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Redetermination of the Hexaamminecobalt(III/II) Electron-Self-Exchange Rate

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Received July 20, 1983

The rate of electron self-exchange for the $[Co(NH_3)_6]^{3+/2+}$ couple has been measured by studying the rate of exchange of ammonia between $[Co(NH_3)_6]^{3+}$ and $NH_3(aq)$ catalyzed by Co(II). The temperature chosen, 40.0 °C, represents a compromise between an inconveniently slow reaction at lower temperature and the increasing contribution to exchange by side reactions at higher temperature. With $CF_3SO_3^-$ and Cl^- as counterions, the second-order specific rates are found to be (8 [illegible] 1) $\times 10^{-6}$ and $(3.9 \pm 1.5) \times 10^{-6}$ M^{-1} s^{-1}, respectively, at ionic strength 2.5 M, much higher than the values suggested in earlier work. There is no significant anomaly in the comparison with the well-established rate of exchange for $[Co(en)_3]^{3+/2+}$.

Introduction

In an earlier study[1,2] of the electron-self-exchange reaction of hexaamminecobalt(III/II) (eq 1) the conclusion was

$$[Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+} = [Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \quad (1)$$

reached that the second-order rate constant for this reaction is less than 1.6×10^{-10} M^{-1} s^{-1} at 64.5 °C. On the basis of several lines of evidence, we have concluded that the rate constant for this reaction is actually at least 5 orders of magnitude greater than this.[3] A good value for the rate constant is important of itself, but it is important also in assessing the magnitude of the spin barrier to electron transfer[4,5] proposed for this reaction.

In the earlier studies[1,2] the electron-exchange reaction was followed with use of radiocobalt. As we have pointed out,[3] in these studies side reactions involving hydrolysis of the complexes, which ultimately lead to cobalt exchange, were not fully taken into account. In the present study, we have chosen to label the ammonia ligands with ^{15}N, which can be assayed by NMR of the ammine protons. In following nitrogen exchange by the NMR method, we are also able to check the corrections we have made for the hydrolysis side reactions, using published data.[6] In the experiments devoted to the electron-self-exchange reaction, the concentration of ammonia covers a wide range. Since the change in the medium itself can be expected to affect the rate of the electron-transfer reaction, we have attempted to gauge it by studying the rate of reduction of $[Ru(NH_3)_6]^{3+}$ by $[Co(en)_3]^{2+}$ as a function of the concentration of NH_3.

Experimental Section

Preparations. Analytical reagents were used unless otherwise specified. Water was purified with a Barnstead "Nanopure" system.

The salt $Co(O_3SCF_3)_2{\cdot}6H_2O$ was synthesized by adding $CoCO_3$ to dilute trifluoromethanesulfonic acid. After filtration, the filtrate was concentrated by rotary evaporation and the pink product was collected, dried by suction, and washed with ether. Anal. Calcd for $Co(O_3SCF_3)_2{\cdot}6H_2O$: Co, 12.7. Found: Co, 12.4.

$NH_4O_3SCF_3$ was synthesized by neutralization of aqueous ammonia with trifluoromethanesulfonic acid, followed by rotary evaporation to dryness.

KO_3SCF_3 was similarly prepared; the residue was dissolved in acetone and reprecipitated with ether.

