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# Aquation and Chromium(II) Reduction Reactions of Sulfonamido Complexes of Pentaamminecobalt(III)

by

Janet Louise Laird

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARC
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OF DOCTOR OF PHILOSOPHY

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EDMONTON, ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled, "Aquation and Chromium(II) Reduction Reactions of Sulfonamido Complexes of Pentaamminecobalt(III)" submitted by Janet Louise Laird in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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Date... October 27, 1983

To Mom and Dad

# ABSTRACT

The aquation and chromium(II) reduction reactions of a variety of sulfonamidopentaamminecobalt(III) complexes have been studied in 1 M $LiClO_4/HClO_4$. The rate law for the aquation of $(NH_3)_5CoNHSO_2NH_2{}^{2+}$ has the form $-d\ln[\text{complex}]/dt = k_{2h}[H^+]/(K_a+[H^+])$, and the aquation kinetics of $(NH_3)_5CoNHSO_2R^{2+}$, ($R = C_6H_4CH_3$-p, $C_6H_4NO_2$-p), are consistent with the same rate law if $K_a >> [H^+]$. The unusually large rate constants obtained, (e.g., $k_{2h} = 1.41 \times 10^{-2}\ s^{-1}$ at 25°C, for $(NH_3)_5CoNHSO_2NH_2{}^{2+}$), are attributed to N-protonation of $(NH_3)_5CoNHSO_2R^{2+}$ followed by facile release of the neutral ligand.

The chromium(II) reduction of $(NH_3)_5CoNH_2SO_3{}^{2+}$ produces $(H_2O)_5CrOSO_2NH_2{}^{2+}$. The nitrogen and oxygen bonded linkage isomers are reduced at indistinguishable rates. Reduction of $(NH_3)_5CoNHSO_2NH_2{}^{2+}$ is competitive with aquation, and $(NH_3)_5CoNH_2SO_2NH_2{}^{3+}$ is reduced much more rapidly than the deprotonated species. 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 $(NH_3)_5CoNHSO_2C_6H_4CH_3$-$p^{2+}$, 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 results.

Chromium(II) reduction of $(NH_3)_5CoNHSO_2C_6H_4NO_2\text{-}p^{2+}$ involves reduction of both the cobalt(III) and the $NO_2$ group. Detection of a p-nitro radical complex has been accomplished by stopped-flow spectrophotometry. A step-wise mechanism consistent with the complex absorbance changes has been proposed and many of the specific rate constants have been measured. Rapid reduction of the nitro group to hydroxylamine occurs concurrently with reduction of the Co(III), the major amount of $Co^{2+}$ coming from reduction of the p-nitroso radical intermediate. Further reduction of the hydroxylamine derivative is much slower. Similar results were found for the chromium(II) reduction of the free ligand, minus those reactions involving reduction of the metal.

# ACKNOWLEDGEMENTS

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## TABLE OF CONTENTS

CHAPTER PAGE

# LIST OF TABLES

# LIST OF FIGURES

FIGURE PAGE

FIGURE PAGE

CHAPTER I

## INTRODUCTION

As early as 1951 [1] the distinction was made between two general types of electron transfer reactions between metal complexes in solution, those in which the electron is transferred within a primary bond system (e.g., (I-1)), and those in which the electron

$$ML_6 + M'L'_6 \longrightarrow [L_5M\text{-}L\text{-}M'L'_5]^{\ddagger} \longrightarrow \text{products} \quad (I\text{-}1)$$

is transferred from one primary bond system to another (e.g., (I-2)). These two types of reactions were later

$$ML_6 + M'L'_6 \longrightarrow [ML_6,M'L'_6]^{\ddagger} \longrightarrow \text{products} \quad (I\text{-}2)$$

named inner-sphere and outer-sphere mechanisms,[2] respectively, on the basis that in the former electron transfer is mediated by one or more ligands shared between the inner coordination spheres of both metal centers, whereas in the latter electron transfer occurs in an activated complex in which both metal ions retain intact inner-coordination spheres.

Identification of the type of activated complex is not always easy, or even possible. In the early studies, the lability or inertness of the reactants and products were controlling factors in the determination of mechanistic type. However, with the advent of rapid reaction techniques, allowing the study of labile species, the ability to distinguish between inner-sphere and outer-sphere mechanisms came to depend more on the relative rate of reduction with respect to the rate of ligand substitution of reactants and products.

It is sufficient for the rate of reduction to be faster than the rate of substitution for at least one oxidation state of each metal ion, in order to obtain information on the type of mechanism directly from kinetic and/or product studies. If both reactants undergo substitution slower than the observed rate of electron transfer, as is the case with a number of oxidants towards vanadium(II), then electron transfer must occur through an outer-sphere activated complex. If the rate of reduction is faster than the rate of substitution for (a) both the reactant and product oxidants (or both reductants), or (b) both products, then product identification, either via isolation and characterization (if substitution inert), or kinetic observation of the decomposition of an initial product (i.e., reduction faster than substitution), or an observation consistent with a concentration of an initial product at some stage in the reaction (i.e., both reactions of comparable rate), will indicate the nature of the activated complex. In case (a), where the reactant and product oxidants are relatively inert, an inner-sphere reaction would result in the transfer of all bridging ligands present in the activated complex from one metal oxidant to the other (e.g. equation 1.1[3]), whereas in

$$\underset{\text{INERT}}{(NH_3)_5CoCl^{2+}} + \underset{\text{LABILE}}{Cr(OH_2)_6^{2+}} \xrightarrow{H^+} 5NH_4^+ + \underset{\text{LABILE}}{Co(OH_2)_6^{2+}} + \underset{\text{INERT}}{(H_2O)_5CrCl^{2+}} \qquad (1.1)$$

case (b), where both products are relatively inert, observations consistent with the presence of a binuclear complex would be indicative of an inner-sphere mechanism (e.g., equation 1.2[4]).

$$Fe(CN)_6^{3-} + Co(CN)_5^{3-} \longrightarrow \underset{\text{INERT}}{(NC)_5CoNCFe(CN)_5^{6-}} \qquad (1.2)$$

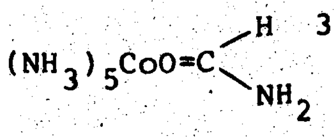
In the remaining cases, (i.e., when both oxidation states of at least one metal ion undergo substitution faster than the observed rate of reduction), attempts to observe the initial products will be either futile, or not indicative of the mechanistic type. Comparison of a variety of rate and thermodynamic parameters with those obtained from authentic inner-sphere and outer-sphere reactions can, in some cases, provide indirect evidence as to the appropriate mechanistic classification.

The nature of the activated complex sometimes can be deduced from the characteristics of the available bridging ligand. If one of the reaction partners does not offer a suitable site to which the labile partner can bond, then the redox reaction must proceed via an outer-sphere mechanism. The potential bridging ligand must possess a minimum of one unshared electron pair after coordination in order to engage the second metal cation. In equation 1.3, coordinated $NH_3$

$$Co(NH_3)_6^{3+} + Cr(OH_2)_6^{2+} \xrightarrow{H^+} Co(OH_2)_6^{2+} + Cr(OH_2)_6^{3+} + 6NH_4^{+} \qquad (1.3)$$

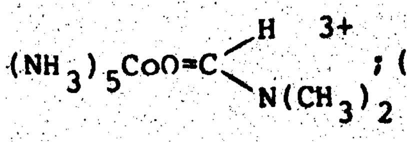
has no unshared electrons to provide a coordinate bond to $Cr^{2+}$, and an outer-sphere mechanism is observed.[5]

In addition, there is evidence that polyatomic bridging ligands must be conjugated in order for facile electron transfer through the ligand. The first examples of this were chromium(II) reduction reactions of the formamide (I-3), N,N-dimethylformamide (I-4), and urea (I-5) complexes of pentaamminecobalt(III).[6,7] These complexes are reduced



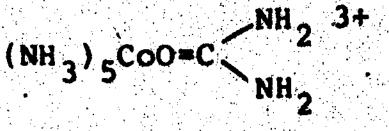
$$(NH_3)_5CoO{=}C\genfrac{}{}{0pt}{}{H}{NH_2}{}^{3+} ;$$

(I-3)



$$(NH_3)_5CoO{=}C\genfrac{}{}{0pt}{}{H}{N(CH_3)_2}{}^{3+} ;$$

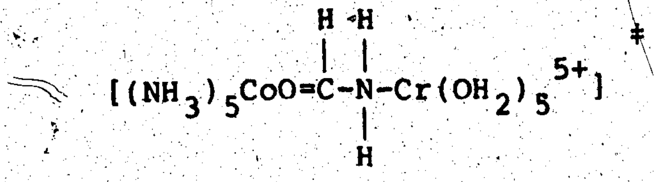
(I-4)



$$(NH_3)_5CoO{=}C\genfrac{}{}{0pt}{}{NH_2}{NH_2}{}^{3+}$$

(I-5)

without ligand transfer in spite of the lone pair of electrons available on the nitrogen atom. The binuclear activated complex which would result from inner-sphere attack at this site, (e.g., (I-6)), does not contain a

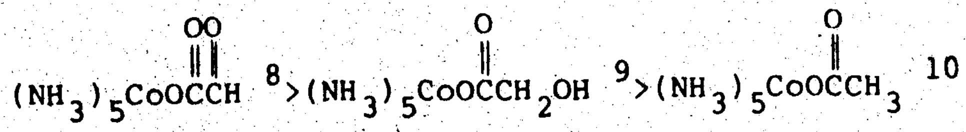


$$[(\mathrm{NH_3})_5\mathrm{CoO{=}}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}\mathrm{-Cr(OH_2)_5}{}^{5+}]^{\ddagger}$$

(I-6)

conjugated bond system to mediate electron transfer.

Suitable lead-in groups and conjugation are not sufficient to ensure an effective bridge. The rate of inner-sphere reduction is influenced by the reducibility of the mediating ligand, although the ligand may not suffer a net reduction during the electron transfer process. Thus the rate of $Cr^{2+}$ reduction decreases in the series:

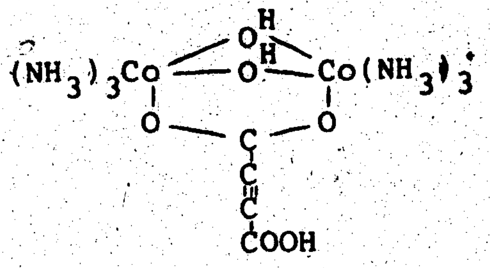


$$(\mathrm{NH_3})_5\mathrm{CoO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H}\ {}^{8}>(\mathrm{NH_3})_5\mathrm{CoO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2OH}\ {}^{9}>(\mathrm{NH_3})_5\mathrm{CoO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}\ {}^{10}$$

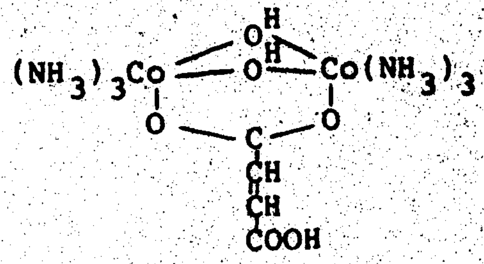
$k, M^{-1}s^{-1}$: $7 \times 10^3$; 3.1 ; 0.35

in spite of the fact that the oxidizing metal center and the reducing agent are identical. The ligands differ in reducibility, the glyoxylate has an unoccupied orbital lying at lower energy, and the difference in rates has been attributed to the difference in reducibility of the ligands.[10]

Finally, the orbital on the bridging ligand which mediates the electron should have an appreciable density in close proximity to the oxidant. Thus (I-7), below, is more reducible than (I-8), but the latter reacts faster with $Cr^{2+}$. This has been ascribed to the decreased ability of the triple bond to delocalize π-electrons with respect to the double bond.[11]



(I-7), k = 0.67 $M^{-1}s^{-1}$

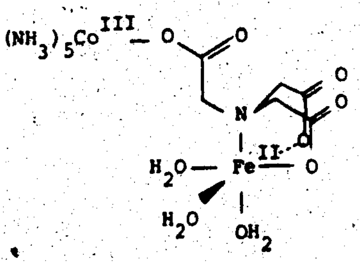


(I-8), k = 2.64 $M^{-1}$ $s^{-1}$

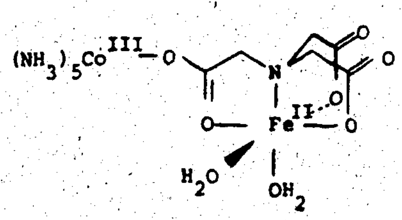
It has been noted[12] that it may be possible for a binuclear precursor complex to form in a system which contains a free-electron pair to engage the second metal ion, but which does not offer a conjugated bridge to mediate electron transfer. If the bridge is sufficiently flexible to allow the two metal ions to approach each other closely, then direct electron transfer via a path which bypasses the bridging ligand, (i.e., an outer-sphere pathway) might occur. Such a reaction, (called bridged-outer-sphere), may be favoured over a conventional outer-sphere pathway, when both mechanistic paths are available.

Prior to the act of electron transfer, bond distortion of the inner coordination spheres of both metal centers must occur in order that the electron can transfer without a change in energy. In a bridged mechanism, (inner- or outer-sphere), distortion of the two metal centers occurs simultaneously, coupled by the formation of the bridged precursor complex. In an unbridged mechanism, distortion of the two metal centers are uncoupled events, which nevertheless must occur simultaneously while the reactants are close together. The improbability of the latter predicts a selectivity for a bridged mechanism over an unbridged mechanism in cases where the amount of distortion required is significant.

Many workers have attempted to observe a bridged-outer-sphere reaction, but few unambiguous cases are known to date. An early example was the study of the ferrous reduction of oxygen bonded nitrilotriacetatopentaammine-cobalt(III).[13] Kinetic evidence was obtained for production of a precursor complex (I-9), but formation of a carboxyl-bridged transition state, (I-10), in which an inner-sphere



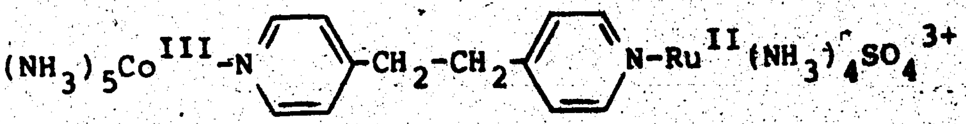
(I-9)



(I-10)

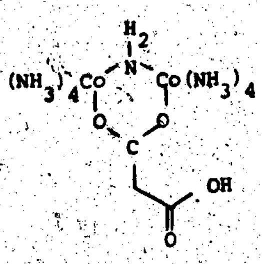
pathway is available was equally consistent with the data.

Taube et al.[14] have proposed a bridged-outer-sphere mechanism for the intramolecular electron transfer reaction in the binuclear complex (I-11).

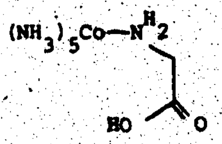


(I-11)

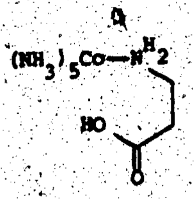
Sykes et al.[12,15] have proposed that the inverse acid dependent pathways observed in the $Cr^{2+}$ reduction of μ-malonato and μ-dimethylmalonato-dicobalt(III) complexes of type (I-12), as well as the nitrogen bonded glycinato- and β-alaninato- complexes of pentaamminecobalt(III), (I-13) and (I-14), are due to acid dissociation and reductant attack at the remote carboxylate. Unfortunately, for complexes of



(I-12)



(I-13)



(I-14)

type (I-12), the diagnostic inner-sphere product was not identified. However, for (I-13) and (I-14), $(H_2O)_5CoO_2CCH_2NH_3{}^{3+}$ and $(H_2O)_5CrO_2CCH_2CH_2NH_3{}^{3+}$ were identified as products of the inverse acid dependent term.

Finally, in a recent study by Kupferschmidt and Jordan,[16] the product of the chromium(II) reduction of the deprotonated cyanoacetate complex, (I-15), was identified as

$(NH_3)_5CoNCCH_2CO_2^{2+}$ (I-15) $(H_2O)_5CrO_2CCH_2CN^{2+}$ (I-16)

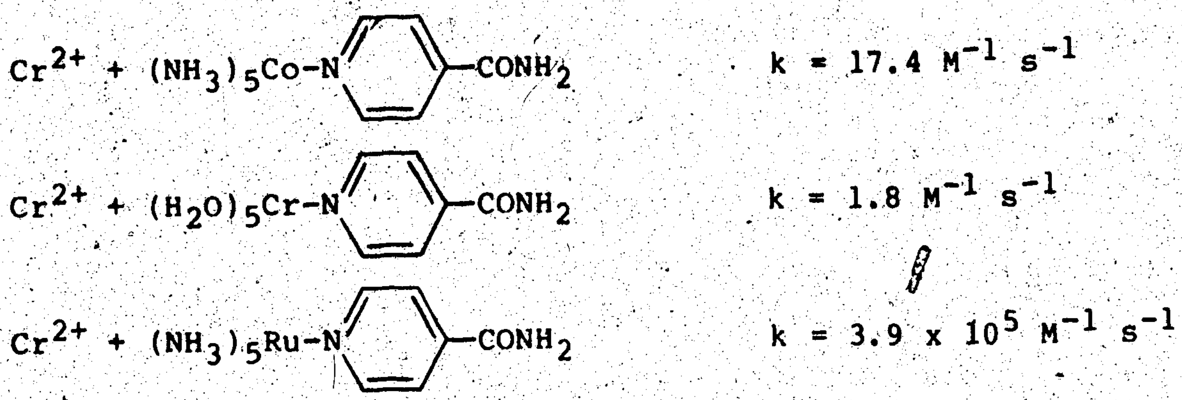
the ligand transfer product, (I-16). Since the reductant and oxidant are linked by a saturated bridge in the above examples, electron transfer must occur via a bridged-outer-sphere mechanism.

It should be noted that other names have been used to denote this mechanism. The original name was direct exchange inner-sphere.[17] Other names have included linked-electron transfer,[18a] and precursor complex formation with outer-sphere reduction.[12]

The above discussion of inner-sphere, outer-sphere, and bridged outer-sphere mechanisms demonstrates the importance of an understanding of how a bridging group aids the inner-sphere passage of electron density between the reacting centers. Subclassifications have emerged which distinguish two limiting modes of inner-sphere reduction. The term <u>chemical mechanism</u> refers to the situation in which either the reducing center is able to reduce the bridging ligand, or the oxidizing agent is able to oxidize the bridging ligand. In the ligand reducing case an electron passes from a well-defined bound state in the reducing agent, to another in the ligand, and subsequently an electron is transferred to the oxidant. Thus the bridge is temporarily reduced to a ligand centered radical. In contrast, the <u>resonance transfer</u> mechanism refers to a process in which the bridging group participates in the mediation of the electron by providing vacant orbitals which accept and transmit the electron, which is viewed as tunnelling from a bound state on the reducing agent directly to another on the oxidant, without occupying a well-defined bound state on the ligand. In both mechanistic extremes the rate of electron transfer is sensitive to the intrinsic reducibility of the bridging ligand. Even when the electron does not occupy a bound state on the ligand, as in the resonance transfer mechanism, the magnitude of the redox rate constant will be affected by the energy of the unoccupied orbital, since this determines the energy barrier to electron tunnelling. However, it has been predicted that as the electron affinity of the bridging ligand is increased, the mechanism may switch from resonance transfer to chemical.[18b,19]

For some systems even the subclassification of mechanism can be determined. The methods of distinction generally make use of the fact that in a resonance transfer mechanism the oxidant is necessarily involved in the rate determining step, and would be favoured in reactions where the acceptor orbitals of the oxidant metal can overlap effectively with those of the bridging ligand; whereas in a two-step chemical mechanism the rate determining step could be electron transfer from the reducing agent to the bridging ligand, and the nature of the oxidant would not be expected to have a large effect on the observed rate of reduction.

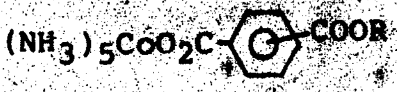
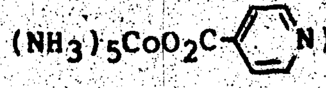
Thus, when reduction of a series of oxidants containing the same potential bridging ligand by the same reducing agent occurs at very similar rates, it seems likely that the oxidant does not play a significant role in the rate determining step. An example would be the $Cr^{2+}$ reduction of isonicotinamido complexes of pentaamminecobalt(III) and pentaaquochromium(III).[20]



Whereas, when the oxidant has a larger influence on the rate constant, as with the pentaammineruthenium(III) complex,[21] a resonance transfer mechanism seems more reasonable.

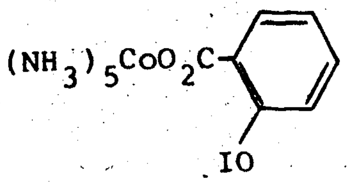
This rationalization is consistent with what is known of the electronic configurations of these three metal ions. The acceptor orbitals of cobalt(III) and chromium(III) have σ-symmetry and cannot interact with the π-acceptor orbitals of the isonicotinamide ligand. Ruthenium, however, has an acceptor orbital of π-symmetry which can overlap with the empty π-orbitals of the bridging ligand. Thus the acceptor orbital in the Ru(III)/Cr(II) couple would be a mixed ligand-metal orbital, and electron transfer to the ligand would be indistinguishable from electron transfer to the metal ion.

Norris and Nordmeyer[22] observed an autocatalytic pathway in the $Eu^{2+}$ reduction of isonicotinamidopentaamminecobalt(III), which enabled them to measure both the rate of $Eu^{2+}$ reduction of the cobalt(III) complex, ($k = 0.83$ $M^{-1}$ $s^{-1}$), and the rate of reduction of the free isonicotinamide ligand, ($k = 1.8$ $M^{-1}$ $s^{-1}$). The similarity of the specific rate constants indicates that electron transfer to the bridging ligand is the primary activation process for the cobalt(III) reduction, and a chemical mechanism was proposed.

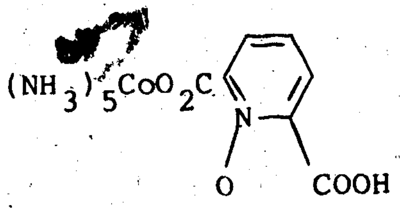
Similarly, when the observed trend in the rates of reduction of a series of complexes, (same metal oxidant, same reductant, variety of potential bridging ligands), is mimicked by the observed trend in the relative rates of reduction of the free ligands by the same reducing agent, this suggests that the metal complex has little influence on the relative rates of reduction and that the mechanism may be chemical. An example of this is a study by Gould and Taube[19] of the chromium(II) reduction of a series of carbonyl-benzoato and pyridinecarboxylato complexes of pentaamminecobalt(III), (e.g.,  and ), and the corresponding free acids. A general correlation between the rates of reduction of the pyridinecarboxylato complexes and their parent acids caused these workers to propose a chemical mechanism for the rapidly reduced complexes, whereas the lack of such a correlation in the carbonylbenzoato series led them to suggest that a resonance mechanism was operative.

In addition, a chemical mechanism seems more reasonable in systems containing polyatomic conjugated or aromatic bridging ligands, which are capable of stabilizing a radical intermediate. If the bridge is monoatomic, such as $F^-$, a chemical mechanism would require reduction of the ligand to $F^{2-}$, or its oxidation to $F^0$, both of which are energetically unfavoured.

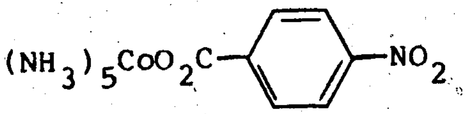
In some cases reduction of the ligand to a radical-ion intermediate has been inferred from stoichiometry studies of complexes containing easily reducible ligands. The chromium(II) reduction of (I-17), (I-18),[23] and a number of nitrobenzene complexes,[19,24,25] e.g., (I-19), resulted in



(I-17) ;



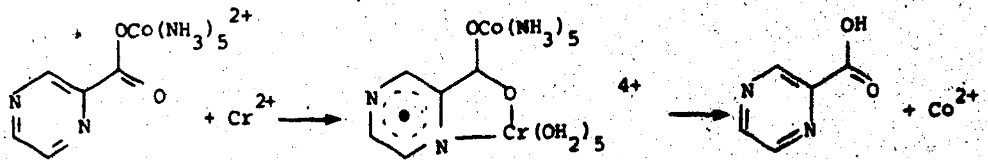
(I-18) ;



(I-19)

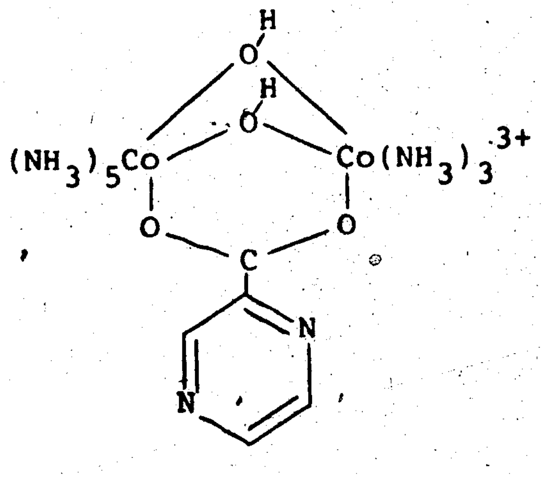
the release of much less than one mole of cobalt(II) per mole of chromium(II) consumed. It was proposed that the ligands themselves are being reduced, transmitting few electrons through the ring to the coordinated cobalt(III).

The most conclusive proof of a chemical mechanism would be actual detection of a transient radical intermediate. Unfortunately, detection and characterization of such transient species is very difficult due to their short lifetimes. In the chromium(II) reduction of (I-20) and the uncomplexed acid, Spiecker and Weighardt[26] observed an E.S.R. signal which they attributed to the cyclic radical intermediate (I-21), and the uncomplexed analog,



(I-20) (I-21) (I-22)

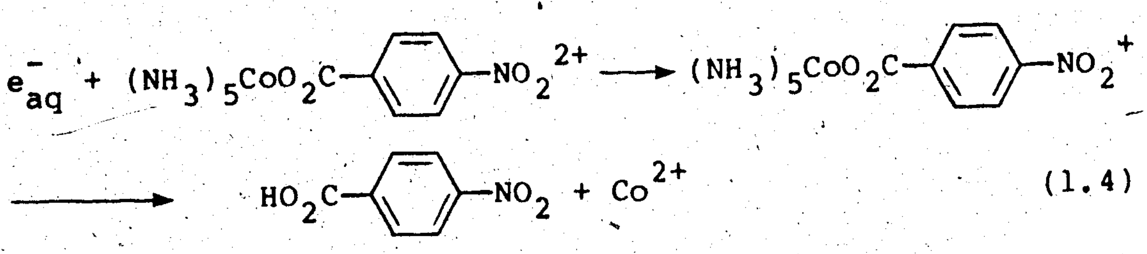
respectively. In a study of the chromium(II) reduction of the similar complex, (I-23),[26] two radical intermediates



(I-23)

were inferred from two rapid increases in absorbance, however, a transient E.S.R. spectrum was not obtained.

Hoffman et al.[27-29] have used pulse radiolysis techniques to study the formation and decay of the radical ion intermediates formed by the reduction of various nitrobenzoatopentaamminecobalt(III) complexes by radiation-generated radicals such as $e_{aq}^-$, $\dot{C}O_2^-$ and $(CH_3)_2\dot{C}OH$, (e.g., equation 1.4).



(1.4)

The study of the p-nitrobenzoato complex, above, was the first reported observation of a radical intermediate produced by the initial reduction of a ligand bound to a metal oxidant, and the first reported measurement of the rate of the subsequent intramolecular electron transfer step.

As well as having empirical foundations, the various classifications and subclassifications defined above have been elaborated by theorists. The theory of outer-sphere reactions has been developed by Libby,[30] Marcus,[31-36] Hush,[37] Levich,[38] Hopfield,[39] Jornter,[40] Schmidt[41] and Dogonadze,[42] and has been reviewed by Marcus,[43] Ruff,[44] Dogonadze[45] and Schmidt.[46] Inner-sphere, chemical and resonance transfer mechanisms are more difficult to treat theoretically, but have been attempted qualitatively by George and Griffith,[47] Halpern and Orgel,[48] Burdett[49] and Larsson.[50]

Gould, Taube and co-workers have investigated the reduction reactions of a wide variety of carboxylato complexes,[51] and the detailed mechanism of electron transfer through a carboxylate linkage is well understood. In contrast, despite the fact that aromatic sulfonamides are used in drugs and are well-known inhibitors of carbonic anhydrase, very little is known about their coordination chemistry, hydrolytic reactions, or the factors affecting electron transfer through a sulfonamide ligand.

The oxygen atoms of a sulfonamide ligand offer a lone pair of electrons capable of bonding to a reductant. However, electron transfer cannot proceed through a saturated $-NH_2-$ group. This led to the expectation that the protonated form of these complexes, $(NH_3)_5CoNH_2SO_2R^{3+}$, should be reduced via an outer-sphere mechanism. However, the deprotonated forms, $(NH_3)_5CoNHSO_2R^{2+}$, may be reduced via an inner-sphere pathway. Consequently, if a ligand-transfer product is observed for the protonated path, then a bridged outer-sphere mechanism must be operative. It is hoped that the results of this study will help elucidate the reaction pathways for reduction of sulfonamide complexes.

A detailed kinetic investigation was also undertaken for the chromium(II) reduction of the p-nitrobenzenesulfonamide complex, (I-24). The ease of reduction of nitro

$$(NH_3)_5CoNHSO_2C_6H_4NO_2^{2+}$$

(I-24)

ligands to nitro radicals[27] suggests that this system may proceed via a chemical mechanism, producing the transient radical intermediate:

$$(NH_3)_5CoNHSO_2C_6H_4\dot{N}O_2^{+}$$

This coordinated radical could react in a number of ways. It could undergo intramolecular electron transfer,

$$(NH_3)_5CoNHSO_2C_6H_4NO_2^{+} \xrightarrow{H^+} 5NH_4^{+} + Co^{2+} + H_2NSO_2C_6H_4NO_2 \qquad (1.5)$$

producing the free ligand.

It could be further reduced by chromium(II), producing

$$(NH_3)_5CoNHSO_2C_6H_4NO_2^{+} + Cr^{2+} \xrightarrow{H^+} (NH_3)_5CoNHSO_2C_6H_4NO^{2+} + Cr^{III} + H_2O \qquad (1.6)$$

the two electron reduction product of the ligand.

Also, the radical could undergo disproportionation,

$$2(NH_3)_5CoNHSO_2C_6H_4NO_2^{+} \xrightarrow{H^+} (NH_3)_5CoNHSO_2C_6H_4NO_2^{2+} + H_2O + (NH_3)_5CoNHSO_2C_6H_4NO^{2+} \quad (1.7)$$

producing the initial reactant, and the p-nitroso derivative.

In all cases, the products of reactions 1.5-1.7 would undergo subsequent reduction reactions in the presence of excess chromium(II), perhaps producing other radical ion intermediates.

Gould and co-workers[24,25] have studied the chromium(II) reduction reactions of a variety of nitrobenzoato and dinitrophenoxyl complexes of pentaamminecobalt(III). Both the nitro substituents and the cobalt(III) metal ions were reduced by chromium(II) and the reactions were found to proceed through a number of intermediates, some of which were proposed to be radical ions. Unfortunately, in all cases, the overall absorption changes were not separated into clean-cut kinetic stages, nor were the inert products characterized.

It was hoped that reduction studies of the sulfonamide derivative may enable the direct measurement of the rate of the intramolecular transfer of an electron from a coordinated ligand radical to the metal oxidant.

To date, ~~only a very~~ few simple inorganic sulfonamide complexes have been prepared. Traube[52,53] first prepared silver(I) complexes of sulfamide. The structure of $Ag_2(N_2H_2SO_2)$ recently has been shown[54] to have two nitrogen atoms from different $N_2H_2SO_2^{2-}$ ions coordinated to silver(I). Ouchi and Moeller[55] prepared some $M(en)_2$-sulfamide derivatives ($M = Cu^{2+}$, $Ni^{2+}$) which are the subject of a recent infrared study.[56] Beck and Cenini and co-workers[57-59] have prepared aromatic sulfonamide derivatives such as $((C_2H_5)_3P)_2(Cl)Pt(NHSO_2C_6H_5)$ and $(bipy)Pd(NHSO_3C_6H_4CH_3)_2$ by reactions of sulfonylazides.

Mann[60] prepared and resolved <u>cis</u>-$[Rh(N_2H_2SO_2)_2(OH_2)_2]^-$. This seems to have been the second example of a purely inorganic optically active species. Mann also prepared $[Pt(OH)(NH_3)(N_2H_2SO_2)_2]^-$, and noted that the rhodium(III) and especially the platinum(IV) complexes are very susceptible to decomposition ~~by even~~ very weak acids used as resolving agents.

Considerably more work has been reported on sulfonamide/carbonic anhydrase inhibition chemistry. Such systems have been studied by a wide range of techniques[61-67] with general agreement that the sulfonamide is complexed as the anion to zinc(II), or cobalt(II) in the modified enzyme. Kinetic studies are consistent with a complex formation mechanism involving pre-association of sulfonamide and the enzyme followed by rate controlling metal-sulfonamide bond formation.[61] However, the sequence of proton transfer steps remains in doubt.

In the present study, a variety of sulfonamido pentaamminecobalt(III) complexes have been prepared and characterized. The acid-base properties, hydrolysis and redox kinetics have been investigated. The results have been related to previous studies on cobalt(III) complexes, as well as to the properties of the sulfonamide-carbonic anhydrase complexes.

## CHAPTER II

## EXPERIMENTAL

### REAGENTS

All solutions were prepared in deionized water redistilled from alkaline permanganate in an all-glass apparatus. Perchloric acid solutions were standardized against sodium hydroxide solutions. Standard solutions of sodium hydroxide and of sodium thiosulfate were prepared from ampoules of concentrated reagent (Fisher Scientific Company). Lithium perchlorate solutions were prepared by filtering aqueous lithium perchlorate through a 0.22 micron Millipore filter and determining the amount of hydrogen ion released from a Dowex 50W-X8 cation exchange column.

Chromium(III) perchlorate solutions were prepared by reducing potassium dichromate with hydrogen peroxide in perchloric acid solution. Primary standard grade potassium dichromate (147.2 g) was dissolved in hot water and added to concentrated perchloric acid (363 mL, 70%). Hydrogen peroxide (30%) was added dropwise with stirring to the ice-cold solution until the yellow dichromate was consumed. The dark blue solution was boiled for 3 h to decompose the excess hydrogen peroxide, chilled to 0°C, filtered through a

0.22 micron Millipore filter to remove the solid potassium perchlorate, and diluted to 2000 mL.

To determine the concentration of acid remaining in the solution an aliquot of the chromium(III) solution (5 mL) was added to a solution of sodium oxalate (2 g) in water (50 mL). The solution was heated for 30 min to complete the conversion of hexaaquochromium(III) to trisoxalatochromium(III), cooled to room temperature and titrated potentiometrically with standard sodium hydroxide solution.

Chromium(II) perchlorate was prepared either by dissolving chromium pellets (99.999% purity, Apache Chemical Inc.) in dilute perchloric acid, or by reducing chromium(III) perchlorate with zinc amalgam. In some cases primary standard grade lithium carbonate was added to the chromium(III) solution to reduce the acidity quantitatively, and the chromous solution was removed from the zinc amalgam after reduction was complete. The total chromium concentration of the chromous solution was determined by chromate analysis. Chromium(II) analyses were carried out periodically on the chromous solutions.

All other reagents were analytical grade, and used without purification. All solutions used in chromous reduction studies were deoxygenated using argon and handled using rubber serum caps and standard syringe techniques.

## ANALYSES

**Chromate:** Chromium species were oxidized to chromate in sodium hydroxide solution with hydrogen peroxide (final solution 1.0 M NaOH). Excess $H_2O_2$ was decomposed by boiling for at least 3 h. The chromate concentration was determined spectrophotometrically ($\lambda$ = 372 nm, $\varepsilon$ = 4.815 x $10^3$ $M^{-1}$ $cm^{-1}$).

**Chromium(II):** Two methods were used. 1) Chromium(II) concentrations were determined iodometrically by reacting an aliquot with an excess of ferric ammonium sulfate solution. The excess ferric ion, as well as the amount present in a blank untreated with chromium(II), was determined by addition of an excess of potassium iodide and titration of the iodine released with a standard sodium thiosulfate solution. 2) An aliquot containing chromium(II) was added to an excess of aquopentaamminecobalt(III) solution. The mixture was analysed for the amount of cobalt(II) produced.

**Cobalt(II):** The concentration of cobalt(II) was determined by treating an aliquot of cobalt(II) (~0.01 mmoles) with aqueous $NH_4SCN$ (2 mL, 65%), acetone (25 mL) and perchloric acid (2 mL, 70%). The solution was cooled to 25°, diluted to 50 mL, and the cobalt(II) concentration determined spectrophotometrically ($\lambda$ = 620 nm, $\varepsilon$ = 1764). The presence of an equivalent amount of cobalt(III) did not interfere and an equivalent amount of chromium(III) caused a 1% increase in absorbance.

Sulfamate: An aliquot containing sulfamate (~0.02 mmoles) was treated with sulfuric acid (20 mL, 1:1 by volume) and sodium nitrite (5 mL, 0.01 M). After 30 min the excess nitrite was oxidized with cerium(IV) ammonium sulfate (10 mL, 0.02 M Ce(IV), 0.18 M $H_2SO_4$) and excess cerium(IV) ion was titrated with iron(II) ammonium sulfate (0.02 M Fe(II), 0.36 M $H_2SO_4$) to an o-phenanthroline iron(II) sulfate indicator end-point. The results were compared to those of [illegible] of equal volume, containing no sulfamate. The [illegible](IV) sulfate solution was standardized iodometrically against a standard sodium thiosulfate solution, and used to determine titrimetrically the normality of the iron(II) solution.

Sulfamide: The sulfamate analysis was also used for sulfamide, but the expected 2:1 stoichiometry of $NO_2^-$ to $SO_2(NH_2)_2$ was not observed and a standard curve was developed from aliquots containing known amounts of sulfamide, (~0.005-0.01 mmoles). The observed stoichiometry was 1.63 moles of nitrite reacted per mole of sulfamide.

C, H, N: Elemental analyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory at the University of Alberta Chemistry Department.

## PREPARATION OF COMPLEXES

### Carbonatopentaamminecobalt(III) nitrate, $[(NH_3)_5CoCO_3](NO_3)$, and aquopentaamminecobalt(III) perchlorate, $[(NH_3)_5CoOH_2](ClO_4)_3$.

