that formerly held the potassium gave enough data to calculate the density.

The densities of four solutions at 25 °C were (concentration of KNH_2 in units of moles per liter of solution, or M, and densities in g/mL) as follows: 0.0751, 0.606; 0.510, 0.614; 0.610, 0.617; 0.728, 0.619. The relation is nearly linear over this range, and the two variables follow the equation $d = 0.604 + 0.020$ M.

Results and Discussion

Table I summarizes the results of the $H_2/KNH_2/Hg$ reaction. The extent of the reaction depends strongly on the amount of stirring, on the length of reaction time, and on the K/Hg ratio. In run 5, in which a glass-enclosed stirring bar was used, two-thirds of the K^+ was reduced. The mole fraction of potassium in the amalgam was 0.044, and the product was a thick paste. It was necessary to dilute this amalgam with more mercury to make filtration possible. The K/Hg phase diagram[12] reveals the amalgams with potassium mole fractions higher than approximately 0.04 are solid at 25 °C. Small differences in stirring and catalysis can affect the extent of reduction strongly, producing irreproducible potassium concentrations in the amalgams. True equilibrium, especially when a viscous amalgam is the product, is reached exceedingly slowly.

When zinc was used as the reducing agent, the KNH_2 concentration was 0.12 M and the reaction time was 75 h. It was found that 17.3% of the K^+ had been reduced to amalgam, presumably $Zn(NH_2)_4^{2-}$ being formed simultaneously. The amalgam contained 4.8 mg of potassium and 0.14 mg of zinc (spectrophotometric analysis), so there was evidently some exchange of the two metals within the mercury phase.

Bergstrom[13] observed earlier that mercury is attacked by potassium amide in liquid ammonia "at an extremely slow rate". The blank experiments confirmed this statement. The 80-day exposure involved 0.093 M KNH_2 and 10.0 g of mercury. The mercury phase was found to contain 4.34 mg of potassium (4.6% of the total). Thus, while the weak reducing agent mercury can reduce K^+ under the experimental conditions, the extent of the reaction is far below that in which hydrogen is present.

Since it is well-known that hexamethylphosphoramide dissolves the alkali metals, this solvent provides an alternative medium for the reaction of interest. Potassium bis(trimethylsilyl)amide was found to dissolve readily in HMPA. With use of concentrations, hydrogen pressures, and reaction times comparable to those in the $H_2/KNH_2/Hg$ experiments, it was found that 11-12% of the total potassium ion was reduced to amalgam. Since hexamethyldisilazane is a stronger acid than ammonia, the driving force for its formation (and K/Hg simultaneously) is less than for the corresponding reaction in ammonia, but no quantitative data were found.

Registry No. KNH_2, 17242-52-3; Hg, 7439-97-6; H_2, 1333-74-0; Zn, 7440-66-6; $KN(SiMe_3)_2$, 40949-94-8; NH_3, 7664-41-7; mercury base, potassium alloy, 39365-58-7.

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Contribution from the Department of Chemistry,
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Kinetics of Chromium(II) Reduction of Sulfamato, *p*-Toluenesulfonamido, and Sulfamido Complexes of Pentaamminecobalt(III)

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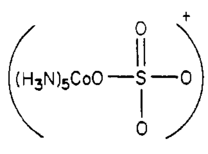
Received September 18, 1981

The kinetics of the chromium(II) reduction of the pentaamminecobalt(III) complexes of sulfamate, sulfamide, and *p*-toluenesulfonamide have been studied in 1 M $LiClO_4/HClO_4$. The reduction rate constant (25 °C), activation enthalpy, and entropy for $(H_3N)_5CoNH_2SO_3^{2+}$ are 3.3 ± 0.1 M^{-1} s^{-1}, 8.5 ± 0.5 kcal mol^{-1}, and −27 ± 2 cal mol^{-1} deg^{-1}, respectively. The reaction produces $(H_2O)_5CrOSO_2NH_2^{2+}$. The O- and N-bonded isomers are reduced at indistinguishable rates. Reduction of the sulfamido complex is competitive with hydrolysis. The kinetic parameters for reduction of $(H_3N)_5CoNH_2SO_2NH_2^{3+}$, in the order given above, are 0.197 ± 0.014 M^{-1} s^{-1}, 9.3 ± 1.2 kcal mol^{-1}, and −30 ± 4 cal mol^{-1} deg^{-1}, and for $(H_3N)_5CoNHSO_2NH_2^{2+}$, $(5.56 \pm 0.26) \times 10^{-2}$ M^{-1} s^{-1}, 11.5 ± 0.9 kcal mol^{-1}, and −26 ± 3 cal mol^{-1} deg^{-1}. The chromium(III) product is too unstable to be fully characterized, but a kinetic–spectrophotometric analysis indicates that ligand transfer does occur. Similar kinetic results were found for the *p*-toluenesulfonamido complex, but the chromium(III) product could not be detected. The kinetic trends for the pentaamminecobalt(III) complexes with SO_4^{2-}, $NH_2SO_3^-$, and $SO_2(NH_2)_2$ are discussed, and a bridged-outer-sphere mechanism is suggested to be most consistent with the formation of ligand-transfer product, greater reactivity of the protonated complex, similar reactivity of O- and N-bonded sulfamato isomers, and lack of electron transfer through an $-NH_2-$ group.

