M).

Under these conditions $A = k_0$ and $B = k_1K_h$ for reactions 1 and 2 and $B/[H^+] = k_1K_h/[H^+] << k_0$ for reactions 4 and 5.

The radical mechanism shown by eq 12–14 is consistent with

$$Co^{3+}{}_{aq} + A \xrightarrow{k_0} Co^{2+}{}_{aq} + A\cdot \tag{12}$$

$$Co^{3+}{}_{aq} + A\cdot \xrightarrow{\text{fast}} \text{products} \tag{13}$$

$$2A\cdot \xrightarrow{\text{fast}} A_2 \tag{14}$$

the stoichiometric and kinetic data for reactions 3 and 6. Step 12 is rate determining and A· is a radical species. This mechanism predicts the identical rate law as the mechanism of eq 9–11 under the same conditions if $B/[H^+] << A = k_0$. The values obtained for k_0,k_1K_h, and corresponding activation parameters[1] are collected in Table II.

Discussion

A comparison of the rate constants and activation parameters for reduction of $Co(NH_3)_2{}^{3+}{}_{aq}$ and $Co(NH_3)_2OH^{2+}{}_{aq}$ species by the six reducing agents of this study with those for substitution-controlled reduction by Br^- and H_2O_2[1,2] (Table II) indicates that substitution into the coordination spheres of the cobalt(III) oxidants is not rate limiting in any of these reactions. The oxidation of substitution-inert[14] tris(o-phenanthroline)iron(II) must therefore be outer sphere. Redox reactions which are limited by substitution at V^{2+} proceed with second-order rate constants in the range 1–90 M^{-1} s^{-1} and activation enthalpies of 11–13 kcal mol^{-1}.[17] The corresponding values for the $Co(NH_3)_2{}^{3+}{}_{aq}$–$V^{2+}{}_{aq}$ reaction are well outside these ranges and clearly indicate the operation of an outer-sphere mechanism in this case also. In addition, the ratio $k_{0_{Cr^{2+}}}/k_{0_{V^{2+}}}$ is 0.045 with $Co(NH_3)_2{}^{3+}{}_{aq}$ as oxidant, and a value as high as 0.044 has been observed for definite outer-sphere reactions.[18] This suggests that the $Co(NH_3)_2{}^{3+}{}_{aq}$–$Cr^{2+}{}_{aq}$ reaction also occurs via an outer-sphere mechanism, although this conclusion is made somewhat uncertain by the high substitutional lability of $Cr^{2+}{}_{aq}$.[19]

The reactions of *fac*-$Co(NH_3)_3{}^{3+}{}_{aq}$ [8] with I^- and $Fe^{2+}{}_{aq}$ are much slower than are those of $Co(NH_3)_2{}^{3+}{}_{aq}$ reported here

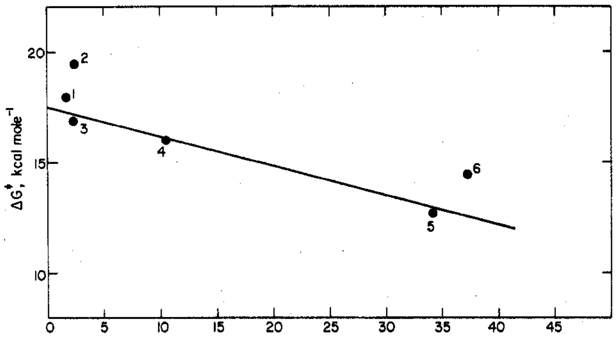

Figure 2. Plot of $\Delta G^{\ddagger}_{\text{obsd}}$ vs. ΔG_{el} for reductions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ at 25 °C. See text for assumptions leading to values of ΔG_{el}. The reductants are indicated as follows: 1, $\text{I}^-{}_{\text{aq}}$; 2, H_2Q; 3, $\text{Fe}(o\text{-phen})_3{}^{2+}$; 4, $\text{Fe}^{2+}{}_{\text{aq}}$; 5, $\text{V}^{2+}{}_{\text{aq}}$; 6, $\text{Cr}^{2+}{}_{\text{aq}}$.

and the lack of redox data for the higher ammines indicates that $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ is a moderately strong oxidant. However, a wide range of data is available for aquocobalt(III) reactions[3] and encourages comparison between these two systems.