Carbonatopentaamminecobalt(III) nitrate was prepared according to the method of Schlessinger.[68] The carbonato complex was converted to the aquo complex by adding the solid to the minimum amount of warm perchloric acid (1.0 M) required to ensure complete conversion. Conversion was complete when the effervescence ceased, and the solution remained acidic. The mixture was cooled, the brick red crystals were collected by filtration, recrystallized from perchloric acid (1.0 M) in order to remove all traces of nitrate, washed with methanol and ether, and air-dried. Anal. Calcd for $[(NH_3)_5CoOH_2](ClO_4)_3$: N, 15.21; H, 3.72. Found: N, 14.55; H, 3.65.

### Aquopentaamminecobalt(III)trifluoromethanesulfonate, $[(NH_3)_5CoOH_2](CF_3SO_3)_3$ and (Trifluoromethanesulfonato)pentaamminecobalt(III)trifluoromethanesulfonate, $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$.

These complexes were prepared according to the method of Kupferschmidt and Jordan.[69]

### Sulfamidopentaamminecobalt(III) perchlorate, $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$.

A solution containing 5 g of sulfamide and 1 mL of 2,6-lutidine in 40 mL of acetone was allowed to stand over molecular sieves for 1 h and then 4 g of $((NH_3)_5CoO_3SCF_3)(O_3SCF_3)_2$ was added. After 14 h the mixture was filtered to remove the molecular sieves and 3 g of LiBr was added. The product was collected, washed with acetone, redissolved in a minimum of warm (50°C) water and precipitated by addition of $NaClO_4$ and cooling. This product was collected and recrystallized from a minimum of warm water to yield dark red crystals which were washed with methanol and air dried.

Anal. Calcd for $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$: N, 23.43; H, 4.33. Found: N, 23.44; H, 4.36.

## p-Toluenesulfamidopentaamminecobalt(III) perchlorate, $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2$.

A solution of aquopentaamminecobalt(III) perchlorate (13.5 g) in dry N,N-dimethylacetamide (40 mL) over molecular sieves (10 g) was heated on a steam bath for 1 h. The p-toluenesulfonamide (10 g) was dissolved in dry N,N-dimethylacetamide (20 mL) containing 3.4 mL of 2,6-lutidine and molecular sieves (10 g) and heated on a steam bath for 1 h. The two solutions were mixed, heated on a steam bath for 6 h, cooled, filtered and dripped into a 50:50 mixture of ether and sec-butanol. The crude product was collected, redissolved in water (500 mL) and purified by cation exchange chromatography on Baker CGC-271 weak acid resin (J.T. Baker Chemical Company) in the sodium ion form (1" x 5.5"). Elution with increasing concentrations of sodium perchlorate up to 0.2 M separated the complex from impurities remaining at the top of the column. The resin containing the desired complex was separated physically and washed with distilled water followed by acetic acid (4 M) in order to remove the complex from the resin. The resulting solution was neutralized with sodium hydroxide and the complex precipitated with $NaClO_4$. The complex was recrystallized from water, washed with ether and air dried to yield a purple crystalline solid.

Anal. Calcd for $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2 \cdot H_2O$: N, 15.82; C, 15.83; H, 4.74. Found: N, 15,91; C, 15.92; H, 4.75.

### p-Nitrobenzenesulfonamidopentaamminecobalt(III) perchlorate $[(NH_3)_5CoNHSO_2C_6H_4NO_2](ClO_4)_2$.

A solution of aquopentaamminecobalt(III) perchlorate (5.7 g) in dry N,N-dimethylacetamide (20 mL) with molecular sieves (10 g) was heated on a steam bath for 2 h. The p-nitrobenzenesulfonamide (5 g) was dissolved in a minimum amount of hot, dry N,N-dimethylacetamide to which 3 mL of 2,6-lutidine and molecular sieves (10 g) had been added. The two solutions were mixed, heated for 3 h on a steam bath, collected, filtered and the solvent extracted with ether. The resulting oil was dissolved in a minimum amount of warm water and the complex precipitated by the addition of sodium perchlorate. The crude product was collected, redissolved in 250 mL of 0.02 M $NaClO_4$ and purified by ion-exchange chromatography and recrystallized as described for the p-toluenesulfonamide complex, yielding dark red crystals.

Anal. Calcd for $[(NH_3)_5CoNHSO_2C_6H_4NO_2](ClO_4)_2 \cdot H_2O$: N, 17.44; C, 12.82; H, 3.94. Found: N, 17.42; C, 12.62; H, 3.66.

## Sulfamatopentaamminecobalt(III) perchlorate, $[(H_3N)_5CoNH_2SO_3](ClO_4)_2$.

This complex was prepared by a more efficient method than those reported previously.[70,71] An aqueous solution (60 mL) containing sulfamic acid (5.8 g) and carbonatopentaamminecobalt(III) nitrate (8 g) 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, redissolved in sodium hydroxide (0.1 M) and allowed to stand for 10 min in order to hydrolyse 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 Company) 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 orange 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,[70,71] (see Tables 2 and 4, respectively).

Azoxybenzenesulfonamide, hydrazobenzenesulfonamide and azobenzenesulfonamide were prepared by the methods of Seikel[72] and hydroxylaminobenzenesulfonamide by the method of Bauer and Rosenthal,[73] with few modifications.

### Azoxybenzenesulfonamide. $H_2NS(O)_2C_6H_4N{=}N(O)C_6H_4S(O)_2NH_2$.

A solution of sulfanilamide (5 g) in hydrogen peroxide (30 mL, 30%) and glacial acetic acid (120 mL) was heated for 30 min on a steam bath and left overnight at room temperature. The yellow crystals were removed by filtration.

Anal. Calcd for $H_2NS(O)_2C_6H_4N{=}N(O)C_6H_4S(O)_2NH_2$: N, 15.72; C, 40.44; H, 3.39. Found: N, 15.73; C, 40.80; H, 3.40. The ultraviolet spectrum in water has a peak at 326 nm ($\epsilon$ $1.89 \times 10^4$ $M^{-1}$ $cm^{-1}$).

### Hydrazobenzenesulfonamide. $H_2NS(O)_2C_6H_4NHNHC_6H_4S(O)_2NH_2$.

A solution of azoxybenzenesulfonamide (2.6 g) in sodium hydroxide (130 mL, 0.2 M) was heated to boiling and treated with sodium dithionite (2 x 4 g). Decolourization appeared complete after the first 4 g sample had been added. The solution was filtered, boiled for 5 min, cooled, and the white precipitate removed by filtration.

Anal. Calcd for $H_2NS(O)_2C_6H_4NHNHC_6H_4S(O)_2NH_2$: N, 16.36; C, 42.10; H, 4.12. Found: N, 15.91; C, 41.33; H, 4.04.

## Azobenzenesulfonamide. $H_2NS(O)_2C_6H_4N{=}NC_6H_4S(O)_2NH_2$.

A hot aqueous solution of hydrazobenzenesulfonamide (2.5 g in 200 mL) was treated with 1 M ferric chloride (20 mL). The solution was filtered and the orange crystals recrystallized twice from 30% pyridine.

Anal. Calcd for $H_2NS(O)_2C_6H_4N{=}NC_6H_4S(O)_2NH_2$: N, 16.46; C, 42.34; H, 3.55. Found: N, 16.28; C, 42.16; H, 3.59. The ultraviolet spectrum in water has a peak at 321 nm ($\varepsilon$ 3.13 x $10^4$ $M^{-1}$ $cm^{-1}$) and a shoulder at 223 nm ($\varepsilon$ 1.30 x $10^4$ $M^{-1}$ $cm^{-1}$).

## p-Hydroxylaminobenzenesulfonamide. $H_2NS(O)_2C_6H_4NHOH$.

To a warm solution of p-nitrobenzenesulfonamide (1 g in 30 mL ethanol) an ammonium chloride solution (1.7 g in 16 mL water) was added. Zinc dust (1.5 g) was added gradually with constant vigorous stirring while the temperature was maintained between 45° and 52°. The mixture was stirred (15 min), chilled in ice (60 min), and filtered to remove the zinc sludge which was washed with ethanol. The yellow filtrate was concentrated under vacuum, and chilled in ice (20 min). The product was collected by filtration and

recrystallized from water, yielding white crystals.
Anal. Calcd for $H_2NS(O)_2C_6H_4NHOH$: N, 14.88; C, 38.29; H, 4.29. Found: N, 14.73; C, 38.30; H, 4.29. The ultraviolet spectrum in $H_2O$ has a peak at 256 nm ($\varepsilon$ 1.564 x $10^4$ $M^{-1}$ $cm^{-1}$). In 1.0 M perchloric acid there is a peak at 256 nm ($\varepsilon$ 8.55 x $10^3$ $M^{-1}$ $cm^{-1}$) and in 0.5 M sodium hydroxide there is a peak at 278 nm ($\varepsilon$ 8.71 x $10^3$ $M^{-1}$ $cm^{-1}$).

### p-Nitrosobenzenesulfonamide. $H_2NS(O)_2C_6H_4NO$.

p-Hydroxylaminobenzenesulfonamide (0.2 g) was dissolved in warm water, filtered, and added dropwise with stirring to an excess of 10% ferric chloride solution. The mixture was stirred (20 min), chilled, and filtered to remove the white precipitate which was crystallized from ethanol.
Anal. Calcd for $H_2NS(O)_2C_6H_4NO$: N, 15.05; C, 38.71; H, 3.25. Found: N, 15.14; C, 39.50; H, 3.37.

## KINETIC MEASUREMENTS

The slow reduction kinetics ($t_{1/2} > 1$ min) were studied by injecting an aqueous solution of the cobalt(III) complex (or the ligand) into a temperature equilibrated aqueous solution containing the required amounts of perchloric acid, lithium perchlorate and chromium(II) perchlorate. This order of mixing was required in the reduction studies due to the rapid aquation of these complexes in acidic solution. The reduction kinetics were followed at 505, 500, 350, and 350 nm for the p-toluenesulfonamido and sulfamido complexes and the slow step of the p-nitrobenzenesulfonamido complex and the p-nitrobenzenesulfonamide ligand, respectively.

The aquation kinetics were done similarly except that the perchloric acid was the last component to be injected for the p-toluenesulfonamido and p-nitrobenzenesulfonamido complexes. The kinetics were observed at 285, 295 and 390 nm for aquation of the sulfamido, p-nitrobenzenesulfonamido and p-toluenesulfonamido complexes, respectively.

The reduction of the sulfamato complex and the fast kinetics in the reduction of the p-nitrobenzenesulfonamido complex and the p-nitrobenzenesulfonamide ligand were studied at 485, 350 and 350 nm, respectively, by mixing an aqueous solution of the cobalt(III) complex (or the ligand) in lithium perchlorate with a solution of chromium(II) in perchloric acid and lithium perchlorate on an Aminco-Morrow stopped-flow system. In the sulfamato complex studies the cobalt(III) solution was made alkaline with sodium bicarbonate (pH ~9) in order to prevent prior linkage isomerization and aquation.[70]

Equilibrium mixtures of nitrogen and oxygen bonded isomers of the sulfamato complex were prepared by allowing the complex to stand in 0.1 M perchloric acid (14 mL, ~1.6 x $10^{-3}$ M cobalt(III)) for 85 min at 21°.[70] Chromium(II) was

~~injected and the~~ reduction kinetics of the isomeric mixture were followed at 288 nm on a Cary 219 spectrophotometer. This instrument could be used because the low ionic strength ($\mu$ = 0.09 m) slowed the reaction. For comparison a few runs were also done on solutions containing the nitrogen 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.

All of the aquation and slow reduction kinetics were studied on a Cary 219 spectrophotometer, except the aquation of the p-toluenesulfonamido complex which was studied on a Bausch and Lomb Precision spectrophotometer. In either case the cell holder of the spectrophotometer was thermostated by water circulating from a constant temperature bath (Colora) connected to a circulating cooler for temperatures below 20° (RHO Scientific Inc., or KR-30 Polyscience Company) and a temperature controller (Fisher Thermistemp 71 or 71A) with the thermistor probe placed either in the cell holder, or in the water bath. The temperature inside the cell was checked periodically with a copper constantan thermocouple connected to a digital thermometer (Doric DS-100-T3). A similar arrangement was employed with the stopped-flow system, in that the temperature inside the drive syringes was controlled by water circulating from a constant temperature bath, and measured periodically by inserting the thermocouple into the drive syringe compartment. The

Aminco-Morrow stopped-flow apparatus had been adapted with two three-way Hamilton valves permitting anaerobic addition of the reagents to the storage syringes, and the compartment containing the observation chamber was flushed continuously with argon.

Except where noted, reactions were studied under pseudo-first order conditions in perchloric acid and chromium(II) (reduction studies only). The observed rate constant, $k_{obsd}$, for reactions which displayed monophasic pseudo-first order behaviour, (equation 2.1), was

$$Abs_t = Abs_\infty + Ae^{-k_{obsd}t} \qquad (2.1)$$

determined either from the slope of a semilogarithmic plot of log $(Abs_t - Abs_\infty)$ versus time, or by fitting the absorbance versus time data to equation 2.1 using a non-linear least-squares program. $Abs_t$ and $Abs_\infty$ are the absorbancies at time t and after the reaction is complete, and the preexponential term, A, is a function of the extinction coefficients. These plots were linear for at least 90% of the reaction. For reactions showing more complex kinetic behaviour, the observed rate constants were determined by fitting the absorbancies to the appropriate functions (described in the Results section) using non-linear least-squares methods.

In the stopped-flow work the transmittance versus time curves were stored on a Tracor NS-570 signal averager. For complex kinetic behaviour the data was output to an X-Y recorder, digitized and fitted as described above. For monophasic exponential behaviour the data was output to a dual trace oscilloscope for comparison to a synthetic exponential decay curve. The time constant for the synthetic curve can be varied by changing the resistance in the circuit. The system was calibrated by recording synthetic curves on an X-Y recorder and calculating the observed rate constant from the usual semilogarithmic plot of absorbance change versus time. Values were within 1% of those expected from resistance settings. An uncertainty of ±5% is expected in matching experimental and synthetic decay curves at typical signal to noise levels.

Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined by a non-linear least-squares fit of the data at various temperatures to the transition state equation:

$$k = \frac{\kappa k_B T}{h} \exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{-\Delta S^{\ddagger}}{R}\right) \qquad (2.2)$$

where k is the specific rate constant, $\kappa$ is the transmission coefficient assumed to be equal to one, $k_B$ is Boltzmann's constant, h is Planck's constant, T is the temperature in °K, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively, and R is the gas constant in units cal $deg^{-1}$ $mole^{-1}$.

## REACTION PRODUCT ANALYSIS

Aquation Studies: The reaction solution for the p-toluenesulfonamido complex typically contained 20 mg of the cobalt(III) complex and 0.10 M or 0.80 M perchloric acid in a total volume of ~15 mL adjusted to a total ionic strength of 1.0 M with lithium perchlorate. The hydrolysis was allowed to proceed for 10 half-times, then the solution was neutralized with 5 M NaOH, diluted to a total volume of ~125 mL and charged onto a ½" x ½" cation exchange column of Baker CGC-271 weak acid resin in the sodium ion form. The resin was cleaned by washing with HCl (6 M) and NaOH (6 M) before use. The initial eluent was collected, acidified to pH ~5 and analysed spectrophotometrically for p-toluenesulfonamide (ε, 528 $cm^{-1}$ $M^{-1}$ at 262 nm, pH < 7). The electronic spectrum of the latter easily distinguishes it from p-toluenesulfonic acid. The resin containing the cobalt(III) product was separated physically and washed with water followed by 4 M $HClO_4$ in order to remove the cobalt(III) complex. The resulting solution was diluted to 1.0 M $HClO_4$ and analysed spectrophotometrically for $(NH_3)_5CoOH_2{}^{3+}$ (ε, 46 $cm^{-1}$ $M^{-1}$ at 345 nm; ε, 49 $cm^{-1}\cdot M^{-1}$ at 492 nm).

A second column was charged with a blank solution containing no cobalt(III). The respective eluents obtained from the identical work-up of this column were used as blan[illegible] spectrophotometric analysis of both products.

[illegible]ion solution for the p-nitrobenzenesulfonamido [illegible]mp[illegible]ned 6 to 14 mg of the cobalt(III) complex and [illegible]0 [illegible].00 M $HClO_4$ in a total volume of ~10 mL (μ = 1.0 [illegible] products were analysed as described above except t[illegible] initial eluent was made 1.0 M in NaOH, and analysed s[illegible]photometrically for $NHSO_2C_6H_4NO_2^-$ (ε, 8.66 x $10^3$ $cm^{-1}$ $M^-$[illegible] 276 nm), allowing distinction between the amide and p-[illegible]obenzenesulfonic acid.

[illegible]e reaction solution for the sulfamido complex cont[illegible]ed ~15 mg of the cobalt(III) complex and 0.05 M or 1.0 M $HClO_4$ in a total volume of ~6 mL, (μ = 1.0 M). Analys[illegible] of the products was carried out as described above excep[illegible] the initial eluent was not analysed for free liga[illegible] because sulfamide has no characteristic absorbance in the UV-visible spectrum.

Reduction Studies: The reactions were allowed to proceed for about seven half-times and then quenched by air oxidation of the chromium(II). Products were separated by cation exchange chromatography at 5° 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 $Cr(OH_2)_6{}^{3+}$.

The initial eluents were analysed spectrophotometrically for p-toluenesulfonamido as described above, and sulfamate and sulfamide concentrations were determined titrimetrically, also as described above. The electronic spectra of the chromium(III) eluents were recorded and the total chromium concentrations were determined by chromate analysis.

A solution containing the N- and O-bonded isomers of the sulfamato complex was produced by allowing $(H_3N)_5CoNH_2SO_3{}^{2+}$ ($1.2 \times 10^{-3}$ M) to react for 2 h in 0.1 M $HClO_4$.[70] 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 ($H^+$) and characterized by its electronic spectrum.

The products of the chromium(II) reduction of the p-nitrobenzenesulfonamide ligand were identified by removing an aliquot of the reaction solution immediately after mixing, and again after the reduction reaction was complete (> 1 h), oxygenating, adjusting to pH ~9 with sodium hydroxide, neutralizing to pH ~7 with perchloric acid, and removing the precipitated chromium(III) by filtration through a 0.22 micron Millipore filter. The filtrate was acidified to 1 M $HClO_4$, as well as adjusted to 0.3 M NaOH and analysed spectrophotometrically for relative concentrations of sulfanilamide and p-hydroxylaminobenzenesulfonamide. The electronic spectra of these ligands are almost identical under neutral conditions. The extinction coefficients at the wavelengths used for this analysis are given below:

| | 1 $M$ $HClO_4$, $\lambda$ = 257 nm $\varepsilon$, ($M^{-1}$ $cm^{-1}$) | 0.3 $M$ NaOH $\lambda$ = 250 nm $\varepsilon$, ($M^{-1}$ $cm^{-1}$) |
|---|---|---|
| $H_2NSO_2C_6H_4NHOH$ | $8.55 \times 10^3$ | $6.31 \times 10^3$ |
| $H_2NSO_2C_6H_4NH_2$ | 568. | $1.615 \times 10^4$ |

This method was employed because conventional column chromatography, (i.e., Dowex 50W-X8, $H^+$ form, eluted with $[H^+]$ = 0.01 to 0.1 $M$ solutions) was shown by means of a blank column (i.e., charged with sulfanilamide) to retain large amounts of sulfanilamide. When the column was modified (i.e., Dowex 50W-X8, $Na^+$ form, eluted with $H_2O$, pH ~ 3) retention of sulfanilamide was observed in the presence of $Cr(OH_2)_6{}^{3+}$ and $(H_2O)_4Cr(OH)_2Cr(OH_2)_4{}^{4+}$.

## STOICHIOMETRY

Stoichiometry studies were carried out at various stages in the chromium(II) reduction of the p-nitrobenzenesulfonamido complex, the p-nitrobenzenesulfonamide ligand and the p-nitrosobenzenesulfonamide ligand by analysing for chromium(II) remaining immediately after mixing, and after the reaction was complete (> 1 h). Also, the amount of cobalt(II) released immediately after mixing, for reaction solutions containing various initial chromium(II) to cobalt(III) ratios, was determined by cobalt(II) analyses.

## PHYSICAL MEASUREMENTS

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

## CHARACTERIZATION OF COMPLEXES

The sulfamide and sulfonamide may coordinate to cobalt(III) through either the nitrogen or oxygen atoms. It must be determined which linkage isomer is under observation before the kinetic results can be interpreted correctly. Previous work with other metal ions such as Pt(II) and Pd(II) and various nitrogen bonded substituted aromatic sulfonamide ligands $R-C_6H_4SO_2NH_2$, (R = H, p-$CH_3$, p-$NHCOCH_3$),[57-59] as well as Cu(II) and Ni(II) and oxygen bonded sulfamide and sulfamide ion ($H_2NSO_2NH^-$),[56] indicates that both nitrogen and oxygen coordination are possible. The observation that sulfamate[71] is nitrogen bonded to

$(NH_3)_5Co^{3+}$ leads one to expect nitrogen coordination to cobalt(III) for sulfamide and the sulfonamides.

The cumulative features of the ultraviolet-visible spectra, infrared spectra, proton magnetic resonance spectra, as well as the charge on the complexes, and their ionization constants provide substantial evidence of the isomer involved. This section describes the various physical and spectral parameters of these complexes.

## Charge and Ionization Constants

Most of the complexes prepared were purified by cation exchange chromatography. The elution characteristics of the complexes indicated at least qualitatively that the charge on each of these complexes was 2+. The compounds separated as single bands on the ion exchange column and in all cases only one isomer was observed. The complexes were also characterized by C, H, N analysis. The stoichiometry confirmed two counter-ions per molecule for each complex. The fact that these ligands coordinate as anions in dilute acid seems more consistent with nitrogen coordination. Kinetic and spectrophotometric observations discussed in the Results indicate that these complexes can be protonated, and the protonated complex of sulfamide has a $Ka = 0.55$ M, while the values for the aromatic sulfonamides are $> 5$ M. Values for the uncoordinated ligands are $Ka = 6.31 \times 10^{-11}$ and

5.02 x $10^{-10}$ for p-toluenesulfonamide, and p-nitrobenzenesulfonamide, respectively.[61,62] Therefore, coordination to $(NH_3)_5Co^{3+}$ has increased the $K_a$ of these ligands by about a factor of $10^{10}$ compared to that of the free ligand. Table 1 lists $pK_a$ values for various free and coordinated ligands. Analogous large changes are noted for other systems in which the atom coordinated to cobalt(III) carries an ionizable hydrogen, such as water,[74] N-bonded sulfamate[71] and N-bonded formamide.[6] Conversely, if the ionizable hydrogen is not on the coordinated atom, much smaller changes in $K_a$ are observed, as noted in the case of carbonate,[75] phosphate,[76] and O-bonded sulfamate.[70]

## Ultraviolet-Visible Spectra

The colour and electronic spectra of pentaamminecobalt(III) compounds indicate qualitatively the bonding mode of the sixth ligand. Table 2 lists the spectral parameters of the complexes studied in this work, and compares them to those of aquopentaamminecobalt(III), hexaamminecobalt(III) and a few other relevant complexes. In general the details of the electronic spectra support the nitrogen bonded structure.

Although the visible spectrum of the sulfamide complex resembles that of the aquo complex more than that of the hexaammine complex, (see Table 2), spectrophotometric

## TABLE 1

## ACID DISSOCIATION CONSTANTS FOR FREE AND BOUND LIGANDS

| Acid | $pK_a$ | ref |
|---|---|---|
| $NH_2SO_3^-$ | >16 | |
| $(NH_3)_5CoNH_2SO_3^{2+}$ | 5.8 | a |
| $(NH_3)_5CoOSO_2NH_2^{2+}$ | 13.1 | b |
| $NH_2SO_2C_6H_4CH_3$-p | 10.2 | c |
| $(NH_3)_5CoNH_2SO_2C_6H_4CH_3\text{-p}^{3+}$ | <-0.7 | this work |
| $NH_2SO_2C_6H_4NO_2$-p | 9.3 | d |
| $(NH_3)_5CoNH_2SO_2C_6H_4NO_2\text{-p}^{3+}$ | <-0.8 | this work |
| $(NH_3)_5CoNH_2CHO^{3+}$ | 2.2 | e |
| $H_2O$ | 15.8 | |
| $(NH_3)_5CoOH_2^{3+}$ | 6.1 | f |
| $HCO_3^-$ | 10.3 | |
| $(NH_3)_5CoOCO_2H^{2+}$ | 6.4 | g |
| $HPO_4^=$ | 12.3 | |
| $(NH_3)_5CoOPO_3H^+$ | 8.5 | h |

FOOTNOTES FOR TABLE 1

a) Po, L.L.; Jordan, R.B. Inorg. Chem. 1968, 7, 526.

b) Sushynski, E.; Van Roodselaar, A.; Jordan, R.B. Inorg. Chem. 1972, 11, 1887.

c) King, R.W.; Burgen, A.S.V. Proc. R. Soc. London, Ser B 1976, 193, 107.

d) Taylor, P.W.; Burgen, A.S.V. Biochemistry 1971, 10, 3859.

e) Balahura, R.J.; Jordan, R.B. J. Am. Chem. Soc. 1970, 92, 1533.

f) Wilkins, R.G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974; p.318.

g) (i) Francis, D.J.; Jordan, R.B. J. Am. Chem. Soc. 1967, 89, 5591.

(ii) Dasgupta, T.P.; Harris, G.M. Ibid. 1969, 91, 3207.

h) Schmidt, W.; Taube, H. Inorg. Chem. 1963, 2, 698.

## TABLE 2

## ELECTRONIC SPECTRA OF PENTAAMMINECOBALT(III) COMPLEXES.[a]

| | $\lambda_{max}$(nm), (ε, $M^{-1}$ $cm^{-1}$) | | |
|---|---|---|---|
| **Unsaturated Nitrogen Bonded** | | | |
| $(NH_3)_5CoNHSO_2NH_2^{2+}$ | 501(78) | 350(119)sh | 270($1.38 \times 10^3$)sh |
| $(NH_3)_5CoNHSO_3^{+}$ [b] | 517(115) | 296($1.78 \times 10^3$)sh | |
| $(NH_3)_5CoNHSO_2C_6H_4CH_3$-$p^{2+}$ | 505(88) | 290($1.74 \times 10^3$)sh | |
| $(NH_3)_5CoNHSO_2C_6H_4NO_2$-$p^{2+}$ | 501(86) | 260($9.75 \times 10^3$) | |
| $(NH_3)_5CoNHCHO^{2+}$ [c] | 484(68) | 348(81) | 250($2.52 \times 10^4$) |
| $(NH_3)_5CoNHCOCH_3^{2+}$ [d] | 486(71) | 351(84) | |
| **Saturated Nitrogen Bonded** | | | |
| $(NH_3)_5CoNH_2SO_2NH_2^{3+}$ [e] | <490 | | |
| $(NH_3)_5CoNH_2SO_3^{2+}$ [f] | 488(60) | 345(50) | |
| $(NH_3)_5CoNH_2CHO^{3+}$ [g] | 478(62) | 340(64) | |
| $(NH_3)_5CoNH_2COCH_3^{3+}$ [h] | 477(62) | 341(58) | |
| $(NH_3)_5CoNH_3$ | 476(56) | 339(46) | |
| **Oxygen Bonded** | | | |
| $(NH_3)_5CoOCHNH_2^{3+}$ [c] | 502(69) | 346(58) | |
| $(NH_3)_5CoO_2CC_6H_4NO_2$-$p^{2+}$ [i] | 502(83) | | |
| $(NH_3)_5CoOH_2^{3+}$ | 492(49) | 345(46) | |

## FOOTNOTES FOR TABLE 2

a) All spectra were run in water at room temperature unless otherwise specified.

b) In 0.1 M NaOH. Po, L.L.; Jordan, R.B. Inorg. Chem. 1968, 7, 526.

c) Balahura, R.J.; Jordan, R.B. J. Am. Chem. Soc. 1970, 92, 1533.

d) Balahura, R.J. Ph.D. Thesis, Department of Chemistry, University of Alberta, 1970, p.39.

e) In 1.0 M $HClO_4$, 15°C

f) In 0.1 M $HClO_4$, (reference given in footnote b).

g) In 1.0 M $HClO_4$, (reference given in footnote c).

h) In 1.0 M $HClO_4$, (reference given in footnote d).

i) Simac, M.G.; Hoffman, M.Z.; Brezniak, N.V. J. Am. Chem. Soc. 1977, 99, 2166.

observations discussed in the Results section indicate that the peak in the visible spectrum of the sulfamido complex shifts from 501 nm to 490 nm in perchloric acid (1.0 M, 15°C), conditions where the complex is predicted to be predominantly (~68%) protonated. Thus the protonated form must have an absorption maximum below 490 nm, a value more consistent with a nitrogen bonded compound. Absorption maxima above 500 nm are known for complexes coordinated via an unsaturated nitrogen. The deprotonated form of the sulfamato complex has a maximum at 517 nm.[71] Also, such a large shift in $\lambda_{max}$ on going from water to 1.0 M perchloric acid would not be expected if the complex were oxygen bonded and the proton were being added to a site remote from the cobalt(III) centre. Thus $(NH_3)_5CoPO_4$, $(NH_3)_5CoPO_4H^+$, $(NH_3)_5CoPO_4H_2^{2+}$ and $(NH_3)_5CoPO_4H_3^{3+}$ have absorption maxima at 525, 521, 518 and 520 nm, respectively.[76] The large shift is analogous however to those found for the formamido,[6] acetamido,[77] and sulfamato[71] complexes.

Although the visible spectra of the protonated forms of the p-toluenesulfonamido and p-nitrobenzenesulfonamido complexes could not be measured, due to the rapid aquation of these complexes in acid coupled with their large ionization constants, the spectral parameters for the deprotonated species are consistent with coordination via an unsaturated nitrogen.

## Infrared Spectra

The assignment of various infrared stretching frequencies in pentaamminecobalt(III) complexes has proven useful in the identification of the coordinating atom when linkage isomers are possible. Bonding modes have been successfully determined from infrared spectral data of many carbonyl and nitrile containing complexes,[6,77,7] where the C=O and N≡C stretching frequencies are easily assigned and sensitive to the bonding position of the metal ion. Unfortunately the S=O stretching bands have not always been so readily identified, and therefore are not as helpful in the assignment of the bonding mode.[78-80] However, for sulfamide and the sulfonamides the shifts of the $SO_2$ and S-N stretching frequencies, relative to the uncoordinated ligand, are useful.

Coordination through the nitrogen atom results in the withdrawal of electrons from the coordinated nitrogen by the cobalt(III) centre. If the coordinated nitrogen is protonated, then all its orbitals are used in the sigma bonding system, and it is not in conjugation with the $SO_2$ $\pi$-bonding system. Although the N-S stretching frequency will be decreased by coordination to the metal ion, only small changes in the $SO_2$ stretching frequencies are expected since the $SO_2$ group is shielded from the cobalt(III) ion by the saturated nitrogen. Unfortunately no examples of such protonated $-NH_2SO_2R$ complexes have been reported, due to their rapid rate of aquation (see Results). However, the N-S and $SO_3$ stretches observed for the sulfamato complex discussed below follow these general trends.

If the coordinated nitrogen is deprotonated, then conjugation of the π-bonding in the $N-SO_2$ system is possible, and withdrawal of electrons from the coordinated nitrogen by the metal ion is compensated by delocalization from the S=O bonds, resulting in a decrease in the $SO_2$ stretching frequencies and an increase in the N-S stretching frequency. Previous examples of deprotonated nitrogen bonded isomers of Pt(II) and Pd(II) complexes have been reported. Beck and Cenini and coworkers[57-59] have prepared aromatic sulfonamide derivatives such as $((C_2H_5)_3P)_2(Cl)Pt(NHSO_2C_6H_4R)$ and $(bipy)Pd(NHSO_2C_6H_4R)_2$. Their $SO_2$ and N-S stretching frequencies are given in Table 3. The $SO_2$ stretching frequencies are increased with respect to those listed for the free ligand, indicating substantial delocalization of the $-SO_2$ electrons.

For oxygen bonded compounds, withdrawal of electrons from the $SO_2$ π-bonding system by the metal centre will be compensated for by donation of electrons from the nitrogen through the N-S bond, causing an increase in the N-S stretching frequency and a much smaller decrease in the $SO_2$ stretching frequencies than would otherwise be expected. A recent infrared study of some oxygen bonded $M(en)_2$-sulfamide

## TABLE 3

## STRETCHING FREQUENCIES OF LIGANDS AND NITROGEN AND OXYGEN BONDED COMPLEXES, ($cm^{-1}$).

| | $SO_2$(asym) | $SO_2$(sym) | $N_2S$(asym) | NS |
|---|---|---|---|---|
| LIGANDS: | | | | |
| $H_2NSO_2NH_2$[a] | 1358 | 1156 | 931 | $904^{e}$ |
| $H_2NSO_2NH^-$ [b] | 1348 | 1165 | 1010 | $912^{e}$ |
| $H_2NSO_2C_6H_4CH_3$-p | 1323 | 1170 | - | 909 |
| $H_2NSO_2C_6H_4NO_2$-p[c] | 1315 | 1165 | - | 901 |
| N-BONDED COMPLEXES | | | | |
| $(NH_3)_5CoNHSO_2NH_2{}^{2+}$ | 1224 | 1132 | 1096 | $993^{e}$ |
| $d_{18}$-$(NH_3)_5CoNHSO_2NH_2{}^{2+}$ | 1275 | 1126 | 1016 | $989^{e}$ |
| $(NH_3)_5CoNHSO_2C_6H_4CH_3$-$p^{2+}$ | 1214 | 1122 | - | 963 |
| $d_{16}$-$(NH_3)_5CoNHSO_2C_6H_4CH_3$-$p^{2+}$ | 1238 | 1122 | - | 1010 |
| $(NH_3)_5CoNHSO_2C_6H_4NO_2$-$p^{2+}$ [c] | 1241 | 1140 | - | 988 |
| $((C_2H_5)_3P)_2(Cl)PtNHSO_2C_6H_4R$[d] | 1320-1240 | 1140-1135 | - | 965-910 |
| $(bipy)Pd(NHSO_2C_6H_4R)_2$[d] | 1275-1260 | 1140 | - | 935-925 |
| O-BONDED COMPLEXES[b] | | | | |
| $(en)_2Ni(H_2NSO_2NH_2)(Cl)^+$ | 1350 | 1158 | 1004 | $920^{e}$ |
| $(en)_2Ni(HNSO_2NH_2)(Cl)$ | 1350 | 1156 | 960 | $922^{e}$ |
| $(en)_2Ni(HNSO_2NH_2)_2$ | 1320 | 1155 | 954 | - |

## FOOTNOTES TO TABLE 3

a) Uno, T.; Machida, K.; Hanai, K. Spectrochim. Acta 1966, **22**, 2065.

b) Giusti, A.; Peyronel, G. Transition Met. Chem. (Weinheim, Ger.) 1979, **4**, 35.

c) $NO_2$ antisym. and sym. stretches occur at 1521 and 1351 $cm^{-1}$ (ligand) and at 1524 and 1354 $cm^{-1}$ (complex), respectively.

d) (i) Beck, W.; Bauder, M. Chem. Ber. 1970, **103**, 583.
(ii) Beck, W.; Bauder, M.; La Monica, G.; Cenini, S.; Ugo, R. J. Chem. Soc. A 1971, 113.
(iii) Cenini, S.; Pezzotti, M.; Porta, F.; La Monica, G. J. Organomet. Chem. 1975, **88**, 237. (R = H, p-$CH_3$, p-$NHCOCH_3$).

e) These frequencies are $N_2S$(sym) stretches.

derivatives, (M = $Ni^{2+}$, $Cu^{2+}$), supports this.[56] The frequencies of the $SO_2$ and N-S stretches for sulfamide, deprotonated sulfamide and their $Ni^{2+}$ complexes are listed in Table 3. All $SO_2$ stretching frequencies are only slightly smaller than those of uncoordinated sulfamide, whereas the N-S stretches are all larger.

The infrared spectra of the pentaamminecobalt(III) complexes studied in this work display the vibrations characteristic of coordinated $NH_3$ at approximately 3000, 1600, 1315 and 830 $cm^{-1}$ due to symmetric and asymmetric N-H stretches, degenerate $NH_3$ deformation, symmetric $NH_3$ deformation and $NH_3$ rocking vibrations, respectively.[81] Deuteration is a useful method for shifting the broad $NH_3$ bands to lower energies, allowing any hidden peaks to be observed. Table 3 gives the symmetric and antisymmetric $SO_2$ and N-S stretches for the sulfonamide and sulfamide complexes prepared. The assignments were made by comparison of the infrared spectra with those of the free ligands, the deuterated complexes, and the previously reported nitrogen and oxygen bonded isomers discussed above. In addition, a linear relationship has been observed[82,83] between the frequency of the $SO_2$ antisymmetric and symmetric modes of several $XSO_2Y$ compounds, and has been proposed as a useful tool in the identification of these infrared bands. The sulfamide and sulfonamide ligands have $\nu SO_2(sym):\nu SO_2(antisym)$ ratios of 0.85-0.89, falling close to the reported range of 0.81-0.88. The complexes have ratios slightly higher at $\nu SO_2$(sym):$\nu SO_2$(antisym) = 0.92.

For the sulfamido and sulfonamido complexes the $SO_2$(antisym), $SO_2$(sym) and N-S vibrations occur in the 1275-1214, 1140-1222 and 1010-963 $cm^{-1}$ regions, respectively. Complexation has caused large decreases in the $SO_2$ stretching frequencies and large increases in the N-S stretching frequency. This is most consistent with nitrogen bonding to the deprotonated form. Comparison to the similarly bonded Pt(II) and Pd(II) complexes given in Table 3 reveals that the Co(III) complexes have weaker S=O and stronger N-S bonds.

The infrared spectrum of the sulfamato complex, $(NH_3)_5CoNH_2SO_3^{2+}$, was also recorded and was analysed by comparison to the spectrum previously reported for sodium sulfamate.[84] Characteristic ligand vibrations in the complex are: $SO_3$ stretch 1270 $cm^{-1}$ (antisym), 1245 $cm^{-1}$ and 1185 $cm^{-1}$ (sym), $SO_3$ deformation 1042 $cm^{-1}$ (sym) and N-S stretch 720 $cm^{-1}$. In sodium sulfamate these vibrations are observed at 1283 $cm^{-1}$, 1240 $cm^{-1}$, 1190 $cm^{-1}$, 1046 $cm^{-1}$ and 788 $cm^{-1}$, respectively. The shift in the N-S stretch to lower frequencies and the relatively small shifts in the $SO_3$ frequencies are consistent with coordination through a saturated nitrogen using arguments similar to those discussed above.