Introduction

The pentaamminecobalt(III) complexes of sulfate (A), sulfamate (B), and sulfamide (C) offer a series in which the structure of the sixth ligand is changed little while the complex charge and coordinating atom are varied. The consequences of these changes on the chromium(II) reduction of these complexes have been studied in this work.



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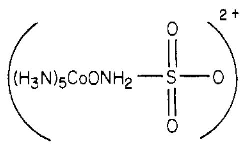

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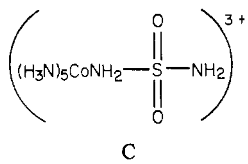

C

The chromium(II) reduction of the sulfato complex was studied previously with reasonable agreement at least on the rate constant at 25 °C.[1,2] It seems to be assumed[3] that the reaction proceeds with sulfate ion transfer to chromium(III), apparently without actual identification of the product. Fraser[2]

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0020-1669/82/1321-4127$01.25/0

found $(H_2O)_5CrOSO_3^+$ as the product from the reduction of $(en)_2CoO_2SO_2^+$. Linear free energy correlations[4] with the rate of reduction by $Ru(NH_3)_6^{2+}$[5] indicate that the chromium(II) reduction of A is not an outer-sphere process. These observations all are consistent with sulfate acting as a bridging ligand in these chromium(II) reductions.

Earlier work in these laboratories[6,7] indicated that electron transfer did not proceed through an $-NH_2-$ group. This leads to the expectation that B and C should be reduced by an outer-sphere mechanism, while their deprotonated forms and the O-bonded isomer[8] of B might use the bridging ligand for electron transfer. This study was designed to test these expectations and produced some unexpected results.

Experimental Section

Reagents. All solutions were prepared in water redistilled from alkaline permanganate in an all-glass apparatus. Lithium perchlorate was prepared and standardized as described previously.[7] Chromium(III) perchlorate solutions were prepared by reducing potassium dichromate with hydrogen peroxide in perchloric acid solution.[9] Excess hydrogen peroxide was decomposed by boiling the solution, and solid $KClO_4$ was removed by filtering the cold solution through a 0.22-μm Millipore filter. The concentration of perchloric acid in the chromium(III) solution was determined by potentiometric titration with standardized sodium hydroxide, after conversion of the hexaaquochromium(III) to tris(oxalato)chromium(III).[9] Chromium(II) perchlorate was prepared either by reducing chromium(III) perchlorate with zinc amalgam or by dissolving chromium pellets (99.999% purity, Apache Chemicals Inc.) in dilute perchloric acid. Chromium(II) concentrations were determined by a titration procedure described previously.[7]

Argon was used to deoxygenate all solutions, which were handled with use of rubber serum caps and standard syringe techniques.

Preparation of Cobalt(III) Complexes. $[(H_3N)_5CoNH_2SO_3](ClO_4)_2$ was prepared by a method more efficient than those reported previously.[8,10] An aqueous solution (60 mL) containing 5.8 g of sulfamic acid and 8 g of (carbonato)pentaamminecobalt(III) nitrate was evaporated to dryness on a steam bath. The crude product was dissolved in a minimum of warm sodium bicarbonate (0.5 M) and crystallized by adding concentrated perchloric acid. The solid product was collected and redissolved in sodium hydroxide (0.1 M), and the solution was allowed to stand for 10 min in order to hydrolyze any $(H_3N)_5CoSO_4^+$. The solution was adjusted to pH 9 and purified by cation-exchange chromatography on Baker CGC-271 weak-acid cation-exchange resin (J. T. Baker Chemical Co.) in the sodium ion form. The sulfamato complex was separated from the $(H_3N)_5CoOH_2^{3+}$ impurity by eluting with 0.1 M Na_2CO_3. The resin containing the desired complex was separated physically and washed with distilled water, followed by 1.0 M $HClO_4$ in order to remove the complex, which was precipitated with sodium perchlorate. Anal. Calcd for $[(H_3N)_5CoNH_2SO_3](ClO_4)_2\cdot H_2O$: N, 18.39; H, 4.19. Found: N, 18.30; H, 4.10. The electronic and NMR spectra agree with those reported previously.[8,10] The infrared spectrum was analyzed by comparison to the spectrum for sodium sulfamate.[11] Characteristic ligand vibrations in the complex are as follows: SO_3 stretch, 1270 (antisym), 1245 and 1185 (sym); SO_3 deformation, 1042 (sym); N–S stretch, 720 cm^{-1}. In sodium sulfamate these vibrations are observed at 1283, 1240, 1190, 1046, and 788 cm^{-1}. The compounds $[(H_3N)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2$,[12] $[(H_3N)_5CoNHSO_2NH_2](ClO_4)_2$,[12] and $[(H_3N)_5CoOSO_3](ClO_4)\cdot H_2O$[8,10] were prepared by methods previously reported from these laboratories.

Kinetic Measurements. The chromium(II) reduction of the *p*-toluenesulfonamido and sulfamido complexes were studied by injecting an aqueous solution of the cobalt(III) complex into a temperature-equilibrated aqueous solution of chromium(II) perchlorate in the required amount of perchloric acid and lithium perchlorate. This order of mixing is necessary because of the rapid aquation of the complexes in acidic solution.[12] The kinetics were followed at 505 and 500 nm, respectively, on a Cary 219 spectrophotometer.

