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KINETICS AND MECHANISMS OF REACTIONS OF CYANOCOBALT AND -CHROMIUM COMPLEXES IN ACIDIC SOLUTION

by

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INTRODUCTION

Taube (1) has pointed out that mechanisms of oxidation-reduction reactions of octahedral transition metal ion complexes can be separated into two classes - inner-sphere (ligand-bridged) and outer-sphere - depending on whether or not the first coordination spheres of the two metal ions have a ligand in common at the time of electron transfer. The identification of a mechanism as inner-sphere is particularly simplified if the bridging ligand is transferred during the course of electron transfer. This product criterion is met if the reactant complex containing the bridging ligand is inert to substitution while the other is labile. After electron transfer, the initially labile metal ion must be more inert than the other product metal ion, so that the ligand is transferred. It must also be sufficiently inert to be detectable as a complex containing the bridging ligand. Among the metal ion reactants which satisfy these criteria are Co(III) and Cr^{2+}, since Co(III) and Cr(III) are inert, while Co^{2+} and Cr^{2+} are labile. The system of reactions of interest here (Eq. 1)[1]

$$Co(NH_3)_5X^{+3-n} + Cr^{2+} + 5H^+ = Co^{2+} + CrX^{+3-n} + 5NH_4^+ \qquad (1)$$

has been studied for a large number of ligands X^{n-} (e.g., I^-, Br^-, Cl^-, F^-, H_2O, NO_3^-, $CH_3CO_2^-$, NCS^-, N_3^-, SO_4^{2-}, etc.)

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[1] Water in the first coordination sphere of octahedral complexes will not generally be shown.

A bridging ligand may function in the electron transfer process in several ways. An ion of opposite charge reduces the coulombic repulsion for approach of two metal ions. If the ligand is an extended polyatomic molecule, there is added benefit in that the metal ions need not approach closely. The ligand may introduce a continuous path of orbital overlap between the metal ions, if it has orbitals of proper symmetry. However, this is not necessary for a bridged transition state - the ligand may function merely to bring the metal ions sufficiently close to allow metal ion orbital overlap.

When the bridging ligand is polyatomic, the second metal ion may coordinate to the same atom (adjacent attack) or to another atom in the ligand (remote attack). In the reduction of pentaammine cobalt(III) complexes by Cr^{2+}, remote attack at the bridging ligand has been suggested as a pathway, but only recently has definite evidence been provided for ligands with extended bond systems (2).

If the polyatomic bridging ligand is unsymmetrical, remote attack by a reducing agent may lead to the formation of an unstable intermediate (a linkage isomer), provided coordination at this remote position is not the stable configuration for the oxidized reducing agent. Formation of such unstable intermediates has been demonstrated for reactions of $Co(CN)_5^{3-}$ with $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5CN^{2+}$ (3), Eq. 2 and Eq. 3, and of Cr^{2+} with $FeNCS^{2+}$ (4) and $Co(en)_2$

$A(NCS)^{n+}$ (5)[1], Eq. 4 and Eq. 5.

$$Co(CN)_5^{3-} + Co(NH_3)_5NO_2^{2+} = Co(CN)_5ONO^{3-} + Co^{2+} + 5NH_3 \qquad (2)$$

$$Co(CN)_5^{3-} + Co(NH_3)_5CN^{2+} = Co(CN)_5NC^{3-} + Co^{2+} + 5NH_3 \qquad (3)$$

$$Cr^{2+} + FeNCS^{2+} = CrSCN^{2+} + Fe^{2+} \qquad (4)$$

$$Cr^{2+} + Co(en)_2A(NCS)^{n+} = CrSCN^{2+} + Co^{2+} + 2en + A^{n-2} \qquad (5)$$

In each of these reactions, the immediate product is an unstable intermediate, postulated to be a linkage isomer of the oxidized metal complex. At about the same time as these reactions were discovered, work was started on the reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, which follows the same pattern. Preliminary results on this system have been published (6). The kinetics and mechanism of this reaction and of the decay of the intermediate produced by this reaction comprise the subject of part of this study.

In addition to the examples cited above, linkage isomerism has been found for a number of other transition metal complexes. Representative examples are nitro and nitrito isomers of various cobalt(III) complexes (7-11) and of rhodium(III), iridium(III) and platinum(IV) (12,13); thiocyanato and isothiocyanato complexes of palladium(II) (14-17), manganese(I) (18), rhodium(III) (19,20) and iridium(III) (19); and oxygen- and sulfur-bonded complexes of thiosulfatopenta-

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[1] The symbol en will be used for ethylenediamine. A = H_2O, NH_3, or NCS^-.

amminecobalt(III) (21). Linkage isomerism was also found in the mixed cyanide polymers $KFeCr(CN)_6$, where cyanide is a bridging ligand (22).

Another extensively studied reaction which proceeds by an inner-sphere mechanism is the electron exchange reaction of Cr^{2+} with Cr(III) species, Eq. 6.

$$CrX^{+3-n} + {}^*Cr^{2+} = Cr^{2+} + {}^*CrX^{+3-n} \qquad (6)$$

Since no net chemical change occurs, these reactions must be followed by radioactive-chromium tracer techniques. This reaction has been studied for $X^{n-} = H_2O$ (23), OH^- (23), F^- (24), Cl^- (24,25), Br^- (24), NCS^- (24), and N_3^- (24,26). As part of this study, the exchange reaction of Cr^{2+} with $CrCN^{2+}$ will be presented.