## Proton Magnetic Resonance Spectroscopy

Proton magnetic resonance spectra are particularly useful in the identification of the bonding atom in pentaamminecobalt(III) complexes. The chemical shift differences between the _cis_ and _trans_ $NH_3$ protons have been found to be in the 0 → 0.6 $\tau$ range for nitrogen bonded ligands and in the 1.0 → 1.5 $\tau$ range for oxygen bonded ligands.[7]

The chemical shifts observed for the complexes prepared are listed in Table 4 and compared to those of a few known nitrogen and oxygen coordinated complexes. The observed chemical shift differences of 0.30, 0.18, 0.30 and 0.30 for the sulfamato, sulfamido, p-nitrobenzenesulfamido and p-toluenesulfonamido complexes, respectively, are consistent with nitrogen bonding.

The resonances due to all other protons in the sixth ligand were assigned by comparison to the spectra of the free ligands, and are given in Table 4. The coordinated -NH- resonance was not observed in the spectrum of the p-nitrobenzenesulfonamido complex.

As a result of the spectral and physical properties discussed above, the subsequent discussion will consider all the ligands to be nitrogen coordinated to $(NH_3)_5Co^{3+}$.

## TABLE 4

## PMR DATA FOR PENTAAMMINECOBALT(III) COMPLEXES.[a]

| Complex[b] | cis-$NH_3$ | trans-$NH_3$ | others |
|---|---|---|---|
| $(NH_3)_5CoNH_3^{3+}$ | 6.78 | | |
| $(NH_3)_5CoNHSO_2NH_2^{2+}$ | 6.70 | 6.88 | NH,8.38;$NH_2$,4.24 |
| $(NH_3)_5CoNHSO_2C_6H_4CH_3\text{-}p^{2+}$ | 6.67 | 6.97 | NH,7.97;$CH_3$,7.64;$C_6H_4$,<br>2.27,2.36,2.62,2.72 |
| $(NH_3)_5CoNHSO_2C_6H_4NO_2\text{-}p^{2+}$ | 6.67 | 6.96 | $C_6H_4$,1.58,1.68,1.96,<br>2.06 |
| $(NH_3)_5CoNH_2SO_3^{2+}$ | 6.47 | 6.77 | $NH_2$,3.46 |
| $(NH_3)_5CoNHSO_3^{+}$ | 6.47 | 6.77 | NH,5.46 |
| $(NH_3)_5CoNH_2CHO^{3+}$ c | 6.68 | 6.68 | $NH_2$,6.18;CH,2.66 |
| $(NH_3)_5CoNHCHO^{2+}$ c | 6.78 | 6.78 | NH,6.14;CH,1.96 |
| $(NH_3)_5CoOH_2^{3+}$ | 6.22 | 7.25 | $OH_2$,4.30 |
| $(NH_3)_5CoOCHNH_2$ | 6.16 | 7.26 | $NH_2$,6.16;CH,2.62 |

(a) All spectra in deuterated dimethylsulfoxide. All values are in τ with respect to $d_6$-DMSO peak at 7.48τ.

(b) All complexes are perchlorate salts except the sulfamido complex which is a bromate perchlorate mixed salt.

(c) Balahura, R.J., Jordan, R.B. J. Am. Chem. Soc. 1970, 92, 1533.

# CHAPTER III

## RESULTS: PARTS A AND B

## PART A: AQUATION STUDIES

### Hydrolysis of $(NH_3)_5CoNHSO_2NH_2^{2+}$.

The hydrolysis of the sulfamido complex was found to follow the rate law

$$\frac{-d\ln[(NH_3)_5CoNHSO_2NH_2^{2+}]}{dt} = k_{obsd} = \frac{a[H^+]}{b+[H^+]} \quad (3.1)$$

The kinetics were followed at 15°, 25° and 35°C in 0.02 to 1.0 M perchloric acid and at a total ionic strength of 1.0 M, adjusted using lithium perchlorate. The experimental results for $k_{obsd}$ are listed in Table B1, Appendix B, where they are compared to the results of a non-linear least-squares fit of the data at each temperature to equation 3.1. The plot of $k_{obsd}^{-1}$ versus $[H^+]^{-1}$ shown in Figure 1 is linear as predicted by equation 3.1. The product analysis resulted in (95 ± 2)% of the cobalt(III) being recovered from the ion-exchange resin and characterized spectrophotometrically as $(NH_3)_5CoOH_2^{3+}$.

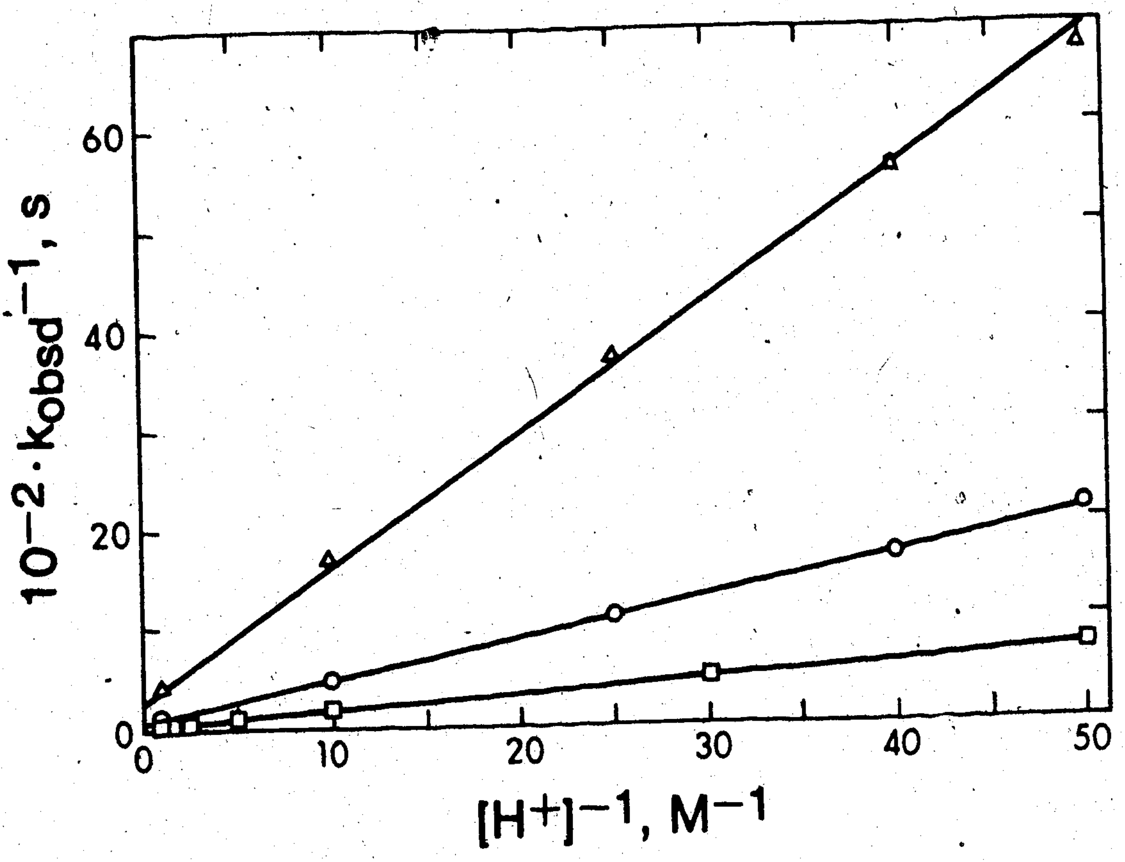


FIGURE 1: Acid dependence of the observed rate constant for aquation of $(NH_3)_5CoNHSO_2NH_2^{2+}$, at 15.0°C (Δ); 25.0°C (O); and 34.9°C ( □ ). Points shown are the average of at least two runs; see Table B1, Appendix B, for complete data set. Lines shown are values calculated by least-squares fit to equation 3.1.

These results are consistent with Co-N bond breaking and the reaction scheme of equation 3.2, with R = $NH_2$.

$$(NH_3)_5CoNHSO_2R^{2+} + H^+ \underset{K_a}{\rightleftharpoons} (NH_3)_5CoNH_2SO_2R^{3+}$$

$$(NH_3)_5CoNHSO_2R^{2+} \xrightarrow{k_{1h}} (NH_3)_5CoOH_2^{3+} + RSO_2NH^- \qquad (3.2)$$

$$(NH_3)_5CoNH_2SO_2R^{3+} \xrightarrow{k_{2h}} (NH_3)_5CoOH_2^{3+} + RSO_2NH_2$$

The rate law consistent with this mechanism is:

$$\frac{-d\ell n[(NH_3)_5CoNHSO_2R^{2+}]}{dt} = k_{obsd} = \frac{k_{1h}K_a + k_{2h}[H^+]}{K_a + [H^+]} \qquad (3.3)$$

and is equivalent to equation 3.1 with a = $k_{2h}$ and b = $K_a$ if $k_{1h}K_a$ is much smaller than $k_{2h}[H^+]$. A least-squares fit of the data in Table B1 to equation 3.3 does indicate that $k_{1h} < 1 \times 10^{-5}$ $sec^{-1}$ at 25°C, and the exact value cannot be reliably established. The specific rate constant, $k_{2h}$, and the acid dissociation constant, $K_a$, were determined at each temperature using equation 3.1. These values are listed in Table 5, and compared to the values calculated from $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H°$, $\Delta S°$, respectively, using the usual transition state theory (equation 2.2) and thermodynamic equations.

The first step of equation 3.2 could be due to protonation at the oxygen atom rather than the coordinated nitrogen, however, the precedent of the similar sulfamato

## TABLE 5

### KINETIC PARAMETERS FOR AQUATION OF SULFAMIDOPENTAAMMINECOBALT(III).[a]

| Temp, °C | $10^2 \cdot k_{2h}$, $sec^{-1}$ obsd.[b] | $10^2 \cdot k_{2h}$, $sec^{-1}$ calcd.[c] | $K_a$, M obsd.[b] | $K_a$, M calcd.[c] |
|---|---|---|---|---|
| 15.0 | 0.35<br>±0.03 | 0.36 | 0.47<br>±0.04 | 0.47 |
| 25.0 | 1.41<br>±0.06 | 1.31 | 0.58<br>±0.03 | 0.55 |
| 34.9 | 4.42<br>±0.20 | 4.38 | 0.65<br>±0.04 | 0.64 |
| $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | 21.7±1.1 | | 2.7±1.4[d] | |
| $\Delta S^{\ddagger}$, cal $mol^{-1}deg^{-1}$ | 5.5±3.7 | | 7.9±4.7[d] | |

a) Errors are 95% confidence limits and are about three times larger than one standard error.

b) Values were determined from a least-squares fit to equation 3.1.

c) Values were calculated from appropriate ΔH and ΔS values retaining extra figures in the recalculation.

d) Values are ΔH° and ΔS°.

complex, which undergoes protonation at the nitrogen atom,[71] makes oxygen protonation seem unlikely. Furthermore, protonation at one of the oxygen atoms would not be expected to have such a large effect on the rate of Co-N bond breaking. For example, $(NH_3)_5CoPO_4H_2^{2+}$ undergoes aquation ($k = 1.57 \times 10^{-5}$ $sec^{-1}$ at 60°C) at a rate just fifteen times greater than that of $(NH_3)_5CoPO_4H^+$ ($k = 1.05 \times 10^{-6}$ $sec^{-1}$ at 60°C), suggesting that protonation at a remote oxygen does not dramatically affect the rate of aquation.[85] Nitrogen protonation is also consistent with the large increase in $K_a$ of the ligand upon coordination to cobalt(III), an increase similar to that observed for the sulfamato complex.[71] If protonation were occurring at the remote oxygen, much smaller increases in $K_a$ would be expected upon coordination, as observed for the carbonato[75] and phosphato[76] complexes.

The sulfamido complex was dissolved in 1.0 M perchloric acid at 15°C, and the visible spectrum was scanned repetitively every 75 seconds from 450-500 nm. Although hydrolysis occurs under these conditions ($t_{1/2}$ ~5 min, 15°C) the sulfamido complex is predicted to be approximately 68% in the protonated form. The results are shown in Figure 2. The peak in the visible spectrum is shifted to 490 nm from 501 nm, implying that the absorption maximum of $(NH_3)_5CoNH_2SO_2NH_2^{3+}$ occurs at less than 490 nm. Both the direction and magnitude of the shift ($\geq -11$ nm) is consistent with protonation at coordinated nitrogen, and

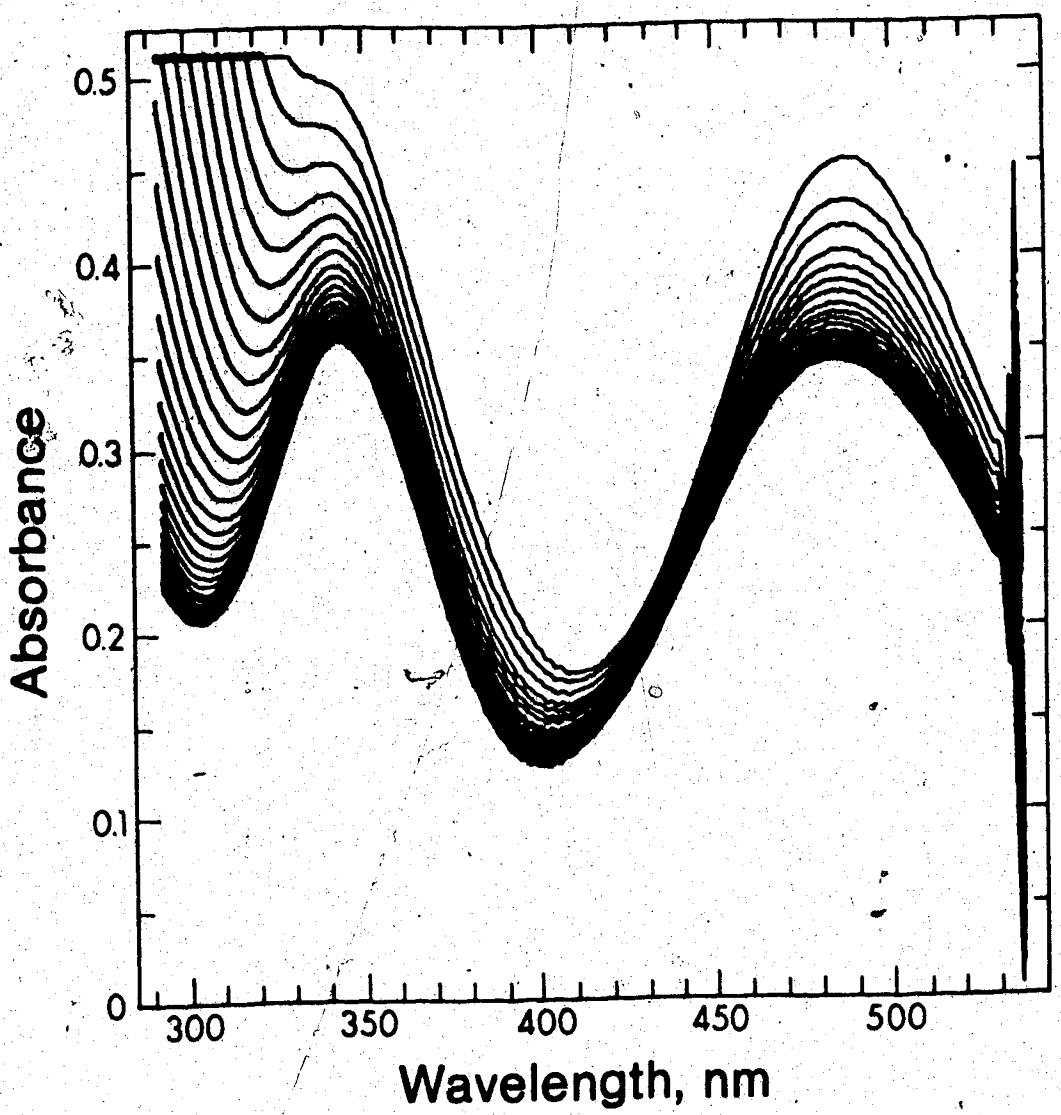


FIGURE 2: Visible spectrum of $(NH_3)_5CoNH_2SO_2NH_2^{3+}$ (1.08 x $10^{-3}$ M; 5 cm cell) in 1.0 M $HClO_4$ at 15°C showing peak at $\lambda_{max}$ = 490 nm. Spectrum scanned every 75 seconds to show hydrolysis.

would not be expected if protonation were occurring at the remote oxygen. The formamido,[6] acetamido[77] and sulfamato[71] complexes show similar shifts of -6 nm, -9 nm and -29 nm, respectively, whereas the phosphato complex[76] shows shifts of -4 nm, -3 nm and -2 nm for the 1+, 2+ and 3+ species, respectively, compared to their respective conjugate bases.

## Hydrolysis of $(NH_3)_5CoNHSO_2R^{2+}$; R = $C_6H_4CH_3$-p, $C_6H_4NO_2$-p.

Both the p-toluenesulfonamido and p-nitrobenzenesulfonamido complexes hydrolyse according to the rate law

$$\frac{-d\ell n[(NH_3)_5CoNHSO_2R^{2+}]}{dt} = k_{obsd} = c[H^+] \qquad (3.4)$$

The kinetics were followed at 15°, 25° and 35° in 0.1 to 0.8 M perchloric acid and the total ionic strength was raised to 1.0 M with lithium perchlorate. The values of $k_{obsd}$ obtained experimentally, as well as those obtained from a least-squares best-fit of the data at each temperature to equation 3.4 are given in Tables B2 and B3, Appendix B. The plots of $k_{obsd}$ versus $[H^+]$ are linear as predicted by equation 3.4 and are shown in Figures 3 and 4. Product analysis studies over a broad range of acid concentrations resulted in (101 ± 4)% of the ligand being recovered as p-toluenesulfonamide or p-nitrobenzenesulfonamide. The sulfonamides are easily distinguished from

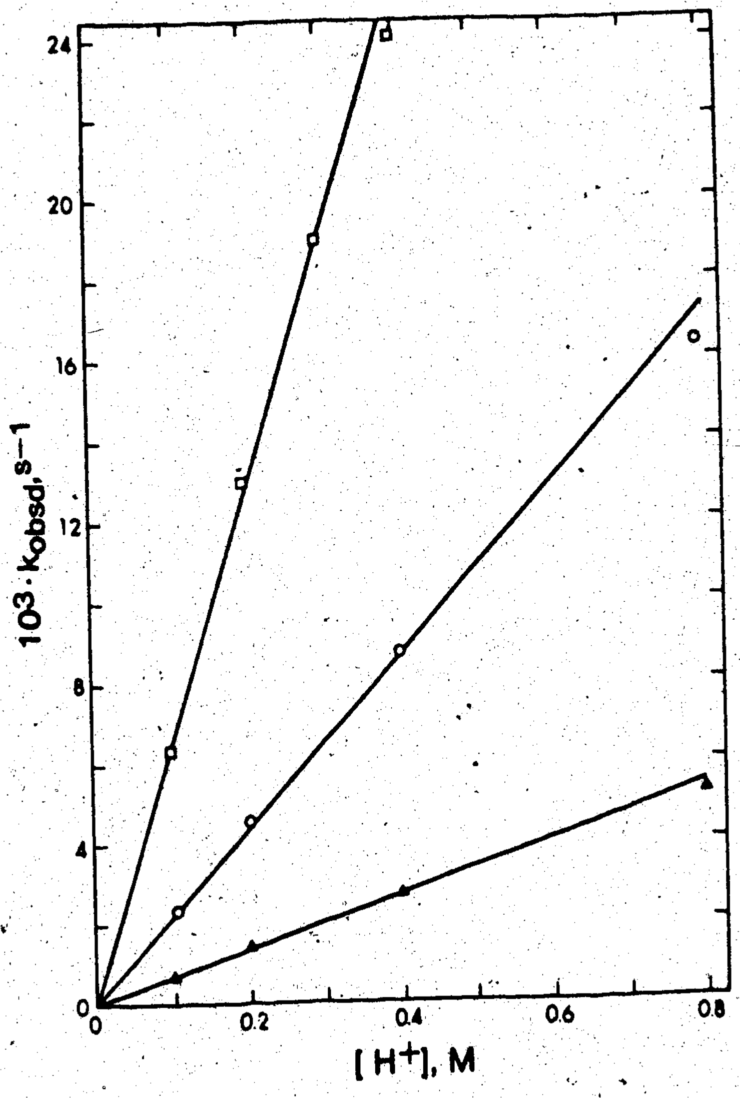


FIGURE 3: Acid dependence of the observed rate constant for aquation of $(NH_3)_5CoNHSO_2C_6H_4CH_3{}^{2+}$, at 14.8°C ( △ ); 25.1°C ( ○ ); and 34.9°C ( □ ). Points shown are the average of at least two runs; see Table B2, Appendix B, for complete data set. Lines shown are values calculated by least-squares fit to equation 3.4.

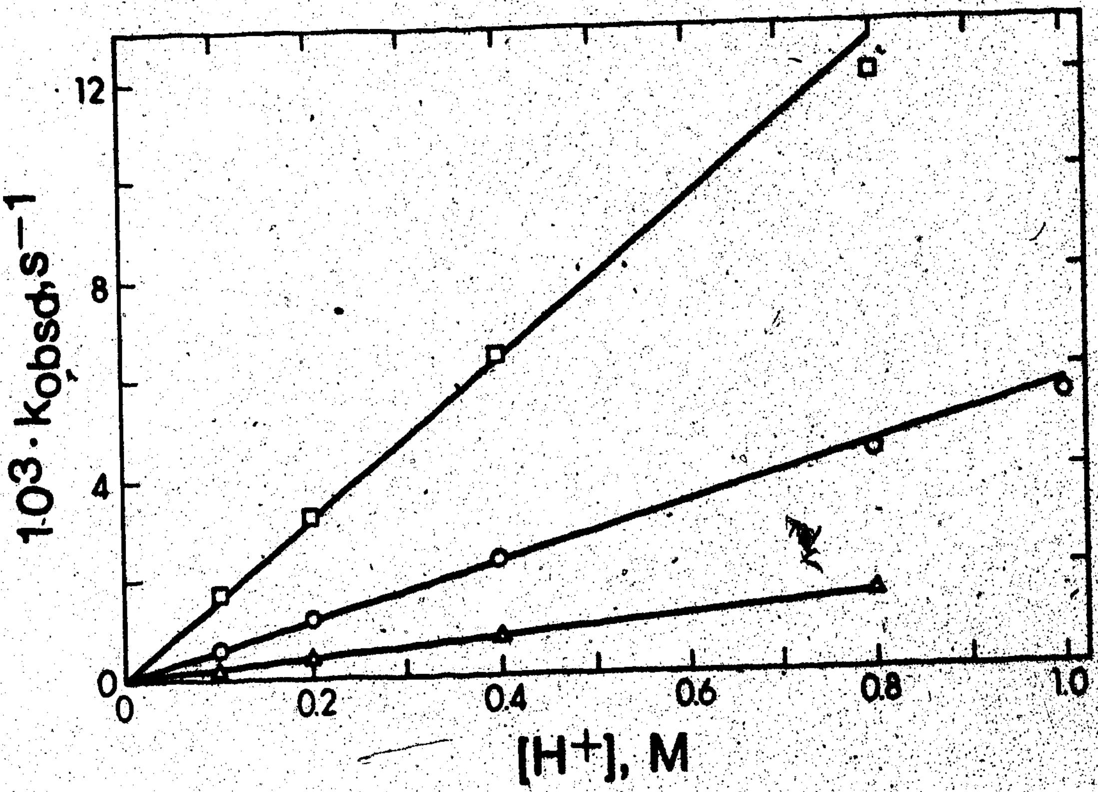


FIGURE 4: Acid dependence of the observed rate constant for aquation of $(NH_3)_5CoNHSO_2C_6H_4NO_2^{2+}$, at 14.9°C ( △ ); 25.0°C ( ○ ); and 35.0°C ( □ ). Points shown are the average of at least two runs; see Table B3, Appendix B, for complete data set. Lines shown are values calculated by least-squares fit to equation 3.4

the corresponding sulfonic acids by their electronic spectra in acid and base, respectively. In both cases (96 ± 8)% of the cobalt(III) was recovered from the ion-exchange column as $(NH_3)_5CoOH_2{}^{3+}$. Therefore these reactions proceed with Co-N bond breaking.

These results are consistent with the reaction scheme of equation 3.2, with R = $C_6H_4CH_3$ and $C_6H_4NO_2$, respectively, and the rate law of equation 3.3, with $c = k_{2h}/K_a$ if $K_a >> [H^+]$ and $k_{1h}\ K_a << k_{2h}[H^+]$. A least-squares analysis of the data in Table B2 and B3 to equation 3.5, (where $k_2' = k_{2h}/K_a$), does indicate that

$$\frac{-d\ell n[(NH_3)_5CoNHSO_2R^{2+}]}{dt} = k_{obsd} = k_{1h} + k_2'\ [H^+] \qquad (3.5)$$

at 25°C $k_{1h}$ (R = $C_6H_4CH_3$) and $k_{1h}$ (R = $C_6H_4NO_2$) are less than $3 \times 10^{-4}$ $sec^{-1}$ and $6 \times 10^{-5}$ $sec^{-1}$, respectively, and the exact values cannot be reliably established in either case. Values for $k_{2h}/K_a$ were determined at each temperature using equation 3.4. The results are listed in Table 6, and compared to those calculated from the transition state equation (equation 2.2) using the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for each complex, also given in Table 6.

Unfortunately values for $K_a$ ($C_6H_4CH_3$) and $K_a$ ($C_6H_4NO_2$) cannot be determined from the experimental data. It may be noted in Table B2 and B3 that there is a tendency for the calculated values to be too small at low acid concentrations

## TABLE 6

## KINETIC PARAMETERS FOR AQUATION OF $(NH_3)_5CoNHSO_2R^{2+}$; $R = C_6H_4CH_3$, $C_6H_4NO_2$.[a]

| R | Temp, °C | $10^2 \cdot k_{2h}/K_a$, $M^{-1}sec^{-1}$ obsd.[b] | calcd.[c] | $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | $\Delta S^{\ddagger}$, cal $mol^{-1}deg^{-1}$ |
|---|---|---|---|---|---|
| $C_6H_4CH_3$ | 14.8 | 0.676<br>±0.024 | 0.667 | | |
| | 25.1 | 2.15<br>±0.07 | 2.17 | | |
| | 34.9 | 6.28<br>±0.14 | 6.22 | 19.0±0.5 | -2.5±1.5 |
| $C_6H_4NO_2$ | 14.9 | 0.192<br>±0.007 | 0.190 | | |
| | 25.0 | 0.571<br>±0.017 | 0.571 | | |
| | 35.0 | 1.59<br>±0.06 | 1.58 | 18.0±0.5 | -8.4±1.7 |

a) Errors are 95% confidence limits and are about three times larger than one standard error.

b) Values were determined from least-squares fit to equation 3.4.

c) Values were calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ using equation 2.2 and retaining extra figures in the recalculation.

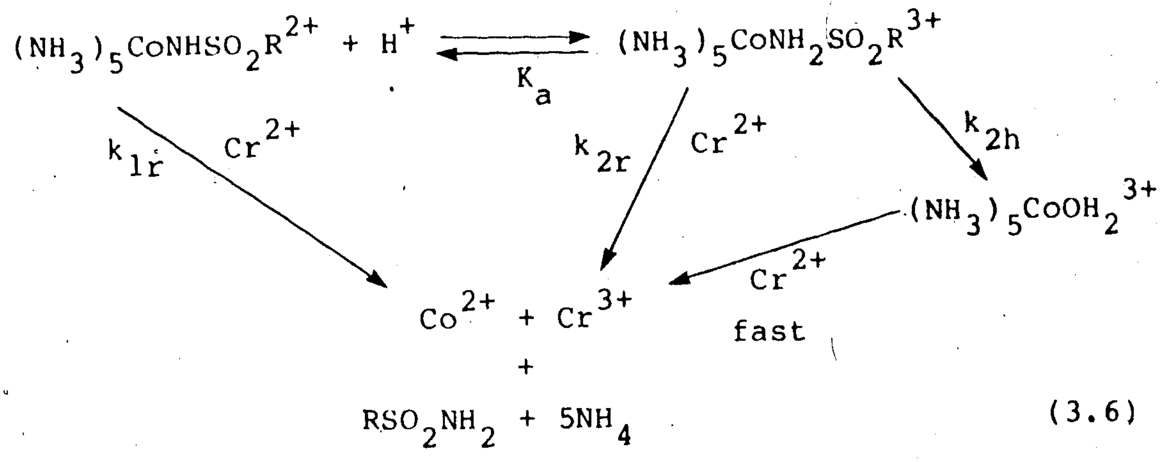
and too large at high acid concentrations. The deviations are consistent with $K_a$' values in the range of 5 to 10 M but the deviations are too small to permit a realistic estimate of $K_a$ for the coordinated aromatic sulfonamides. If it is assumed that a >15% deviation from equation 3.4 would be real and large enough to be accurately fitted, then $[H^+]$ must be smaller than 15% of $K_a$. This allows for lower limits of 5.3 M and 6.6 M to be given to $K_a$ for the p-toluenesulfonamido and p-nitrobenzenesulfonamido complexes, respectively.

## PART B: REDUCTION STUDIES

### Chromium(II) Reduction of $(NH_3)_5CoNHSO_2NH_2^{2+}$.

The acid catalysed aquation of this cobalt(III) complex is unusually rapid (see Results: Part A), and is competitive with reduction. Aquation produces $(NH_3)_5CoOH_2^{3+}$ which is reduced much more rapidly[86] so that aquation of the sulfamido complex is also a rate controlling process for the total cobalt(III) reduction.

The kinetic data at 25°C are shown in Figures 5 and 6; essentially similar studies have been done at 15° and 35°. To provide a more economical presentation the usual kinetic logic will be circumvented by first suggesting the following reaction scheme (where $R = NH_2$)



(3.6)

The hydrolysis study discussed in Part A has provided values of $k_{2h}$ and $K_a$. With the assumption that proton dissociation represents a rapidly established pre-equilibrium, this scheme gives the rate law

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

$$= \frac{k_{2h}[\mathrm{H}^+]}{K_a + [\mathrm{H}^+]} + \left(\frac{k_{1r}K_a + k_{2r}[\mathrm{H}^+]}{K_a + [\mathrm{H}^+]}\right)[\mathrm{Cr}^{2+}] \tag{3.7}$$

where the chromium(II) independent term, $k_h$, is due to the hydrolysis reaction, and $k_r$ represents the term due to reduction. The results at 25° are plotted in Figure 5 to show clearly the importance and the acid dependence of the chromium(II) independent term. The saturation effect on hydrolysis, which occurs when $[\mathrm{H}^+] \gg K_a$ can be seen from the less than first order dependence on $[\mathrm{H}^+]$ of the intercepts in Figure 5. Since $k_{2h}$ and $K_a$ are known from the aquation study, (see Part A), it is possible to subtract $k_h$ from $k_{obsd}$ and divide the difference by [Cr(II)] to obtain

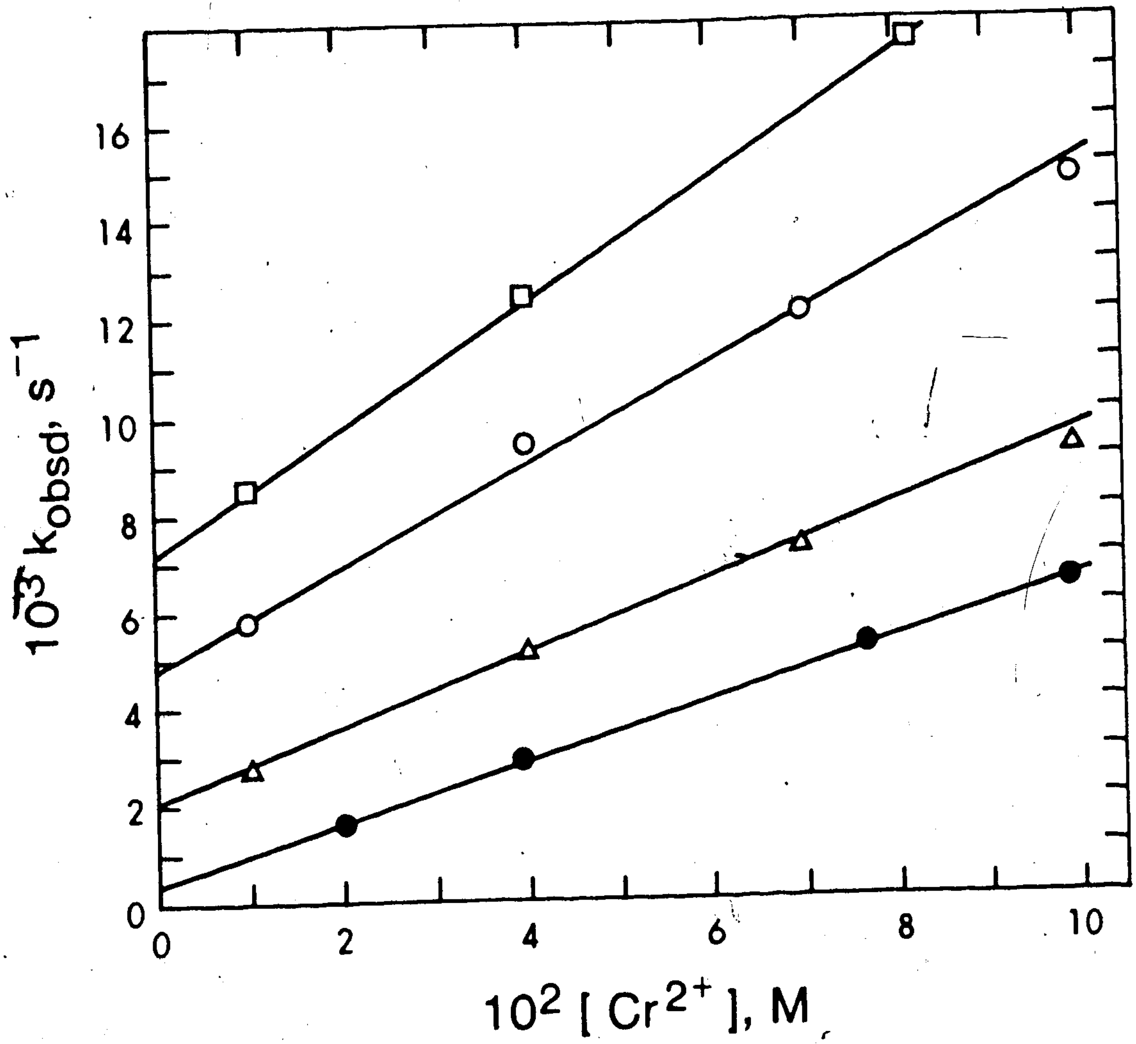


FIGURE 5: The chromium(II) dependence of the observed rate constant for disappearance of $(NH_3)_5CoNHSO_2NH_2{}^{2+}$, at 25°, at hydrogen ion concentrations of 0.020 M ( ● ); 0.100 M ( △ ); 0.300 M ( ○ ); 0.600 M ( □ ). Some points shown are the average of more than one run; see Table B4, Appendix B, for complete data set. Lines shown are values calculated by least-squares fit to equation 3.7.

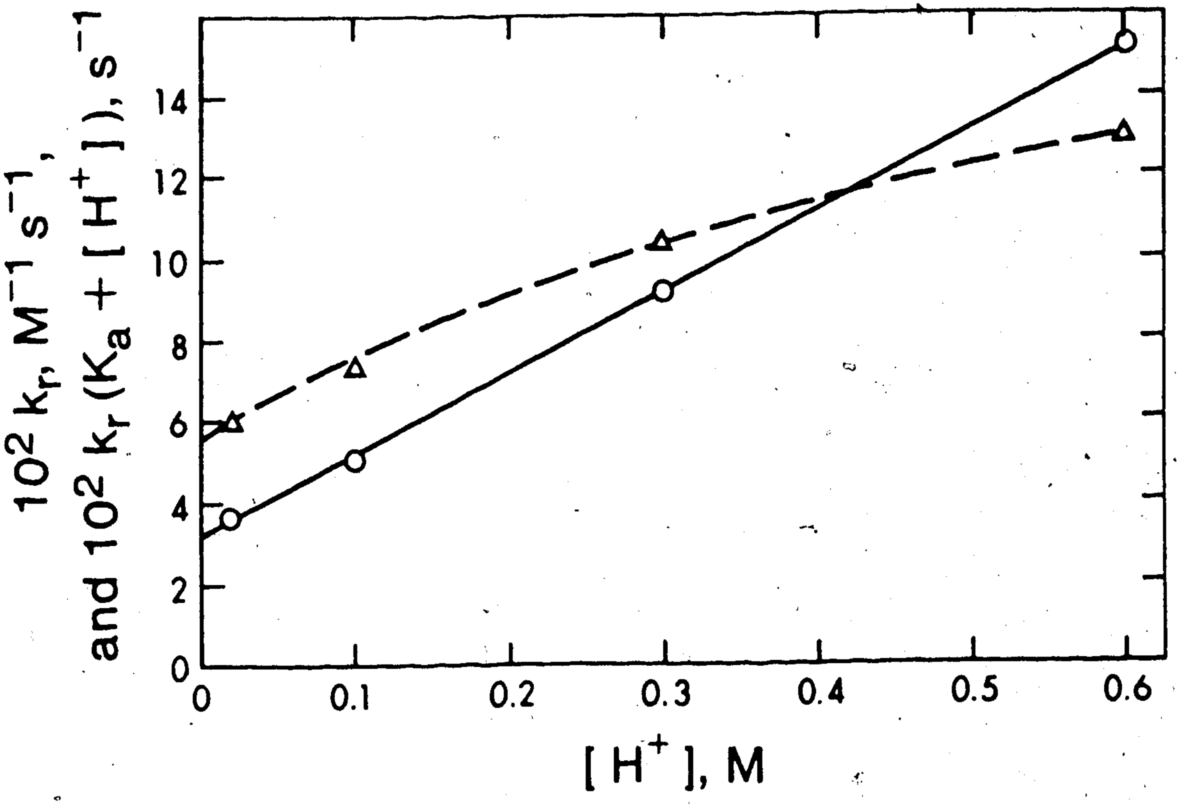


FIGURE 6: The hydrogen ion dependence of the chromium(II) reduction of $(NH_3)_5CoNHSO_2NH_2^{2+}$ at 25°C: $k_r$ versus $[H^+]$ ( △ ); $k_r$ $(K_a + [H^+])$ versus $[H^+]$ ( ○ ). Lines shown were calculated using values for $k_{1r}$, $k_{2r}$ and $K_a$ given in Tables 7 and 5.

$k_r$. The dependence of $k_r$ on $[H^+]$ at 25° is shown in Figure 6, where it is clear that a plot of $k_r$ versus $[H^+]$ is curved, but $k_r(K_a + [H^+])$ versus $[H^+]$ is linear, as expected from equation 3.7. The curvature in Figure 6 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 chromium(II) concentration cannot be increased because of ionic strength limitations. The results were fitted to equation 3.7 by least-squares methods, keeping both $K_a$ and $k_{2h}$ fixed at the values obtained in the aquation study (see Part A). The calculated and observed values of $k_{obsd}$ are compared in Table B4, Appendix B. A summary of the specific rate constants, $k_{1r}$ and $k_{2r}$, and the activation parameters is given in Table 7.