The reduction of the sulfamato complex was studied at 485 nm by mixing an alkaline solution (pH ~9 with $NaHCO_3$) of the cobalt(III) complex in lithium perchlorate with a solution of chromium(II) in perchloric acid and lithium perchlorate on an Aminco-Morrow stopped-flow system. The complex solution must be alkaline in order to prevent prior linkage isomerization and aquation.

An equilibrium mixture of N- and O-bonded isomers of the sulfamato complex was prepared by allowing the complex to stand in 0.01 M $HClO_4$ (14 mL; ~1.6×10^{-3} M cobalt(III)) for 85 min at 21 °C.[8] Chromium(II) was injected, and the reduction of the isomeric mixture was followed at 288 nm on a Cary 219 spectrophotometer. This instrument could be used because the low ionic strength (μ = 0.09 M) slowed the reaction. For comparison a few runs were also carried out on solutions containing the N-bonded isomer only under identical conditions. In this case the complex was dissolved in sodium hydroxide (pH ~9) in order to prevent prior isomerization and aquation.

Except where noted, reactions were studied under pseudo-first-order conditions in chromium(II) and perchloric acid. The rate constants were determined from the usual semilogarithmic plots of absorbance change vs. time, which were linear for at least 90% of the reaction. In the stopped-flow work rate constants were determined by an analog comparison technique described previously.[13] The temperature was controlled by a water circulation system described elsewhere,[7] and the temperature inside the cell was checked periodically with a thermocouple. A similar arrangement was employed in the stopped-flow system, and the temperature in the drive syringe compartment was measured with a thermocouple.

Reaction Product Analysis. The reactions were allowed to proceed for about 7 half-times and then quenched by air oxidation of the chromium(II). Products were separated by cation-exchange chromatography at 5 °C on Dowex 50W-X8 resin in the hydrogen ion form. The resin was washed successively with 6 M HCl, distilled water, 50% acetone, ethanol, and distilled water before use.

The amount of free ligand produced could be assessed most rapidly by using a column volume just sufficient to absorb all of the chromium(III). A relatively high flow rate was used, and the free ligand could be collected in 10–20 min. If the chromium(III) product was to be investigated, longer columns and slower flow rates were necessary to ensure resolution of possible products. Such studies typically required several hours of elution with 0.10 M $HClO_4$ and concentrations of $NaClO_4$ increasing up to 0.5 M to elute $Cr(OH_2)_6^{3+}$.

Sulfamate was determined by the titrimetric method reported by Whitman.[14] This method was also used for sulfamide, but the expected 2:1 stoichiometry of NO_2^- and $SO_2(NH_2)_2$ was not observed, and a standard curve was developed from solutions of known sulfamide concentration. A direct spectrophotometric method was used for *p*-toluenesulfonamide (ϵ 528 cm^{-1} M^{-1} at 262 nm, pH <7). The electronic spectrum distinguishes the amide from *p*-toluenesulfonic acid. The electronic spectrum of the chromium(III) eluent was recorded, and the total chromium was determined as chromate (ϵ 4815 cm^{-1} M^{-1} at 372 nm).

A solution containing the N- and O-bonded isomers of the sulfamato complex was produced by allowing $(H_3N)_5CoNH_2SO_3^{2+}$ (1.2×10^{-3} M) to react for 2 h in 0.1 M $HClO_4$.[8] A 10-mL aliquot of this solution was treated with 0.6 mL of 0.42 M chromium(II), and after 3.5 min the solution was aerated and ion exchanged. The initial eluent was analyzed for sulfamate ion. This analysis was corrected for sulfamate ion produced by aquation of the cobalt(III) complex by the simultaneous removal of a second 10-mL aliquot of the cobalt(III) reactant solution, ion exchange, and analysis of the initial eluent for sulfamate ion. The dipositive chromium(III) product of the reduction was isolated in solution by ion exchange and characterized by the electronic spectrum.

The chromium(III) product of the chromium(II) reduction of the sulfato complex was separated by ion exchange on Dowex 50W-X8

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Table I. Kinetic Data for the Reduction of $(H_3N)_5CoNH_2SO_3^{2+}$ [a]

temp, °C	[H⁺], M	$10^2[Cr^{2+}]$, M	10^2k_{obsd}, s^{-1} exptl	calcd[b]
14.9	0.050	4.62	8.63	9.01
14.9	0.050	8.38	16.5	16.3
15.0	0.100	4.57	8.92	8.91
15.3	0.150	8.38	17.0	16.3
25.0	0.050	4.70	15.7	15.5
25.0	0.103	4.70	15.7	15.5
25.0	0.202	4.70	15.7	15.5
25.0	0.400	1.63	5.40	5.39
35.2	0.025	4.67	24.8	25.9
35.2	0.050	4.73	25.1	26.2
35.1	0.100	4.73	27.1	26.2
35.2	0.200	4.73	26.1	26.2
35.1	0.400	1.58	9.44	8.75
25.0[c]	0.01	1.59	0.80	
25.0[c]	0.01	1.48	0.76	
25.0[c,d]	0.01	1.65	0.83	
25.0[c,d]	0.01	1.72	0.81	

[a] All runs in 1.0 M $LiClO_4/HClO_4$, with [Co(III)] = (4.4-7.8) × 10^{-4} M and with the N-bonded isomer unless otherwise indicated. [b] Calculated according to eq 1 with k_{1r} = 1.95 ± 0.07, 3.30 ± 0.11, and 5.54 ± 0.32 M^{-1} s^{-1} at 15, 25, and 35.2 °C, respectively, from a least-squares analysis. Errors are 95% confidence limits and are about 3 times 1 standard error. [c] Ionic strength was 0.09 M and [Co(III)] = (1.4-1.6) × 10^{-3} M. [d] Oxidant was a mixture of O- and N-bonded isomers.