$[Co(^{15}NH_3)_6]Cl_3$. A solution was prepared by dissolving $^{15}NH_4Cl$ (2.00 g, 95 atom %, Merck Sharp and Dohme Canada, Ltd.), $CoCl_2{\cdot}6H_2O$ (0.86 g), and NaOH (1.20 g) in ice-cold water (3.0 mL) with cooling in ice. Decolorizing charcoal (10 mg) and H_2O_2 (30%, 0.20 mL) were added, and the suspension was stirred in a covered vessel for 5 h. The mixture was then diluted with 50 mL of 0.5 M HCl, filtered through Celite, and passed down a column (2.5 × 3.0 cm) of cation-exchange resin (AG50W-X1, H^+ form). The column was washed with 100 mL of 1 M HCl and the eluate saved for recovery of unreacted $^{15}NH_4Cl$ by sublimation. After elution of a minor purple band ($[Co(^{15}NH_3)_5Cl]^{2+}$) with 2.0 M HCl, the main orange-colored band was eluted with 3.0 M HCl and the eluate rotary evaporated to dryness. The solid residue was dissolved in water and sorbed onto a column (4 × 15 cm) of SP-Sephadex C-25 cation exchanger in the sodium ion form. Elution with 0.25 M sodium acetate revealed a leading red band ($[Co(^{15}NH_3)_5OH^{2+}$) and a trailing yellow band ($[Co(^{15}NH_3)_6]^{3+}$). The eluates of the two bands were separately passed down a column of AG50W-X7 resin and washed with 1 M HCl to remove Na^+, and the complex was eluted with 3 M HCl. The eluate containing $[Co(^{15}NH_3)_6]^{3+}$ was rotary evaporated to ~10 mL, whereupon crystallization occurred. The solution was cooled to 0 °C and the crystals were collected, washed with ethanol and ether, and air-dried: yield 0.71 g. Anal. Calcd for $[Co(^{15}NH_3)_6]Cl_3$ (95 atom %): H, 6.64; N, 30.75; Cl, 38.93. Found: H, 6.4; N, 30.7; Cl, 38.6. The eluates containing the pentaammine side products were combined and evaporated to dryness and were used as a source of $^{15}NH_3$ in subsequent preparations of the hexaammine complex.

$[Co(NH_3)_6]^{3+/2+}$ Self-Exchange. The studies consisted of following the loss of ^{15}N label in $[Co(NH_3)_6]^{3+}$ in ammoniacal cobalt(II) solutions. Stock solutions of $[Co(^{15}NH_3)_6]Cl_3$, NH_4Cl, $NH_4O_3SCF_3$, KCl, and KO_3SCF_3 were prepared by weight, and solutions of $CoCl_2$ and CoO_3SCF_3 were assayed by atomic absorption. A solution (2 mL) containing the desired concentrations of $[Co(^{15}NH_3)_6]Cl_3$ and $CoCl_2$ (or CoO_3SCF_3) was placed in a bubbler flash and purged with argon deaerated by prebubbling through a solution of $Cr^{2+}(aq)$. A solution (13 mL) of the desired concentrations of NH_4Cl (or $NH_4O_3SCF_3$), KCl (or KO_3SCF_3), and ammonia was placed in a second bubbler. This solution was purged with deoxygenated argon that had been bubbled through concentrated ammonia. The solutions were mixed through a Teflon cannula. The resulting solution was loaded in 2-mL aliquots by cannula into seven serum-capped, argon-purged neutra glass ampules (Wheaton VACULES, 2 mL). (These had been pretreated with concentrated nitric acid for 1 h, rinsed with distilled water, and dried at 110 °C before use.) The ampules were flame sealed soon after filling and then were submerged in a water bath at 40.0 ± 0.1 °C.

At intervals, an ampule was removed and opened, and its content were quickly acidified with 4 M HCl. (For at least two ampules of every run, a 1.00-mL sample was drawn first and added to a known excess of HCl and then back-titrated with NaOH to a bromocresol blue endpoint, to determine total ammonia.) The acidified contents were poured down a column of AG50W-X7 cation-exchange resin in the H^+ form, washed with 1.5 M HCl, and then eluted with 3 M HCl. The yellow $[Co(NH_3)_6]^{3+}$ eluate was rotary evaporated to dryness and dissolved in 3 mL of hot water, and the perchlorate salt was precipitated by addition of $NaClO_4{\cdot}H_2O$ followed by cooling at room temperature. The crystals were collected, washed with ethanol and ether, and air-dired.