The activation parameters for some reduction reactions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ and $\text{Co}^{3+}{}_{\text{aq}}$ are shown in Table III. It appears that, for both oxidants, $\Delta H^{\ddagger}_{0}$ values for the reactions with I^- and H_2Q are much larger than are those for reactions with $\text{Fe}^{2+}{}_{\text{aq}}$ and $\text{Cr}^{2+}{}_{\text{aq}}$. The values of $\Delta S^{\ddagger}_{0}$ increase as the charge product of the reactant pairs becomes more negative; however, $\Delta S^{\ddagger}_{0}$ values for $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ reactions are consistently more negative than those for $\text{Co}^{3+}{}_{\text{aq}}$ reactions and are closer to those observed for outer-sphere reactions between inert species.[20] It is also notable that the enthalpies of activation for reduction of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ by $\text{Cr}^{2+}{}_{\text{aq}}$ and $\text{Fe}^{2+}{}_{\text{aq}}$ are significantly smaller than are those for reduction of $\text{Co}^{3+}{}_{\text{aq}}$. Although outer-sphere mechanisms are suggested by the data for all these systems (see below) and $\text{Co}^{3+}{}_{\text{aq}}$ is undoubtedly the stronger oxidant, the origin of these differences is still uncertain. The "limiting" behavior suggested for $\text{Co}^{3+}{}_{\text{aq}}$ reactions[4] does not appear to be appropriate here, since a plot of $\Delta H^{\ddagger}_{0}$ vs. ΔH_{ip}, where ΔH_{ip} is the enthalpy of ion association,[4] does not correlate the data for these $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ reactions.

Figure 2 shows a plot of the observed free energy of activation, $\Delta G^{\ddagger}_{\text{obsd}}$, for reactions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ vs. the overall free energy change, ΔG_{el},[21] for process 15, where Red and Ox

$$\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}} + \text{Red} \rightleftharpoons \text{Co(NH}_3)_2{}^{2+}{}_{\text{aq}} + \text{Ox} \quad \Delta G_{\text{el}} \tag{15}$$

are the initial and one-electron oxidized forms of the reductant, respectively. No account has been made for the differences in the free energy of precursor formation.[26] The electrode potential, $\mathcal{E}°$, for the $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}\text{–Co(NH}_3)_2{}^{2+}{}_{\text{aq}}$ couple has been assumed to be 1.2 V in order to give $\Delta G_{\text{el}} \leq 0$, but this choice is completely arbitrary and the use of any other value would not affect the shape or slope of the line (see below).

Figure 2 illustrates that a line of slope ca. 0.14 can be drawn through most of the data for reduction by 2+ ions. This correlation suggests that all of these reactions occur by a similar mechanism and that reduction by $\text{Fe}^{2+}{}_{\text{aq}}$ is outer-sphere, although the substitutional lability[19] of $\text{Fe}^{2+}{}_{\text{aq}}$ makes this conclusion somewhat uncertain.

There is one basic problem associated with attempts to estimate $\mathcal{E}°$ from data for reduction of amminecobalt(III) centers. This difficulty arises from the fact that these reactions are virtually irreversible because of the thermodynamically favorable, rapid dissociation of the primary product $\text{Co(NH}_3)_n{}^{2+}{}_{\text{aq}}$ to $\text{Co}^{2+}{}_{\text{aq}}$ and $\text{NH}_4{}^+$ in acid solution. For example, the calculated free energy change for process 16 is −18.1 kcal mol⁻¹ at 25 °C.[27] In general, this represents a major contribution to the overall free energy change, ΔG_0, for transformation of reactants to final products and in some redox systems may provide the *only* driving force for electron transfer. A case in point is the measurable rate constant for reduction of $\text{Co(NH}_3)_6{}^{3+}{}_{\text{aq}}$ by $\text{Ru(NH}_3)_6{}^{2+}{}_{\text{aq}}$, for which ΔG_{el} is greater than zero.[29] Thus, it is conceivable that $\Delta G°_{\text{el}} > 0$ for the reactions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ with I^-, H_2Q, $\text{Fe}(o\text{-phen})_3{}^{2+}$, and $\text{Fe}^{2+}{}_{\text{aq}}$.

$$\text{Co(NH}_3)_2{}^{2+}{}_{\text{aq}} + 2\text{H}^+ \rightleftharpoons \text{Co}^{2+}{}_{\text{aq}} + 2\text{NH}_4{}^+ \tag{16}$$