(H^+) and characterized by its electronic spectrum.

Physical Measurements. Electronic spectra were recorded on a Cary 219 or a Unicam SP1700 spectrophotometer. The ^1H NMR spectra were obtained in deuterated dimethyl sulfoxide on Varian A56/60 or Perkin-Elmer R32 spectrometers. Infrared spectra were recorded on Perkin-Elmer 421 grating or Nicolet FT-7000 spectrometers in KBr pellets.

Results

Chromium(II) Reduction of $(H_3N)_5CoNH_2SO_3^{2+}$. Previous work has shown that the sulfamato complex has a pK_a of 5.7 (1 M $NaClO_4$)[10] and undergoes linkage isomerism and aquation with rate constants in the range of 10^{-3}–10^{-4} s^{-1} at 25 °C.[8] From the reduction kinetic results given in Table I, it is clear that aquation and isomerization are much slower than reduction for the chromium(II) concentrations used. The rate law for reduction is given by

$$d[Co(III)]/dt = k_{obsd}[Co(III)] = k_{1r}[Cr(II)][Co(III)] \qquad (1)$$

with k_{1r} = 3.30 ± 0.11 M^{-1} s^{-1} at 25 °C in 1 M $LiClO_4/HClO_4$ for the N-bonded isomer.

Some studies were done on equilibrium mixtures of the N- and O-bonded isomers. So that the reaction could be slowed for more precise spectrophotometric examination, these studies were done at lower ionic strength. The results are given and compared to the N-bonded isomer studied under the same conditions in Table I. Because aquation is competitive with isomerization, the isomer mixture solutions contain some $(H_3N)_5CoOH_2^{3+}$. However, the latter is reduced much faster[15] than the sulfamato species so that this is not a complicating factor. It was hoped that the isomer mixture would show biphasic kinetics, but only one process could be resolved kinetically with a rate constant at most 9% above that of the N isomer (see Table I). Reduction of the O isomer cannot be rapid and complete on mixing because the initial absorbance of the solution at 488 nm on adding chromium(II) was within 2% of that of the initial isomer mixture. Since the mixture is about 25% O isomer,[8] and the latter has almost the same absorbance as the N isomer at 488 nm, the initial absorbance would have been ~25% below that of the reactants if there had been rapid reduction of O isomer. Isomerization is over 10 times slower than reduction under the experimental conditions; therefore all of the observations require that the O and N isomers are reduced at very similar rates.

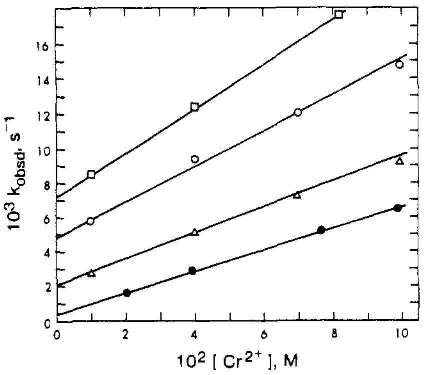

Figure 1. Chromium(II) dependence of the observed rate constant for disappearance of $(H_3N)_5CoNHSO_2NH_2^{2+}$, at 25 °C, at hydrogen ion concentrations of 0.020 (●), 0.100 (△), 0.300 (○), and 0.600 M (□).

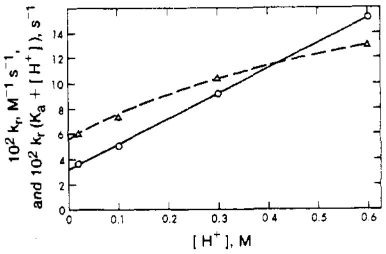

Figure 2. Hydrogen ion dependence of the chromium(II) reduction of $(H_3N)_5CoNHSO_2NH_2^{2+}$: k_r vs. [H^+] (△); k_r (K_a + [H^+]) vs. [H^+] (○).

The results of product analysis studies are summarized in Table II. The analyses for free sulfamate ion in the initial eluent clearly show that >93% of the ligand remains bound to chromium(III) after reaction. A dipositive chromium(III) product was identified by its ion-exchange properties. This product has absorption maxima at 416 and 591 nm with extinction coefficients of 16.8 and 15.5 cm^{-1} M^{-1}, respectively, and a shoulder at ~672 nm. Reduction of the N- and O-bonded isomer mixture gave the same products as the N isomer (see Table II).