Each such $[Co(NH_3)_6](ClO_4)_3$ sample was dissolved in 1% D_2SO_4 in Me_2SO-d_6 and its proton NMR spectrum determined with a Varian XL-100 spectrometer. The spectrum consists of three peaks, a doublet

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Table I. Electron-Self-Exchange Rate Data for the $[Co(NH_3)_6]^{3+/2+}$ System at 40 °C, $I = 2.5$ M[a]

run	[Co(II)], mM	$[NH_4^+]$, M	$[NH_3]$,[b] M	no. of ampules studied	no. of $t_{1/2}$ periods	$[Co(NH_3)_6^{2+}]$,[g] mM	10^7k_{obsd},[c] s^{-1}	10^7k_{cor},[g] s^{-1}
1	80[d]	2.00	9.3	5	2.7	55	4.7 (3)	4.6 (3)
2	50	2.02	9.2	5	2.3	34	1.86 (6)	1.78 (6)
3[e]	50	1.60	8.9	3	0.7	34	1.0 (2)	0.9 (2)
4	50	1.20	7.3	4	0.6	31	0.8 (1)	0.7 (1)
5[e]	40[d]	2.00	10.2	5	2.0	28	2.4 (2)	2.3 (2)
6[e,f]	40[d]	0.20	8.9	1				
7	40	1.98	11.6	5	2.1	29	1.56 (6)	1.47 (6)
8[e]	30	2.01	10.5	4	1.1	21	1.2 (1)	1.1 (1)
9[e]	30	1.00	8.9	5	1.4	20	1.29 (2)	1.16 (2)
10[e]	30	0.67	10.3	4	0.7	21	0.9 (1)	0.7 (1)
11[e]	30	0.50	9.7	4	0.6	21	0.7 (1)	0.4 (1)
12[e]	30	1.84	9.9	4	0.6	21	0.64 (3)	0.55 (3)
13	30	1.65	8.5	5	1.2	21	1.11 (3)	1.03 (3)
14	30	1.25	7.7	3	0.9	19	0.87 (2)	0.57 (2)
15	20	1.99	10.3	3	0.4	14	0.9 (2)	0.8 (2)
16	0	1.20	6.6	2	0.2	0	0.07 (5)	0.01
17	0	0.30	4.7	2	0.4	0	0.21 (5)	0.02
18	0	0.20	1.1	2	0.1	0	0.04 (3)	−0.04
19	0	0.10	4.8	2	0.8	0	0.40 (6)	−0.18

[a] $[Co(NH_3)_6Cl_3] = 12 \pm 2$ mM; chloride medium (KCl), unless specified. The figure in parentheses following each rate constant value is the estimated standard deviation in the last significant figure. [b] $[NH_3] = C_{NH_3} - 6C_{Co(II)}$; C_{NH_3} is the average of at least two measurements. [c] Observed first-order rate constant for NH_3 exchange in the $[Co(NH_3)_6]^{3+}$ complex. [d] $CF_3SO_3^-$ ion medium (KO_3SCF_3). [e] Analyzed for $[Co(NH_3)_6]^{3+}$ ion at end of run. [f] No $[Co(NH_3)_6]^{3+}$ complex detected after 25 days of reaction. [g] See text.

corresponding to protons of coordinated $^{15}NH_3$ surrounding a singlet due to the $^{14}NH_3$ protons.[7] These peaks were integrated by using the utility curve-fitting program NFTCAP of the XL-100FT software package, to give the best visual fit. The ratio of the central peak area to the total area of all three peaks was taken to be $^{14}X_t$, the mole fraction of ^{14}N at the time the ampule was opened.

The data were reduced with use of the McKay treatment,[8] where the fraction of exchange at time t is $F = (^{14}X_t - {}^{14}X_0)/(^{14}X_\infty - {}^{14}X_0)$. The infinity value $^{14}X_\infty$ was calculated from the known concentrations of total $^{15}NH_3$ and $^{14}NH_3$ in the reaction solution, including the natural abundance of 0.37% ^{15}N. The data were fitted to the function $\ln(1 - F) = -k_{obsd}t$, with k_{obsd} and $^{14}X_0$ being treated as variables.