Table IV. Derived Ratios of Second-Order Rate Constants for Reduction of Hydroxo- and Aquocobalt(III) Species in Perchlorate Media at 25 °C

Reductant	$k_{\text{Co(NH}_3)_2\text{OH}^{2+}{}_{\text{aq}}}/k_{\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}}$ [a]	$k_{\text{CoOH}^{2+}{}_{\text{aq}}}/k_{\text{Co}^{3+}{}_{\text{aq}}}$ [b]
$\text{I}^-{}_{\text{aq}}$	≤24	180
H_2O	≤44	290
$\text{V}^{2+}{}_{\text{aq}}$	≤40	
$\text{Cr}^{2+}{}_{\text{aq}}$	1.3 × 10⁴	260
$\text{Fe}^{2+}{}_{\text{aq}}$	720	560
$\text{Co}^{2+}{}_{\text{aq}}$		160

[a] This work, at ionic strength 2 M. K_{h} is assumed to be 2.5 × 10⁻⁴ M. [b] Data are from ref 3 and 17 at ionic strength 3.0 M, assuming $K_{\text{h}} = 2 \times 10^{-3}$ M.

In addition, no kinetic data are available for electron exchange in the $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}\text{–Co(NH}_3)_2{}^{2+}{}_{\text{aq}}$ system and the standard electrode potential, $\mathcal{E}°$, for this couple is unknown. However, reduction of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ will only be thermodynamically favorable if $\Delta G_{\text{el}} < 18.1$ kcal mol⁻¹. This requires that $\mathcal{E}°$ be greater than 0.35 V based on the data for the weakest reductant in this series ($\text{I}^-\text{–I}_2{}^{\cdot-}$, $\mathcal{E}$ = 1.13 V).[23] Since reduction reactions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ are generally *much faster* than those of $\text{Co(NH}_3)_5\text{H}_2\text{O}^{3+}{}_{\text{aq}}$,[30] which has an estimated oxidation potential of 0.33 V,[31] it is plausible that $\mathcal{E}° > 0.35$ V for the $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}\text{–Co(NH}_3)_2{}^{2+}{}_{\text{aq}}$ couple.

A more reasonable estimate of the minimum $\mathcal{E}°$ for the diammine system can be obtained as follows. The free energy for electron exchange, $\Delta G^{\ddagger}_{11}$, in the aquocobalt(III) system is 16.6 kcal mol⁻¹.[3] Since $\Delta G^{\ddagger}_{11}$ increases in the $\text{Co(NH}_3)_n(\text{H}_2\text{O})_{6-n}{}^{3+}{}_{\text{aq}}$ series as n increases from 0 to 6,[32] it is likely that $\Delta G^{\ddagger}_{11}$ for the $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}\text{–Co(NH}_3)_2{}^{2+}{}_{\text{aq}}$ system is at least as large as that for the $\text{Co}_{\text{aq}}{}^{3+}\text{–Co}^{2+}{}_{\text{aq}}$ couple. The intercept at $\Delta G°_{\text{el}} = 0$ for a plot such as that shown in Figure 2 should, by definition, be equal to $\Delta G^{\ddagger}_{11}$. In order for $\Delta G^{\ddagger}_{11}$ to be >16.6 kcal mol⁻¹ in the diammine system, $\mathcal{E}°$, must be at least 0.91 V, which is intermediate between those for the $n = 5$ and $n = 0$ couples[31,33] (see above).

We now turn to a consideration of the effect of inner-sphere hydroxide on the reactivity of the $\text{Co(NH}_3)^{3+}{}_{\text{aq}}$ species. If the values of K_{h} for $\text{Co}^{3+}{}_{\text{aq}}$, $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$, and $\text{Co(NH}_3)_5\text{OH}_2{}^{3+}{}_{\text{aq}}$ are taken to be 2 × 10⁻³,[3] 2.5 × 10⁻⁴,[8] and 2.5 × 10⁻⁷ M,[34] respectively at 25 °C, then one can obtain values of k_1 from the experimentally determined k_1K_{h} products in each system.