The spectrum of the product is very similar to that of $(H_2O)_5CrOSO_3^{+}$,[16] which has maxima at 417 and 587 nm with extinction coefficients of 18.8 and 19.0 cm^{-1} M^{-1}, respectively, and a shoulder at 671 nm. This similarity indicates that the reaction product is the O-bonded isomer $(H_2O)_5CrOSO_2NH_2^{2+}$. The aquation rate of this product was studied spectrophotometrically in the ion-exchange eluent and had a rate constant of 2.8 × 10^{-5} s^{-1} [17] (25 °C, 0.05–0.10 M H^+, 0.5 M $NaClO_4$). Aquation during ion exchange can account for the <7% sulfamate ion product so that electron transfer may well proceed completely with transfer of sulfamate to chromium(III).

Chromium(II) Reduction of $(H_3N)_5CoNH_2SO_2NH_2^{3+}$. The acid-catalyzed aquation of this cobalt(III) complex is unusually rapid[12] and is competitive with the reduction. Aquation produces $(H_3N)_5CoOH_2^{3+}$, which is reduced much more rapidly,[15] so that aquation of the sulfamido complex is also

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(17) This rate constant happens to be nearly identical with that for aquation of $(H_3N)_5CoNH_2SO_3^{2+}$, 2.6 × 10^{-5} s^{-1}.

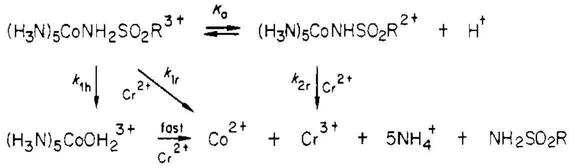
Table II. Product Analysis Results for $(H_3N)_5Co(ligand)$ Reduction[a]

ligand	[Co(III)], M	[Cr(II)], M	$[H^+]$, M	reacn time, min	% free ligand	Cr(III) product
$NH_2SO_3^-$	0.010[b]	0.020	0.10	3.8	5.7	
	0.010[b]	0.020	0.20	3.5	5.3	
	0.010[b]	0.020	0.50	4.5	6.4	
	0.010[b]	0.020	0.50	3.8	6.6	
	0.0087	0.0097	0.20	17		$(H_2O)_5CrOSO_2NH_2^{2+}$ [e]
	0.012[d]	0.023	0.10	3.5	4.5	$(H_2O)_5CrOSO_2NH_2^{2+}$ [e]
	0.012[d]	0.025	0.10	3.0	4.4	
$SO_2(NH_2)(NH)^-$	0.010	0.20	0.05	15	97	
	0.010	0.20	0.05	13	105	$Cr(OH_2)_6^{3+}$ [e]
	0.010	0.20	0.05	10	91	$Cr(OH_2)_6^{3+}$ [e]
	0.003	0.20	0.05	8	96	
	0.007	0.33	0.60	3	100	
$H_3CC_6H_4SO_2NH^-$	0.0025[c]	0.39	0.05	15	100	
	0.0025[c]	0.39	0.05	10	97	
	0.0024[c]	0.36	0.33	7	106	
SO_4^{2-}	0.0072	0.12	0.20	3		$(H_2O)_5CrOSO_3^+$ [e]

[a] Experiments done at ambient temperature (21 °C) unless otherwise indicated. [b] Temperature was 25 °C. [c] Temperature was 5 °C. [d] Oxidant was a mixture of N- and O-bonded isomers. [e] Identified by ion exchange and electronic spectra as described in the text.

a rate-controlling process for total cobalt(III) reduction.

The kinetic data at 25 °C are shown in Figures 1 and 2; essentially similar studies have been done at 15 and 35 °C. So that a more economical presentation can be provided, the usual kinetic logic will be circumvented by first suggesting the reaction scheme given in eq 2 (where R ≡ NH_2). The



(2)

aquation study[12] has provided values of k_{1h} and K_a. With the assumption that proton dissociation represents a rapidly established preequilibrium this scheme gives the rate law

$$\frac{-d(\ln [Co(III)])}{dt} = k_{obsd} = k_h + k_r[Cr^{2+}]$$
$$= \frac{k_{1h}[H^+]}{K_a + [H^+]} + \frac{k_{1r}[H^+] + k_{2r}K_a}{K_a + [H^+]}[Cr^{2+}] \quad (3)$$

where the chromium(II)-independent term (k_h) is due to the hydrolysis reaction.

The results at 25 °C are plotted in Figure 1 to show clearly the importance and the acid dependence of the chromium(II)-independent term. The saturation effect on the hydrolysis, which occurs when $[H^+] \gtrsim K_a$, can be seen from the less than first-order dependence on $[H^+]$ of the intercepts in Figure 1. Since k_h is known independently,[12] it is possible to subtract k_h from k_{obsd} and divide the difference by $[Cr^{2+}]$ to obtain k_r. The dependence of k_r on $[H^+]$ is shown in Figure 2, where it is clear that a plot of k_r vs. $[H^+]$ is curved, but $k_r(K_a + [H^+])$ vs. $[H^+]$ is linear, as expected from eq 3. The skeptical reader may surmise correctly that the curvature in Figure 2 is not sufficient to permit an accurate determination of K_a. Unfortunately, the reduction cannot be studied at much higher acidity because hydrolysis becomes too important, and the $[Cr^{2+}]$ cannot be increased because of ionic strength limitations. Therefore, the K_a values from the hydrolysis study,[12] determined for 0.02–1.0 M $[H^+]$ at 15, 25, and 35 °C, have been used in the analysis here. The results were fitted to eq 3 by least-squares methods, with k_{1h} and K_a fixed, and the results are summarized in Table III.