The product analysis studies, summarized in Table 8, 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 $k_{1r}$ path, or at 0.60 M $H^+$, where it proceeds 67% by the $k_{2r}$ path.

The simplest explanation for the observed products is that the sulfamide ligand is not transferred to chromium(III). However, the unusual acid lability of $(H_3N)_5CoNH_2SO_2NH_2{}^{3+}$ ($k_{2h} = 1.4 \times 10^{-2}$ s$^{-1}$) suggests that a

## TABLE 7

## KINETIC PARAMETERS FOR REDUCTION OF SULFAMIDOPENTAAMMINECOBALT(III)[a]

| Temp, °C | $10^2 \cdot k_{1r}$, $M^{-1}sec^{-1}$ obsd.[b] | $10^2 \cdot k_{1r}$, $M^{-1}sec^{-1}$ calc.[c] | $k_{2r}$, $M^{-1}sec^{-1}$ obsd.[b] | $k_{2r}$, $M^{-1}sec^{-1}$ calc.[c] |
|---|---|---|---|---|
| 15.0 | 2.76 | 2.75 | 0.110 | 0.110 |
| | ±0.14 | | ±0.006 | |
| 24.9 | 5.56 | 5.53 | 0.197 | 0.195 |
| | ±0.26 | | ±0.014 | |
| 35.0 | 11.0 | 10.8 | 0.340 | 0.338 |
| | ±0.8 | | ±0.039 | |
| $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | | 11.5±0.9 | | 9.3±1.2 |
| $\Delta S^{\ddagger}$, cal $mol^{-1}$ $deg^{-1}$ | | -26±3 | | -30±4 |

a) All runs in 1 M $LiClO_4/HClO_4$. Errors are 95% confidence units and are about three times larger than one standard error.

b) Values were determined from least-squares fit to equation 3.7, holding $k_{2h}$ and $K_a$ fixed (see aquation study, part A).

c) Values were calculated from the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values using equation 2.2, and retaining [illegible] figures in the recalculation.

## TABLE 8

PRODUCT ANALYSIS RESULTS FOR CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNHSO_2NH_2^{2+}$ at 21°C.

| [Co(III)], M | [Cr(II)], M | $[H^+]$, M | Reaction Time, min | %Free Ligand | Chromium(III) Product |
|---|---|---|---|---|---|
| 0.010 | 0.20 | 0.05 | 15 | 97% | - |
| 0.010 | 0.20 | 0.05 | 13 | 105% | $Cr(OH_2)_6^{3+}$ a |
| 0.010 | 0.20 | 0.05 | 10 | 91% | $Cr(OH)_6^{3+}$ a |
| 0.003 | 0.20 | 0.05 | 8 | 96% | - |
| 0.007 | 0.33 | 0.60 | 3 | 100% | - |

a) Identified by ion-exchange and electronic spectra as described in text.

chromium(III)-sulfamide could be formed, but then hydrolysed during the ion exchange separation. This possibility is given some credence by the very similar hydrolysis rates of $(NH_3)_5CoOSO_3^+$ ($k = 8.9 \times 10^{-7}$ $sec^{-1}$)[87] and $(H_2O)_5CrOSO_3^+$ ($k = 7.9 \times 10^{-7}$ $sec^{-1}$)[88] at 25°C and the similarity of the corresponding sulfamato complexes discussed below ($(NH_3)_5CoNH_2SO_3^{2+}$, $k = 2.6 \times 10^{-5}$ $sec^{-1}$; $(H_2O)_5CrOSO_2NH_2$, $k = 2.8 \times 10^{-5}$ $sec^{-1}$). On this basis one estimates a hydrolysis rate constant for $(H_2O)_5CrOSO(NH_2)_2^{3+}$ of ~$1.4 \times 10^{-2}$ $s^{-1}$ 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 <u>in situ</u> method under conditions such that the reduction has a half-time of $\lesssim$ 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 spectrum 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 $X \rightarrow Y \rightarrow Z$ kinetic system. 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 versus time should appear linear up to three 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 $5.1 \times 10^{-3}$ M cobalt(III); in a 9 cm spectrophotometer cell. The semilogarithmic plot for one of the experiments is shown in Figure 7. At 400 nm the half-times were 39.1 s and 42.6 s, while at 430 nm the half-times were 57.7 s 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.

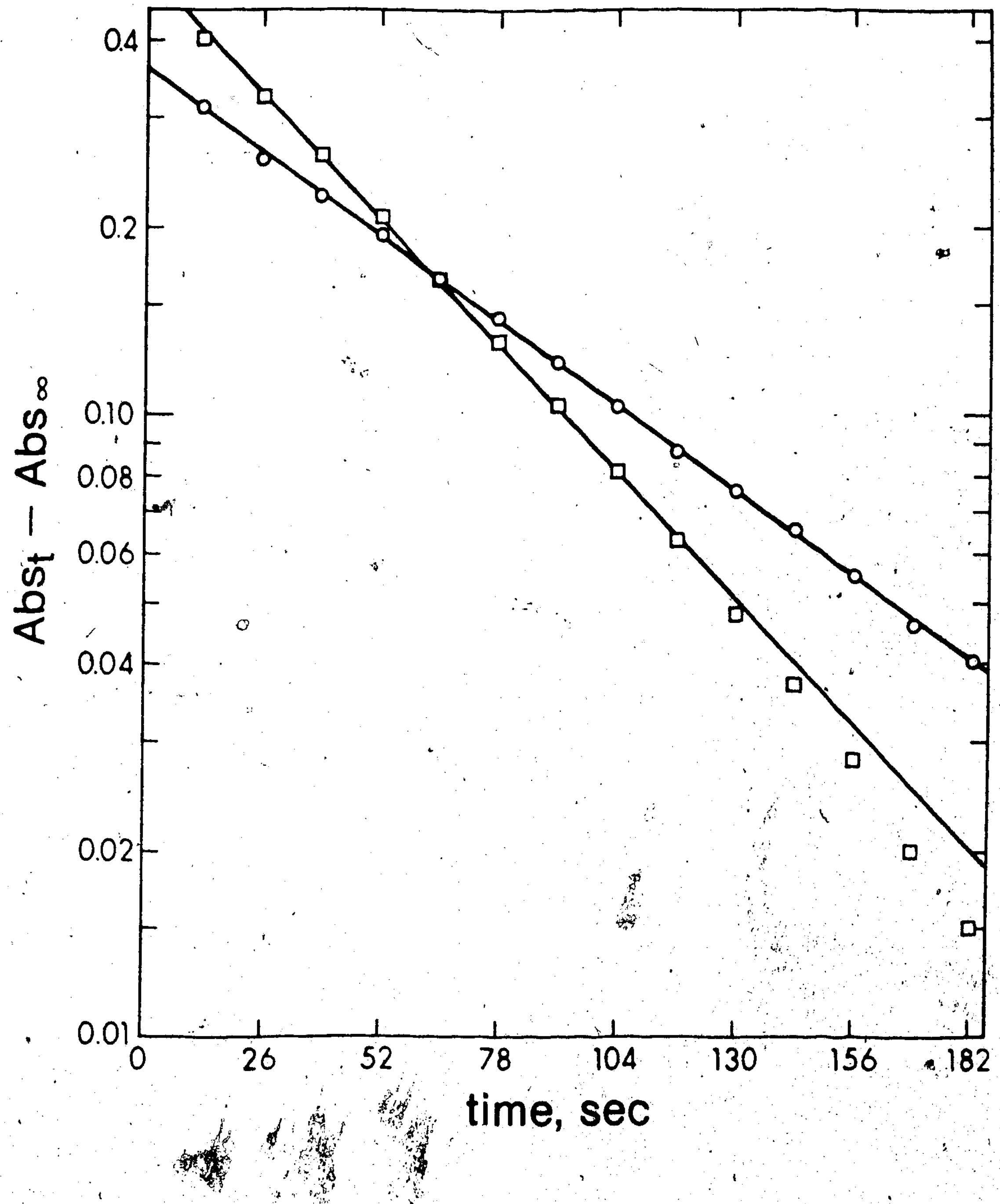


FIGURE 7: Time dependence of the absorbance change during the chromium(II) reduction of $(NH_3)_5CoNHSO_2NH_2^{2+}$ at 25°C; $\mu$ = 1.0 M. Observed at $\lambda$ = 400 nm (□); $\lambda$ = 430 nm (○).

## Chromium(II) Reduction of $(NH_3)_5CoNHSO_2C_6H_4CH_3\text{-}p^{2+}$.

This system is analogous to the sulfamido complex in that aquation is competitive with reduction. The kinetic results are consistent with the reaction scheme of equation 3.6, with R = $C_6H_4CH_3$ and give the rate law

$$\frac{-d\ln[\text{Cobalt(III)}]}{dt} = k_{obsd} = k_h + k_r[Cr^{2+}] \qquad (3.8)$$
$$= \frac{k_{2h}[H^+]}{K_a} + [k_{1r} + \frac{k_{2r}[H^+]}{K_a}][Cr^{2+}]$$

The rate law results from equation 3.7 if $K_a >> [H^+]$, a condition already verified by the aquation study for $[H^+] \leq 0.80$ M (see Part A). A plot of $k_{obsd}$ versus [Cr(II)] at 25° (Figure 8) shows the first order acid dependence of the chromium(II) independent term, $k_h$. The acid dependence of $k_r$ at 15°, 25° and 35° is shown in Figure 9, where $k_r$ versus $[H^+]$ yields a straight line with slope $k_{2r}/K_a$ and intercept $k_{1r}$, as expected from equation 3.8. The values of $k_{2h}/K_a$ were fixed at those obtained in the aquation study (see Part A) at 15°, 25° and 35° and the data were fitted to equation 3.8 by least-squares analysis methods. The observed and calculated values for $k_{obsd}$ are compared in Table B5, Appendix B. The values obtained for $k_{1r}$ and $k_{2r}/K_a$ at three temperatures, and their corresponding activation parameters are listed in Table 9.

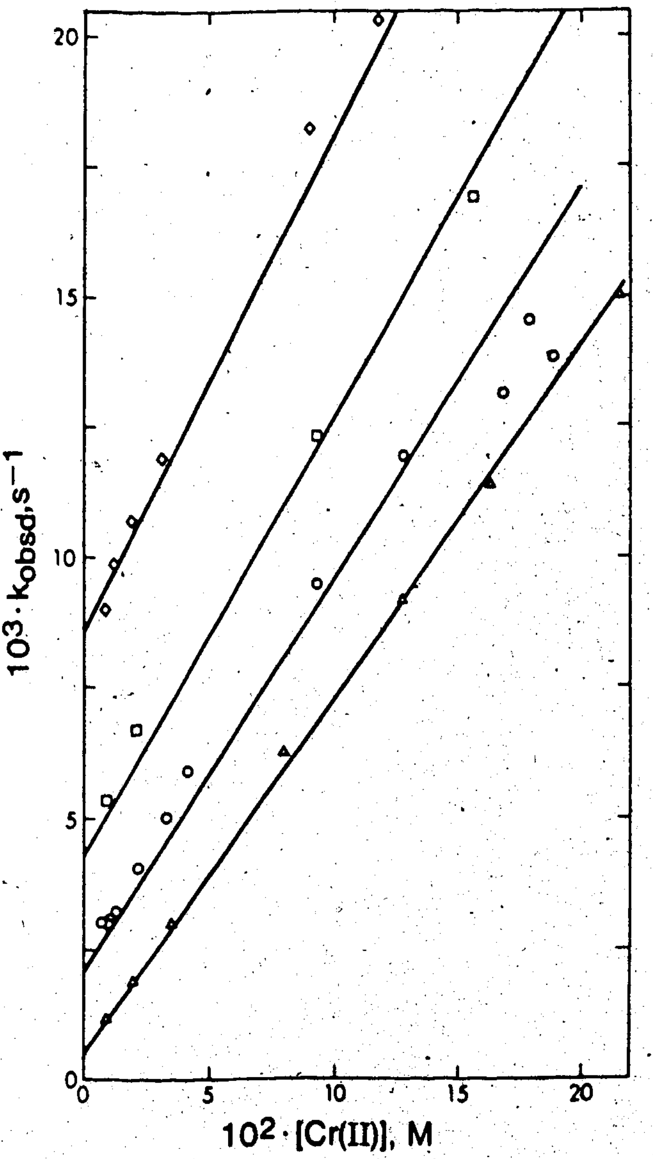


FIGURE 8: Chromium(II) dependence of the observed rate constant for reduction of $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$ at 25°, at hydrogen ion concentrations of 0.025 M ( △ ); 0.100 M ( ○ ); 0.200 M ( □ ); and 0.400 M (◇). Most points shown are the average of at least two runs; see Table B5, Appendix B, for complete data set. Lines shown are values calculated by least-squares fit to equation 3.8.

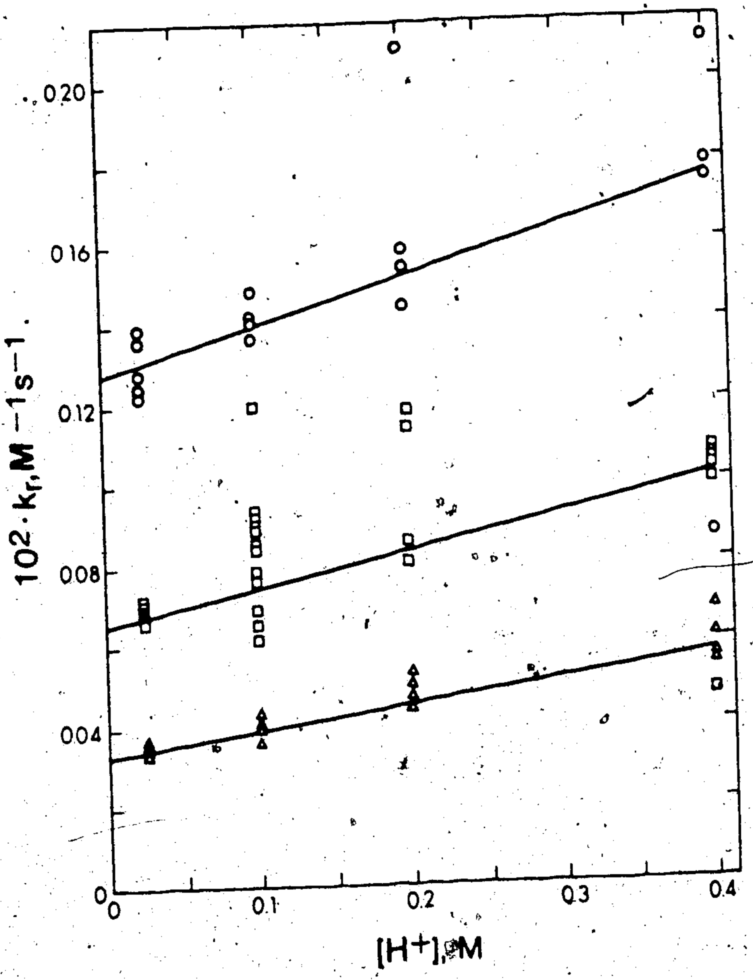


FIGURE 9: Acid dependence of the second order rate constant for reduction of $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$, at 14.9°C ( △ ); 25.0°C ( □ ); and 35.0°C ( ○ ). Lines shown were calculated using values for $k_{1r}$ and $k_{2r}/K_a$ given in Table 9. Most points shown are the average of at least two runs done at the same chromium(II) concentration. Those points showing the largest deviation from the line are those at the lowest chromium(II) concentrations (see Table B5, Appendix B).

## TABLE 9

## KINETIC PARAMETERS FOR CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$.[a]

| Temp, °C | $10^2 \cdot k_{1r}, M^{-1}sec^{-1}$ obsd.[c] | calcd.[d] | $10^2 \cdot k_{2r}/K_a, sec^{-1}$[b] obsd.[c] | calcd.[d] |
|---|---|---|---|---|
| 14.9 | 3.33 ±0.17 | 3.34 | 6.0 ±1.1 | 6.0 |
| 24.0 | 6.57 ±0.41 | 6.68 | 8.9 ±3.5 | 8.3 |
| 35.0 | 12.8 ±0.5 | 12.7 | 12.0 ±3.9 | 11.3 |
| $\Delta H^{\ddagger}$, kcal mol$^{-1}$ | | 11.1±0.8 | | 5±5 |
| $\Delta S^{\ddagger}$, cal mol$^{-1}$ deg$^{-1}$ | | -27±3 | | -46±18 |

a) All runs in 1 M $LiClO_4/HClO_4$. Errors are 95% confidence limits and are about three times larger than one standard error.

b) $K_a \geq 5$ M, so that $k_{2r} \geq 0.45$ $M^{-1}$ $sec^{-1}$ at 25°C.

c) Values were determined from l[illegible]-squares fit to equation 3.8, holding $k_{2h}/K_a$ fixed (see aquation study, part A).

d) Values were calculated from the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, using equation 2.2, and retaining extra figures in the recalculation.

The product analysis results are given in Table 10 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 $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$ yielded values of $k_{2h}/K_a = 2.15 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $K_a > 5$ M, so that $k_{2h} \geq 0.1\ s^{-1}$. 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 nm to 300 nm at 160 s intervals for a solution initially containing 0.08 M chromium(II), 0.052 M hydrogen ion and $4.7 \times 10^{-3}$ M cobalt(III) in a 9 cm path length cell.

## Chromium(II) Reduction of $(NH_3)_5CoNH_2SO_3^{2+}$.

Previous work has shown that the sulfamato complex has a $pK_a$ of 5.7 (1 M $NaClO_4$)[71] and undergoes linkage isomerization and aquation with rate constants in the range of $10^{-3}$ to $10^{-4}$ $sec^{-1}$ at 25°.[70] From the reduction kinetic results discussed below it is clear that aquation and isomerization are much slower than reduction for the

## TABLE 10

## PRODUCT ANALYSIS RESULTS FOR CHROMIUM(II) REDUCTION

## $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$ at 5°C.

| [Co(III)], M | [Cr(II)], M | [H+], M | Reaction time, min | % Free Ligand |
|---|---|---|---|---|
| 0.0025 | 0.39 | 0.05 | 15 | 100% |
| 0.0025 | 0.39 | 0.05 | 10 | 97% |
| 0.0024 | 0.36 | 0.33 | 7 | 106% |

chromium(II) concentrations used ($k_{obsd} \approx 0.1\ sec^{-1}$ at 25°).

The rate of reduction of the nitrogen bonded sulfamato complex was found to be independent of hydrogen ion concentration, and to obey the rate law

$$\frac{-d\ell n[\text{Cobalt(III)}]}{dt} = k_{obsd} = k_{2r}[Cr^{2+}]. \qquad (3.9)$$

The experimental results at 1.0 M ionic strength are given in Table B6, Appendix B, where they are compared to the results of a least-squares fit to equation 3.9. The specific rate constant, $k_{2r}$, and the enthalpy and entropy of activation are given in Table 11.

These results are consistent with the reaction scheme of equation 3.6 with R = $O^-$, and the rate law

$$\begin{aligned}\frac{-d\ell n[\text{Cobalt}]}{dt} &= k_h + \underbrace{k_r}[Cr^{2+}] \\ &= k_h + \left(\frac{k_{1r}K_a + k_{2r}[H^+]}{K_a + [H^+]}\right)[Cr^{2+}]\end{aligned} \qquad (3.10)$$

where $k_h$ has been previously defined,[70] if $k_h << k_r[Cr^{+2}]$, $K_a << [H^+]$ and $k_{1r}\ K_a << k_{2r}\ [H^+]$. The first two conditions have already been verified by the aquation study.[70,71] For both the sulfamido and p-toluenesulfonamido complexes discussed above $k_{1r} < k_{2r}$. With $K_a = 2 \times 10^{-6}$ M and $k_{2r} = 3.30\ M^{-1}\ sec^{-1}$ at 25°, any reasonable value for $k_{1r}$ would satisfy the third condition for the acid range under

## TABLE 11

## KINETIC PARAMETERS FOR REDUCTION OF SULFAMATOPENTAAMMINECOBALT(III).[a]

| Temp, °C | $k_{2r}$, $M^{-1}sec^{-1}$ obsd.[b] | $k_{2r}$, $M^{-1}sec^{-1}$ calcd.[c] | $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | $\Delta S^{\ddagger}$, cal $mol^{-1}$ $deg^{-1}$ |
|---|---|---|---|---|
| 15.0 | 1.95<br>±0.07 | 1.95 | | |
| 25.0 | 3.30<br>±0.11 | 3.32 | | |
| 35.2 | 5.54<br>±0.32 | 5.53 | 8.5±0.5 | -27±2 |
| 25.0[d] | 0.51 | | | |
| 25.0[d,e] | 0.49 | | | |

a) All runs in 1.0 M $LiClO_4/HClO_4$ and on the N-bonded isomer unless indicated otherwise. Errors are 95% confidence limits and are about three times one standard error.

b) Values were determined from least-squares fit to equation 3.9.

c) Values were calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ using equation 2.2 and retaining extra figures in the recalculation.

d) Ionic strength was 0.09 M. Observed first order rate constant divided by [Cr(II)].

e) Oxidant was mixture of O- and N-bonded isomers.

consideration, $[H^+] = 0.025 - 0.40$ M.

Kinetic studies were also done on equilibrium mixtures of the nitrogen and oxygen bonded linkage isomers. In order to slow the reaction for more precise spectrophotometric examination, these studies were carried out at lower ionic strength ($\mu = 0.09$ M). Because aquation is competitive with isomerization, the isomer mixture solutions contain some $(NH_3)_5CoOH_2^{3+}$. However, the latter is reduced much faster[86] ($k \sim 10^2$ $M^{-1}$ $sec^{-1}$ in 0.01 M $HClO_4$ at 25°C) than the sulfamato species, so that this was 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 nitrogen isomer alone. The results are given, and compared to those of the nitrogen isomer studied under the same conditions in Table B6, Appendix B. The specific rate constants, $k_{2r}$, are given in Table 11. Reduction of the oxygen 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. It has been estimated that the equilibrium constant for equation 3.11, $K_{eq}$, is greater than or equal to

$$(NH_3)_5CoNH_2SO_3^{2+} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} (NH_3)_5CoOSO_2NH_2^{2+} \qquad (3.11)$$

0.3 at 24° in 0.90 M $HClO_4$.[70] Therefore, the isomer mixture is at least 25% oxygen bonded, and since the latter has almost the same absorbance as the nitrogen isomer at 488 nm, the initial absorbance would have been at least 25% below that of the reactants if there had been rapid reduction of the oxygen isomer. Isomerization is over ten times slower than reduction under the experimental conditions, therefore all the observations require that the oxygen and nitrogen isomers are reduced at very similar rates.

Repeated scans of the visible spectrum with chromium(II) in approximately 10% excess over cobalt(III) at low ionic strength ($\mu$ = 0.025 M) and low acidity ($H^+$ = 0.020 M) showed the growth of two peaks at approximately 415 nm and 575 nm (Figure 10). Isosbestic points occurring at 383, 422 and 547 nm imply the existence of only one product.

The results of product analysis studies are summarized in Table 12. 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 nm and 591 nm with extinction coefficients of 16.8 $cm^{-1}$ $M^{-1}$ 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 12).

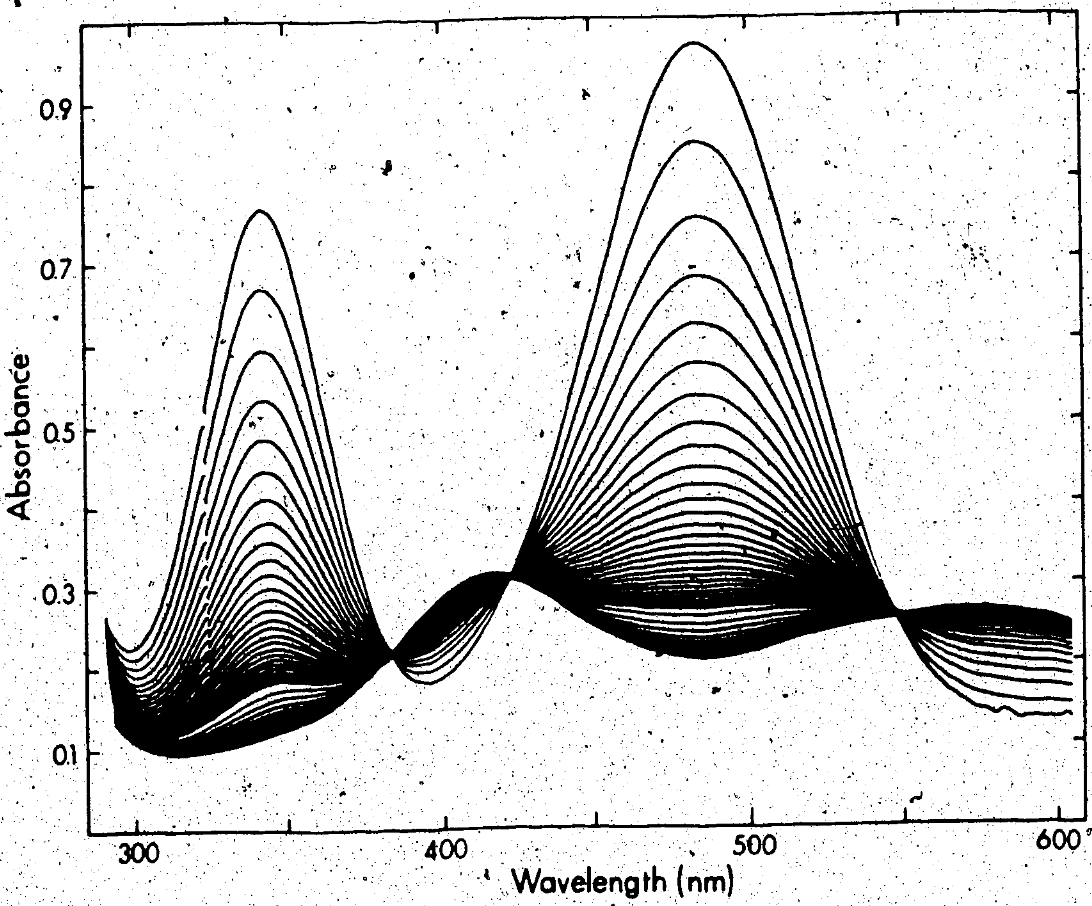


FIGURE 10: Change in visible spectrum during reduction of $(NH_3)_5CoNH_2SO_3^{2+}$ ($2.96 \times 10^{-3}$ M) by $Cr^{2+}$ ($3.26 \times 10^{-3}$ M); $[H^+] = 0.020$ M; $\mu = 0.025$ M; T = 21°C; 5 cm cell. The absorbance is decreasing at ~342 nm and ~485 nm due to consumption of cobalt(III) complex, and increasing at ~415 and ~575 nm due to production of chromium(III) complex. Isosbestic points occur at 383, 422 and 547 nm.

## TABLE 12

## PRODUCT ANALYSIS RESULTS FOR CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNH_2SO_3^{2+}$ at 25°C.

| Ligand | [Co(III)], M | [Cr(II)], M | $[H^+]$, M | Reaction time, min | Products |  |
|---|---|---|---|---|---|---|
|  |  |  |  |  | Free Ligand | Chromium(III) |
| $NH_2SO_3^-$ | 0.010 | 0.020 | 0.10 | 3.8 | 5.7% | - |
|  | 0.010 | 0.020 | 0.20 | 3.5 | 5.3% | - |
|  | 0.010 | 0.020 | 0.50 | 4.5 | 6.4% | - |
|  | 0.010 | 0.020 | 0.50 | 3.8 | 6.6% | - |
|  | 0.0087[a] | 0.0097 | 0.20 | 17.0 | - | $(H_2O)_5CrOSO_2NH_2^{2+}$ [c] |
|  | 0.012[a,b] | 0.023 | 0.10 | 3.5 | 4.5% | $(H_2O)_5CrOSO_2NH_2^{2+}$ [c] |
|  | 0.012[a,b] | 0.025 | 0.10 | 3.0 | 4.4% | - |
| $SO_4^=$ | 0.0072[a] | 0.12 | 0.20 | 3.0 | - | $(H_2O)_5CrOSO_3^+$ [c] |

a) Experiments done at ambient temperature (21°).

b) Oxidant was a mixture of N- and O-bonded isomers.

c) Identified by ion-exchange and electronic spectra as described in text.

The spectrum of the product is very similar to that of $(H_2O)_5CrOSO_3^+$ [89] which has maxima at 417 nm and 587 nm with extinction coefficients of 18.8 $cm^{-1}$ $M^{-1}$ and 19.0 $cm^{-1}$ $M^{-1}$, respectively and a shoulder at 671 nm. This similarly 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 x $10^{-5}$ $sec^{-1}$, (25°, 0.05 to 0.10 M $H^+$, 0.5 M $NaClO_4$). Interestingly, this rate constant is nearly identical to that for aquation of $(NH_3)_5CoNH_2SO_3^{2+}$, 2.6 x $10^{-5}$ $sec^{-1}$ at 25°.[70] 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 $(NH_3)_5CoOSO_3^+$.

The kinetics of this system were studied previously,[90,91] and only the chromium(III) product was identified in this work (see Table 12). The product had ion exchange properties typical of a +1 charged ion. The electronic spectrum of the product in 0.1 M $HClO_4$ shows maxima at 672 nm (shoulder), 586 nm and 416 nm, with extinction coefficients of 5.32 $M^{-1}$ $cm^{-1}$, 19.1 $M^{-1}$ $cm^{-1}$ and 20.6 $M^{-1}$ $cm^{-1}$, respectively, in good agreement with the spectrum of $(H_2O)_5CrOSO_3^+$ reported by Finholt et al.[89] The yield of this product was 98% based on the original amount of cobalt(III).

## CHAPTER IV

## DISCUSSION: PARTS A AND B

### PART A: AQUATION STUDIES

Ligand substitution reactions of coordination compounds may be represented by the generalized equation

$$MX_n + Y \rightleftharpoons MX_{n-1}Y + X \quad (4.1)$$

where M is the metal ion and X and Y are any two ligands. When Y is $H_2O$, the reaction is called aquation or hydrolysis.

Substitution reactions of metal complexes have been intensively studied, with general agreement that aquation of cobalt(III) ammine complexes in acidic aqueous solution is a dissociative process.[92] This label implies that the main activation energy comes from weakening of the bond to the leaving group, with little, if any, participation of the entering ligand. Consequently, the rate of a dissociative reaction is sensitive to variation in the nature of the leaving group. The numerous studies on the aquation of cobalt(III) ammine systems have shown definite trends between the rate of aquation and the Lewis basicity of the leaving group which support the dissociative activation hypothesis.

Unfortunately, there is no general measure of Lewis basicity, so that these trends remain qualitative. If attention is confined to a similar set of ligands, such as the carboxylate anions,[93] the rate of aquation of the pentaamminecobalt(III) complexes parallels the basicity, toward the proton, of the free carboxylate ions.

In the present study, a homologous series of leaving groups have been examined for which the basicity toward the cobalt(III) of the coordinated ligand nitrogen atom might be related to the coordinated ligand $K_a$, e.g.,

$$(NH_3)_5CoNH_2S(O)_2R \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNHS(O)_2R + H^+ \qquad (4.2)$$

On this basis the aquation of the sulfamato complex ($R = O^-$; $K_a = 2 \times 10^{-6}$ M) should be much slower than aquation of the sulfamido complex ($R = NH_2$; $K_a = 0.55$ M), which in turn should aquate more slowly than the aromatic sulfonamido complexes ($R = C_6H_4CH_3$, $C_6H_4NO_2$; $K_a \geq 5$ M). The kinetic data summarized in Table 13 conform to these predictions.

It is noteworthy that the protonated sulfamido and aromatic sulfonamido complexes have aquation rate constants in the same range as the perchlorato and trifluoromethanesulfonato complexes (see Table 13). This high level of lability for the sulfamido derivatives was initially

Table 13

KINETIC RESULTS FOR HYDROLYSIS OF $(NH_3)_5CoL$ COMPLEXES IN AQUEOUS ACID

| L | k, $sec^{-1}$ (25°) | $\Delta H^{\ddagger}$, kcal $mol^{-1}$ | $\Delta S^{\ddagger}$, cal $mol^{-1}$ $deg^{-1}$ | Reference |
|---|---|---|---|---|
| $ClO_4^-$ | ~0.1 | - | - | a |
| $NH_2SO_2C_6H_4CH_3$ | ≥0.11 | - | - | this work |
| $NH_2SO_2C_6H_4NO_2$ | ≥0.038 | - | - | this work |
| $F_3CSO_3^-$ | 0.027 | - | - | a |
| $NH_2SO_2NH_2$ | 0.013 | 21.7 | 5.5 | this work |
| $OP(OCH_3)_3$ | $2.5 \times 10^{-4}$ | - | - | b |
| $NH_2SO_3^-$ | $2.6 \times 10^{-5}$ | 24.2 | 1.4 | c |
| $NO_3^-$ | $2.0 \times 10^{-5}$ | 24.3 | 1.9 | d |
| $OS(CH_3)_2$ | $1.8 \times 10^{-5}$ | 24.6 | 2.3 | e |
| $SO_4^{2-}$ | $8.9 \times 10^{-7}$ | 22.7 | -10 | f |

## FOOTNOTES TO TABLE 13

a) Harrowfield, J.; Mac, B.; Sargeson, A.M.; Singh, B.; Sullivan, J.C. Inorg. Chem. 1975, **14**, 2864.

b) Taube, H.; Schmidt, W. Inorg. Chem. 1963, **2**, 698.

c) Sushynski, E.; Van Roodselaar, A.; Jordan, R.B. Inorg. Chem. 1972, **11**, 1887.

d) Jones, W.E.; Jordan, R.B.; Swaddle, T.W. Inorg. Chem. 1969, **8**, 2504.

e) Palmer, D.A.; Kelm, H. Inorg. Chem. 1977, **16**, 3139.

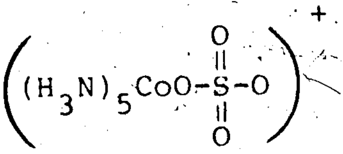
f) Monacelli, F. Inorg. Chim. Acta 1973, **7**, 65.

unexpected and might seem unusual. However, if the simplest assumption is made, that the aquation rate constant is directly proportional to the coordinated ligand $K_a$, then the sulfamato rate constant and $K_a$ can be used to predict a rate constant of $0.55 \times 2.6 \times 10^{-5}/2 \times 10^{-6} = 7\ \mathrm{sec}^{-1}$ for the sulfamido complex compared to the value of $0.013\ \mathrm{sec}^{-1}$. Of course, this argument is very simplistic, but it indicates that there is no excuse for invoking special effects to explain the kinetic lability of the sulfamido and sulfonamido complexes in aqueous acid.

The present results have some bearing on the coordination chemistry of sulfonamides and carbonic anhydrase. It is clear that the sulfonamide anion prefers to bond through nitrogen to the metal. Furthermore, the neutral sulfonamides are not strongly bonded by the metal. It would be useful to be able to estimate the $pK_a$ of metal-bound sulfonamides in carbonic anhydrase. This could be done by comparison of the $pK_a$ of the cobalt(III) sulfonamide complexes and that of $(NH_3)_5CoOH_2^{3+}$ ($pK_a \simeq 6$)[74] and (enzyme)$ZnOH_2$. Unfortunately, the latter value is not available unambiguously. The enzyme has a $pK \simeq 7$ involved in catalytic activity, but it is not clear if this is for ionization of a histidine or a metal bound water.[94,95] In any case, the high acidity of $(NH_3)_5CoNH_2SO_2C_6H_4X^{3+}$ is consistent with complete ionization of the enzyme-sulfonamide complex at and above physiological pH values.

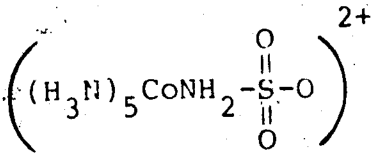
## PART B: REDUCTION STUDIES

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.



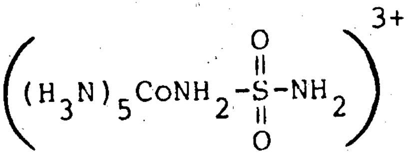
$\left((H_3N)_5CoO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\right)^{+}$

A



$\left((H_3N)_5CoNH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O\right)^{2+}$

B



$\left((H_3N)_5CoNH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-NH_2\right)^{3+}$

C

The chromium(II) reduction of the sulfato complex, (A), was studied previously with reasonable agreement at least on the rate constant at 25°C.[90,91] It seems to be assumed[96] that the reaction proceeds with sulfate ion transfer to chromium(III), apparently without actual identification of the product. Fraser[91] found $(H_2O)_5CrOSO_3^+$ as the product from the reduction of $en_2CoO_2SO_2^+$. Linear free energy correlations[97] with the rate of reduction by $Ru(NH_3)_6^{2+}$ [98] 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.

In the present work, the chromium(III) product of the chromous reduction of complex (A) has been separated and characterized by its electronic spectrum as the ligand transfer product, $(H_2O)_5CrOSO_3^+$. This is in agreement with the above observations.

The chromous reduction reactions of the sulfamato complex, (B), and the sulfamido complex, (C) also proceed with ligand transfer to chromium, (see Table 12).

The kinetic results of this and related work are summarized in Table 14. There are several puzzling features of 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 $(k_{2r})$[99] larger than those for the deprotonated form $(k_{1r})$ when charge and conjugation seem to favor the deprotonated form?

The rate constants, $k_{2r}$, given in Table 14 decrease in the order $(NH_3)_5CoOSO_3^+ > (NH_3)_5CoNH_2SO_3^{2+} > (NH_3)_5CoNH_2SO_2NH_2^{3+}$. For a reaction between two ions of charge $Z_A$ and $Z_B$ the rate constant k (reduced to zero ionic strength) is given by:

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{DKTr_{\ddagger}} \qquad (4.3)$$

where $k_0$ is the rate constant in a medium of infinite dielectric constant, D is the dielectric constant, e is the

## TABLE 14

SUMMARY OF KINETIC DATA FOR REDUCTION OF $(H_3N)_5Co(LIGAND)$ COMPLEXES BY CHROMIUM(II).[a]

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

a) Values at 25° in 1 M $LiClO_4/HClO_4$ unless otherwise indicated.

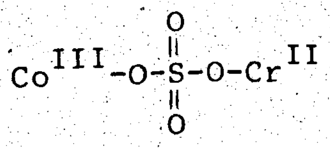
b) Values in 1 M $NaClO_4/HClO_4$ from reference 90.

c) Value of $(k_{1r}/K_a)$ is given, but $K_a \gtrsim 5$ M so that $k_{1r} \gtrsim 0.45$ $M^{-1}$ $s^{-1}$.

charge of an electron, T is the temperature in °K, K is Boltzmann's constant and $r_{\ddagger}$ is the internuclear distance in the activated complex.