$[Ru(NH_3)_6]^{3+}$ + $[Co(en)_3]^{2+}$. The reaction of $[Ru(NH_3)_6]^{3+}$ with $[Co(en)_3]^{2+}$ was followed spectrophotometrically (466 nm) at 25.0 ± 0.1 °C, in mixtures of aqueous ammonia (0–10 M) and ethylenediamine (1.0 M) with (2-aminoethyl)ammonium chloride (1.0 M) being used to adjust the ionic strength. Before each set of kinetic runs, two solutions containing freshly distilled ethylenediamine, HCl, and aqueous ammonia were purged with deoxygenated, NH_3-scrubbed argon. Solid samples of $CoCl_2 \cdot 2H_2O$ and $[Ru(NH_3)_6]Cl_3$ (Matthey Bishop, Inc.) were added to the purged solutions, and the resulting solutions were purged 5 min. The solutions were mixed with a hand-operated stopped-flow device connected to a 1-cm quartz cell in a Cary 15 spectrophotometer. This device, capable of measuring half-lives down to about 1 s, is described elsewhere.[9] The ruthenium complex was used in excess, and plots of $\ln(A_\infty - A_t)$ vs. time were linear for at least 2 half-lives, yielding values of k_{obsd}.

Results

In the McKay treatment for the exchange of ^{15}N, $\ln(1 - F) = Rt(a + b)/ab$, where R is the rate of exchange of label and a and b are the concentrations of the two chemical forms of the label, which remain constant in a pure exchange reaction.[8] In this case, a and b represent the concentrations of nitrogen coordinated in $[Co(NH_3)_6]^{3+}$ ion and uncoordinated, respectively. The rate of N exchange is thus

$$R_N = \frac{6[Co(NH_3)_6^{3+}][N_f]}{6[Co(NH_3)_6^{3+}] + [N_f]}$$

where N_f represents nitrogen in ammonia not complexed to cobalt(III). The rate of cobalt exchange, R_{Co}, is $R_N/6$, since exchanging six ammonias effectively exchanges one cobalt. Since, under our conditions, $[Co(NH_3)_6^{3+}] << [N_f]$, the equation simplifies to $R_{Co} = k_{obsd}[Co(NH_3)_6^{3+}]$, so the observed rate constant for cobalt exchange can be taken as equal to that for nitrogen exchange.

The conditions and observed rate constants for cobalt exchange in our 19 kinetic runs are summarized in Table I. However, to determine the rate of the hexaamminecobalt self-exchange reaction (1), the contributions of other reactions that lead to exchange must be subtracted. These reactions are shown in eq 2–5.

$$[Co(^*NH_3)_6]^{3+} + OH^- = [Co(^*NH_3)_5(OH)]^{2+} + {}^*NH_3 \quad (2)$$

$$[Co(^*NH_3)_5(OH)]^{2+} + NH_3 = [Co(^*NH_3)_4(NH_3)(OH)]^{2+} + {}^*NH_3 \quad (3)$$

$$[Co(^*NH_3)_5(OH)]^{2+} + [Co(NH_3)_5(OH_2)]^{2+} = [Co(^*NH_3)_5(OH_2)]^{2+} + [Co(NH_3)_5OH]^{2+} \quad (4)$$

$$[Co(^*NH_3)_6]^{3+} + [Co(NH_3)_5(OH_2)]^{2+} + OH^- = [Co(^*NH_3)_6]^{2+} + [Co(NH_3)_5(OH)]^{2+} \quad (5)$$

The hydrolysis of hexaamminecobalt(III), reaction 2, and the reverse ammonolysis represent an exchange of ammonia label with the solvent. The ammonia-exchange reaction (3), and the redox reaction (4) represent ammonia-exchange mechanisms for $[Co(NH_3)_5OH]^{2+}$, which lead to observed exchange for hexaamminecobalt(III). Reaction 5 involves reduction of $[Co(NH_3)_6]^{3+}$.