The product analysis studies, summarized in Table II, indicate that all of the sulfamide ligand appears in the initial ion-exchange eluent and that the chromium(III) product is tripositive with the same electronic spectrum as $Cr(OH_2)_6^{3+}$. The products are the same whether the reaction is done at 0.05 M H^+, proceeding 70% by the k_{2r} path, or at 0.60 M H^+, where it proceeds 67% by the k_{1r} path.

Table III. Kinetic Results for the Reduction of $(H_3N)_5CoNHSO_2NH_2^{2+}$ in 1 M $LiClO_4/HClO_4$[a]

temp, °C	10^2k_{1h}, M^{-1} s^{-1}	K_a, M	k_{1r},[b] M^{-1} s^{-1}	10^2k_{2r},[b] M^{-1} s^{-1}
15.0	0.35	0.47	0.110 ± 0.006	2.76 ± 0.14
24.9	1.41	0.58	0.197 ± 0.014	5.56 ± 0.26
35.0	4.42	0.65	0.340 ± 0.039	11.0 ± 0.80

[a] Data were fitted to eq 3 to obtain k_{1r} and k_{2r} while holding k_{1h} and K_a constant at previously determined values.[12] [b] Errors are 95% confidence limits.

The simplest explanation for the observed products is that the sulfamide ligand is not transferred to chromium(III). However, the unusual acid lability of $(H_3N)_5CoNH_2SO_2NH_2^{3+}$ ($k_{1h} = 1.4 \times 10^{-2}$ s^{-1}) suggests that a chromium(III)–sulfamide product could be formed but then hydrolyzed during the ion-exchange separation. This possibility is given some credence by the very similar hydrolysis rates of $(H_3N)_5CoOSO_3^+$ ($k = 8.9 \times 10^{-7}$ s^{-1})[18] and $(H_2O)_5CrOSO_3^+$ ($k = 8.5 \times 10^{-7}$ s^{-1})[19] and the already noted similarity of the corresponding sulfamato complexes.[17] On this basis one estimates a hydrolysis rate constant for $(H_2O)_5CrOSO(NH_2)_2^{3+}$ of $\sim 1.4 \times 10^{-2}$ s^{-1} or a half-time of ~50 s. If these estimates are approximately correct, then hydrolysis would certainly be complete even during the charging of the ion-exchange column.

The above arguments suggest that the only way to detect a ligand-transfer product would be by an in situ method under conditions such that the reduction has a half-time of ≲50 s. Model calculations indicated that the best conditions would be with ~0.2 M chromium(II) and 0.1 M H^+. Then the reaction proceeds 88% by direct reduction of the sulfamido complex with a half-time of 40 s, while maintaining 1 M ionic strength and pseudo-first-order conditions. If the electronic spectra of $(H_2O)_5CrOSO_2NH_2^{2+}$ and $(H_2O)_5CrOSO(NH_2)_2^{3+}$ are similar, then the latter should be isosbestic with $Cr(OH_2)_6^{3+}$ at ~400 nm and show a maximum difference in absorbance at ~430 nm, with extinction coefficients of 14.5 and 11.5 M^{-1} cm^{-1}, respectively.

The feasibility of detecting the ligand-transfer product was tested by model calculations on the X→Y→Z kinetic system.

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Table IV. Kinetic Data for the Reduction of $(H_3N)_5CoNHSO_2C_6H_4CH_3^{2+}$ at 25 °C in 1.0 M $LiClO_4/HClO_4$[a]

$[H^+]$, M	$10^2[Cr^{2+}]$, M	$10^3 k_{obsd}$, s^{-1} exptl	$10^3 k_{obsd}$, s^{-1} calcd[b]
0.025	0.885	1.15	1.14
0.025	1.96	1.89	1.87
0.025	3.47	3.01	2.89
0.025	7.97	6.26	5.95
0.025	12.8	9.22	9.27
0.025	16.4	11.4	11.7
0.025	21.6	15.0	15.2
0.100	0.709	3.00	2.68
0.100	0.894	2.99	2.82
0.100	0.968	3.04	2.88
0.100	1.24	3.19	3.08
0.100	2.13	4.04	3.75
0.100	3.27	4.95	4.54
0.100	4.12	5.88	5.23
0.100	9.29	9.46	9.08
0.100	12.8	11.9	11.7
0.100	16.9	13.2	14.8
0.100	17.9	14.5	15.5
0.100	18.9	13.8	16.2
0.200	0.896	5.36	5.06
0.200	2.11	6.70	6.07
0.200	9.35	12.3	12.1
0.200	15.74	16.9	17.5
0.400	0.882	9.01	9.51
0.400	1.22	9.87	9.85
0.400	1.96	10.7	10.6
0.400	3.22	11.9	11.9
0.400	9.11	18.2	17.9
0.400	11.8	20.3	20.5

[a] The cobalt(III) concentration was $(0.24-2.8) \times 10^{-3}$ M.
[b] Calculated from eq 4 with $k_{1h}/K_a = 2.15 \times 10^{-2}\ M^{-1}\ s^{-1}$,[12] while $k_{1r}/K_a = (8.9 \pm 3.5) \times 10^{-2}\ s^{-1}$ and $k_{2r} = (6.57 \pm 0.41) \times 10^{-2}\ M^{-1}\ s^{-1}$ were determined by least-squares fitting. Errors are 95% confidence limits.