The calculated ratios of k_1/k_0 for $\text{Co(NH}_3)_2\text{OH}^{2+}{}_{\text{aq}}\text{–Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ and $\text{CoOH}^{2+}{}_{\text{aq}}\text{–Co}^{3+}{}_{\text{aq}}$ oxidant pairs are shown in Table IV. In the case of the acid-independent diammine reactions, the ratios are upper limits obtained from the assumption that $k_1K_{\text{h}} \leq 0.1k_0[\text{H}^+]$ at the lowest respective experimental acidities. The ratios of k_1/k_0 for reactions of aquocobalt(III) species are all similar, whereas a marked differentiation is evident in the ratios for the aquodiamminecobalt(III) species. Since OH^- has little effect on the rates of reactions of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ with I^-, H_2Q, and $\text{V}^{2+}{}_{\text{aq}}$, a general outer-sphere mechanism is indicated for reaction of the hydroxo form. Of the remaining two cases, the reduction of $\text{Co(NH}_3)_2{}^{3+}{}_{\text{aq}}$ by Cr^{2+} is the more subject to base catalysis, which points to an inner-sphere mechanism for the $\text{Co(NH}_3)_2\text{OH}^{2+}{}_{\text{aq}}\text{–Cr}^{2+}{}_{\text{aq}}$ reaction. The values of $10^{-6}k_1$ for reduction of $CoOH^{2+}_{aq}$, $Co(NH_3)_2OH^{2+}_{aq}$, and $Co(NH_3)_5OH^{2+}_{aq}$ by Cr^{2+}_{aq} are 3.3,[10] 3.0, and 1.5 $M^{-1}\ s^{-1}$,[35] respectively at 25 °C, suggesting a common rate-determining step, presumably substitution at Cr^{2+}_{aq}, for these systems. It is worth noting that oxygen atom exchange has been observed in other Cr^{2+}_{aq} reductions of cobalt ammines.[36]

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Registry No. Co, 7440-48-4; I^-, 20461-54-5; hydroquinone, 106-51-4; $Fe(o\text{-phen})_3^{2+}$, 14708-99-7; Fe^{2+}, 15438-31-0; V^{2+}, 15121-26-3; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Table I, showing kinetic data for the reduction of $Co(NH_3)_2{}^{3+}_{aq}$ species (6 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Anation of Hexaaquorhodium(III) Ion by Bromide Ion in Acidic Aqueous Solution. Kinetic Trans Effect as a Mechanistic Criterion for Ligand Water Replacement Processes[1]

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Rate constants over the temperature range 50–80 °C have been obtained for the title reaction at I = 2.00 M, with $[H^+]$ varied between 0.50 and 2.00 M and $[Br^-]$ varied between 0.10 and 1.00 M. The data have been interpreted in a manner analogous to that employed for previous studies of aquorhodium(III) complex ions and show that the rate-limiting process for bromide anation is identical within experimental error with that for the corresponding chloride reaction and very close to the water-exchange rate of the parent complex ion. These findings, reinforced by some observations on the kinetic trans-effect phenomenon for anation of complexes of the form $Rh(H_2O)_5X^{2+}$ (X^- = OH^-, Cl^-, or Br^-), support the simple dissociative (D) mechanism concept for reactions of this type. Comparisons are also made with rate constant and trans-effect data for various reactions of the species $Rh(en)_2X(H_2O)^{3+}$ (X = H_2O, OH^-, Cl^-, or Br^-) and $Rh(NH_3)_5H_2O^{3+}$ and discussed in terms of possible mechanisms.

Introduction

Previous studies originating in this laboratory have dealt with the chloride anation kinetics of the complete family of chloroaquorhodium(III) complex ions, including the hexaaquo,[2] chloropentaaquo,[3] *trans*- and *cis*-dichlorotetraaquo,[4] *mer*- and *fac*-trichlorotriaquo,[4] *trans*-tetrachlorodiaquo,[4] *cis*-tetrachlorodiaquo,[5] and the pentachloroaquo species.[6] An argument based on the acid dependence of the anation kinetics of the monochloro congener[3] provides effective evidence that a five-coordinate intermediate or dissociative (D)[7] mechanism is to be preferred for at least two members of the series. This type of kinetic analysis has also supported the D-mechanism concept for chloride anation of the related species *trans*-diaquobis(ethylenediamine)rhodium(III) complex.[8] Furthermore, the recently reported study[4] of the dichloro, trichloro, and tetrachloro species offers additional kinetic evidence for the D mechanism and also for a fixed square-pyramidal geometry of the assumed five-coordinate intermediate.

If, in truth, anation of the hexaaquorhodium(III) ion is purely dissociative, use of some other similar anion in place