Corrections for Side Reactions. Data in the literature lead to good estimates of the rates of reactions 2–4. The hydrolysis reaction (2) has been found to follow a rate law of the form[6] $R_2 = k_2'K_a[Co(NH_3)_6^{3+}]/[H^+]$, with $k_2' = 2.8 \times 10^{-4}$ M^{-1} s^{-1}, and $K_a = 1.9 \times 10^{-13}$ M at 61.8 °C, $I = 2.0$ M, and $E_a = 35.0$ kcal/mol. With use of the energy of activation and the value[10] of $pK_a(NH_4^+) = 9.10$ at 40 °C, $I = 2.5$ M, the rate can be expressed as $R_2 = k_2[Co(NH_3)_6^{3+}][NH_3]/[NH_4^+]$, with $k_2 = 1.6 \times 10^{-9}$ s^{-1} at 40 °C, $I = 2.5$ M.

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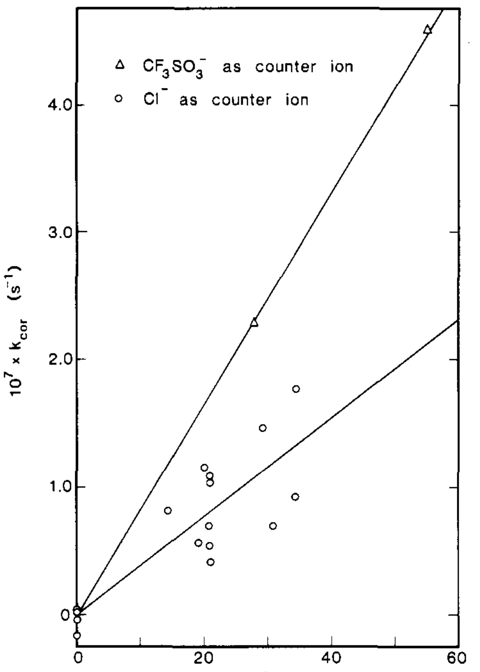

Figure 1. Plot of corrected rate constants vs. $[Co(NH_3)_6^{2+}]$ (data from Table I).

Williams and Hunt[11] have studied ammonia exchange in $[Co(NH_3)_5OH]^{2+}$, reaction 3, and found the rate of reaction to be independent of pH in alkaline solution. The value for the first-order rate constant was reported as 9.2×10^{-6} s^{-1} at 44.4 °C, $I = 2.28$ M, with $\Delta H^{\ddagger} = 32$ kcal/mol, so that $k_3 = 4.2 \times 10^{-6}$ s^{-1} at 40 °C.

The redox reaction of the pentaamminecobalt(III/II) system, reaction 4, has been studied by Appelman, Anbar, and Taube[12] and later by Williams and Hunt.[13] The reaction appears to fit the rate law $R_4 = k_4[Co(NH_3)_5(OH)^{2+}][Co(NH_3)_5(OH_2)^{2+}]$. When ^{18}O-labeled $[Co(NH_3)_5(OH)]^{2+}$ was used,[11] no exchange with solvent water was seen on the time scale of the redox reaction, consistent with a mechanism involving a hydroxo-bridged activated complex with transfer of oxygen upon reaction. Appelman et al. used the association constants obtained by Bjerrum[14] for the Co(II)–ammine system at $I = 2.28$ M, in calculating k_4 (4.4×10^{-4} and 6.0×10^{-4} M^{-1} s^{-1} at 35.5 and 45 °C, respectively) from their data. Williams and Hunt obtained $k_4 = 4.4 \times 10^{-4}$ and 1.4×10^{-3} M^{-1} s^{-1} at 35.5 and 44.4 °C, respectively, also making use of Bjerrum's equilibrium values. The activation parameters given in the latter study ($\Delta H^{\ddagger} = 20 \pm 4$ kcal/mol, $\Delta S^{\ddagger} = 7.3 \pm 12$ cal mol^{-1} K^{-1}) seem more reasonable, and using them, we calculate $k_4 = 7 \times 10^{-4}$ M^{-1} s^{-1} at 40 °C.

The rate of reaction 5 has not been measured. It should be noted through that it is an outer-sphere electron-transfer reaction and is considerably uphill thermodynamically. This can be seen by noting that, at equilibrium under our reaction conditions, the dominant form of Co(III) is $[Co(NH_3)_6]^{3+}$, not $[Co(NH_3)_5(OH)]^{2+}$. We assume therefore that the rate of reaction 5 is small compared to the rate of reaction 1, and we neglect it.