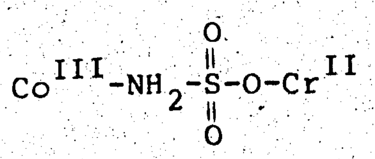
The relative reactivities ($k_{2r}$) of the sulfato, sulfamato and sulfamido complexes are consistent with a dependence of the rate constant on the exponential of the charge product of the reactants, as described by equation 4.3. This predicts relative rate constants of 1:0.14:0.018, respectively, compared to the observed ratios of 1:0.18:0.011.

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 ($k_{2r}$) difference between the sulfato and sulfamato complexes can be accounted for by reactant charge, then electron transfer appears to be about equally facile for



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

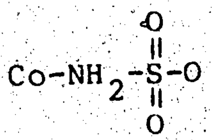
and



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

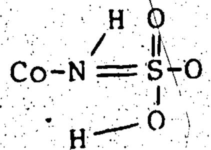
The similar reactivity of the N- and O-bonded isomers of the sulfamato complex leads to a similar conclusion. The implication is that electron transfer is possible through a coordinated $-NH_2-$ group, but this is contrary to our previous experience[6,7] that $-NH_2$ groups, either coordinated, or as a 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



$$\mathrm{Co{-}NH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O}$$

D



$$\mathrm{Co{-}\overset{H}{N}{=}\overset{\overset{O}{\|}}{\underset{\underset{O{-}H}{|}}{S}}{-}O}$$

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 sulphur 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 favourable, and thereby increase the rate constant for outer-sphere electron transfer.[43] Similar reactivity increases were observed by Gould *et al.*[100] for the reduction by vanadium(II) of several protonated carboxylatopenta-amminecobalt(III) complexes.

# CHAPTER V

## RESULTS AND DISCUSSION PART C:

## CHROMIUM(II) REDUCTION of P-NITROBENZENESULFONAMIDE AND P-NITROBENZENESULFONAMIDOPENTAAMMINE COBALT(III).

### Stoichiometry Studies

The results of the chromium(II) stoichiometry studies carried out on the reduction of the p-nitrobenzenesulfonamide ligand, and the cobalt(III) complex are given in Tables 15 and 16, respectively. The stoichiometry for the ligand was found to be four chromium(II) ions oxidized per p-nitrobenzenesulfonamide ligand reduced immediately after mixing, (reaction stopped by injection into Fe(III) or Co(III) solution within 1-4 minutes), and six chromium(II) ions oxidized per ligand reduced after the reaction was complete (≥ 1 h). Similarly chromium(II) reacted 2:1 with p-nitrosobenzenesulfonamide immediately upon mixing (~ 2 min).

For the cobalt(III) complex, the stoichiometry was found to be five chromium(II) ions oxidized per p-nitrobenzenesulfonamido complex reduced immediately after mixing, (reaction stopped by injection into Fe(III) solution within

## TABLE 15

## STOICHIOMETRY STUDIES: CHROMIUM(II) REDUCTION OF LIGANDS.[a]

| $H_2NSO_2C_6H_4X$-p | $10^3$ [Lig], M | $10^2$ [Cr(II)], M | [$H^+$], M | moles of Cr(II) reacted per mole of Ligand | |
|---|---|---|---|---|---|
| | | | | initial | final |
| X = $NO_2$ | 4.66 | 4.69 | 0.2 | 3.7[b] | 6.3[d] |
| | 4.66 | 4.69 | 0.2 | 3.9[b] | 6.3[d] |
| | 2.34 | 4.65 | 0.2 | 4.4[c] | 6.1[e] |
| | 2.45 | 4.65 | 0.2 | 4.0[c] | 5.9[e] |
| X = NO | 5.00 | 3.28 | 0.1 | 2.1[c] | |

a. Done at ambient temperature, ~21°C.

b. Allowed to react ~4 minutes before injection into Fe(III).

c. Allowed to react ~1 min before injection into Co(III).

d. Allowed to react 24 hours before injection into Fe(III).

e. Allowed to reaction ~1 hour before injection into Co(III).

# TABLE 16

## STOICHIOMETRY STUDIES: CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNHS(O)_2C_6H_4NO_2$-p$^{2+}$.[a]

| $10^4$ [Co(III)], M | $10^3$ [Cr(II)], M | [$H^+$], M | moles of Cr(II) reacted per mole of cobalt(III) initial[b] | final[c] |
|---|---|---|---|---|
| 7.98 | 9.49 | 0.01 | 4.8 | 6.8 |
| 7.98 | 9.49 | 0.01 | 5.0 | 7.1 |

a. Done at ambient temperature, ~21°C.

b. Allowed to react ≲ 3 minutes before injection into Fe(III) solution.

c. Allowed to react ~24 hours before injection into Fe(III) solution.

~ 2 minutes), and seven chromium(II) ions oxidized per complex reduced after the reaction was complete, (≥ 1 h).

In Table 17 are summarized the yields of cobalt(II) as both the ratio of the initial concentration of the reactants and the acidity are varied. The reaction was stopped after 1-2 minutes by air oxidation. Approximately one fifth of the added chromium(II) reduces the cobalt(III), the majority being consumed in reduction of the ligand. At low acidities the larger values obtained when 3 or 4 equivalents of chromium(II) are added suggest that intramolecular electron transfer through one or more of the intermediates is more rapid than through the p-nitro derivative itself, and that protonation of one or more of these intermediates inhibits intramolecular electron transfer. At high acidities the cobalt(III) is not entirely reduced within 1 → 2 minutes even under a 50-fold excess of chromium(II). This indicates that at high acid concentrations and under pseudo-first order conditions, reduction of the ligand to an intermediate which does not rapidly undergo intramolecular electron transfer occurs in competition with intramolecular electron transfer throughout the initial stages.

Under the pseudo first order conditions employed in the kinetic studies, ≥ 90% of the cobalt is released as cobalt(II) within 1 or 2 minutes.

It should be noted that reduction of the p-toluenesulfonamido complex, discussed above, has a t $_{1/2}$ ≥ 30

# TABLE 17

## COBALT(II) STOICHIOMETRY STUDIES OF REDUCTION OF $(NH_3)_5CoNHSO_2C_6H_4NO_2\text{-}p^{2+}$.

| $10^4$ [Complex], M | $10^4$ [Cr(II)], M | [Cr(III)]/ [Complex] | $[H^+]$, M | % Recovery as Co(II) |
|---|---|---|---|---|
| 8.33 | 8.54 | 1 | 0.01 | 19 |
| 10.0 | 10.3 | 1 | 0.80 | 19 |
| 6.73 | 13.5 | 2 | 0.02 | 37 |
| 10.0 | 20.5 | 2 | 0.80 | 38 |
| 8.19 | 24.8 | 3 | 0.01 | 69 |
| 10.0 | 29.9 | 3 | 0.80 | 53 |
| 8.05 | 32.2 | 4 | 0.01 | 92 |
| 10.0 | 41.1 | 4 | 0.80 | 83 |
| 10.0 | 50.4 | 5 | 0.80 | 85 |
| 8.04 | 94.9 | 12 | 0.01 | 100 |
| 10.0 | 120. | 12 | 0.80 | 90 |
| 9.99 | 500. | 50 | 0.80 | 87 |

minutes, so that direct reduction of cobalt(III) is not likely a competitive pathway for the p-nitro complex.

## Product Studies

The product studies for the chromium(II) reduction of the p-nitrobenzenesulfonamide ligand were carried out by oxygenating an aliquot of the reaction solution immediately after mixing, and again after the reduction reaction was complete (t > 1 h), precipitating the chromium(III) by the addition of base, and filtration of the mixture through a Millipore filter. Analysis of the resulting solution was carried out spectrophotometrically, (see Experiment section for details). Similar studies were performed on p-hydroxylaminobenzenesulfonamide and sulfanilamide.

The results of these studies are listed in Table 18. When p-hydroxylaminobenzenesulfonamide or p-nitrobenzenesulfonamide are reacted with an excess of chromium(II), and allowed to react to completion, 99% and 93% of the ligand, respectively, was recovered as sulfanilamide, the six electron reduction product, in agreement with the stoichiometry studies.

Unfortunately, similar reaction solutions analysed immediately after mixing, in an attempt to identify the four electron reduction product did not yield consistent results. Samples containing either the p-nitro or the

## TABLE 18

## PRODUCT STUDIES: CHROMIUM(II) REDUCTION OF LIGANDS AT 21°C.[a]

| $H_2NSO_2C_6H_4X$-p, | $10^3$ [Lig], M | $10^2$ [Cr(II)], M | [Cr(II)]/[Lig] | $[H^+]$, M | % Recovery as p-$H_2NSO_2C_6H_4R$ R=NHOH | R=$NH_2$ |
|---|---|---|---|---|---|---|
| X = $NO_2$ | 4.66 | 7.5 | 16 | 0.2 | 2 | 93 |
| | 4.66 | 7.5 | 16 | 0.2 | 3 | 94 |
| | 2.28 | 0.91 | 4 | 0.2 | 89 | 12 |
| X = NHOH | 2.34 | 7.5 | 32 | 0.2 | 1 | 99 |
| X = $NH_2$[b] | 2.35 | 4.5 | 19 | 0.2 | 1 | 102 |

a. Allowed to react ≥ 24 hours.

b. Blank experiment, no reaction.

p-hydroxylamino ligand which were oxygenated immediately (t ~ 30 sec), and which subsequently had aliquots removed for analysis yielded ≥ 85% sulfanilamide with ≥ 90% total recovery. However, in the p-nitro case, aliquots removed anaerobically from the reaction solution prior to oxygenation (t ~ 3 min) yielded 3-45% p-hydroxylaminobenzenesulfonamide and 91-15% sulfanilamide.

In all cases where > 90% of the ligand was recovered, the majority of it, (> 85%), was sulfanilamide. A blank experiment using sulfanilamide as the starting material was carried out under similar conditions (see Table 18 for details). The results showed that 100% of the sulfanilamide present can be recovered using this method. In all studies, the ligand was separated from the chromium(III) by precipitation of the chromium(III) under basic conditions as the highly charged polymeric $[(Cr(III))_x(OH)_y(OH_2)_z]^{(3x-y)+}$ species. The low yields obtained in some of the studies are consistent with the trapping of a negatively charged partially reduced ligand species, e.g.

$$^{-}HNS(O)_2C_6H_4NHOH$$

within the cationic polymeric chromium(III) precipitate.

When product studies were carried out under a 4:1 ratio of chromium(II) to p-nitrobenzenesulfonamide ligand, and allowed to react to completion, 89% of the reactant is recovered as p-hydroxylaminobenzenesulfonamide, and only 12% as sulfanilamide. This indicates that reduction to p-hydroxylaminobenzenesulfonamide is faster than the subsequent reduction to sulfanilamide, in agreement with the stoichiometry studies. These results also indicate that the problem with the product studies performed under conditions of a large excess of chromium(II) must occur at the oxidation stage. It appears that oxidation of excess chromium(II) by oxygen produces some intermediate which can rapidly reduce $H_2NS(O)_2C_6H_4NHOH$ to sulfanilamide. One possibility is:

$$Cr^{2+} + O_2 \longrightarrow Cr^{3+} + O_2^{\bullet -}$$

$$p\text{-}H_2NS(O)_2C_6H_4NHOH + 2O_2^{\bullet -} \xrightarrow{2H^+} p\text{-}H_2NS(O)_2C_6H_4NH_2 + 2O_2 + 2H_2O$$

Kinetic Studies

The kinetic results for the reduction of free and complexed p-nitrobenzenesulfonamide ligand can be divided into two general categories. The fast reactions were studied by stopped-flow techniques and were complete within ~ 1 minute. The slow reactions were studied on a Cary 219 spectrophotometer and required several hours to reach completion. For both rate categories and both reactant systems the kinetics did not display simple monophasic behaviour.

Stopped-flow Studies: The stopped-flow studies showed an initial rapid increase in absorbance which was too fast to measure, ($t_{1/2} \lesssim 10^{-3}$ s). The product could not be identified due to rapid subsequent reactions, but the absorption spectrum was measured on the stopped-flow system at ~ 30 nm intervals between 270-500 nm. These measurements showed an absorbance maximum at 330 ± 20 nm with an apparent extinction coefficient of ~ 2.5 x $10^3$ $M^{-1}$ $cm^{-1}$ at pH 0.7 for both the free ligand and the cobalt(III) complex.

This reaction was followed by a kinetically measureable decrease in absorbance with rate constants $k_{1L}$ and $k_{1C}$ for the free ligand and complexed ligand, respectively.

For the free ligand there was a subsequent slower decrease in absorbance, but the absorbance change was small and the rate constant, $k_{2L}$, could not be determined. The data were fitted by least-squares to:

$$Abs_t = Abs_\infty + A_{1L}e^{-k_{1L}t} + A_{2L}e^{-k_{2L}t} \qquad (5.1)$$

where $Abs_t$ and $Abs_\infty$ are the absorbancies at time t and after the reaction is complete, and the preexponential terms, $A_{1L}$ and $A_{2L}$, are functions both of the extinction coefficients and the rate constants, $k_{1L}$ and $k_{2L}$, (see Appendix A). The value of $k_{2L}$ was fixed at 1 $sec^{-1}$, which generally best described the data. Since $k_{1L} >> k_{2L}$, the values of $k_{1L}$ were quite insensitive to assumptions about the magnitude of $k_{2L}$ below this upper limit.

For the complex, the second kinetically measureable reaction on the stopped-flow involved an increase in absorbance and the values of $k_{2C}$ could be determined. This behaviour represents the most obvious difference between the free ligand and the complex. The two reactions were sufficiently separable so that the data for each reaction could be fitted by least-squares to equation 5.2, using the data up to 0.4 seconds to obtain $k = k_{1C}$ and the data obtained between ~ 0.5 and ~ 12 seconds for $k = k_{2C}$.

$$Abs_t = Abs_\infty + Ae^{-kt} \qquad (5.2)$$

For both the free ligand and the complex, the values obtained for $k_1$ are consistent with the rate law

$$k_1 = \left( \frac{a}{[H^+]} + b \right) [Cr^{2+}] \qquad (5.3)$$

The values obtained for $k_1$ from a least-squares fit to equation 5.3 are compared to the experimental values in Table B7 and B8, Appendix B, for the ligand and the complex, respectively. For the free ligand a = 95 ± 10 $sec^{-1}$ and b = $2.69 \pm 0.14 \times 10^3\ M^{-1}\ s^{-1}$, while for the complex a = 84 ± 10 $sec^{-1}$ and b = $2.36 \pm 0.19 \times 10^3\ M^{-1}\ s^{-1}$ at 25°C. Plots of $k_1/[Cr^{2+}]$ versus $[H^+]^{-1}$ are linear as shown in Figure 11. The identical rate law and very similar rate parameters indicate that the same process is being observed for $k_1$ in both systems.

These observations are consistent with a reaction sequence in which the initial reaction involves formation of the nitro radical anion, at a rate too large to measure

$$p\text{-X-NHS(O)}_2C_6H_4NO_2Cr^{2+} \longrightarrow p\text{-X-NHS(O)}_2C_6H_4\dot{N}O_2^{-} + Cr^{2+} \qquad (5.4)$$

followed by reduction of the protonated and unprotonated forms of the radical anion with the observed rate constant $k_1$

$$p\text{-X-NHS(O)}_2C_6H_4\dot{N}O_2^{-} + H^+ \underset{K_a}{\rightleftharpoons} p\text{-X-NHS(O)}_2C_6H_4\dot{N}O_2H$$

$$p\text{-X-NHS(O)}_2C_6H_4\dot{N}O_2^{-} + Cr^{2+} \xrightarrow{k'} \text{product} \qquad (5.5)$$

$$p\text{-X-NHS(O)}_2C_6H_4\dot{N}O_2H + Cr^{2+} \xrightarrow{k''} \text{product}$$

where X ≡ H for the free ligand, and X ≡ $(NH_3)_5Co^{3+}$ for the complex.

This scheme predicts that

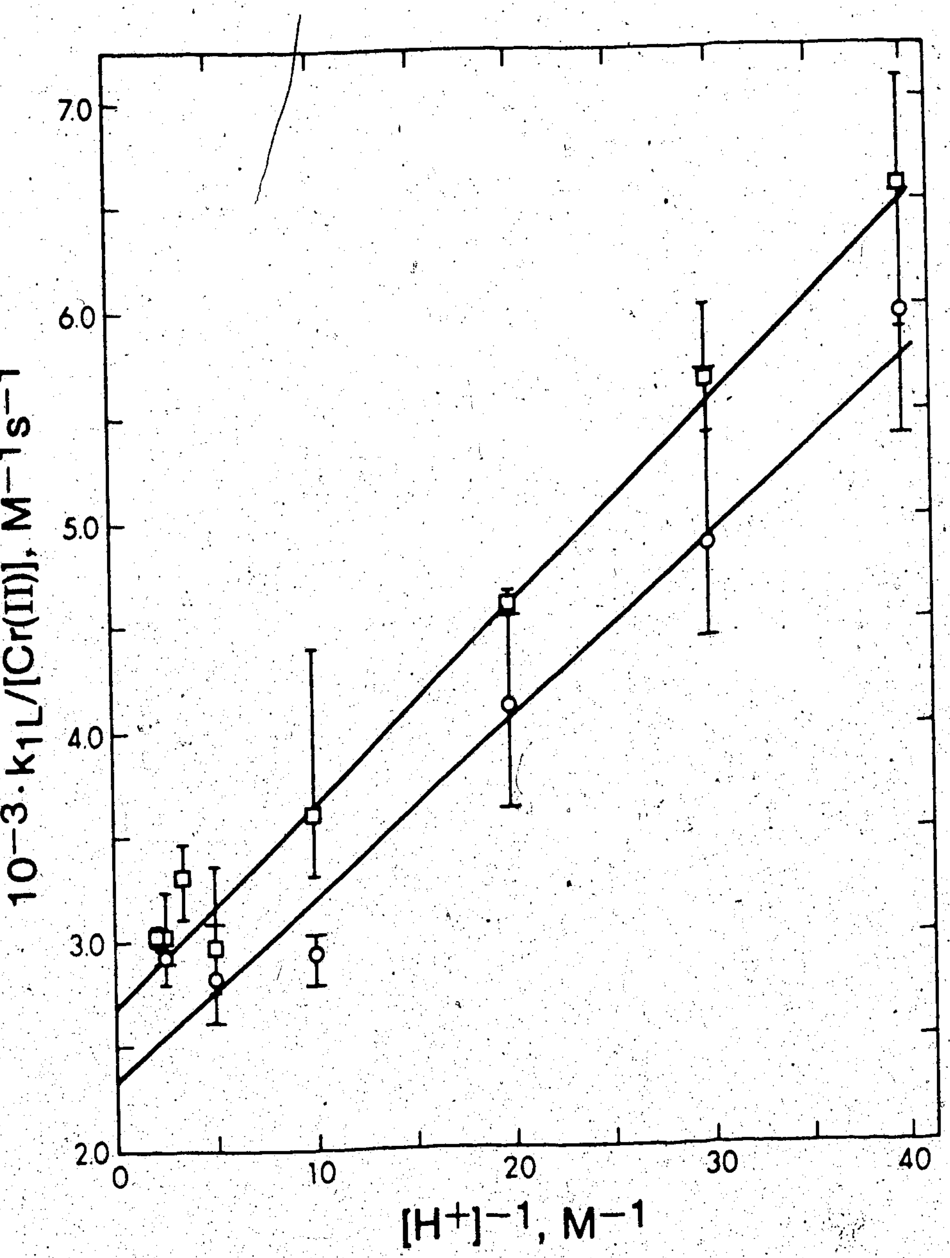


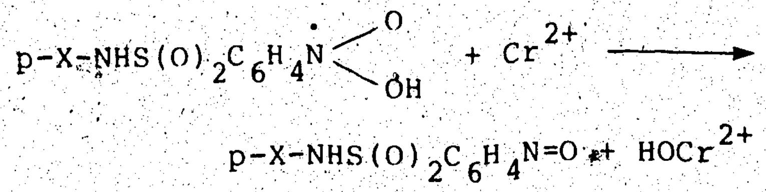
FIGURE 11: Acid dependence of the second order rate constant for reduction at 25°C of p-$NH_2SO_2C_6H_4NO_2$ ( □ ); and $(NH_3)_5CoNHSO_2C_6H_4NO_2$-$p^{2+}$ ( ○ ). Lines shown represent values calculated by least-square fit to equation 5.3. Points shown are average values. Error bars represent the range of values. (See Appendices B7 and B8, respectively).

$$k_1 = \left( \frac{k'K_a + k''[H^+]}{K_a + [H^+]} \right) [Cr^{2+}] \qquad (5.6)$$

If $[H^+] >> K_a$ then equation 5.6 reduces to the same form as equation 5.3 with $a = k'K_a$ and $b = k''$.

This proposed sequence is consistent with the observation of Hoffman et al[28] who found that $p\text{-}HO_2CC_6H_4\dot{N}O_2H$ either free or coordinated to $(NH_3)_5Co^{3+}$ has $\lambda_{max} = 310$ nm, $\varepsilon = 2 \times 10^4\ M^{-1}\ cm^{-1}$ and both the free and coordinated radicals have a $K_a = 1.6 \times 10^{-3}$ M. Thus the assumption that $[H^+] >> K_a$ is justified in the present study where the $[H^+]$ range is from 0.025-0.50 M.

The product of this reaction, (equation 5.5), could not be identified, but is probably the p-nitrosobenzene derivative. For example, this could be obtained from the protonated radical by hydroxy radical abstraction

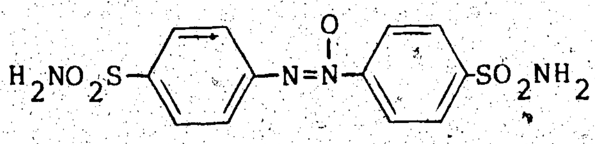


$$p\text{-}X\text{-}NHS(O)_2C_6H_4\dot{N}\genfrac{}{}{0pt}{}{\diagup O}{\diagdown OH} + Cr^{2+} \longrightarrow p\text{-}X\text{-}NHS(O)_2C_6H_4N{=}O + HOCr^{2+} \qquad (5.7)$$

A chromium(III)-ligand product is also possible.

The slower stopped-flow reaction, $k_2$, involved a substantial increase in absorbance for the complex, but a small decrease in absorbance for the ligand which could not be characterized kinetically. It is possible that this small decrease also occurs with the complex, but is completely masked by the larger absorbance increase. It might be noted at this point that the studies on the Cary 219 spectrophotometer, to be discussed later indicated that at the beginning of the slow kinetics the initial absorbance is 2 to 3 times larger for the complex than for the free ligand, and that the initial absorbance increases with decreasing acidity for the complex, but is relatively independent of the acidity for the free ligand. This is consistent with the qualitative observation that the absorbance increase for the complex on the stopped-flow was larger at lower acidity. Furthermore, the apparent extinction coefficient at 350 nm is in the range of 2 - 3.5 x $10^3$ $M^{-1}$ $cm^{-1}$ for the complex at the end of the stopped-flow study.

A consideration of the electronic spectra and known chemistry of various possible reduced derivatives of p-$NH_2S(O)_2C_6H_4NO_2$ indicates that the most likely product in the cobalt reduction study with substantial absorbance at 350 nm is the azoxybenzene derivative (V-1).



(V-1)

The molar extinction coefficient of (V-1) is 1.31 x $10^4$ $M^{-1}$ $cm^{-1}$ at 350 nm, so that only ~ 20% need be formed to cause the observed absorbance increase. This is not inconsistent with the stoichiometry results, since a small amount of the azoxy product would not be detectable from the stoichiometry studies.

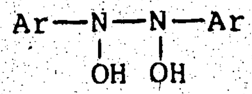
Formation of azoxybenzene derivatives has substantial precedence in a number of studies in which reduced nitro derivatives in several oxidation states are present. The formation kinetics have been studied[101-104] by reaction of aromatic, (Ar), nitroso and hydroxylamine derivatives:

$$\mathrm{ArNO + ArNHOH \longrightarrow ArN_2OAr + H_2O} \qquad (5.8)$$

The rate constant is first order in each reactant ($k \sim 1\ M^{-1}\ s^{-1}$; 25°C)[102] and shows acid catalysis ($k \sim 1 \times 10^{2}\ M^{-2}\ s^{-1}$; 25°C).[102] A disproportionation and radical coupling mechanism has been suggested[103]

$$\mathrm{ArNO + ArNHOH \overset{K}{\rightleftharpoons} 2ArNHO^{\bullet} \xrightarrow{k} ArN_2OAr + H_2O} \qquad (5.9)$$

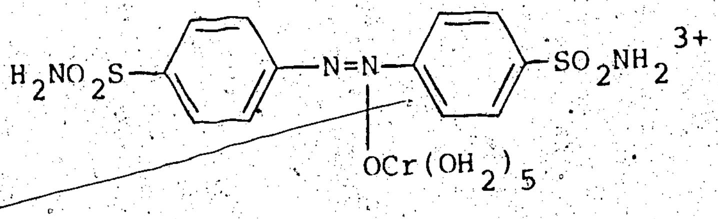
For the phenyl system ($Ar = C_6H_5$), $K \sim 10^{-5}$ [105] and kinetic studies yield $kK = 0.3\ M^{-1}\ sec^{-1}$ at 19°C,[103] so that $k = 0.3/10^{-5} = 3 \times 10^{4}\ M^{-1}\ s^{-1}$. On the other hand, a recent study[104] of the acid and base catalysis has suggested a direct coupling mechanism through an intermediate of the form (V-2).



$$\mathrm{Ar{-}\underset{OH}{N}{-}\underset{OH}{N}{-}Ar}$$

(V-2)

If the absorbance increase with the complex is to be accounted for by an azoxy derivative (V-1), then the reaction scheme should be consistent with the kinetic results discussed below, and should explain the fact that more of it is formed at lower acidity, and explain why more forms with the complex than with the free ligand. In regard to the latter it should be noted that (V-1) is reduced rapidly by chromium(II), so that the product from the complex might simply be stabilized in some way relative to further reduction, compared to the corresponding free ligand product. For example, the chromium(III) coordinated species (V-3) might be stable to reduction if reduction is



(V-3)

normally by hydroxy radical abstraction.

The kinetic results are given in Table B9, Appendix B. The absorbance data show a simple exponential time dependence with an apparent first order rate constant which is independent of the concentration of chromium(II), but which does vary with the initial cobalt concentration (a less than first order dependence), as well as slightly with the acidity. It seems peculiar that the time dependence shows first order behaviour, but the apparent rate constant varies with the concentration of the limiting reagent.

The simplest way to account for the apparent pseudo-first order behaviour would be a reaction between two cobalt(III) species, (P1 and P2), with one of them, (P1), being dominant. If P1 and P2 couple to give the azoxy derivative, then the kinetics could be pseudo-first order, and the rate constant would depend on the initial cobalt(III) concentration because the concentration of P1 would be proportional to the concentration of cobalt(III).

Reaction of product with residual reactant might also be a possibility, but seems unlikely since the absorbance change for $k_{2C}$ is independent of the initial chromium(II) conc[illegible]ation, but the rate of $k_{1C}$ is first order in [illegible]II). Less reactant would be present at higher [illegible](II) concentrations and then less azoxy product [illegible]orm.

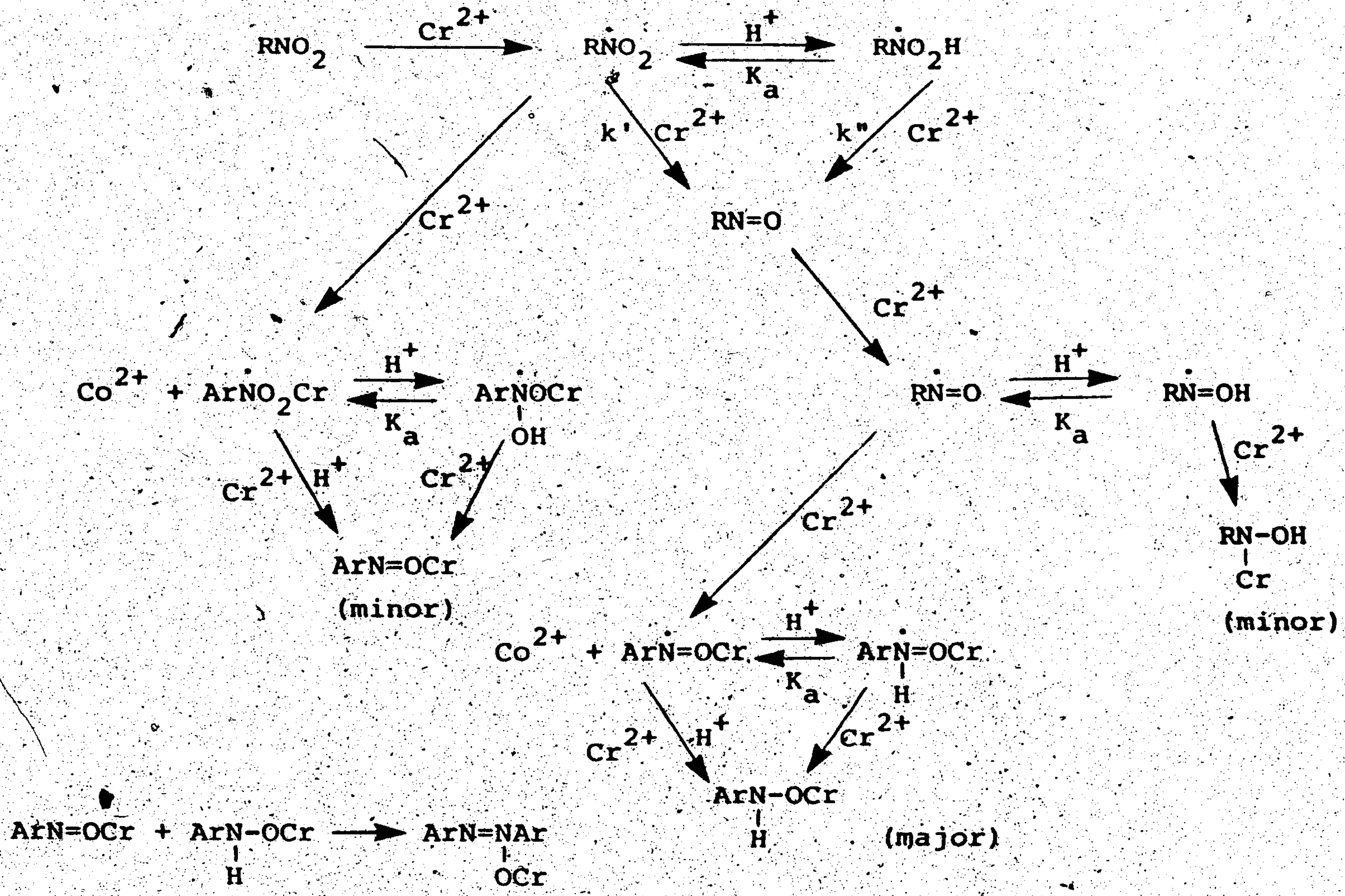
An explanation for the formation of a chromium(III) b[illegible] azoxy intermediate with the complex, and the acid d[illegible]ndency of the amount formed will start with the most l[illegible]ely initial reduction products of both the protonated and u[illegible]rotonated forms of the p-nitro radical complex. The un[illegible]ue[illegible]eature of the complex, compared to the free ligand, is suggested to be inner-sphere reduction of the unprotonated p-nitro radical complex, resulting in reduction of the cobalt(III) center. This pathway would result eventually in production of a chromium(III) bound p-nitrosobenzenesulfonamide product, which is proposed to be inhibited from further reduction by the bound chromium(III), but which is subject to nucleophilic attack by an hydroxylamine product (see below) to form chromium(III) bound azoxybenzenesulfonamide.

It is proposed that when possible, reduction will occur by hydroxy radical abstraction. Thus, the protonated p-nitro radical complex might react by hydroxy radical abstraction (see equation 5.7, X ≡ $(NH_3)_5Co^{3+}$), yielding the unbound p-nitroso derivative. Therefore, the amount of chromium(III) bound p-nitroso product will depend on the amount of the $k_1$ reaction proceeding via the unprotonated pathway, although it is not the sole product of that reduction (see Scheme I).

It is proposed further, that only a small fraction of the cobalt(III) is reduced at the p-nitro radical stage, the predominant two electron reduction product being the p-nitrosobenzenesulfonamido cobalt(III) complex. This nitroso derivative can be reduced to the radical, which can protonate, and both forms will be reduced further. If the protonated form undergoes reduction producing $(NH_3)_5CoNHS(O)_2C_6H_4N(OH)Cr(OH_2)_5{}^{4+}$, a relatively unreactive N-bonded chromium(III) species, then this might account for the less than quantitative yield of cobalt(II) at high acidity, (see Co(II) stoichiometry results, Table 17). The unprotonated form might undergo inner sphere reduction of

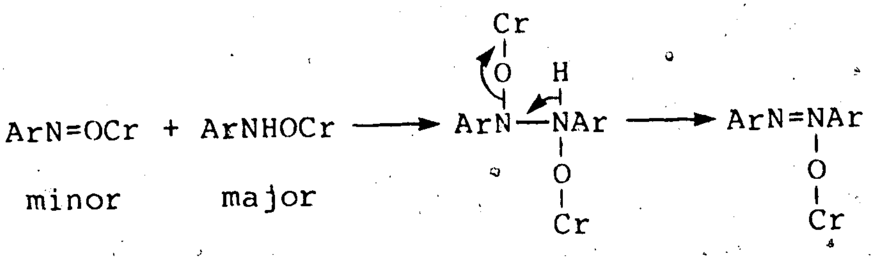
## SCHEME I

$R \equiv (NH_3)_5CoNHSO_2C_6H_4-$ $Ar \equiv H_2NSO_2C_6H_4-$ $Cr \equiv (H_2O)_5Cr^{3+}$



the cobalt(III) center in a step similar to that proposed above for the p-nitro radical species, producing eventually chromium(III) bonded p-hydroxylaminobenzenesulfonamide (see Scheme I).

It is proposed that the major portion of the cobalt(III) is reduced at the p-nitroso radical stage, in agreement with the cobalt(II) stoichiometry results. The final products of the two intramolecular electron transfer steps couple to give chromium(III) bonded azoxybenzenesulfonamide.



$$\underset{\text{minor}}{\mathrm{ArN{=}OCr}} + \underset{\text{major}}{\mathrm{ArNHOCr}} \longrightarrow \mathrm{ArN}\overset{\overset{\mathrm{Cr}}{|}}{\underset{}{\overset{|}{\mathrm{O}}}}\!-\!\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{Cr}}{|}}{\underset{|}{\mathrm{NAr}}}}\!\!\!\!\!\!\!\!\underset{\mathrm{O}}{} \longrightarrow \mathrm{ArN{=}}\underset{\underset{\underset{\mathrm{Cr}}{|}}{\mathrm{O}}}{\underset{|}{\mathrm{NAr}}} \qquad (5.10)$$

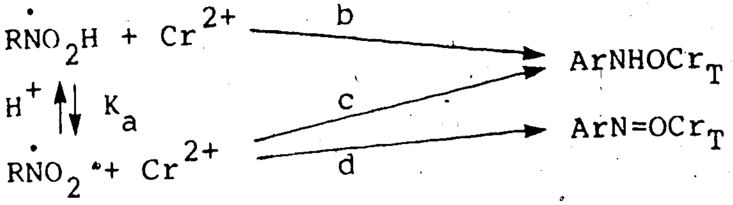
The pseudo first order rate constants, ($k_{2C}$), for this coupling reaction (see Table B9, Appendix B) were found to vary slightly with the acidity, showing a minimum value of ~ 0.43 $sec^{-1}$ at 0.1 M $H^+$ and increasing to ~ 0.51 $s^{-1}$ and 0.60 $s^{-1}$ at 0.4 M $H^+$ and 0.025 M $H^+$, respectively. Although the variation with acidity is not large, it seems to be outside the range of experimental error, judging from the reproducibility of the runs at any particular acidity.

The data for $k_{2C}$ were best-fitted to equation 5.11, and the results are compared in Table B9, Appendix B.

$$k_{2C} = \left( \frac{x}{[H^+]} + y\,[H^+] \right) [Co]_T + z = k_{Co}[Co]_T + z \qquad (5.11)$$

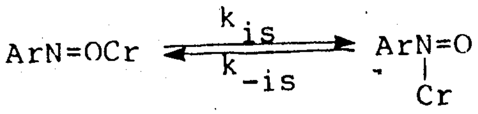
The values obtained for x, y, and z were 46 ± 8 $s^{-1}$, 3.25 ± 0.71 x $10^3$ $M^{-2}$ $s^{-1}$ and 0.268 ± 0.025 $s^{-1}$, respectively.

The reaction scheme (scheme 1), proposed for production of the two reactants involved in the cobalt dependent term of equation 5.11 may be abbreviated to



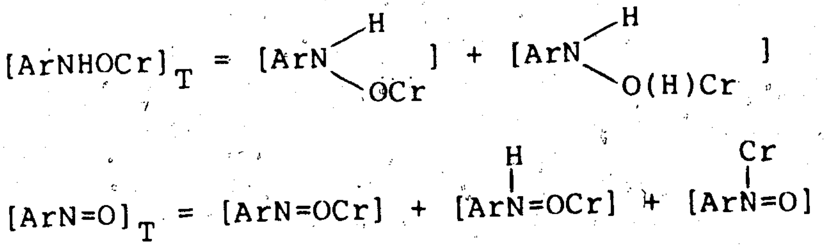
$$\begin{tikzcd} \dot{R}NO_2H + Cr^{2+} \arrow[r, "b"] \arrow[d, shift left, "K_a"] & ArNHOCr_T \\ \dot{R}NO_2 + Cr^{2+} \arrow[u, shift left, "H^+"] \arrow[ur, "c"] \arrow[r, "d"'] & ArN{=}OCr_T \end{tikzcd} \qquad (5.12)$$

where R ≡ $(NH_3)_5CoNHS(O)_2C_6H_4$, Ar ≡ $H_2NS(O)_2C_6H_4$, Cr ≡ $Cr(OH_2)_5{}^{3+}$ and c + d = a; and where "a" and "b" have the same meaning as in equation 5.3. Both the hydroxylamino and nitroso species can protonate, and it is proposed that the unprotonated nitroso derivative can isomerize according to equation 5.13.



$$ArN{=}OCr \underset{k_{-is}}{\overset{k_{is}}{\rightleftharpoons}} \underset{\displaystyle Cr}{ArN{=}O} \qquad (5.13)$$

The terms $[ArNHOCr]_T$ and $[ArN{=}OCr]_T$ refer to the total concentration of each species, i.e.