These calculations indicate that a maximum of about 36% of the sulfamide would be present as the ligand-transfer intermediate (Y) after about 65 s. However, the normal semilogarithmic plot of absorbance change vs. time should appear linear up to 3 half-times, but the apparent half-time would be about 60 s compared to the reduction half-time of 40 s. Since the detection of the intermediate ultimately depends only on this half-time difference, the experiment was monitored at two wavelengths at 13-s intervals at each wavelength. At the isosbestic point (400 nm) the reduction half-time of 40 s should be observed while at 430 nm a longer half-time should be found if the ligand-transfer product is formed and has the approximate properties described above.

Two experiments were carried out under similar conditions: 0.20 M chromium(II), 0.10 M perchloric acid, and 5.1×10^{-3} M cobalt(III) in a 9-cm spectrophotometer cell. At 400 nm the half-times were 39.1 and 42.6 s, while at 430 nm the half-times were 57.7 and 59.3 s, respectively. These results are almost embarassingly close to the predictions made and confirm that reduction of the sulfamido complex does produce substantial amounts of chromium(III)–sulfamido product.

Chromium(II) Reduction of $(H_3N)_5CoNHSO_2C_6H_4CH_3^{2+}$. This system is analogous to that of the sulfamido complex in that hydrolysis is competitive with reduction. The kinetic data at 25 °C are given in Table IV, and similar studies were done at 15 and 35 °C. The results are consistent with the reaction scheme in eq 2 ($R \equiv C_6H_4CH_3$) and give the rate law

$$\frac{-d(\ln [Co(III)])}{dt} = k_{obsd} = k_h + k_r[Cr^{2+}]$$

$$= \frac{k_{1h}}{K_a}[H^+] + \left(\frac{k_{1r}[H^+]}{K_a} + k_{2r}\right)[Cr^{2+}] \tag{4}$$

This rate law results from eq 3 if $K_a >> [H^+]$, a condition found to be true in the hydrolysis study[12] for $[H^+] \leq 0.80$ M. The value of k_{1h}/K_a was fixed at that obtained in the hydrolysis study, and the data were fitted to eq 4 by least-squares methods. The observed and calculated values are compared in Table IV.

The product analysis results are given in Table II and show that all of the *p*-toluenesulfonamide appears in the initial ion-exchange eluent. The observations are consistent with no ligand transfer to chromium(III) or with rapid hydrolysis of an initial ligand-transfer product by arguments parallel to those given for the sulfamido complex. The hydrolysis study of $(H_3N)_5CoNHSO_2C_6H_4CH_3^{2+}$ yielded values of $k_{1h}/K_a = 2.15 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $K_a > 5$ M, so that $k_{1h} \geq 0.1\ s^{-1}$. If a similar rate constant applies to the $(H_2O)_5Cr^{3+}$ complex, then it will aquate in a matter of seconds and never be an identifiable reduction product. This is consistent at least with our failure to detect any evidence of a chromium(III) intermediate when the spectrum was scanned repetitively from 600 to 300 nm at 160-s intervals for a solution initially containing 0.08 M chromium(II), 0.052 M hydrogen ion, and 4.7×10^{-3} M cobalt(III) in a 9-cm path length cell.

Chromium(II) Reduction of $(H_3N)_5CoOSO_3^+$. The kinetics of this system were studied previously,[1,2] and only the chromium(III) product was identified in this work. The product had ion-exchange properties typical of a 1+ charged ion. The electronic spectrum in 0.1 M $HClO_4$ shows maxima at 672 (shoulder), 586, and 416 nm, with extinction coefficients of 5.32, 19.1, and 20.6 $M^{-1}\ cm^{-1}$ in good agreement with the spectrum of $(H_2O)_5CrOSO_3^+$ reported by Finholt et al.[16] The yield of this product was 98% based on the original cobalt(III).

Discussion

The kinetic results of this and related work are summarized in Table V. There are several puzzling features to the results on these seemingly simple and structurally related systems. How do the protonated sulfamato and sulfonamido complexes achieve bridged electron transfer through a saturated $-NH_2-$ group coordinated to cobalt(III)? Why are the rate constants for the N-bonded and O-bonded sulfamato complexes quite similar? Why are the rate constants for the protonated sulfamido and *p*-toluenesulfonamido complexes (k_{1r})[20] larger than

Table V. Summary of Kinetic Data for Reduction of $(H_3N)_5Co(ligand)$ Complexes by Chromium(II)[a]

	ligand			
	SO_4^{2-} [b]	$H_2NSO_3^-$	$SO_2(NH_2)_2$	$H_2NSO_2C_6H_4CH_3$
k_{1r}, $M^{-1}\ s^{-1}$	18	3.30 ± 0.11	0.197 ± 0.014	$(8.9 \pm 3.5) \times 10^{-2}$ [c]
k_{2r}, $M^{-1}\ s^{-1}$			$(5.56 \pm 0.26) \times 10^{-2}$	$(6.57 \pm 0.41) \times 10^{-2}$
$\Delta H^{\ddagger}_{1r}$, kcal mol^{-1}	6.2	8.5 ± 0.5	9.3 ± 1.2	5 ± 5[c]
$\Delta S^{\ddagger}_{1r}$, cal mol^{-1} deg^{-1}	−32	−27 ± 2	−30 ± 4	−46 ± 18[c]
$\Delta H^{\ddagger}_{2r}$, kcal mol^{-1}			11.5 ± 0.9	11.1 ± 0.8
$\Delta S^{\ddagger}_{2r}$, kcal mol^{-1}			−26 ± 3	−27 ± 3