The contribution of the side reactions to the observed rate of exchange of ^{15}N label can be assessed if a steady-state isotope distribution is assumed for the $[Co(NH_3)_5(OH)]^{2+}$ species. The following symbols will be used: $X_{(6)}$ is the mole fraction of ^{15}N in $[Co(NH_3)_6]^{3+}$ and $X_{(5)}$ in $[Co(NH_3)_5(OH)]^{2+}$. The equilibrium ratio of $[Co(NH_3)_5(OH)^{2+}]$ to $[Co(NH_3)_6^{3+}]$ will be denoted as α. From the work of Bjerrum,[14] $\alpha = 0.0209$ M/$[NH_4^+]$ at 30 °C, and at 65 °C it is found to be[15] $\alpha = 0.025$ M/$[NH_4^+]$, with $I = 2.5$ M. For our work at 40 °C, a value of $\alpha = 0.022$ M/$[NH_4^+]$ will be used.

It will be assumed in this treatment that the equilibrium in the formation of $[Co(NH_3)_5(OH)]^{2+}$ is established rapidly relative to the time scale of the exchange reaction. Since the buildup time is actually finite, our treatment tends to overestimate this concentration and hence the contribution of the side reactions to the observed exchange.

At equilibrium then, the hexaammine and hydroxopentaammine species will interconvert at the rate $R_2 = k_2[Co(NH_3)_6^{3+}][NH_3][NH_4^+]^{-1}$. The rate of change of ^{15}N label in the $[Co(NH_3)_5(OH)]^{2+}$ species is then expressed by eq 6. On introduction of the steady-state condition

$$\frac{d[^{15}N_{(5)}]}{dt} = (X_{(6)} - X_{(5)})5k_2\frac{[NH_3]}{[NH_4^+]}[Co(NH_3)_6^{3+}] - (k_3 + 5k_4[Co(NH_3)_5(OH_2)^{2+}])X_{(5)}[Co(NH_3)_5(OH)^{2+}] \quad (6)$$

eq 7 follows. As expected, if the contributions of reactions

$$\frac{X_{(5)}}{X_{(6)}} = \frac{5k_2[NH_3][NH_4^+]^{-1}}{5k_2[NH_3][NH_4^+]^{-1} + \alpha k_3 + 5\alpha k_4[Co(NH_3)_5(OH_2)^{2+}]} \quad (7)$$

3 and 4 are negligible, the fractions of label in $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5(OH)]^{2+}$ are equal. If reactions 3 and 4 are rapid compared to reaction 2, the ratio is small—$[Co(NH_3)_5(OH)]^{2+}$ has lost its label.

The rate of change of label in the $[Co(NH_3)_6]^{3+}$ ion by the hydrolysis pathway is $d[^{15}N_{(6)}]/dt = [5X_{(5)} - 6X_{(6)}]k_2[Co(NH_3)_6^{3+}][NH_3][NH_4^+]^{-1}$. The first-order rate constant for exchange of label becomes $d(\ln X_{(6)})/dt = d[^{15}N_{(6)}]/[^{15}N_{(6)}]dt = k_2([NH_3][NH_4^+]^{-1})((5X_{(5)}/6X_{(6)}) - 1)$. Thus, for $X_{(5)}/X_{(6)}$ small, the exchange proceeds at the hydrolysis rate, and for $X_{(5)}/X_{(6)} = 1$, there is one-sixth exchange with each hydrolysis event.

With the known values for k_2, k_3, k_4, and α, the contribution of the side reactions can be calculated. A vast simplification occurs when even a small amount of cobalt(II) is present. For $[NH_3] = 5$ M, $[NH_4^+] = 2$ M, and $[Co(NH_3)_5(OH_2)^{2+}] = 0.01$ M, the ratio $X_{(5)}/X_{(6)} = 0.023$. Thus with a least this much Co(II) present, the contribution of the side reactions essentially is governed by the hydrolysis rate of reaction 2.