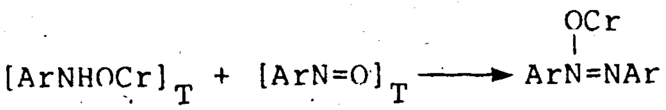
$$[ArNHOCr]_T = [ArN\begin{smallmatrix} H \\ OCr \end{smallmatrix}] + [ArN\begin{smallmatrix} H \\ O(H)Cr \end{smallmatrix}]$$

$$[ArN{=}O]_T = [ArN{=}OCr] + [Ar\overset{H}{N}{=}OCr] + [Ar\overset{Cr}{N}{=}O] \qquad (5.14)$$

The acid dissociation constants are defined by:

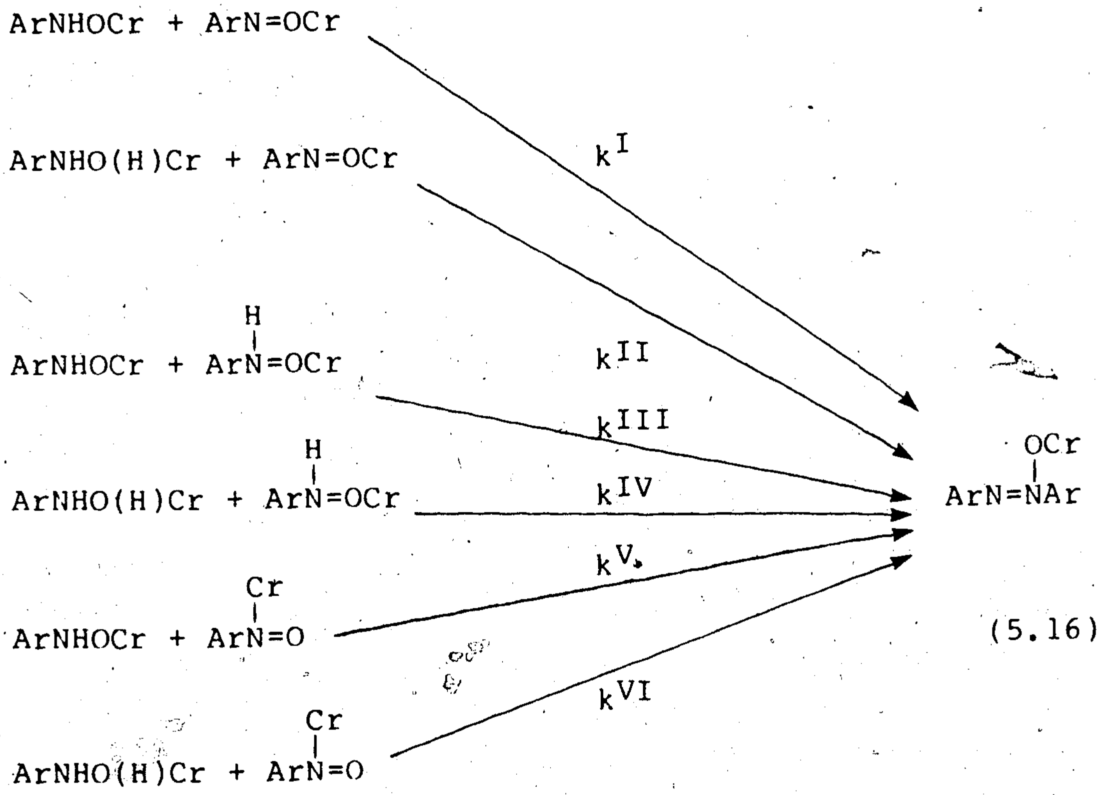
$$K_{a1} = \frac{[ArNHOCr][H^+]}{[ArNHO(H)Cr]} \; ; \; K_{a2} = \frac{[ArN{=}OCr][H^+]}{[ArN(H){=}OCr]} \qquad (5.15)$$

The reaction of equation 5.12 would be followed by the coupling reactions



$$[ArNHOCr]_T + [ArN{=}O]_T \longrightarrow Ar\overset{OCr}{\overset{|}{N}}{=}NAr$$

which represents the six possible pathways



(5.16)

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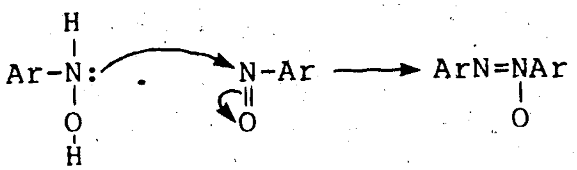
The reaction between hydroxylamino and nitroso compounds can be viewed as nucleophilic attack of the hydroxylamino nitrogen at the nitroso nitrogen atom:



(5.17)

Therefore, the N-bonded isomer of the nitroso compound, $\text{Ar-}\overset{\text{Cr}}{\text{N}}\text{=O}$, might be expected to react more rapidly than its oxygen bonded counterpart, due to the increased electrophilicity of the nitroso nitrogen. If steady-state conditions are assumed for $\text{Ar}\overset{\text{Cr}}{\text{N}}\text{=O}$, and if $k^{V}[\text{ArNHOCr}] + k^{VI}[\text{ArNHO(H)Cr}] \gg k_{-is}$, then it can be shown that the steady-state concentration of $\text{Ar}\overset{\text{Cr}}{\text{N}}\text{=O}$ is given by:

$$[\text{ArN(Cr)=O}]_{\text{S.S.}} = \frac{k_{is}[\text{ArN=OCr}]}{k^{V}[\text{ArNHOCr}] + k^{VI}[\text{ArNHO(H)Cr}]} \tag{5.18}$$

If the steady-state concentration of $\text{Ar}\overset{\text{Cr}}{\text{N}}\text{=O}$ is much smaller than that of the O-bonded isomer, then,

$$[\text{ArN=O}]_{T} = [\text{ArN=OCr}] + [\text{ArN(H)=OCr}] \tag{5.19}$$

Combining equations 5.14, 5.15,5.18 and 5.19 it can be shown that

$$[\text{ArNHOCr}] = \frac{K_{a1}}{K_{a1}+[\text{H}^{+}]}\,[\text{ArNHOCr}]_{T} \tag{5.20}$$

$$[\text{ArNHO(H)Cr}] = \frac{[\text{H}^{+}]}{K_{a1}+[\text{H}^{+}]}\,[\text{ArNHOCr}]_{T} \tag{5.21}$$

$$[\mathrm{ArN{=}OCr}] = \frac{K_{a2}}{K_{a2}+[\mathrm{H}^+]}\,[\mathrm{ArN{=}O}]_T \qquad (5.22)$$

$$[\mathrm{ArN(H){=}OCr}] = \frac{[\mathrm{H}^+]}{K_{a2}+[\mathrm{H}^+]}\,[\mathrm{ArN{=}O}]_T \qquad (5.23)$$

$$[\mathrm{ArN(Cr){=}O}]_{S.S.} = \frac{k_{is}K_{a2}(K_{a1}+[\mathrm{H}^+])}{(k^{V}K_{a1}+k^{VI}[\mathrm{H}^+])(K_{a2}+[\mathrm{H}^+])}\;\frac{[\mathrm{ArN{=}O}]_T}{[\mathrm{ArNHOCr}]_T} \qquad (5.24)$$

Employing equations 5.20-5.24, the total rate of production of chromium(III) bonded azoxybenzenesulfonamide by the reaction scheme of equation 5.16 is given by:

$$\frac{d[\mathrm{Azoxy}]}{dt} = \left(\frac{k^{I}K_{a1}K_{a2}+k^{II}K_{a2}[\mathrm{H}^+]+k^{III}K_{a1}[\mathrm{H}^+]+k^{IV}[\mathrm{H}^+]^2}{(K_{a1}+[\mathrm{H}^+])(K_{a2}+[\mathrm{H}^+])}\right) \times \left([\mathrm{ArNHOCr}]_T[\mathrm{ArN{=}O}]_T\right) + \left(\frac{k_{is}K_{a2}}{K_{a2}+[\mathrm{H}^+]}\right)[\mathrm{ArN{=}O}]_T \qquad (5.25)$$

The hydroxylamino species is the reactant in excess, so the observed first-order rate constant, $k_{2C}$, is given by:

$$k_{2C} = \left(\frac{k^{I}K_{a1}K_{a2}+k^{II}K_{a2}[\mathrm{H}^+]+k^{III}K_{a1}[\mathrm{H}^+]+k^{IV}[\mathrm{H}^+]^2}{(K_{a1}+[\mathrm{H}^+])(K_{a2}+[\mathrm{H}^+])}\right)[\mathrm{ArNHOCr}]_T + \frac{k_{is}K_{a2}}{(K_{a2}+[\mathrm{H}^+])} \qquad (5.26)$$

The product distribution predicted by equation 5.12 is given by:

$$\frac{[\mathrm{ArNHOCr}]_T}{[\mathrm{ArN{=}OCr}]_T} = \frac{b[H^+] + c}{d} \tag{5.27}$$

If it is assumed that these are the major reactants present prior to the rise in absorbance then:

$$\text{Total [Cobalt]} = [\mathrm{Co}]_T = [\mathrm{ArNHOCr}]_T + [\mathrm{ArN{=}OCr}]_T \tag{5.28}$$

By combining equation 5.27 and 5.28 it can be shown that:

$$[\mathrm{ArNHOCr}]_T = \left(\frac{b[H^+] + c}{b[H^+] + c + d}\right) [\mathrm{Co}]_T \tag{5.29}$$

However, the hydroxylamino species is the major product of equation 5.12. Therefore $b[H^+] + c >> d$ and

$$[\mathrm{ArNHOCr}]_T = [\mathrm{Co}]_T \tag{5.30}$$

Substitution of equation 5.30 into equation 5.26 gives

$$k_{2C} = \left(\frac{k^I K_{a1} K_{a2} + k^{II} K_{a2}[H^+] + k^{III} K_{a1}[H^+] + k^{IV}[H^+]^2}{(K_{a1}+[H^+])(K_{a2}+[H^+])}\right)[\mathrm{Co}]_T + \frac{k_{is} K_{a2}}{K_{a2}+[H^+]} \tag{5.31}$$

If $K_{a1} << [H^+]$, $K_{a2} >> [H^+]$ and $k^{II} + k^{III}K_{a1}/K_{a2} <<$ $k^I K_{a1}/[H^+] + k^{IV}[H^+]/K_{a2}$, then equation 5.31 reduces to:

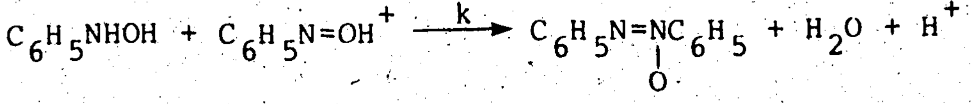
$$k_{2C} = \left( \frac{k^{I}K_{a1}}{[H^{+}]} + \frac{k^{IV}[H^{+}]}{K_{a2}} \right) [Co]_{T} + k_{is} \qquad (5.32)$$

which is equivalent to equation 5.11 with $x = k^{I}K_{a1}$, $y = k^{IV}/K_{a2}$ and $z = k_{is}$.

Although the reaction scheme of equation 5.16 yields a rate law consistent with the results, it is always advisable to consider if the approximations used, and the rate constants obtained are reasonable. As discussed in the Characterization of Complexes section above, coordination of a metal ion to an atom containing an ionizable hydrogen generally results in an increase in the $K_a$ by a factor of ~ $10^{10}$ compared to the uncoordinated ligand. Thus, the $K_{a1}$ of ArNHO(H)Cr should be ~ $10^{10}$ larger than that of ArNHOH. Hydroxylamine ligands are not expected to be very acidic. In fact no measurements of the $K_a$ of such ligands have been reported to date. A value as small as $K_a < 10^{-13}$ is not unreasonable, allowing an estimate of $K_{aI} \leq 10^{-3}$ M.

Considering the assumption that $K_{a2} >> [H^{+}]$, Ogata et al[101] have reported that the $K_a$ of $C_6H_5N{=}OH^{+}$ is ~ 0.8 M. Since the oxygen atom is more basic that the nitrogen atom, the $K_a$ of $C_6H_5\overset{H}{N}{=}O^{+}$ must be > 0.8 M. Addition of a chromium(III) ion, yielding $C_6H_5\overset{H}{N}{=}OCr(OH_2)_5{}^{4+}$ can only serve to increase the $K_a$ further. If $K_{a1} \leq 10^{-3}$ M and $K_{a2} \geq 0.8$ M then the values of x and y can be used to calculate $k^{I} \geq 5 \times 10^{4}\ M^{-1}\ s^{-1}$ and $k^{IV} \geq 3 \times 10^{3}\ M^{-1}\ s^{-1}$.

Ogata et al[101] have reported a value of $k = 0.4 \times 10^3\ M^{-1}\ s^{-1}$ for the reaction

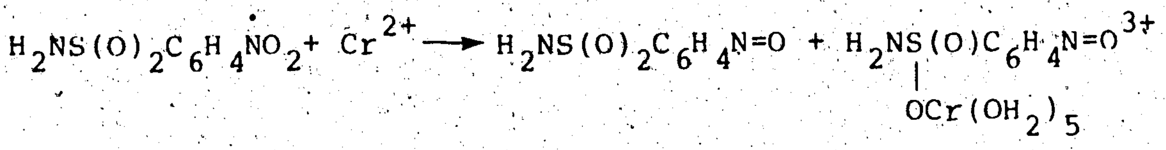


$$C_6H_5NHOH + C_6H_5N{=}OH^+ \xrightarrow{k} C_6H_5N{=}\underset{\displaystyle O}{\overset{|}{N}}C_6H_5 + H_2O + H^+$$

Therefore the values for $k^I$ and $k^{IV}$ do not seem unreasonable.

It is proposed that the free ligand undergoes reduction by the same steps as that described above for the cobalt(III) complex, except that those steps involving reduction of the cobalt(III) center are not available, and in the absence of the bulky and highly charged $(NH_3)_5Co^{3+}$ group, chromium(II) might be able to attack the ligand at the sulfonamido oxygen atom, as well as at the p-nitro oxygen, on the stopped-flow time scale.

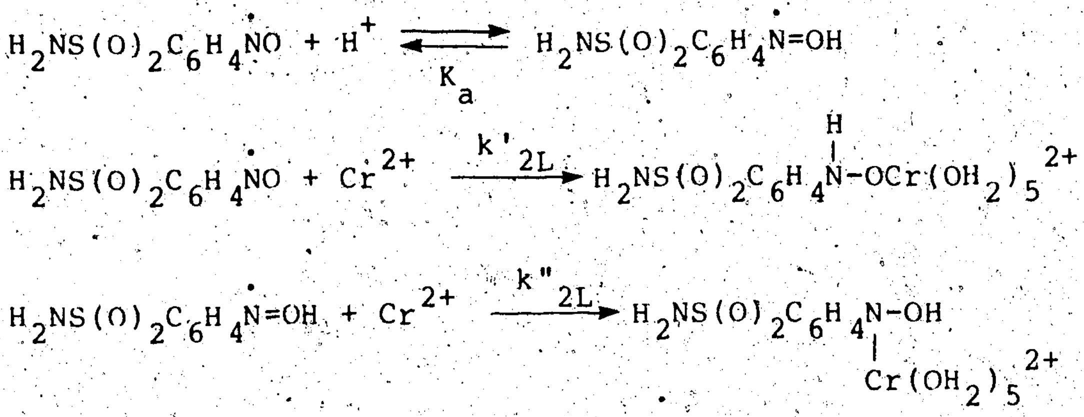
As discussed above, the results of the faster ligand stopped-flow study, ($k'_{1L}$), are consistent with reduction according to equations 5.4 and 5.5, with X ≡ H, as well as with the rate law of equation 5.6. The protonated p-nitro radical species most likely undergoes reduction via the hydroxy radical abstraction reaction of equation 5.7, (X = H). However, it is proposed that the unprotonated p-nitro radical might react to produce both the free and chromium(III) coordinated p-nitroso compound, i.e.,



$$H_2NS(O)_2C_6H_4\dot{N}O_2 + Cr^{2+} \longrightarrow H_2NS(O)_2C_6H_4N{=}O + H_2N\underset{\underset{OCr(OH_2)_5}{|}}{S}(O)C_6H_4N{=}O^{3+}$$

(5.33)

The slower stopped-flow reaction, ($k_{2L}$), which involved a small decrease in absorbance is most likely due to reduction of both the unprotonated and protonated forms of the p-nitroso radical compound.



$$\begin{aligned}
&H_2NS(O)_2C_6H_4\dot{N}O + H^+ \underset{K_a}{\rightleftharpoons} H_2NS(O)_2C_6H_4\dot{N}{=}OH \\
&H_2NS(O)_2C_6H_4\dot{N}O + Cr^{2+} \xrightarrow{k'_{2L}} H_2NS(O)_2C_6H_4\overset{\overset{H}{|}}{N}\text{-}OCr(OH_2)_5^{2+} \\
&H_2NS(O)_2C_6H_4\dot{N}{=}OH + Cr^{2+} \xrightarrow{k''_{2L}} H_2NS(O)_2C_6H_4\underset{\underset{Cr(OH_2)_5^{2+}}{|}}{N}\text{-}OH
\end{aligned}$$

(5.34)

Although the product of this reaction is unknown, the unprotonated radical would most likely react to produce the oxygen bonded chromium(III) complex, whereas the protonated species might be expected to produce the nitrogen bonded isomer. Again, some or all of the product could have a second $Cr(OH_2)_5^{3+}$ center coordinated to the sulfonamide oxygen atom.

The mechanism of equation 5.34 is consistent with the rate law

$$k_{2L} = \left(\frac{k'_{2L}K_a + k''_{2L}[H^+]}{K_a + [H^+]}\right).[Cr^{2+}] \qquad (5.35)$$

Asmus et al[106] reported the p$K_a$ of the similar $C_6H_5\dot{N}OH$ radical to be 11.7. Assuming a p$K_a$ of similar magnitude for the sulfonamido species equation 5.35 reduces to

$$k_{2L} = \left(\frac{k'_{2L}K_a}{[H^+]} + k''_{2L}\right)[Cr^{2+}] \qquad (5.36)$$

Unfortunately, the acid and chromium(II) dependence of the rate constant $k_{2L}$ could not be determined, but an upper limit of $k_{2L} \leq 1$ sec$^{-1}$ was obtained.

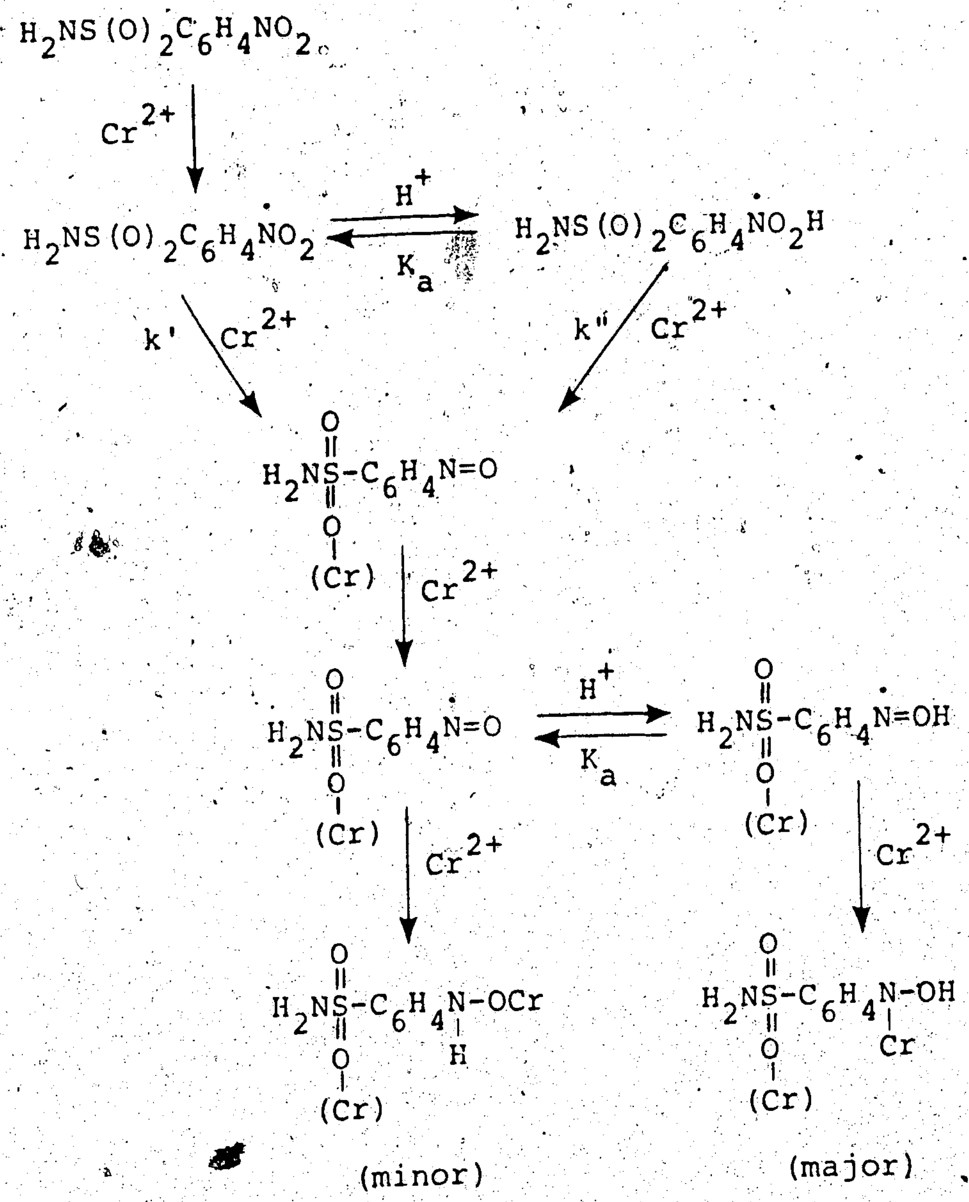
The results of the slower reduction studies, ($t_{1/2} \geq 1$ min), discussed below, suggest that the major product present at the end of the stopped-flow studies is the N-bonded chromium(III) complex. This implies that $k'_{2L}K_a/[H^+] \ll k''_{2L}$, and that $k''_{2L}[Cr^{2+}] \leq 1$ sec$^{-1}$. Since the average concentration of chromium(II) was $8.5 \times 10^{-3}$ M, this allows an upper limit for $k''_{2L}$ of ~ $10^2$ to be calculated.

The overall mechanism proposed for the stopped-flow reduction of the free ligand is shown in scheme II.

Cary 219 Studies: The stoichiometry results, (see Tables 15, 16, and 17), indicated that the ligand has

## SCHEME II

$[Cr = Cr(OH_2)_5^{3+}]$



unde[illegible]-electron reduction at the start of the slow kine[illegible] that a further 2-electron reduction occurs [illegible]rin[illegible]ow stages to yield the sulfanilamide product. [illegible] co[illegible](III) complex has undergone a 5-electron reduction [illegible] th[illegible]tart of the slow kinetics, with the extra electron c[illegible] in reducing the cobalt(III) to cobalt(II). The s[illegible]t interpretation would be that the ligand has been re[illegible]d primarily to p-hydroxylaminobenzenesulfonamide in bot[illegible]ases, although it may be present as a chromium(III) comp[illegible].

[illegible]e slower kinetics were followed on a standard Cary 219 spectrophotometer. In general these absorbance changes showed [illegible] triphasic time dependence, and were fitted by least[illegible]es to the equation

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + A_3e^{-k_3t} + A_4e^{-k_4t} + A_5e^{-k_5t} \qquad (5.37)$$

For five of the twelve runs with the ligand under various conditions, only biphasic behaviour could be resolved by computer fitting. Subsequent analysis indicated that for four of these runs this occurred because $k_{4L}$ was within a factor of 2 of $k_{5L}$, due to the differing concentration dependencies of $k_{4L}$ and $k_{5L}$. In the fifth case, the overall absorbance change was smaller because half the normal ligand concentration was used, but at normal or higher ligand concentrations, otherwise identical runs showed triphasic behaviour. For the complex the successive rate constants generally differ by a factor of 6 to 10 and the triphasic character could always be resolved.

It should be noted at the outset that extraction of rate constants from polyphasic systems inevitably is less accurate than from monophasic systems because there is always some correlation between rate constants and between pre-exponential factors. The degree of correlation is reduced for a particular step if the pre-exponential factor is large and if the rate constant is quite different from that of preceding and succeeding steps. It should also be remembered that other reactions may be going on, but may not be detected, either because they have similar rate constants, or small absorbance changes.

The results of the least-squares fits are summarized in Tables 19 and 20 for the cobalt(III) complex and the free ligand, respectively. Before these results are discussed in detail, some qualitative features should be mentioned. First of all, the most obvious difference between the two systems is that $k_{4L}$ is first order in chromium(II), while $k_{4C}$ is independent of chromium(II). Secondly, $k_{5C}$ and $k_{5L}$ are of similar magnitude, and show the same lack of $[H^+]$ and $[Cr^{2+}]$ dependence. Finally the absorbance is higher with the complex initially ($Abs_\infty + A_3 + A_4 + A_5$), and also at the end of the first, ($Abs_\infty + A_4 + A_5$), and second, ($Abs_\infty + A_5$) reactions, than it is with the ligand.

## Table 19

KINETIC PARAMETERS: CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNHSO_2C_6H_4NO_2\text{-}p^{2+}$ AT 25°C; (SLOW KINETICS; TRIPHASIC FIT).[a]

| $10^4$ [Co(III)], M | $10^3$ [Cr(II)], M | $[H^+]$, M | $Abs_\infty$ | $A_{3C}$ | $A_{4C}$ | $A_{5C}$ | $10^2$ $k_{3C}$, $sec^{-1}$ | $10^3$ $k_{4C}$, $sec^{-1}$ | $10^4$ $k_{5C}$, $sec^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.72 | 8.49 | 0.799 | 0.048 | 0.394 | 0.825 | 0.469 | 0.794 | 1.63 | 1.60 |
| 1.72 | 8.49 | 0.400 | 0.036 | 0.601 | 0.970 | 0.567 | 1.59 | 2.31 | 1.77 |
| 1.72 | 8.49 | 0.201 | 0.037 | 1.03 | 0.827 | 0.576 | 1.61 | 2.63 | 2.22 |
| 1.72 | 17.0 | 0.099 | 0.106 | 1.95 | 0.631 | 0.413 | 1.46 | 2.00 | 2.88 |
| 0.844[b] | 8.49 | 0.099 | 0.074 | 1.69 | 0.682 | 0.536 | 1.61 | 2.34 | 2.52 |
| 1.72 | 4.2[illegible] | 0.099 | 0.054 | 1.50 | 0.677 | 0.651 | 1.72 | 2.38 | 1.71 |
| 1.72 | 8.38 | 0.0497 | 0.066 | 2.12 | 0.465 | 0.491 | 1.20 | 1.33 | 2.63 |

a. Data fitted by least-squares to equation 3.48.

b. Values listed for $Abs_\infty$, $A_{3C}$, $A_{4C}$, and $A_{5C}$ are the observed values multiplied by 2; for easy comparison to runs done at $10^4\cdot$[Co(III)] = 1.72 M.

## Table 20

KINETIC PARAMETERS: CHROMIUM(II) REDUCTION OF $NH_2SO_2C_6H_4NO_2$-p AT 25°C; (SLOW KINETICS).[a]

| $10^4$ [Lig], M | $10^3$ [Cr(II)], M | $[H^+]$, M | $Abs_\infty$ | $A_{3L}$ | $A_{4L}$ | $A_{5L}$ | $10^2$ $k_{3L}$,[b] $sec^{-1}$ | $10^3$ $k_{4L}$,[c] $sec^{-1}$ | $10^4$ $k_{5L}$,[d] $sec^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.70 | 8.49 | 0.801 | 0.019 | 0.404 | 0.500 | - | 0.475 | 0.169 | - |
| 1.70 | 8.49 | 0.401 | 0.008 | 0.349 | 0.619 | - | 0.612 | 0.196 | - |
| 1.70 | 8.49 | 0.200 | 0.027 | 0.358 | 0.698 | - | 0.922 | 0.255 | |
| 1.70 | 34.0 | 0.101 | 0.041 | 0.338 | 0.579 | 0.166 | 1.47 | 1.60 | 2.12 |
| 1.70 | 17.0 | 0.101 | 0.094 | 0.373 | 0.596 | 0.159 | 1.44 | 0.866 | 1.87 |
| 1.70 | 17.0 | 0.101 | 0.041 | 0.335 | 0.621 | 0.154 | 1.39 | 0.866 | 1.54 |
| 3.40[e] | 8.49 | 0.100 | 0.052 | 0.302 | 0.379 | 0.371 | 1.30 | 0.468 | 1.71 |
| 1.70 | 8.49 | 0.101 | 0.024 | 0.323 | 0.536 | 0.234 | 1.32 | 0.443 | 1.56 |
| 0.823[f] | 8.49 | 0.100 | 0.057 | 0.309 | 0.737 | - | 1.29 | 0.426 | - |
| 1.70 | 4.25 | 0.101 | 0.017 | 0.340 | 0.754 | - | 1.21 | 0.138 | - |
| 1.70 | 8.49 | 0.0492 | 0.076 | 0.328 | 0.448 | 0.311 | 1.55 | 0.643 | 2.17 |

Footnotes for Table 20

a. Values obtained by fitting data by least-squares to equation 5.37.

b. $k_{3L} = a/(b+[H^+])$; see Table B10, Appendix B for fits.

c. $k_{4L} = (c+d[H^+]^{-1})[Cr^{2+}]$; see Table B11, Appendix B for fits.

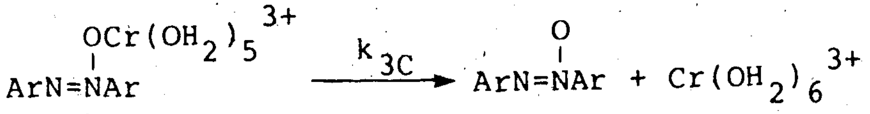
d. $k_{5L} = 1.8 \times 10^{-4}$ $sec^{-1}$; average value.

e. Values listed for $Abs_\infty$, $A_{3L}$, $A_{4L}$ and $A_{5L}$ are the observed values divided by 2; for easy comparison to runs done at $10^4 \cdot [Lig] = 1.70$ M.

f. Values listed for $Abs_\infty$, $A_{3L}$, $A_{4L}$ and $A_{5L}$ are the observed values multiplied by 2; for easy comparison to runs done at $10^4 \cdot [Lig] = 1.70$ M.

For each oxidant, a relationship has already been noted, (see pages 117-118), between the initial absorbance prior to the first slow reaction, and the direction, magnitude and acid dependence of the absorbance change for the last stopped-flow reaction, (reaction $k_{2C}$ and $k_{2L}$). Data in Tables 19 and 20 further reveal that the absorbance decrease during the first slow reaction with the complex, $A_{3C}$, is larger than that with the ligand, $A_{3L}$. In addition, $A_{3C}$ increases with decreasing acidity while $A_{3L}$ remains relatively constant. These results also parallel the absorbance changes for the last stopped-flow reaction.

These observations indicate that the initial slow reactions are different for complex and ligand, despite their similar rate constants. The rate constant, $k_{3C}$, is independent of $[Cr^{2+}]$ and appears to be independent of $[H^+]$ except possibly at the highest acidity. These observations are consistent with the slow reaction being aquation of the chromium(III)-azoxybenzenesulfonamide complex, proposed to form in the last stopped-flow step.



$$\overset{\overset{\displaystyle \mathrm{OCr(OH_2)_5^{3+}}}{|}}{\mathrm{ArN{=}NAr}} \xrightarrow{k_{3C}} \overset{\overset{\displaystyle \mathrm{O}}{|}}{\mathrm{ArN{=}NAr}} + \mathrm{Cr(OH_2)_6^{3+}} \qquad (5.38)$$

Experiments starting with the proposed azoxybenzenesulfonamide product of equation 5.38 indicate that it would be reduced rapidly to products that are essentially transparent at 350 nm.

The first slow reaction with the ligand, $k_{3L}$, shows an absorbance change, $A_{3L}$, which is essentially independent of the acidity and about equal to the smallest change observed with the complex, $A_{3C}$, (i.e., at the highest acidity). If the azoxybenzenesulfonamide derivative were formed and hydrolysed during the first slow step with the ligand, then an increase in absorbance during the stopped-flow study should have been observed with both the ligand and the cobalt complex, ($k_{2C}$ and $k_{2L}$). No increase was observed with the ligand, indicating that little or no azoxy derivative is produced from the ligand.

A consideration of the acid dependence of $k_{3L}$ and the acid independence of $k_{3C}$ further indicates that the first slow step for the ligand and the complex are due to different reactions. The values of $k_{3L}$ are independent of $[Cr^{2+}]$, but the acid dependence can be described by equation 5.39. The experimental values for $k_{3L}$ are given in Table B10,

$$k_{3L} = \frac{a}{b + [H^+]} \qquad (5.39)$$

Appendix B, where they are compared to the results of a least-squares fit to equation 5.39.

This rate law is consistent with a reaction scheme of the form:

$$AH \underset{}{\overset{K_a}{\rightleftarrows}} A^- + H^+$$

$$A^- \xrightarrow{k'_{3L}} \text{products} \qquad (5.40)$$

$$AH \xrightarrow{k''_{3L}} \text{products}$$

for which

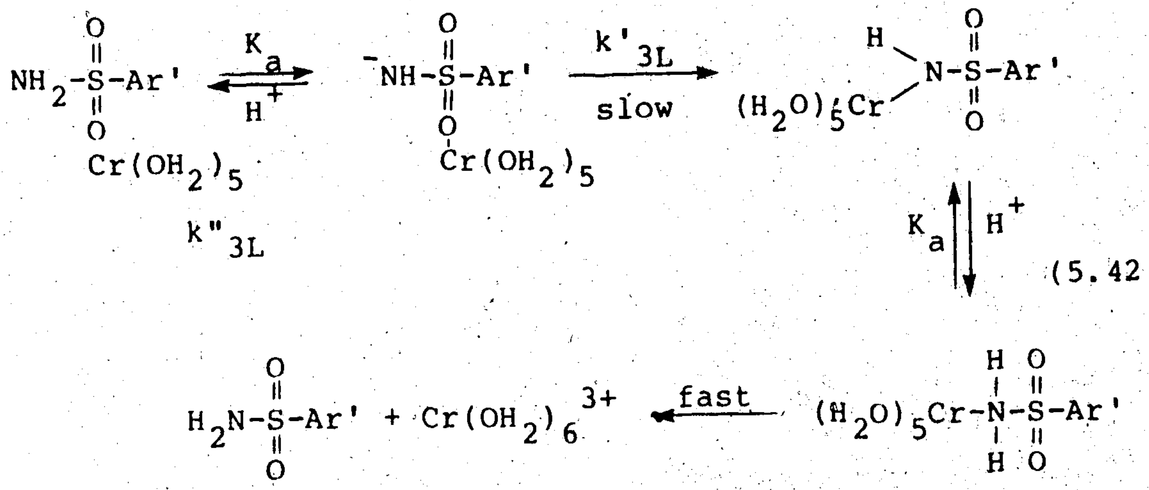
$$k_{3L} = \frac{k'_{3L}K_a + k''_{3L}[H^+]}{K_a + [H^+]} \qquad (5.41)$$

which is consistent with equation 5.39 if $k'_{3L}K_a >> k''_{3L}[H^+]$. A least-squares fit to equation 5.39 gives $b = K_a = 0.22 \pm 0.10$ M, $10^2 \cdot a = 0.42 \pm 0.12$ M $s^{-1}$ from which $k'_{3L} = 1.9 \times 10^{-2}$ $s^{-1}$.

The reaction characterized by $k_{3L}$ appears to be an aquation reaction, since the rate constant is independent of $[Cr^{2+}]$ and initial ligand concentration. However, it is unusual that aquation of the deprotonated form is much faster than the protonated form. Normally the ligand protonated form of a chromium(III) - ligand complex aquates more rapidly.[107] An inverse acid dependency of the rate is observed for some $(H_2O)_5Cr^{III}X$ complexes, due to reaction of the conjugate base $(H_2O)_4Cr(OH)(X)$. However, the acid dissociation constant for the system is expected to be < $10^{-3}$ M, which is not consistent with the value of $K_a$ =

0.22 M.

The rate law for $k_{3L}$ is consistent with the following reaction scheme, where Ar' might be $-C_6H_4NHOH$ or a chromium(III)-hydroxylamine complex.



(5.42)

It is proposed that dissociation of the $-NH_2$ proton is followed by rate controlling linkage isomerization to the nitrogen bonded chromium(III) complex, which aquates relatively rapidly in a manner analogous to the corresponding $(NH_3)_5Co^{3+}$ complexes discussed in Part A. The nitrogen bonded $N_3^-$ and $NCS^-$ complexes of $Cr(OH_2)_5^{3+}$ aquate 25 to 200 times, respectively, more rapidly than the corresponding $(NH_3)_5Co^{3+}$ complexes. If a similar factor applies to the N-bonded sulfonamide $Cr(OH_2)_5^{3+}$ complex, then aquation would be rapid relative to the observed rate constant $k_{3L}$.

A least-squares fit of the data to equation 5.41 indicates that $k''_{3L} \sim 2 \times 10^{-3}\ s^{-1}$ and cannot be accurately determined.[108]

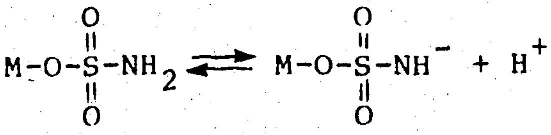
The proposed reaction scheme could be substantiated if the $K_a$ value could be estimated independently. This seems roughly possible from the following results:

$(NH_3)_5CoNH_2SO_3^{2+} \rightleftharpoons (NH_3)_5CoNHSO_3^{+} + H^{+} \quad K_a = 2 \times 10^{-6}$ M[71]

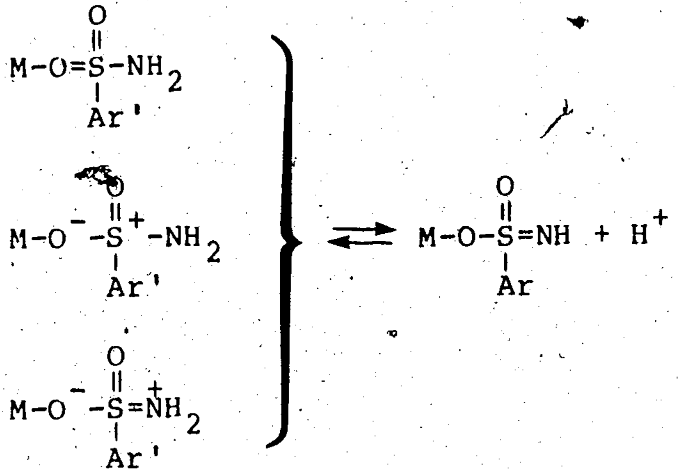
$(NH_3)_5CoOSO_2NH_2^{2+} \rightleftharpoons (NH_3)_5CoOSO_2NH^{+} + H^{+} \quad K_a = 8.5 \times 10^{-14}$ M[70]

$(NH_3)_5CoNH_2SO_2Ar' \rightleftharpoons (NH_3)_5CoNHSO_2Ar' + H^{+} \quad K_a \gtrsim 5$ M

From the first two reactions, the change from nitrogen to oxygen coordination reduces the $K_a$ by ~ $10^8$, and if the same factor is applied to the third reaction, then a value of $K_a \gtrsim 5 \times 10^{-8}$ M can be predicted for $(NH_3)_5CoOSO(NH_2)Ar'$. Replacement of $(NH_3)_5Co^{3+}$ by $(H_2O)_5Cr^{3+}$ might increase the value somewhat, but it is still smaller than the observed $K_a$ = 0.22 M. However, a more detailed examination of the sulfamate and sulfonamide systems indicates that the O-isomer acidities might not be as analagous as implied above. This may be seen from the following simple valence bond structures, where M ≡ $(H_2O)_5Cr^{3+}$.