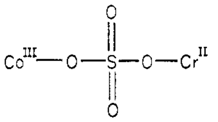
[a] Values at 25 °C in 1 M $LiClO_4/HClO_4$ unless otherwise indicated. [b] Values in 1 M $NaClO_4$ from ref 1. [c] Value of k_{1r}/K_a is given, but $K_a \gtrsim 5$ M so that $k_{1r} \gtrsim 0.45\ M^{-1}\ s^{-1}$.

those for the deprotonated form (k_{2r}) when charge and conjugation seem to favor the deprotonated form?

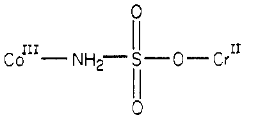
First, it should be noted that it now has been shown that reduction of $(H_3N)_5CoOSO_3^+$ proceeds with sulfate ion transfer to chromium. This is consistent with previous assumptions[3] and linear free energy relationships based on the relative rates of chromium(II) and $Ru(NH_3)_6^{2+}$ reduction.[4,5]

The relative reactivities (k_{1r}) of the sulfato, sulfamato, and sulfamido complexes are consistent with a dependence of the rate constant on the charge product of the reactants of the form $k \propto \exp(-z_1 z_2)$. This predicts relative rate constants of 1:0.14:0.018, respectively, compared to observed ratios of 1:0.18:0.011. The rate constant differences are due mainly to changes in ΔH^* while ΔS^* remains essentially constant. These reductions all proceed with ligand transfer to chromium.

The above observations are indicative of a common reaction mechanism for the sulfato, sulfamato, and protonated sulfamido complexes with a ligand bridging between cobalt(III) and chromium(II). But if the rate constant (k_{1r}) difference between the sulfato and sulfamato complexes can be accounted for by reactant charge, then electron transfer appears to be about equally facile for

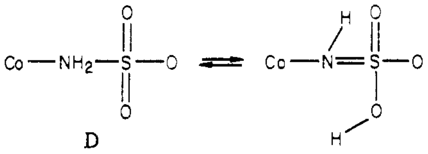


$$\mathrm{Co^{III}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}Cr^{II}}$$



$$\mathrm{Co^{III}{-}NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O{-}Cr^{II}}$$

The similar reactivity of the N- and O-bonded isomers of the sulfamato complex leads to a similar conclusion. The implication is that electron transfer is possible through a coordinated $-NH_2-$ group, but this is contrary to our previous experience[6,7] that $-NH_2$ groups, either in coordination to a metal or as lead-in groups on a ligand, do not provide an inner-sphere electron-transfer path. This difficulty could be explained by a tautomeric equilibrium such as



D E

Then the E tautomer and its sulfamide analogue could be the forms active in the bridged electron transfer between chromium(II) and cobalt(III). However, the deprotonated sulfamido complex, which would be analogous to tautomer E, is less reactive than the protonated form; therefore it is difficult to assign much enhanced reactivity to E. In addition, it is difficult to explain the similar reactivity of the N- and O-bonded sulfamato complexes, since only the N isomer must go through this tautomeric equilibrium.

An explanation for these problems is to suppose that the electron transfer does not occur through the $-NH_2-$ group. This would be possible with a bridged-outer-sphere mechanism in which the bridging ligand simply serves to hold the cobalt(III) and chromium(II) in proximity so that outer-sphere electron transfer occurs. The tetrahedral geometry about the nitrogen and sulfur atoms allows the first coordination spheres of the cobalt(III) and chromium(II) to be in close contact. This proposal also is consistent with the similar reactivities of the N- and O-bonded sulfamato complexes.

The larger rate constants for the protonated forms of the sulfamido and *p*-toluenesulfonamido complexes can be rationalized with a bridged-outer-sphere electron-transfer mechanism. Protonation of the nitrogen atom coordinated to cobalt(III) should make reduction thermodynamically more favorable and thereby increase the rate constant for outer-sphere electron transfer.[21] Similar reactivity increases were observed by Gould et al.[22] for the reduction by vanadium(II) of several protonated (carboxylato)pentaamminecobalt(III) complexes.

Acknowledgment. The authors wish to acknowledge financial support and fellowship support (J.L.L.) from the Natural Sciences and Engineering Council of Canada.

Registry No. $[(H_3N)_5CoNH_2SO_3]^{2+}$, 19508-44-2; $[(H_3N)_5CoNHSO_2NH_2]^{2+}$, 78891-48-2; $[(H_3N)_5CoNHSO_2C_6H_4CH_3]^{2+}$, 78891-46-0; $[(H_3N)_5CoOSO_3]^+$, 18661-07-9; Cr, 7440-47-3; $[(H_2O)_5CrOSO_2NH_2]^{2+}$, 83152-21-0; $Cr(H_2O)_6$, 14873-01-9; $[(H_2O)_5CrOSO_3]^+$, 19163-97-4.

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(20) See footnote *c* of Table V.

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