Analysis of Data. The observed first-order rate constants of exchange in our 19 runs, presented in Table I, are corrected by subtracting the calculated contributions of side reactions 2–4, as explained in the previous section. These values of k_{cor} then represent the exchange of label due to electron transfer between the cobalt species.

Also tabulated are the concentrations of $[Co(NH_3)_6]^{2+}$ for each run as calculated from [Co(II)] and $[NH_3]$ by using association constants interpolated from those of Bjerrum:[14] $K_5 = 1.46$ M^{-1} and $K_6 = 0.23$ M^{-1} at 40 °C and $I = 2.5$ M. Under our conditions, usually about two-thirds of the cobalt(II) is in the hexaammine form.

In runs 16–19, with [Co(II)] = 0, the values of k_{cor} average to $(-0.5 \pm 3.0) \times 10^{-8}$ s^{-1} (95% confidence limit), close to the expected zero. The correction factors in runs 1–15 are gen-

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Table II. Kinetic Data for Oxidation of $[Co(en)_3]^{2+}$ with $[Ru(NH_3)_6]^{3+}$ in Ammoniacal Solution (25 °C, I = 1.0 M)[a]

$[NH_3]$, M	$[Ru(NH_3)_6Cl_3]$, mM	k_{obsd},[b] s^{-1}	k,[c] $M^{-1}\ s^{-1}$
8-10	5.1	0.36 ± 0.01	71 ± 3
8-10	9.9	0.74 ± 0.02	75 ± 3
3	4.9	0.35 ± 0.03	71 ± 5
0	5.0	0.33 ± 0.02	67 ± 4

[a] Conditions: $[CoCl_2]$ = 0.5 mM, [en] = 1.0 M, [enHCl] = 1.0 M, λ = 466 nM. [b] Average of five separate determinations. [c] $k = k_{obsd}/[Ru(NH_3)_6{}^{3+}]$.

erally less than 20% of the observed rates, and therefore the precision of the correction factor is not a crucial issue here. However, at higher temperatures, owing to the high activation energy of reaction 2, the side reactions become major contributors to the observed exchange, and the accuracy of k_{cor} would decrease.

In Figure 1, the data for the runs are plotted as k_{cor} vs. $[Co(NH_3)_6{}^{2+}]$, with separate symbols for the chloride and $CF_3SO_3^-$ counterion runs. The straight line through the two $CF_3SO_3^-$ points passes through the origin as expected for a second-order reaction, and it has the slope (8 ± 1) × 10^{-6} M^{-1} s^{-1}.

For the 16 points with chloride as counterion, the least-squares line through the data has slope (3.9 ± 1.5) × 10^{-6} M^{-1} s^{-1}, (95% confidence limit). There is no correlation between k_{cor} and the value of $[NH_3]/[NH_4{}^+]$; thus there is no pH dependence, but there seems to be a correlation with reaction time. The data actually appear to fall into two groups. The data points that lie below the least-squares line tend to be those runs that were followed for less than 0.7 half-life, and it appears that some systematic error is introduced if the observations are restricted to the early reaction phase. The slope through the points that represent data extending over more than 1 half-life plus the origin is about 5.1 × 10^{-6} M^{-1} s^{-1}.

In an earlier paper[3] on the exchange, some preliminary results were quoted based on experiments in which much higher concentrations of Co(II) were used than in the present series. This was done to increase the rate, as well as to minimize the contribution to the exchange by the hydrolytic path. The continuation of the experiments at high [Co(II)] showed that the results did not conform to the expected variation of rate with [Co(II)]. This observation and others made in the course of the studies suggest condensation reactions involving Co(II), which complicate the interpretation of the exchange data when [Co(II)] is high.

Rate of Oxidation of $[Co(en)_3]^{2+}$ by $[Ru(NH_3)_6]^{3+}$. The kinetic data for the oxidation of $[Co(en)_3]^{2+}$ by $[Ru(NH_3)_6]^{3+}$ in ammoniacal solutions are presented in Table II. As can be seen, at three different ammonia concentrations, the second-order rate constants for the reaction do not change significantly from the average 71 M^{-1} s^{-1}, and we believe therefore that the change in medium as the ratio H_2O/NH_3 changes is not a significant variable in our exchange studies.