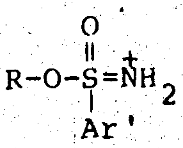


$$M\text{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}NH_2 \rightleftharpoons M\text{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}NH^- + H^+ \qquad (5.43)$$



$$\left.\begin{array}{l} M\text{-}O{=}\underset{\underset{Ar'}{|}}{\overset{\overset{O}{\|}}{S}}\text{-}NH_2 \\ M\text{-}O^-\text{-}\underset{\underset{Ar'}{|}}{\overset{\overset{O}{\|}}{S^+}}\text{-}NH_2 \\ M\text{-}O^-\text{-}\underset{\underset{Ar'}{|}}{\overset{\overset{O}{\|}}{S}}{=}\overset{+}{N}H_2 \end{array}\right\} \rightleftharpoons M\text{-}O\text{-}\underset{\underset{Ar}{|}}{\overset{\overset{O}{\|}}{S}}{=}NH + H^+ \qquad (5.44)$$

The oxygen coordination of a metal ion favours the two lower structures with the aromatic sulfonamide, increasing the positive charge on the nitrogen, and thereby increasing the acidity of the $-NH_2$ protons. Analogous structures are not required for the oxygen bonded sulfamato complex. It remains debatable what the magnitude of this effect should be, but the acidity might be similar to that of



$$R\text{-}O\text{-}\underset{\underset{Ar'}{|}}{\overset{\overset{O}{\|}}{S}}{=}\overset{+}{N}H_2$$

Unfortunately, no $K_a$ values are available to date for such imidoarylsulfonic acid esters.

These results imply that aquation of the $(H_2O)_5CrOSO(NH_2)_2{}^{3+}$ inner-sphere product, (observed briefly as reported in Part B, see pages 76-78), should also occur via the mechanism of equation 5.42, and that our earlier assumption that the observed aquation rate constant should be independent of $[H^+]$, is suspect on the basis of this new proposal. The valence bond structures for the aromatic sulfonamides, (equation 5.44), are applicable to the sulfonamido derivative, with Ar ≡ $NH_2$. Therefore a comparison of the following $K_a$ values should be meaningful

| | |
|---|---|
| $(NH_3)_5CoNH_2SO_2C_6H_4CH_3\text{-}p^{3+}$ | $K_a > 5.3$ M |
| $(H_2O)_5CrOSO(NH_2)C_6H_4CH_3\text{-}p^{3+}$ | $K_a = 0.22$ M |
| $(NH_3)_5CoNH_2SO_2NH_2^{3+}$ | $K_a = 0.55$ M |

from which a value of $K_a \sim 0.02$ M can be predicted for $(H_2O)_5CrOSO(NH_2)_2^{3+}$. Then equation 5.41 reduces to

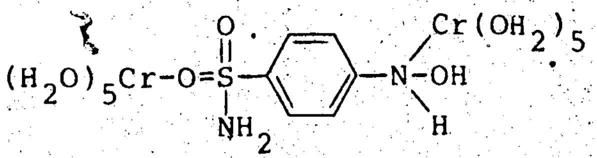
$$k_{3L} = \frac{k'_{3L}K_a}{[H^+]} + k''_{3L} \qquad (5.45)$$

if $[H^+] >> K_a \sim 0.02$ M. This analysis predicts that the rate of aquation of $(H_2O)_5CrOSO(NH_2)_2^{3+}$ should decrease with increasing acidity under normal conditions.

To test this prediction an experiment similar to that described in Part B (pages 76-78) was repeated with $[Cr^{2+}] = 0.20$ M as before, but $[H^+]$ was increased to 0.40 M. Under these conditions a reduction half-time of 24 sec is predicted at λ = 400 nm. The semilogarithmic plot produced a $t_{1/2} = 20$ sec at λ = 400 nm and a $t_{1/2} = 240$ sec at

430 nm. The increase in $t_{1/2}$ at 430 nm from 60 sec to 240 sec as $[H^+]$ is increased from 0.1 to 0.4 M verifies that aquation of the transient $(H_2O)_5CrOSO(NH_2)_2{}^{3+}$ inner sphere product is indeed slower at higher acidity. This substantiates the assignment of the $k_{3L}$ reaction to aquation of a chromium(III) coordinated sulfonamido product.

A second problem with the proposed mechanism, (equation 5.42), is the substantial absorbance change associated with $k_{3L}$. An initially $1.7 \times 10^{-4}$ M solution of ligand shows about a 0.30 absorbance change in a 5 cm path length cell. This corresponds to a change in molar extinction coefficient of ~ 350 $M^{-1}$ $cm^{-1}$ at 350 nm. It has been noted previously that the visible spectra of $(H_2O)_5CrOSO_3{}^+$, $(H_2O)_5CrOSO_2NH_2{}^{2+}$, and probably $(H_2O)_3CrOSO(NH_2)_2{}^{3+}$ are similar and do not have significant absorbance at 350 nm. Therefore the change of ~350 $M^{-1}$ $cm^{-1}$ in the molar extinction coefficient must be attributed to the presence of the aryl-hydroxylamine function:

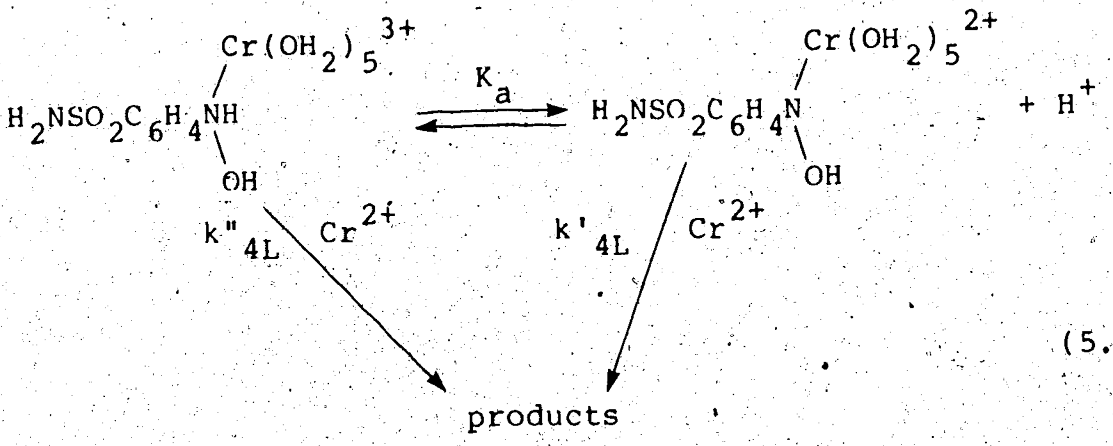


The data obtained for the second slow reaction with the ligand could be accurately fitted to

$$k_{4L} = \left( \frac{c}{[H^+]} + d \right) [Cr^{2+}] \qquad (5.46)$$

The experimental results for $k_{4L}$ are compared to the results of a least-squares fit to equation 5.46 in Table B11, Appendix B. When $[H^+]$ = 0.2, 0.4 or 0.8 M this reaction cannot be resolved from the last slow reaction, ($k_{5L}$), consistent with the value of $k_{4L}$ falling to less than 2 times $k_{5L}$ at high acidity. There is a similar problem at the lowest $[Cr^{2+}]$, also caused by $k_{4L} \simeq k_{5L}$. From the results at higher $[Cr^{2+}]$ and lower $[H^+]$, when these two reactions are well resolved, it appears that the absorbance change for $k_{4L}$ is 2 → 3 times larger than that observed for $k_{5L}$, so that when the two reactions cannot be resolved, the absorbance change is dominated by the $k_{4L}$ contribution.

The rate law for $k_{4L}$, (equation 5.46), is consistent with the following reaction scheme involving reduction of the hydroxylamine function.



(5.47)

This scheme predicts that

$$k_{4L} = \left(\frac{k'_{4L}\,K_a + k''_{4L}[H^+]}{K_a + [H^+]}\right)[Cr^{2+}] \qquad (5.48)$$

which is consistent with equation 5.46, with $c = k'_{4L}K_a$ and $d = k''_{4L}$ if $[H^+] \equiv 0.05 \gg K_a$. The values obtained for $k'_{4L}K_a$ and $k''_{4L}$ from the least-squares fit to equation 5.46 were $3.0 \pm 1.1 \times 10^{-3}\ s^{-1}$ and $1.6 \pm 0.8 \times 10^{-2}\ M^{-1}\ s^{-1}$, respectively. An estimate of $K_a$ can be made from the following results.

$$NH_3OH^+ \rightleftharpoons NH_2OH + H^+ \qquad pK_a = 6$$

$$(NH_3)_5IrNH_2OH \rightleftharpoons (NH_3)_5IrNHOH + H^+ \qquad pK_a = 9.4$$ [109]

$$C_6H_5NH_2OH^+ \rightleftharpoons C_6H_5NHOH + H^+ \qquad pK_a \sim 1$$ [110]

On this basis the $pK_a$ of $(H_2O)_5CrNH\genfrac{}{}{0pt}{}{Ar}{OH}$ should be 3 to 4 units larger than for free $ArNH_2OH^+$, or $K_a \sim 10^{-4}$ to $10^{-5}$. This estimate is consistent with the above condition that $K_a \ll 0.05$ M, and gives a magnitude for $k'_{4L}$ of the order of 0.03 to 0.3 $M^{-1}\ s^{-1}$.

Schmidt et al.[111] have studied the reduction of hydroxylamine and a variety of amine oxides in aqueous acid. Oxygen-18 tracer experiments, radical polymerization initiation, and failure to detect a chromium(III)-amine product are consistent with direct attack by chromium(III) on the oxygen atom, followed by hydroxy radical abstraction. The amine radical produced could then react by [illegible]g a hydrogen atom from the coordination sphere of [illegible] i.e.

$$\begin{aligned} R_1R_2R_3NOH^+ \; Cr^{2+} &\xrightarrow{slow} R_1R_2R_3\dot{N}^+ + Cr^{III}OH^{2+} \\ R_1R_2R_3\dot{N}^+ + Cr^{2+} &\longrightarrow R_1R_2R_3NH^+ + Cr^{III}OH^{2+} \end{aligned} \qquad (5.49)$$

Their results are given in Table 21, along with the results of the present study. The $Cr(OH_2)_5^{3+}$ would be expected to destabilize the $R_1R_2R_3\dot{N}^+$ radical intermediate and reduce the rate relative to $(CH_3)_3NOH^+$ and $(CH_3)_2C_6H_5NOH^+$ as observed. The lack of an $[H^+]^{-1}$ term in the rate law for the systems studied by Schmidt et al.[111] can be attributed to the absence of an NH proton in two cases, and to the smaller $K_a$ and high acid range, (0.095-0.485 M), studied with $NH_3OH^+$.

The final slow step has a rate constant, $k_{5L}$, in the range of $1.5 \times 10^{-4}$ to $2.2 \times 10^{-4}$ $s^{-1}$. The smaller absorbance change and sometimes similar rate to the preceding step did not allow the rate to be resolved at all acidities. However, the range of values at 0.1 M $H^+$ and the single value at 0.05 M $H^+$ do not indicate any acid dependency for $k_{5L}$. Similarly $k_{5L}$ does not appear to have any chromium(II) dependence. This reaction is tentatively assigned to aquation of a chromium(III)-amine complex,

$$(H_2O)_5CrNH_2C_6H_4SO_2NH_2^{3+} + H_2O \xrightarrow{H^+} Cr(OH_2)_6^{3+} + NH_3C_6H_4SO_2NH_2^{+} \qquad (5.50)$$

A separate study of the chromium(II) reduction of p-

# Table 21

## RATE CONSTANTS FOR CHROMIUM(II) REDUCTION OF AMINE OXIDES, $R_1R_2R_3NOH^+$

| $R_1$ | $R_2$ | $R_3$ | $pK_a$ at 25°C | k, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| H | H | H | 6 | 0.0141[a] |
| $CH_3$ | $CH_3$ | $CH_3$ | 4.65 | 0.66[a] |
| $CH_3$ | $CH_3$ | $C_6H_5$ | 4.21 | 36.0[a] |
| $Cr(OH_2)_5^{3+}$ | H | $C_6H_4SO_2NH_2$ | $\geq$ 4 | 0.016 |

a. Schmidt, W.; Swinehart, J.H.; Taube, H. Inorg. Chem. 1968, 7, 1984.

nitrosobenzenesulfonamide confirms the observations on the slow kinetics for the ligand reduction and indicates that the nitroso derivative is an intermediate in the reduction of p-nitrobenzenesulfonamide. No attempt was made to study the first slow reaction, and the results of a least-squares best-fit to a biphasic exponential equation are given in Table 22. It was found that the step corresponding to $k_{4L}'$, referred to as $k_{4NO}$, was first order in [Cr(II)], showed the same acid dependence, essentially the same rate constant and a similar absorbance change of ~ 0.4 to 0.5 units at the same oxidant concentrations. The data analysis was complicated in the same way in that $k_{4NO}$ and $k_{5NO}$ could not be resolved at the three highest acidities, and the lowest [Cr(II)], apparently because the rates are too similar.

Since the $k_{5NO}$ step could only be detected for $[H^+] <$ 0.1 M and $[Cr(II)] > 8.5 \times 10^{-3}$ M, it could not be characterized, but the rate constant was fixed at $1.8 \times 10^{-4}$ $sec^{-1}$, consistent with the p-nitro ligand results. Then the value of $A_{5NO}$ was in the range of 0.14 to 0.19, consistent with the $A_{5L}$ values from the p-nitro ligand study.

The first slow reaction for the complex already has been assigned to decomposition of the azoxybenzenesulfonamido chromium(III) byproduct. The second and third slow reactions for the complex do not seem to show any chromium(II) dependence. This is surprising since the stoichiometry studies indicate that 2 moles of chromium(II)

## Table 22

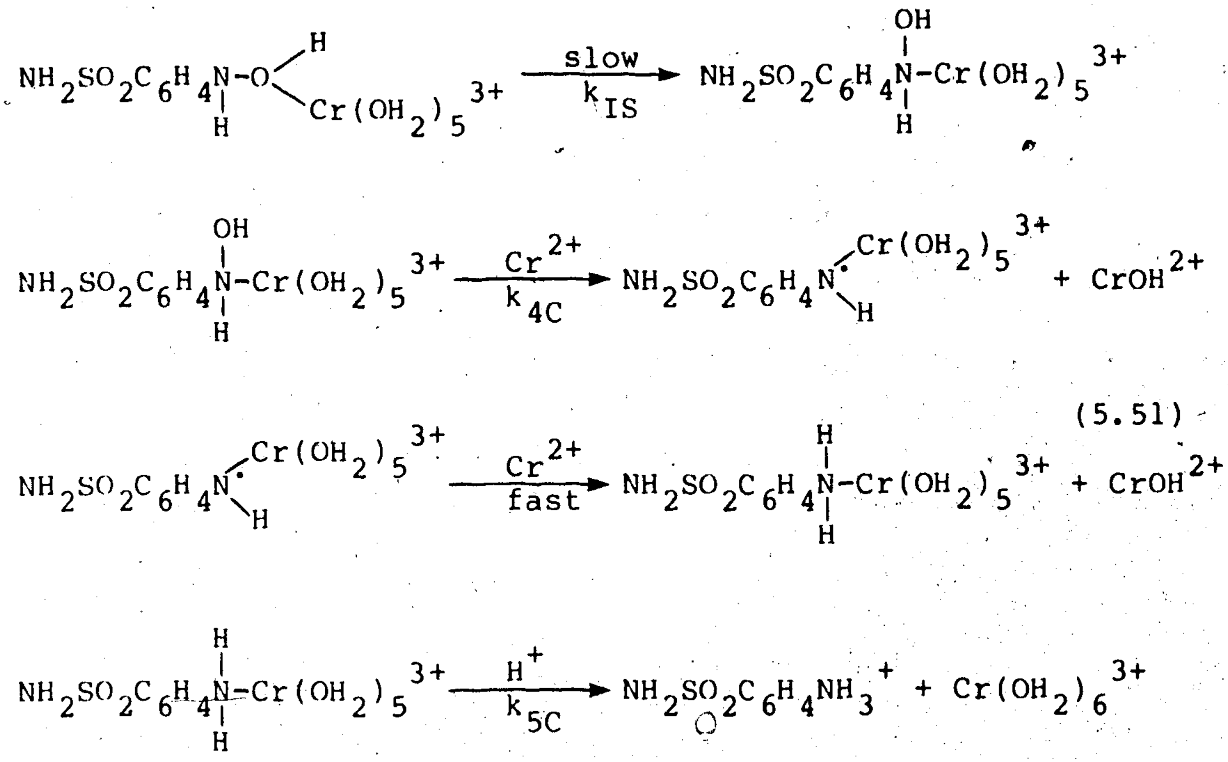
KINETIC PARAMETERS: CHROMIUM(II) REDUCTION OF $NH_2SO_2C_6H_4NO$-p AT 25°C.[a]

| $10^4$ [Lig], M | $10^3$ [Cr(II)], M | $[H^+]$, M | $Abs_\infty$ | $A_{4NO}$ | $A_{5NO}$ | $10^3$ $k_{4NO}$, $sec^{-1}$ | $10^2$ $k_{4NO}/[Cr]$, $M^{-1}sec^{-1}$ | $10^2$ $k_{4L}/[Cr]$, $M^{-1}sec^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1.70 | 8.52 | 0.800 | 0.094 | 0.425 | - | 0.216 | 2.54 | 1.99 |
| 1.70 | 8.52 | 0.400 | 0.132 | 0.542 | - | 0.231 | 2.71 | 2.31 |
| 1.70 | 8.52 | 0.200 | 0.110 | 0.520 | - | 0.285 | 3.34 | 3.00 |
| 1.70 | 25.6 | 0.100 | 0.081 | 0.400 | 0.147 | 1.43 | 5.58 | 4.70 |
| 1.70 | 17.0 | 0.100 | 0.099 | 0.398 | 0.160 | 0.868 | 5.10 | 5.09 |
| 1.70 | 8.57 | 0.100 | 0.126 | 0.454 | 0.184 | 0.377 | 4.40 | 5.25 |
| 1.70 | 4.03 | 0.100 | 0.181 | 0.530 | - | 0.181 | 4.49 | 3.25 |
| 1.70 | 8.52 | 0.050 | 0.107 | 0.324 | 0.189 | 0.663 | 7.78 | 7.57 |

a. Data fitted by least-squares to: $Abs_t = Abs_\infty + A_{4NO}e^{-k_{4NO}t} + A_{5NO}e^{-k_{5NO}t}$ holding $k_{5NO}$ fixed at 1.8 x $10^{-2}$ $sec^{-1}$, the value obtained for $k_{5L}$ in the p-nitrobenzenesulfonamide study, (see Table 18).

must be consumed per mole of cobalt(III) during these slow stages, and the second stage with the ligand is first order in chromium(II). The lack of a chromium(II) dependence for $k_{4C}$ and $k_{5C}$ could be due to other reactions with similar rates, but larger absorbance changes, and/or to some slower step preceding, and rate limiting, the reduction step. The latter possibility does not seem entirely consistent with the fact that the $k_{4C}$ reduction rate is always greater than the $k_{4L}$ rate under similar conditions of $[H^+]$ and $[Cr(II)]$. The other noteable difference between ligand and complex is that $A_{5C}$ is 2 to 3 times larger than $A_{5L}$, i.e., the absorbance change for the last reaction is much larger with the complex than it is with the ligand.

The qualitative observations outlined above seem most consistent with failure to resolve a reduction step in the absorbance-time data for the cobalt complex. A consideration of the proposals for the fast steps indicate that the major product at the start of the Cary 219 studies on the complex should be the O-bonded p-hydroxylaminobenzenesulfonamido chromium(III) complex, $p\text{-}NH_2SO_2C_6H_4N(H)OCr(OH_2)_5{}^{2+}$. Chromium(II) reduction of this species should be slow if the hydroxy radical abstraction mechanism, discussed above, is the favoured path. This is consistent with the observations of Schmidt et al.[111] that $NH_3OCH_3{}^+$ is reduced much slower than $NH_3OH^+$ under similar conditions. Linkage isomerization would produce the same N-bonded p-hydroxylaminobenzenesulfonamido chromium(III) complex, as proposed with the ligand, and this would be reduced as in the ligand systems



$$NH_2SO_2C_6H_4\underset{H}{N}\text{-}O\begin{smallmatrix}H\\Cr(OH_2)_5\end{smallmatrix}{}^{3+} \xrightarrow[k_{IS}]{\text{slow}} NH_2SO_2C_6H_4\overset{OH}{\underset{H}{N}}\text{-}Cr(OH_2)_5{}^{3+}$$

$$NH_2SO_2C_6H_4\overset{OH}{\underset{H}{N}}\text{-}Cr(OH_2)_5{}^{3+} \xrightarrow[k_{4C}]{Cr^{2+}} NH_2SO_2C_6H_4\dot{N}\begin{smallmatrix}Cr(OH_2)_5{}^{3+}\\H\end{smallmatrix} + CrOH^{2+}$$

(5.51)

$$NH_2SO_2C_6H_4\dot{N}\begin{smallmatrix}Cr(OH_2)_5{}^{3+}\\H\end{smallmatrix} \xrightarrow[\text{fast}]{Cr^{2+}} NH_2SO_2C_6H_4\overset{H}{\underset{H}{N}}\text{-}Cr(OH_2)_5{}^{3+} + CrOH^{2+}$$

$$NH_2SO_2C_6H_4\overset{H}{\underset{H}{N}}\text{-}Cr(OH_2)_5{}^{3+} \xrightarrow[k_{5C}]{H^+} NH_2SO_2C_6H_4NH_3{}^+ + Cr(OH_2)_6{}^{3+}$$

If the linkage isomerization step were rate limiting then the observed reaction would be independent of $[Cr^{2+}]$.

Before trying to support such a reaction scheme it must be admitted that fitting of the absorbance-time data clearly indicate three kinetically distinguishable steps with rate constants differing by about a factor of ten. The only peculiarities in the fitting parameters are that the values of $k_{4C}$ are significantly lower at the highest and lowest acidities, an unusual but not impossible situation, and the values of $A_{5C}$ increase with decreasing [Cr(II)], while $k_{5C}$ decreases somewhat with decreasing [Cr(II)]. Bearing in mind the complexity of the fits, these peculiarities are at best hints, rather than compelling reasons, for suggesting even more complex kinetic behaviour.

If the proposed reaction scheme is to be consistent with the results, the absorbance-time data actually consists of four steps, and should be described by the equation

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + A^*_{3C} e^{-k_{3C} t} + A_{IS} e^{-k_{IS} t} + A^*_{4C} e^{-k^*_{4C} t} + A^*_{5C} e^{-k^*_{5C} t} \quad (5.52)$$

where $k_{3C}$, $k_{IS}$, $k^*_{4C}$ and $k^*_{5C}$ are the rate constants for aquation of the chromium(III)-azoxybenzenesulfonamide byproduct, isomerization of the O-bonded p-hydroylaminobenzenesulfonamido chromium(III) complex, reduction of the N-bonded p-hydroxylaminobenzenesulfonamido chromium(III) complex, and aquation of the chromium(III)-sulfanilamide product, respectively. The last two reactions, $k^*_{4C}$ and $k^*_{5C}$, should have the same rate as the corresponding reactions in the ligand study, i.e., $k_{4L}$ and $k_{5L}$. Therefore, $k^*_{4C}$ should be given by equation 5.46 and $k^*_{5C} \simeq 1.8 \times 10^{-4}$ sec$^{-1}$; also $A^*_{4C} \simeq A_{4L} \simeq 0.58$ and $A^*_{5C} \simeq A_{5L} \simeq 0.2$, based on mid-range values from the ligand study. The absorbance-time data were refitted to equation 5.52 with fixed parameters $k_{3C} = 1.6 \times 10^{-2}$ sec$^{-1}$, a typical value from the triphasic fits, and $k^*_{4C}$, $k^*_{5C}$ and $A^*_{5C}$ as obtained in the ligand study for $k_{4L}$, $k_{5L}$ and $A_{5L}$, (see Table 20).

The resulting values of $Abs_\infty$, $A^*_{3C}$, $A_{IS}$, $A^*_{4C}$ and $k_{IS}$ are given in Table 23. For two of the seven runs, the parameters $A^*_{3C}$, $A_{IS}$ and $k_{IS}$ were undefined as judged by their 95% confidence limits. These two runs are at the lowest acidity and the highest chromium(II) concentration, respectively. It remains unclear why these do not fit satisfactorily, but it may be related to the fact that they have the largest $k^*_{4C}$ values, and these are within about a factor of 3 of the $k_{IS}$ values expected on the basis of the other runs. Aside from these two runs, the values obtained for $k_{IS}$ are reasonably constant, and well defined judging from the confidence limits. The values of $A^*_{4C}$ at 0.10 M $H^+$ (~ 0.48) are also similar to the values of $A_{4L}$ from the free ligand system (~ 0.58), considering that the pre-exponential term $A^*_{5C}$ was fixed here, but was a fitting parameter for the ligand system.

It is concluded from this analysis that the data at least are not inconsistent with a qualitatively unobservable intermediate slow step, ($k_{4C}$), in the cobalt(III) system, attributed to isomerization followed by reduction and aquation steps with the same kinetic features as observed with the ligand. Although this proposal is more speculative than one might like, it seems more reasonable than other triphasic mechanistic schemes which would require rapid reduction of intermediates in order to explain the apparent lack of chromium(II) dependence of the slow steps observed

## Table 23

KINETIC PARAMETERS: CHROMIUM(II) REDUCTION OF $(NH_3)_5CoNHSO_2C_6H_4NO_2\text{-}p^{2+}$ AT 25°C; (TETRAPHASIC FIT).[a]

| $10^4$ [Co(III)], M | $10^3$ [Cr(II)], M | $[H^+]$, M | $Abs_\infty$ | $A^*_{3C}$ | $A_{IS}$ | $A^*_{4C}$ | $10^3$ $k_{IS}$, $sec^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1.72 | 8.49 | 0.799 | 0.054 | 0.296 | 0.955 | 0.291 | 2.00 |
| 1.72 | 8.49 | 0.400 | 0.045 | 0.560 | 0.957 | 0.399 | 2.54 |
| 1.72 | 8.49 | 0.201 | 0.037 | 0.996 | 0.815 | 0.408 | 2.84 |
| 1.72 | 17.0 | 0.099 | 0.098 | 1.66 | 0.573 | 0.575 | 5.93 |
| 0.844[b] | 8.49 | 0.099 | 0.073 | 1.59 | 0.618 | 0.470 | 3.40 |
| 1.72 | 4.25 | 0.099 | 0.068 | 1.44 | 0.609 | 0.495 | 2.71 |
| 1.72 | 8.38 | 0.0497 | 0.066 | 0.836 | 1.40 | 0.691 | 10.2 |

a. Values obtained by fitting data by least-squares to equation 3.63, holding $k_{3C} = 1.6 \times 10^{-2}$ $sec^{-1}$ and $k^*_{4C}$, $k^*_{5C}$ and $a^*_{5C}$ as obtained in ligand study, see Table 18.

b. Values listed for $Abs_\infty$, $A^*_{3C}$, $A_{IS}$ and $A^*_{4C}$ are the observed values multiplied by 2; for easy comparison to runs done at $10^4 \cdot [Co(III)] = 1.72$ M.

with the cobalt(III) complex. Rapid reduction of the O-bonded p-hydroxylaminobenzenesulfonamido chromium(III) species seems inconsistent with the observations on the free ligand, and with the observations of Schmidt et al.[111] on hydroxylamine analogues.

# CHAPTER VI

## SUMMARY AND CONCLUSIONS PART C

There are many similarities between the chromium(II) reduction reactions of p-nitrobenzenesulfonamide and its $(NH_3)_5Co(III)$ complex. In both cases reduction to the p-hydroxylamino derivative occurs on the stopped-flow time scale, and further reduction and aquation yielding free sulfanilamide requires several hours. In both systems the first detectable intermediate is the p-nitro radical derivative, and reduction of this species has the same rate law and rate constants, within experimental error, for both systems. The final slow reaction also is kinetically the same in both systems, and has been assigned to aquation of a chromium(III) sulfanilamide product.

At the intermediate stages of reduction the major differences arise because reduction of the cobalt(III) results in the incorporation of one more chromium(III) than is present in the free ligand system. This extra chromium(III) generally serves to inhibit further reduction. Thus, the chromium(III)-nitroso intermediate, $p\text{-}NH_2SO_2C_6H_4N{=}OCr(OH_2)_5{}^{3+}$, is not rapidly reduced and can couple with the chromium(III)-hydroxylamino intermediate to produce the azoxybenzenesulfonamide derivative. Similarly, the chromium(III)-hydroxylamino intermediate, p-$NH_2SO_2C_6H_4NHO(H)Cr(OH_2)_5^{3+}$, is not readily reduced, but isomerizes to the nitrogen-bonded isomer prior to reduction. Reduction of this intermediate would normally proceed by hydroxy-radical abstraction, but this is prevented by the oxygen bonded chromium(III).

One purpose of this study was to obtain information on the intramolecular electron transfer rate, ($k_{e.t.}$), in the initial p-nitrobenzenesulfonamido radical, i.e.,

$$\underset{\text{(VI-1)}}{(NH_3)_5CoNHSO_2C_6H_4\dot{N}O_2\text{-}p^+} \xrightarrow[H^+]{k_{e.t.}} Co^{2+} + 5NH_4^+ + NH_2SO_2C_6H_4NO_2\text{-}p \qquad (6.1)$$

Such rates have been measured with the analagous carboxylate complex $(NH_3)_5CoO_2CC_6H_4\dot{N}O_2\text{-}p^+$, ($k_{e.t.} = 2.6 \times 10^3\ sec^{-1}$ at 25°C and pH 7).[27,28] Although the initial report suggested that the carboxylate group facilitates electron transfer,[27] it is now believed to act as an insulator, retarding the transfer of an electron through the bridging ligand.[28,112,113] It was hoped that the present study would indicate the relative insulating capacity of the $-NHSO_2-$ group.

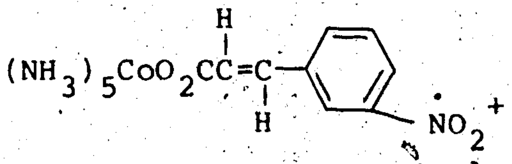
The p-nitrobenzenesulfonamido radical intermediate, (VI-1), was identified by the similarity of its electronic spectrum to that reported for the $(NH_3)_5CoO_2CC_6H_4\dot{N}O_2\text{-}p^+$ radicals generated by pulse radiolysis.[28] The similiarity of the absorption spectra of the free and $Co^{III}$ coordinated nitro radical indicates that coordination of the electron withdrawing 3+ metal center has little effect on the electronic energy levels involved in the observed transitions of the ligand radical, implying that the $-NHSO_2-$ linkage does insulate the nitro and aromatic electronic systems from the metal ion.

Unfortunately, the intramolecular electron transfer rate constant for the reaction represented by equation 6.1 was not obtainable for this system. This reaction must be slow compared to further reduction by Cr(II), since even when equivalent amounts of chromium(II) and cobalt(III) are employed, only 20% of the cobalt(III) is reduced.[114] In addition, if intramolecular electron transfer rates were fast, subsequent reactions in the cobalt(III) system should be identical to those observed with the free ligand, which they were not.

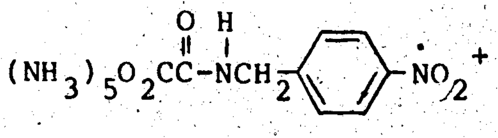
If it is assumed, consistent with Hoffman's observations,[28] that only the deprotonated nitro radical undergoes intramolecular electron transfer, then an upper limit for the rate constant $k_{e.t.}$ of equation 6.1 is given by:

$$k_{e.t.} < \frac{k'K_a[Cr^{2+}]}{[H^+]} = \frac{84.3\ (8.61 \times 10^{-3})}{0.4} = 1.8\ \text{sec}^{-1}$$

This value is ~ $10^3$ times smaller than the corresponding value reported for the carboxylate derivative,[28] ($2.6 \times 10^3$ $s^{-1}$), suggesting that the $-NHSO_2^-$ group is an even less favourable bridge for electron transfer. In fact, $k_{e.t.}$ is closer in magnitude to the analogous rate constants reported for (VI-2) and (VI-3) for non-resonance assisted through chain electron transfer.[29] Hoffman has attributed the increased value of $k_{e.t.}$ for the p-nitrobenzoato derivative with respect to (VI-2) and (VI-3) to the substantial electron spin density at the carbon atom para to the nitro group (~ 16-17%),[28,29] determined via E.S.R. spectroscopy.[115] For the sulfonamide derivative the present results suggest either a lower electron spin density on the para carbon, or lower electron permeability of the sulfonamide linkage with respect to the carboxylate group.



(VI-2); $k_{e.t.} = 3.1\ s^{-1}$



(VI-3); $k_{e.t.} = 5.8\ s^{-1}$

Finally, the observations in this system also provide potentially useful information for the preparation of amine and hydroxylamine derivative complexes of $Cr(OH_2)_5^{3+}$. It appears that with appropriate control of the stoichiometry and reaction times, these complexes can be prepared in solution by reduction of the appropriate nitro or nitroso ligand derivative.

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108. Although the lower limit estimated in Part A for aquation of the analogous $(H_2O)_5CrOSO(NH_2)C_6H_4CH_3\text{-}p^{3+}$ complex was $k_{2h} > 0.1\ s^{-1}$, (see page 83), this prediction assumed direct aquation of the O-bonded isomer. It now seems that aquation occurs via prior isomerization to the N-bonded form, as shown in equation 5.42.

The attempt to observe a Cr(III) intermediate during reduction of $(NH_3)_5CoNHSO_2C_6H_4CH_3\text{-}p^{2+}$, (page 83), assumed that aquation of the intermediate was independent of $[H^+]$. However the additional information available now indicates that the rate of aquation of $(H_2O)_5CrOSO(NH_2)C_6H_4CH_3\text{-}p^{3+}$ should be given by equation 5.39, with $a = k'_{3L}\ K_a \approx 0.4\ s^{-1}$ and $b = K_a \approx 0.2$ M. Under the conditions empl[illegible] $[H^+]$ 0.05~~2 M;~~ $[Cr^{2+}] = 0.08$ M), $k_{3L} \approx 1.6 \times 10$[illegible] whereas reduction of the Co(III) reactant,

$k_r = 5.6 \times 10^{-3}$ sec$^{-1}$. Calculations show that a maximum of ~ 17% of the p-toluenesulfonamide would be present as the Cr(III) intermediate after ~ 100 sec.

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114. Note that the 20% Cobalt(II) obtained is attributed to chromium(II) reduction of the p-nitro radical complex (VI-1), and the p-nitroso radical complex (see Scheme I), not the intramolecular electron transfer reaction of equation 6.1

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# APPENDIX A

## TREATMENT OF DATA FOR CONSECUTIVE REACTIONS

Considering the sequence of two irreversible pseudo first order reactions,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{(A-1)}$$

where $k_1$ and $k_2$ are the observed pseudo first order rate constants, the differential rate equations are:

$$\frac{-d[A]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \text{(A-2)}$$

$$\frac{d[C]}{dt} = k_2[B]$$

Integration of these equations, assuming that at $t=0$ $[A] = [A]_0$ and $[B] = [C] = 0$, then the concentrations at any time t in terms of $[A]_0$ are:

$$[A] = [A]_0 \, e^{-k_1 t}$$

$$[B] = [A]_0 \frac{k_1}{k_2-k_1} (e^{-k_1 t} - e^{-k_2 t}) \qquad \text{(A-3)}$$

$$[C] = [A]_0 \, (1 - \frac{k_2}{k_2-k_1} e^{-k_1 t} + \frac{k_1}{k_2-k_1} e^{-k_2 t}$$

The absorbance at time t, $(Abs_t)$, of the reacting solution in a cell of path length 1 cm, is given by:

$$\mathrm{Abs}_t = \varepsilon_a[\mathrm{A}] + \varepsilon_b[\mathrm{B}] + \varepsilon_c[\mathrm{C}] \qquad \text{(A-4)}$$

where $\varepsilon_a$, $\varepsilon_b$ and $\varepsilon_c$ are the molar absorptivities of A, B and C, respectively. Substitution of equations A-3 into equation A-4 followed by rearrangement of terms gives:

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \qquad \text{(A-5)}$$

where $\mathrm{Abs}_\infty = \varepsilon_c[\mathrm{A}]_0$ and:

$$A_1 = [\mathrm{A}]_0\left(\varepsilon_a + \frac{\varepsilon_b k_1 - \varepsilon_c k_2}{k_2 - k_1}\right)$$

$$\text{(A-6}$$

$$A_2 = [\mathrm{A}]_0 \frac{k_1}{k_1 - k_2}(\varepsilon_b - \varepsilon_c)$$

The data were fitted by non-linear least-squares to equation A-5, where $\mathrm{Abs}_t$ and t are the knowns and $\mathrm{Abs}_\infty$, $A_1$, $k_1$, $A_2$ and $k_2$ are the fitting parameters.

# APPENDIX B

## Table B1

## AQUATION KINETIC DATA FOR $(NH_3)_5CoNHSO_2NH_2^{2+}$.[a]

| temp, | $[H^+]$, | $10^4[Co(III)]$, | $10^3 \cdot k_{obsd}$, $sec^{-1}$ | |
|---|---|---|---|---|
| °C | M | M | obsd | calc[b] |
| 15.0 | 0.0200 | 1.48 | 0.148 | 0.144 |
| | 0.0200 | 1.48 | 0.148 | 0.144 |
| | 0.0250 | 1.39 | 0.181 | 0.178 |
| | 0.0250 | 1.47 | 0.180 | 0.178 |
| | 0.0400 | 1.47 | 0.268 | 0.276 |
| | 0.0400 | 1.47 | 0.273 | 0.276 |
| | 0.0999 | 1.48 | 0.602 | 0.617 |
| | 0.0999 | 1.47 | 0.597 | 0.617 |
| | 0.999 | 2.48 | 2.40 | 2.38 |
| | 0.999 | 2.48 | 2.41 | 2.38 |
| 25.0 | 0.0200 | 1.47 | 0.474 | 0.470 |
| | 0.0200 | 1.47 | 0.462 | 0.470 |
| | 0.0250 | 1.34 | 0.585 | 0.583 |
| | 0.0250 | 1.34 | 0.599 | 0.583 |
| | 0.0400 | 1.48 | 0.906 | 0.909 |
| | 0.0400 | 1.48 | 0.910 | 0.909 |
| | 0.0999 | 1.43 | 2.05 | 2.07 |
| | 0.0999 | 1.43 | 2.06 | 2.07 |
| | 0.999 | 2.40 | 8.95 | 8.93 |
| | 0.999 | 2.40 | 8.95 | 8.93 |
| 34.9 | 0.0200 | 1.47 | 1.36 | 1.33 |
| | 0.0200 | 1.47 | 1.33 | 1.33 |
| | 0.0333 | 1.47 | 2.13 | 2.17 |

| | | | |
|---|---|---|---|
| 0.0333 | 1.47 | 2.15 | 2.17 |
| 0.0999 | 1.48 | 6.10 | 5.92 |
| 0.0999 | 1.48 | 5.93 | 5.92 |
| 0.200 | 1.48 | 10.3 | 10.4 |
| 0.200 | 1.48 | 10.3 | 10.4 |
| 0.400 | 1.48 | 17.1 | 16.9 |
| 0.400 | 1.48 | 16.5 | 16.9 |
| 0.799 | 1.48 | 24.4 | 24.5 |
| 0.799 | 1.48 | 24.9 | 24.5 |
| 0.999 | 2.46 | 27.0 | 26.9 |
| 0.999 | 2.46 | 26.8 | 26.9 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 3.1 with $10^2 \cdot a = 0.35 \pm 0.03$, $1.41 \pm 0.06$, and $4.42 \pm 0.20$ $sec^{-1}$ and $b = 0.47 \pm 0.04$, $0.58 \pm 0.03$, and $0.65 \pm 0.04$ M at 15.0°, 25.0° and 34.9°C, respectively. Errors are 95% confidence limits, which are about three times larger than the standard error.

## Table B2

AQUATION KINETIC DATA FOR $(NH_3)_5NHSO_2C_6H_4CH_3^{2+}$, [a]

| temp, °C | $[H^+]$, M | $10^4[Co(III)]$, M | $10^3 \cdot k_{obsd}$, $sec^{-1}$ obsd | calc[b] |
|---|---|---|---|---|
| 14.8 | 0.100 | 2.44 | 0.691 | 0.676 |
| | 0.100 | 2.44 | 0.701 | 0.676 |
| | 0.200 | 2.91 | 1.40 | 1.35 |
| | 0.200 | 2.91 | 1.41 | 1.35 |
| | 0.400 | 2.91 | 2.71 | 2.70 |
| | 0.400 | 2.91 | 2.71 | 2.70 |
| | 0.800 | 2.98 | 5.11 | 5.40 |
| | 0.800 | 2.98 | 5.04 | 5.40 |
| 25.1 | 0.104 | 2.57 | 2.37 | 2.24 |
| | 0.104 | 2.99 | 2.37 | 2.24 |
| | 0.202 | 2.78 | 4.44 | 4.35 |
| | 0.203 | 2.78 | 4.66 | 4.35 |
| | 0.399 | 2.99 | 8.59 | 8.60 |
| | 0.399 | 2.99 | 8.75 | 8.60 |
| | 0.781 | 3.21 | 16.0 | 16.8 |
| | 0.798 | 3.28 | 16.9 | 17.2 |
| | 0.798 | 3.28 | 16.6 | 17.2 |
| | 0.798 | 3.28 | 15.9 | 17.2 |
| 34.9 | 0.102 | 2.92 | 6.28 | 6.40 |
| | 0.100 | 2.92 | 6.45 | 6.28 |
| | 0.100 | 2.84 | 6.28 | 6.28 |
| | 0.200 | 2.91 | 13.0 | 12.6 |
| | 0.200 | 2.91 | 13.1 | 12.6 |

|  |  |  |  |
|---|---|---|---|
| 0.302 | 2.91 | 19.0 | 19.0 |
| 0.302 | 2.91 | 19.0 | 19.0 |
| 0.400 | 2.91 | 24.1 | 25.1 |
| 0.400 | 2.91 | 24.3 | 25.1 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 3.4 with $10^2 \cdot c$ = 0.676 ± 0.024, 2.15 ± 0.07 and 6.28 ± 0.14 $M^{-1}$ $sec^{-1}$ at 14.8°, 25.1°, and 34.9°C, respectively. Errors are as in Table Bl.

## Table B3

AQUATION KINETIC DATA FOR $(NH_3)_5CoNHSO_2C_6H_4NO_2{}^{2+}$.[a]

| temp, °C | $[H^+]$, M | 10[illegible]$[Co(III)]$, M | $10^3 \cdot k_{obsd}$, $sec^{-1}$ obsd | calc[b] |
|---|---|---|---|---|
| 14.9 | 0.100 | 3.75 | 0.191 | 0.192 |
| | 0.100 | 5.73 | 0.202 | 0.192 |
| | 0.200 | 3.85 | 0.361 | 0.384 |
| | 0.200 | 3.39 | 0.423 | 0.384 |
| | 0.400 | 4.53 | 0.808 | 0.767 |
| | 0.400 | 4.18 | 0.724 | 0.767 |
| | 0.400 | 4.36 | 0.802 | 0.767 |
| | 0.400 | 3.80 | 0.788 | 0.767 |
| | 0.800 | 3.58 | 1.41 | 1.53 |
| | 0.800 | 3.46 | 1.54 | 1.53 |
| | 0.800 | 4.14 | 1.50 | 1.53 |
| 25.0 | 0.0997 | 4.46 | 0.597 | 0.571 |
| | 0.0998 | 7.28 | 0.590 | 0.571 |
| | 0.200 | 3.27 | 1.20 | 1.14 |
| | 0.199 | 3.39 | 1.18 | 1.14 |
| | 0.400 | 5.37 | 2.31 | 2.28 |
| | 0.400 | 5.96 | 2.33 | 2.28 |
| | 0.800 | 4.65 | 4.38 | 4.57 |
| | 0.800 | 5.13 | 4.42 | 4.57 |
| | 1.000 | 4.97 | 5.40 | 5.71 |
| | 1.000 | 5.89 | 5.48 | 5.71 |
| 35.0 | 0.100 | 4.94 | 1.68 | 1.59 |
| | 0.100 | 5.20 | 1.71 | 1.59 |

| | | | |
|---|---|---|---|
| 0.100 | 4.35 | 1.74 | 1.59 |
| 0.200 | 3.63 | 3.22 | 3.19 |
| 0.200 | 5.93 | 3.30 | 3.19 |
| 0.400 | 6.68 | 6.44 | 6.37 |
| 0.400 | 4.65 | 6.42 | 6.37 |
| 0.800 | 5.25 | 11.9 | 12.7 |
| 0.800 | 3.91 | 11.9 | 12.7 |
| 0.800 | 4.47 | 12.0 | 12.7 |
| 0.800 | 4.65 | 12.3 | 12.7 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 3.4 with $10^2 \cdot c$ = 0.192 ± 0.007, 0.571 ± 0.017, and 1.59 ± 0.06 $M^{-1}$ $sec^{-1}$ at 14.9°, 25.0°, and 35.0°, respectively. Errors are as in Table B1.

## Table B4

REDUCTION KINETIC DATA FOR $(NH_3)_5CoNHSO_2NH_2^{2+}$.[a]

| temp, °C | $[H^+]$ M | $10^2$ [Cr(II)] M | $10^4$ [Co(III)] M | $10^3 \cdot k_{obsd}$, $sec^{-1}$ | |
|---|---|---|---|---|---|
| | | | | obsd | calc[b] |
| 15.0 | 0.0200 | 1.02 | 7.81 | 0.462 | 0.459 |
| | | 4.01 | 7.68 | 1.40 | 1.38 |
| | | 7.25 | 7.96 | 2.33 | 2.39 |
| | | 9.88 | 7.70 | 3.25 | 3.20 |
| | 0.100 | 1.00 | 7.67 | 1.02 | 1.03 |
| | | 3.99 | 7.61 | 2.36 | 2.29 |
| | | 6.99 | 7.56 | 3.55 | 3.55 |
| | | 9.87 | 7.70 | 4.60 | 4.76 |
| | 0.300 | 0.944 | 7.75 | 1.95 | 1.96 |
| | | 4.03 | 7.73 | 3.84 | 3.77 |
| | | 7.02 | 7.71 | 5.53 | 5.55 |
| | | 10.1 | 7.84 | 7.19 | 7.36 |
| | 0.600 | 0.990 | 7.71 | 2.85 | 2.69 |
| | | 4.04 | 7.74 | 5.17 | 4.94 |
| | | 5.99 | 7.70 | 6.49 | 6.38 |
| | | 8.31 | 7.83 | 7.73 | 8.08 |
| | | 8.31 | 7.83 | 8.08 | 8.08 |
| 24.9 | 0.0200 | 2.00 | 8.16 | 1.65 | 1.68 |
| | | 3.94 | 7.98 | 2.92 | 2.85 |
| | | 7.68 | 8.24 | 5.20 | 5.11 |
| | | 9.91 | 8.02 | 6.51 | 6.45 |
| | 0.100 | 1.00 | 6.24 | 2.80 | 2.84 |
| | | 3.97 | 6.43 | 5.11 | 5.11 |

| | | | | | |
|---|---|---|---|---|---|
| | | 6.97 | 6.39 | 7.22 | 7.40 |
| | | 9.81 | 6.29 | 9.17 | 9.58 |
| | 0.300 | 0.985 | 7.95 | 5.81 | 5.83 |
| | | 3.98 | 7.96 | 9.30 | 8.95 |
| | | 3.98 | 7.96 | 9.45 | 8.95 |
| | | 6.97 | 7.95 | 12.0 | 12.0 |
| | | 9.93 | 8.00 | 14.8 | 15.1 |
| | 0.600 | 0.995 | 8.02 | 8.53 | 8.44 |
| | | 3.97 | 7.94 | 12.4 | 12.2 |
| | | 8.19 | 7.93 | 18.0 | 17.6 |
| | | 8.19 | 7.93 | 17.3 | 17.6 |
| 35.0 | 0.0200 | 1.02 | 8.17 | 2.46 | 2.50 |
| | | 3.99 | 7.89 | 6.19 | 5.97 |
| | | 7.87 | 8.11 | 10.5 | 10.5 |
| | | 9.84 | 7.91 | 12.3 | 12.8 |
| | 0.100 | 0.993 | 8.01 | 7.40 | 7.29 |
| | | 4.01 | 7.96 | 11.7 | 11.5 |
| | | 6.98 | 7.90 | 15.9 | 15.7 |
| | | 10.0 | 8.08 | 20.0 | 20.0 |
| | 0.200 | 1.00 | 7.57 | 12.4 | 12.0 |
| | | 3.96 | 7.54 | 17.2 | 16.9 |
| | | 6.97 | 7.62 | 21.4 | 21.8 |
| | | 9.87 | 7.70 | 26.2 | 26.6 |
| | 0.300 | 0.986 | 7.61 | 16.9 | 15.8 |
| | | 1.00 | 7.95 | 16.9 | 15.8 |
| | | 1.02 | 7.95 | 17.2 | 15.8 |
| | | 4.00 | 7.60 | 22.0 | 21.3 |
| | | 4.05 | 7.94 | 22.3 | 21.3 |
| | | 6.96 | 7.57 | 27.2 | 26.7 |
| | | 6.93 | 7.92 | 27.5 | 26.6 |
| | | 10.0 | 8.05 | 32.0 | 32.2 |
| | | 9.92 | 7.94 | 31.9 | 32.1 |
| | | 9.92 | 7.94 | 32.1 | 32.1 |
| | | 14.5 | 8.02 | 38.3 | 40.3 |

|  |  |  |  |
|---|---|---|---|
| 14.4 | 7.67 | 38.5 | 40.2 |

## FOOTNOTES FOR TABLE B4

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 3.7 with $10^2 \cdot k_{1r}$ = 2.76 ± 0.14, 5.56 ± 0.26 and 11.0 ± 0.8 $M^{-1}$ $sec^{-1}$ and $k_{2r}$ = 0.110 ± 0.006, 0.197 ± 0.014 and 0.340 ± 0.039 $M^{-1}$ $sec^{-1}$ at 15.0°, 24.9° and 35.0°, respectively, while holding $k_{2h}$ and $K_a$ constant at values determined by aquation study (see Table 5). Errors are as in Table B1.

## Table B5

REDUCTION KINETIC DATA FOR $(NH_3)_5CoNHSO_2C_6H_4CH_3^{2+}$.[a]

| temp, °C | $[H^+]$ M | $10^2$ [Cr(II)], M | $10^4$ [Co(III)], M | $10^3 \cdot k_{obsd}$, sec$^{-1}$ | |
|---|---|---|---|---|---|
| | | | | obsd | calc[b] |
| 14.9 | 0.0250 | 0.912 | 6.02 | 0.486 | 0.486 |
| | | 0.912 | 6.02 | 0.485 | 0.486 |
| | | 3.18 | 6.86 | 1.34 | 1.27 |
| | | 3.23 | 6.94 | 1.27 | 1.29 |
| | | 9.52 | 6.85 | 3.67 | 3.48 |
| | | 9.52 | 6.85 | 3.85 | 3.48 |
| | | 9.57 | 6.85 | 3.47 | 3.50 |
| | | 15.85 | 6.85 | 5.81 | 5.69 |
| | | 15.85 | 6.85 | 5.62 | 5.69 |
| | | 15.93 | 6.85 | 5.22 | 5.71 |
| | 0.100 | 0.917 | 5.98 | 1.05 | 1.04 |
| | | 3.26 | 7.00 | 2.07 | 1.96 |
| | | 3.26 | 7.00 | 2.11 | 1.96 |
| | | 9.64 | 6.91 | 4.51 | 4.47 |
| | | 9.64 | 6.91 | 4.53 | 4.47 |
| | | 9.64 | 6.91 | 4.44 | 4.47 |
| | | 16.30 | 7.00 | 6.42 | 7.08 |
| | | 16.30 | 7.00 | 6.64 | 7.08 |
| | | 16.30 | 7.00 | 6.66 | 7.08 |
| | 0.200 | 0.906 | 6.05 | 1.78 | 1.76 |
| | | 0.906 | 6.05 | 1.83 | 1.76 |
| | | 2.99 | 6.94 | 3.12 | 2.70 |
| | | 3.00 | 6.94 | 2.78 | 2.71 |
| | | 3.00 | 6.94 | 2.94 | 2.71 |

| | | | | | |
|---|---|---|---|---|---|
| | | 9.69 | 6.98 | 5.95 | 5.74 |
| | | 9.69 | 6.98 | 5.97 | 5.74 |
| | | 9.74 | 6.98 | 5.89 | 5.76 |
| | | 16.04 | 6.93 | 8.48 | 8.62 |
| | | 16.04 | 6.93 | 9.05 | 8.62 |
| | | 16.13 | 6.93 | 7.77 | 8.66 |
| | 0.400 | 0.906 | 6.05 | 3.21 | 3.22 |
| | | 0.906 | 6.05 | 3.19 | 3.22 |
| | | 0.907 | 6.05 | 3.32 | 3.22 |
| | | 0.907 | 6.05 | 3.31 | 3.22 |
| | | 3.07 | 6.95 | 4.62 | 4.46 |
| | | 3.07 | 6.95 | 4.70 | 4.46 |
| | | 3.07 | 6.95 | 5.05 | 4.46 |
| | | 3.07 | 6.95 | 4.82 | 4.46 |
| | | 9.73 | 6.97 | 7.96 | 8.28 |
| | | 9.74 | 6.96 | 8.14 | 8.28 |
| | | 9.74 | 6.97 | 8.36 | 8.28 |
| | | 12.95 | 6.96 | 9.69 | 10.1 |
| | | 12.96 | 6.96 | 9.75 | 10.1 |
| | | 12.96 | 6.96 | 9.71 | 10.1 |
| 25.0 | 0.025 | 0.879 | 8.21 | 1.15 | 1.14 |
| | | 0.892 | 2.37 | 1.16 | 1.15 |
| | | 1.96 | 6.72 | 1.89 | 1.87 |
| | | 1.96 | 6.72 | 1.89 | 1.87 |
| | | 3.47 | 7.17 | 3.01 | 2.89 |
| | | 7.97 | 7.80 | 6.26 | 5.95 |
| | | 12.85 | 6.98 | 9.22 | 9.27 |
| | | 16.32 | 6.87 | 11.46 | 11.6 |
| | | 16.55 | 8.63 | 11.35 | 11.8 |
| | | 21.63 | 8.39 | 15.14 | 15.2 |
| | | 21.59 | 6.96 | 14.94 | 15.2 |
| | 0.100 | 0.705 | 4.65 | 3.02 | 2.68 |
| | | 0.705 | 4.65 | 3.04 | 2.68 |
| | | 0.715 | 4.71 | 2.94 | 2.69 |

| | | | | |
|---|---|---|---|---|
| | 0.886 | 5.88 | 2.97 | 2.81 |
| | 0.894 | 5.88 | 3.03 | 2.82 |
| | 0.894 | 5.88 | 3.07 | 2.81 |
| | 0.902 | 6.02 | 2.90 | 2.83 |
| | 0.902 | 6.02 | 2.96 | 2.83 |
| | 0.968 | 8.03 | 3.04 | 2.88 |
| | 1.21 | 8.16 | 3.14 | 3.06 |
| | 1.21 | 8.16 | 3.46 | 3.06 |
| | 1.25 | 8.39 | 3.29 | 3.08 |
| | 1.26 | 8.24 | 2.89 | 3.09 |
| | 1.26 | 8.24 | 3.15 | 3.09 |
| | 2.12 | 10.6 | 4.25 | 3.73 |
| | 2.15 | 8.23 | 3.83 | 3.76 |
| | 3.26 | 8.34 | 4.93 | 4.59 |
| | 3.27 | 21.8 | 4.97 | 4.59 |
| | 4.12 | 19.4 | 5.84 | 5.23 |
| | 4.12 | 19.4 | 5.92 | 5.23 |
| | 9.29 | 20.0 | 9.22 | 9.08 |
| | 9.29 | 20.0 | 9.71 | 9.08 |
| | 12.8 | 6.87 | 11.93 | 11.7 |
| | 12.8 | 6.87 | 11.93 | 11.7 |
| | 16.9 | 27.9 | 13.17 | 14.8 |
| | 16.9 | 27.9 | 13.25 | 14.8 |
| | 17.9 | 6.75 | 14.47 | 15.5 |
| | 17.9 | 6.75 | 14.50 | 15.5 |
| | 18.9 | 19.5 | 13.75 | 16.2 |
| 0.200 | 0.896 | 5.91 | 5.35 | 5.06 |
| | 0.896 | 5.91 | 5.38 | 5.06 |
| | 2.10 | 6.94 | 6.42 | 6.06 |
| | 2.11 | 6.74 | 6.44 | 6.07 |
| | 2.11 | 6.74 | 6.91 | 6.07 |
| | 2.12 | 10.6 | 7.04 | 6.08 |
| | 9.31 | 6.77 | 12.08 | 12.1 |
| | 9.39 | 6.99 | 12.46 | 12.2 |
| | 15.7 | 6.94 | 17.07 | 17.4 |

| | | | | | |
|---|---|---|---|---|---|
| | | 15.7 | 6.72 | 16.41 | 17.4 |
| | | 15.8 | 28.1 | 17.07 | 17.5 |
| | 0.400 | 0.882 | 5.96 | 8.62 | 9.51 |
| | | 0.882 | 5.96 | 9.41 | 9.51 |
| | | 1.22 | 6.75 | 9.71 | 9.85 |
| | | 1.22 | 6.75 | 10.03 | 9.85 |
| | | 1.96 | 6.75 | 10.73 | 10.6 |
| | | 1.96 | 6.75 | 10.77 | 10.6 |
| | | 3.22 | 6.74 | 11.83 | 11.9 |
| | | 3.22 | 6.74 | 11.93 | 11.9 |
| | | 9.11 | 6.76 | 18.20 | 17.9 |
| | | 11.8 | 6.84 | 20.19 | 20.5 |
| | | 11.8 | 6.84 | 20.48 | [illegible].5 |
| 35.0 | 0.0250 | 0.861 | 6.02 | 2.59 | 2.69 |
| | | 0.861 | 6.02 | 2.70 | 2.69 |
| | | 3.05 | 6.87 | 5.68 | 5.55 |
| | | 3.12 | 6.86 | 5.95 | 5.65 |
| | | 3.12 | 6.86 | 6.02 | 5.65 |
| | | 9.37 | 6.86 | 14.2 | 13.8 |
| | | 9.37 | 6.86 | 14.4 | 13.8 |
| | | 15.6 | 6.86 | 20.9 | 22.0 |
| | | 15.6 | 6.86 | 22.2 | 22.0 |
| | | 16.1 | 6.86 | 21.3 | 22.6 |
| | 0.100 | 0.924 | 6.12 | 7.44 | 7.57 |
| | | 0.924 | 6.12 | 7.75 | 7.59 |
| | | 3.15 | 7.01 | 10.8 | 10.7 |
| | | 3.15 | 7.01 | 11.1 | 10.7 |
| | | 9.44 | 6.91 | 19.0 | 19.5 |
| | | 9.44 | 6.91 | 19.4 | 19.5 |
| | | 15.8 | 7.01 | 27.8 | 28.3 |
| | | 15.8 | 7.01 | 28.7 | 28.3 |
| | | 15.8 | 7.01 | 29.0 | 28.3 |
| | 0.200 | 0.912 | 6.05 | 14.4 | 13.9 |
| | | 0.912 | 6.05 | 14.5 | 13.9 |

| | | | | |
|---|---|---|---|---|
| | 3.02 | 6.94 | 17.2 | 17.1 |
| | 3.02 | 6.94 | 17.5 | 17.1 |
| | 9.59 | 6.98 | 26.7 | 27.1 |
| | 9.59 | 6.98 | 27.8 | 27.1 |
| | 16.2 | 6.93 | 36.0 | 37.2 |
| | 16.2 | 6.93 | 36.0 | 37.2 |
| 0.400 | 0.892 | 5.70 | 25.8 | 26.7 |
| | 0.892 | 5.70 | 26.0 | 26.7 |
| | 3.02 | 6.95 | 31.1 | 30.4 |
| | 3.02 | 6.95 | 31.8 | 30.4 |
| | 9.58 | 6.97 | 41.7 | 41.9 |
| | 9.58 | 6.97 | 42.8 | 41.9 |
| | 12.7 | 6.96 | 47.2 | 47.5 |
| | 12.7 | 6.96 | 47.5 | 47.5 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 3.8 with $10^2 \cdot k_{1r}$ = 3.33 ± 0.17, 6.57 ± 0.41 and 12.8 ± 0.5 $M^{-1}$ $sec^{-1}$ and $10^2 \cdot k_{2r}/K_a$ = 6.0 ± 1.1, 8.9 ± 3.5 and 12.0 ± 3.9 $sec^{-1}$ at 14.9°, 25.0° and 35.0°, respectively, while holding $k_{2h}/K_a$ constant at values determined by aquation study (see Table 6). Errors are as in Table B1.

## Table B6

REDUCTION KINETIC DATA FOR $(NH_3)_5CoNH_2SO_3^{2+}$.[a]

| temp, °C | $[H^+]$, M | $10^2$ [Cr(II)], M | $10^4$ [Co(III)], M | $10^2 \cdot k_{obsd}$, $sec^{-1}$ obsd | calc[b] |
|---|---|---|---|---|---|
| 15.0 | 0.0500 | 4.62 | 4.60 | 8.63 | 9.01 |
| | | 8.38 | 7.80 | 15.8 | 16.3 |
| | | 8.38 | 5.85 | 17.1 | 16.3 |
| | 0.100 | 4.57 | 5.05 | 9.00 | 8.91 |
| | | 4.57 | 5.20 | 8.83 | 8.91 |
| | 0.15 | 8.38 | 4.82 | 17.0 | 16.3 |
| 25.0 | 0.0500 | 4.70 | 5.43 | 15.2 | 15.5 |
| | 0.102 | 4.70 | 6.17 | 15.7 | 15.5 |
| | 0.202 | 4.70 | 6.17 | 16.2 | 15.5 |
| | | 4.70 | 5.69 | 15.2 | 15.5 |
| | 0.400 | 1.63 | 5.73 | 5.40 | 5.39 |
| 35.2 | 0.0250 | 4.67 | 4.77 | 24.8 | 25.9 |
| | 0.050 | 4.73 | 5.21 | 25.1 | 26.2 |
| | 0.100 | 4.73 | 5.12 | 27.1 | 26.2 |
| | 0.200 | 4.73 | 4.38 | 26.1 | 26.2 |
| | 0.400 | 1.58 | 4.68 | 9.44 | 8.75 |
| 25.0 | 0.0100 | 1.59 | 14.8 | 0.80[c] | |
| | | 1.48 | 13.9 | 0.76[c] | |
| | | 1.65 | 14.9 | 0.83[c,d] | |
| | | 1.72 | 15.6 | 0.81[c,d] | |

## FOOTNOTES FOR TABLE B6

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$) and with N-bonded isomer unless otherwise indicated.

b. Caluclated from equation 3.9 with $k_{2r}$ = 1.95 ± 0.07, 3.30 ± 0.11, and 5.54 ± 0.32 $M^{-1}$ $sec^{-1}$ at 15.0°, 25.0° and 35.2°, respectively, by least-squares analysis. Errors are as in Table B1.

c. Ionic strength was 0.09 M.

d. Oxidant was a mixture of O- and N-bonded isomers.

## Table B7

STOPPED-FLOW REDUCTION KINETIC DATA FOR $H_2NSO_2C_6H_4NO_2$ at 25°C.[a,b]

| $[H^+]$, | $10^3[Cr(II)]$, | $k_{1L}$, $sec^{-1}$ | |
|---|---|---|---|
| M | M | obsd | calc[c] |
| 0.500 | 16.7 | 51.38 | 48.22 |
| | 16.7 | 49.86 | 48.22 |
| 0.400 | 8.61 | 26.81 | 25.2 |
| | 8.58 | 25.29 | 25.1 |
| | 8.58 | 23.96 | 25.1 |
| | 8.58 | 27.75 | 25.1 |
| 0.300 | 8.56 | 28.53 | 25.8 |
| | 8.56 | 26.70 | 25.8 |
| | 8.56 | 29.66 | 25.8 |
| 0.200 | 8.61 | 28.97 | 27.2 |
| | 8.58 | 24.71 | 27.2 |
| | 8.58 | 24.73 | 27.2 |
| | 8.58 | 23.74 | 27.2 |
| 0.100 | 8.20 | 31.75 | 29.8 |
| | 8.20 | 31.44 | 29.8 |
| | 8.20 | 31.78 | 29.8 |
| | 8.20 | 29.42 | 29.8 |
| | 8.20 | 33.15 | 29.8 |
| | 8.20 | 31.30 | 29.8 |
| | 8.20 | 28.01 | 29.8 |
| | 8.20 | 27.14 | 29.8 |
| | 8.20 | 29.21 | 29.8 |
| | 8.20 | 27.37 | 29.8 |
| | 8.20 | 27.65 | 29.8 |

| | | | |
|---|---|---|---|
| | 8.20 | 27.97 | 29.8 |
| | 8.38 | 30.10 | 30.5 |
| | 8.58 | 30.69 | 31.2 |
| | 8.58 | 29.79 | 31.2 |
| 0.0500 | 8.61 | 39.46 | 39.4 |
| | 8.61 | 39.95 | 39.4 |
| | 8.61 | 39.20 | 39.4 |
| 0.0331 | 8.53 | 51.12 | 47.4 |
| | 8.53 | 47.36 | 47.4 |
| | 8.53 | 48.25 | 47.4 |
| | 17.1 | 92.97 | 94.8 |
| | 17.1 | 100.4 | 94.8 |
| | 17.1 | 96.51 | 94.8 |
| | 4.27 | 23.01 | 23.7 |
| | 4.27 | 23.19 | 23.7 |
| | 4.27 | 24.91 | 23.7 |
| 0.0250 | 8.61 | 60.91 | 55.7 |
| | 8.61 | 60.36 | 55.7 |
| | 8.37 | 53.47 | 54.2 |
| | 8.37 | 53.38 | 54.2 |
| | 8.37 | 49.22 | 54.2 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. $[\text{Ligand}]^{o}$ = $1.71 \times 10^{-4}$ M, all runs.

c. Calculated from equation 5.3 with a = 94.7 ± 9.7 $sec^{-1}$ and $10^{-3} \cdot b = 2.69 \pm 0.14\ M^{-1}\ sec^{-1}$ at 25°C. Errors are as in Table Bl.

## Table B8

STOPPED-FLOW REDUCTION KINETIC DATA FOR $(NH_3)_5CoNHSO_2C_6H_4NO_2^{2+}$ at 25°C. (ABSORBANCE DECREASING).[a,b]

| $[H^+]$, M | $10^3[Cr(II)]$, M | $k_{1C}$, $sec^{-1}$ obsd | $k_{1C}$, $sec^{-1}$ calc[c] |
|---|---|---|---|
| 0.400 | 8.61 | 25.3 | 22.1 |
| | 8.61 | 25.3 | 22.1 |
| 0.200 | 8.60 | 23.6 | 23.9 |
| | 8.60 | 26.5 | 23.9 |
| | 8.60 | 24.8 | 23.9 |
| | 8.60 | 25.4 | 23.9 |
| | 8.60 | 25.5 | 23.9 |
| | 8.60 | 22.8 | 23.9 |
| | 8.60 | 23.2 | 23.9 |
| | 8.60 | 22.4 | 23.9 |
| 0.100 | 8.38 | 25.2 | 26.8 |
| | 8.38 | 24.7 | 26.8 |
| | 8.38 | 23.3 | 26.8 |
| | 8.38 | 25.4 | 26.8 |
| 0.0500 | 8.61 | 39.0 | 34.8 |
| | 8.61 | 35.0 | 34.8 |
| | 8.61 | 35.2 | 34.8 |
| | 8.60 | 36.4 | 34.8 |
| | 8.60 | 31.1 | 34.8 |
| 0.0336 | 17.2 | 77.3 | 83.8 |
| | 17.2 | 75.8 | 83.8 |
| | 17.2 | 75.9 | 83.8 |
| | 8.60 | 46.4 | 41.9 |
| | 8.60 | 42.3 | 41.9 |

| | | | |
|---|---|---|---|
| | 8.60 | 48.9 | 41.9 |
| | 8.60 | 39.0 | 41.9 |
| | 4.30 | 20.4 | 21.0 |
| | 4.30 | 21.0 | 21.0 |
| | 4.30 | 22.0 | 21.0 |
| 0.0250 | 8.61 | 51.2 | 49.3 |
| | 8.61 | 50.4 | 49.3 |
| | 8.61 | 46.2 | 49.3 |
| | 8.61 | 52.6 | 49.3 |
| | 8.61 | 49.4 | 49.3 |
| | 8.61 | 54.9 | 49.3 |
| | 8.61 | 47.5 | 49.3 |
| | 8.61 | 56.3 | 49.3 |
| | 8.61 | 52.6 | 49.3 |

---

a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. [Cobalt(III)] = $1.71 \times 10^{-4}$ M, all runs.

c. Calculated from equation 5.3 with a = 84.3 ± 10.1 $sec^{-1}$ and $10^{-3} \cdot b = 2.36 \pm 0.19$ $M^{-1}$ $sec^{-1}$ at 25°C. Errors are as in Table B1.

# Table B9

STOPPED-FLOW REDUCTION KINETIC DATA FOR

$(NH_3)_5CoNHSO_2C_6H_4NO_2{}^{2+}$ at 25°C. (ABSORBANCE INCREASING).[a]

| $[H^+]$, M | $10^3$ [Cr(II)], M | $10^4$ [Co(III)], M | $k_{2C}$, $sec^{-1}$ | |
|---|---|---|---|---|
| | | | obsd | calc[b] |
| 0.400 | 17.2 | 1.71 | 0.479 | 0.510 |
| | 17.2 | 1.71 | 0.509 | 0.510 |
| | 17.2 | 1.71 | 0.482 | 0.510 |
| | 8.61 | 1.71 | 0.542 | 0.510 |
| | 8.61 | 1.71 | 0.527 | 0.510 |
| | 8.61 | 1.71 | 0.524 | 0.510 |
| | 4.30 | 1.71 | 0.510 | 0.510 |
| | 4.30 | 1.71 | 0.500 | 0.510 |
| 0.200 | 8.52 | 1.71 | 0.508 | 0.419 |
| | 8.52 | 1.71 | 0.498 | 0.419 |
| | 8.52 | 1.71 | 0.545 | 0.419 |
| 0.100 | 8.38 | 1.71 | 0.444 | 0.402 |
| | 8.38 | 1.71 | 0.415 | 0.402 |
| | 8.38 | 1.71 | 0.455 | 0.402 |
| | 8.38 | 1.71 | 0.406 | 0.402 |
| 0.0500 | 8.61 | 1.71 | 0.446 | 0.453 |
| | 8.61 | 1.71 | 0.434 | 0.453 |
| | 8.61 | 1.71 | 0.437 | 0.453 |
| | 8.60 | 1.71 | 0.467 | 0.453 |
| | 8.60 | 1.71 | 0.495 | 0.453 |
| | 8.60 | 1.71 | 0.477 | 0.453 |
| 0.0336 | 17.2 | 1.71 | 0.529 | 0.521 |
| | 17.2 | 1.71 | 0.538 | 0.521 |

| | | | | |
|---|---|---|---|---|
| | 17.2 | 1.71 | 0.540 | 0.521 |
| | 8.60 | 1.71 | 0.553 | 0.521 |
| | 8.60 | 1.71 | 0.550 | 0.521 |
| | 8.60 | 1.71 | 0.547 | 0.521 |
| | 4.30 | 1.71 | 0.510 | 0.521 |
| | 4.30 | 1.71 | 0.523 | 0.521 |
| | 4.30 | 1.71 | 0.529 | 0.521 |
| 0.0250 | 8.60 | 1.71 | 0.601 | 0.597 |
| | 8.60 | 1.71 | 0.589 | 0.597 |
| | 8.60 | 1.71 | 0.598 | 0.597 |
| 0.100 | 8.60 | 3.42 | 0.464 | 0.537 |
| | 8.60 | 3.42 | 0.459 | 0.537 |
| | 8.60 | 3.42 | 0.448 | 0.537 |
| | 8.60 | 0.855 | 0.333 | 0.335 |
| | 8.60 | 0.855 | 0.320 | 0.335 |
| | 8.60 | 0.855 | 0.319 | 0.335 |
| | 8.60 | 0.855 | 0.325 | 0.335 |
| | 8.60 | 0.430 | 0.302 | 0.302 |
| | 8.60 | 0.430 | 0.294 | 0.302 |
| | 8.60 | 0.430 | 0.295 | 0.302 |
| | 8.60 | 0.210 | 0.280 | 0.285 |
| | 8.60 | 0.210 | 0.272 | 0.285 |
| | 8.60 | 0.210 | 0.275 | 0.285 |

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a. Ionic Strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 5.11 with $x = 46.0 \pm 7.8\ sec^{-1}$, $10^{-3} \cdot y = 3.25 \pm 0.71\ M^{-2}\ sec^{-1}$ and $z = 0.268 \pm 0.025\ sec^{-1}$.

## Table B10

KINETIC DATA FOR FIRST SLOW REACTION, Cr(II) REDUCTION OF $NH_2SO_2C_6H_4NO_2$-p AT 25°C.[a]

| $[H^+]$, M | $10^3$ [Cr(II)], M | $10^4$ [Lig], M | $10^2 \cdot k_{3L}$, $sec^{-1}$ obsd | $10^2 \cdot k_{3L}$, $sec^{-1}$ calc[b] |
|---|---|---|---|---|
| 0.801 | 8.49 | 1.70 | 0.475 | 0.412 |
| 0.401 | 8.49 | 1.70 | 0.612 | 0.678 |
| 0.200 | 8.49 | 1.70 | 0.922 | 1.00 |
| 0.101 | 34.0 | 1.70 | 1.47 | 1.31 |
| 0.101 | 17.0 | 1.70 | 1.44 | 1.31 |
| 0.101 | 17.0 | 1.70 | 1.39 | 1.31 |
| 0.100 | 8.49 | 3.40 | 1.30 | 1.31 |
| 0.101 | 8.49 | 1.70 | 1.32 | 1.31 |
| 0.100 | 8.49 | 0.823 | 1.29 | 1.31 |
| 0.101 | 4.25 | 1.70 | 1.21 | 1.31 |
| 0.0492 | 8.49 | 1.70 | 1.55 | 1.57 |

a. Ionic strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 5.39 with $10^3 \cdot a = 4.21 \pm 1.2$ M $sec^{-1}$ and $b = 0.22 \pm 0.10$ M.

## Table B11

KINETIC DATA FOR SECOND SLOW REACTION, Cr(II) REDUCTION OF $NH_2SO_2C_6H_4NO_2$-p at 25°C.[a]

| $[H^+]$, M | $10^3$ [Cr(II)], M | $10^4$ [Lig], M | $10^3 \cdot k_{4L}$, $sec^{-1}$ obsd | $10^3 \cdot k_{4L}$, $sec^{-1}$ calc.[b] |
|---|---|---|---|---|
| 0.801 | 8.49 | 1.70 | 0.169 | 0.166 |
| 0.401 | 8.49 | 1.70 | 0.196 | 0.198 |
| 0.200 | 8.49 | 1.70 | 0.255 | 0.261 |
| 0.101 | 34.0 | 1.70 | 1.597 | 1.539 |
| 0.101 | 17.0 | 1.70 | 0.866 | 0.770 |
| 0.101 | 17.0 | 1.70 | 0.866 | 0.770 |
| 0.100 | 8.49 | 3.40 | 0.468 | 0.387 |
| 0.101 | 8.49 | 1.70 | 0.443 | 0.384 |
| 0.100 | 8.49 | 0.823 | 0.426 | 0.387 |
| 0.101 | 4.25 | 1.70 | 0.138 | 0.192 |
| 0.0492 | 8.49 | 1.70 | 0.643 | 0.647 |

a. Ionic strength 1.0 M ($LiClO_4/HClO_4$).

b. Calculated from equation 5.46 with $10^2 \cdot d = 1.6 \pm 0.8\ M^{-1}$ $sec^{-1}$ and $10^3 \cdot c = 3.0 \pm 1.1\ sec^{-1}$.