Discussion

Our results indicate that the exchange of label in $[Co(NH_3)_6]^{3+}$, corrected for side reactions 2–4, conforms reasonably well to the rate law rate = $k_1[Co(NH_3)_6{}^{3+}][Co(NH_3)_6{}^{2+}]$ and that it is independent of pH in the range covered. At 40 °C, I = 2.5 M, k_1 = (8 ± 1) × 10^{-6} M^{-1} s^{-1} with $CF_3SO_3^-$ as counterion and k_1 = (3.9 ± 1.5) × 10^{-6} M^{-1} s^{-1} with Cl^- as counterion.

Our results are incompatible with the conclusions reached by Biradar, Stranks, and Vaidya,[2] who reported that the rate law for the dominant exchange reaction is rate = $k[Co(NH_3)_6{}^{3+}][Co(NH_3)_n{}^{2+}]/[H^+]$, with k = 2.3 × 10^{-14} s^{-1} at 64.5 °C, I = 1.0 M. They report E_a as 30.1 ± 0.8 kcal mol^{-1}. Elsewhere,[3] we have discussed the possibility that this observed rate law represents the contribution of side reactions 2 and 4, which was not considered in their study and which is prominent at higher temperatures.

It is worthwhile to compare our results for the hexaamminecobalt(III/II) couple to those of the related tris(ethylenediamine)cobalt(III/II) couple. The data of Dwyer and Sargeson[16] indicate that k for the $[Co(en)_3]^{3+/2+}$ electron-self-exchange reaction is 2.4 × 10^{-4} M^{-1} s^{-1} at 40 °C, I = 1.0 M (chloride medium), thus roughly 4 × 10^{-4} M^{-1} s^{-1} at I = 2.5 M, and so 100 times that which we have obtained here for the $[Co(NH_3)_6]^{3+/2+}$ couple.

It should be noted that the value of k_1 calculated for the hexaamminecobalt electron self-exchange is strongly dependent on the value used for the association constant K_6 governing the addition of the sixth ammonia to Co(II). Elsewhere[3,15] we have cited evidence which suggests that the literature value of K_6 for Co(II) is too high. If this is true, then the concentration of $[Co(NH_3)_6]^{2+}$ is lower than we have calculated, and the value of k_1 we report is a lower limit. It should be noted that the electron-self-exchange rate for $[Ru(en)_3]^{3+/2+}$ is greater than that of $[Ru(NH_3)_6]^{3+2+}$, but by less than a factor of 100.

Conclusion

We have measured the rate of ammonia exchange between hexaamminecobalt(III) and ammoniacal Co(II) solutions, which has led to estimates of the electron-self-exchange rate constant for $[Co(NH_3)_6]^{3+/2+}$. At 40.0 °C, I = 2.5 M, the second-order rate constant was found to be (8 ± 1) × 10^{-6} M^{-1} s^{-1}, with $CF_3SO_3^-$ as counterion, and (3.9 ± 1.5) × 10^{-6} M^{-1} s^{-1}, with Cl^- as counterion.

These results are inconsistent with earlier work, which set an upper limit of 1.6 × 10^{-10} M^{-1} s^{-1} at 64.5 °C on the rate constant. Our results show the rate constant for tris(ethylenediamine)cobalt(III/II) self-exchange is less than 100-fold greater than that for the hexaamminecobalt(III/II) self-exchange.

Acknowledgment. Support of this work by National Science Foundation Grant No. CHE82-11275 is gratefully acknowledged. Assistance in purchasing the XL-100 NMR spectrometer under National Science Foundation Grant No. GP28142 and the Nicolet Computer Station under National Science Foundation Grant No. CHE77-08810 is also gratefully acknowledged.

Registry No. $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_6]^{2+}$, 15365-75-0; NH_3, 7664-41-7; Co, 7440-48-4; $[Ru(NH_3)_6]^{3+}$, 18943-33-4; $[Co(en)_3]^{2+}$, 23523-25-3.

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(16) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892–1894.