The mechanisms of ligand substitution reactions of octahedral transition metal complexes have received considerable attention, but are as yet not fully understood. In particular, the degree of participation of the entering ligand in the activated complex of substitution reactions in acidic solution is a matter of considerable disagreement. This subject has been reviewed most recently by Sutin (27).

The reactions of particular interest to this study are aquation (substitution by water) reactions of chromium(III) complexes. The kinetics and mechanisms of the aquation of $CrCN^{2+}$, Eq. 7, and of the catalysis of this aquation by Hg^{2+}

$$CrCN^{2+} + H^+ = Cr^{3+} + HCN \qquad (7)$$

and Cr^{2+}, will be presented as part of this study.

Previous to the preparation of $CrCN^{2+}$, reported in a preliminary account of this work (6), the only known cyanochromium(III) complex reported in the literature was $K_3Cr(CN)_6$ (28,29). Since that time, the complexes $Cr(CN)_4^-$, $Cr(CN)_3$, $Cr(CN)_2^+$ and $CrCN^{2+}$ have been prepared by the stepwise aquation of $Cr(CN)_6^{3-}$ in acidic solution (30).

EXPERIMENTAL

Preparation and Analysis of Reagents

Water

Water used in all reagent purifications and solutions and in all rate studies was the product of a double redistillation of laboratory distilled water from alkaline permanganate in a tin-lined Barnstead still. Conductance of the water was $\leq 1\mathrm{x}10^{-6}$ ohm^{-1}.

Lithium perchlorate

Lithium perchlorate was prepared by dissolving reagent grade lithium carbonate in a slight excess of 72% perchloric acid, followed by boiling to expel CO_2. Hydrated lithium perchlorate precipitated on cooling and was recrystallized twice. Stock solutions ca. 2 M in $LiClO_4$ were analyzed by passing aliquots through a column of Dowex 50W-X8 cation resin in the H^+ form. The resin was rinsed with water and the rinsings were titrated with standard sodium hydroxide.

Sodium perchlorate

Sodium perchlorate was prepared from sodium carbonate and analyzed in the same manner as lithium perchlorate.

Perchloric acid

Dilutions of 72% perchloric acid were used without further purification. Solutions were titrated directly with standard sodium hydroxide.

Chromium(III) perchlorate

Reagent grade potassium dichromate or chromium(VI) oxide was reduced in perchloric acid solution with an excess of formic acid or hydrogen peroxide. When $K_2Cr_2O_7$ was used, $KClO_4$ was first removed by filtration through a sintered glass funnel after the solution was cooled in a dry ice-acetone bath. Excess reducing agent was destroyed by boiling and the hydrated $Cr(ClO_4)_3$ isolated on cooling was recrystallized two or three times. The solid was stored over $CaSO_4$ dessicant.

Nitrogen

Nitrogen gas was purified by passage through a series of five gas-washing bottles equipped with sintered glass bubblers. The first two bottles contained Cr^{2+} over amalgamated zinc, the third dilute sodium hydroxide and the fourth, distilled water. The fifth bottle contained no solution and acted as a moisture trap.

Chromium(II) perchlorate

Chromium(II) perchlorate solutions were prepared by three methods.

(1) Solutions of chromium(III) perchlorate were reduced electrolytically at a mercury cathode. The anode consisted of a platinum electrode immersed in ~1.0$\underline{M}$ $HClO_4$ separated from the chromium(III) solution by a sintered glass disk. The applied potential was kept $\leq$10 volts to avoid reduction of perchlorate ion. Solutions were tested for the presence of chloride ion by adding silver nitrate to air-oxidized aliquots. Only those solutions which gave no detectable precipi-

tate were used.

(2) High purity chromium metal, obtained from United Mineral and Chemical Corporation,was dissolved in a slight excess of perchloric acid under a nitrogen atmosphere. The solution was filtered through a fine sintered glass disk to remove any undissolved metal.

(3) Acidic solutions of chromium(III) perchlorate were deoxygenated and reduced by stirring over amalgamated zinc. Solutions contained Zn^{2+} at concentrations of $\frac{1}{2}[Cr^{2+}]$.

Chromium(II) concentration was determined by reaction of aliquots of the solution with excess $Co(NH_3)_5Cl^{2+}$ in perchloric acid under nitrogen (31). The Co^{2+} produced was analyzed spectrophotometrically as the thiocyanate complex in 50 vol % acetone at 6230Å, where the absorbancy index is $1842\underline{M}^{-1}cm^{-1}$.

Total chromium was determined by oxidation of aliquots with hydrogen peroxide in basic solution. Solutions were analyzed spectrophotometrically at 3720Å, where chromate has an absorbancy index of $4803\underline{M}^{-1}cm^{-1}$ (32). Total chromium concentration was generally very close to chromium(II) concentration.

Perchloric acid was determined by titration of the acid released when air-oxidized aliquots of the solution were passed through Dowex 50W-X8 cation resin in the acid form. The acid concentration was then calculated as the total amount of acid titrated less that displaced by the dimeric chromium (III) species $Cr_2(OH)_2^{4+}$ (33) formed by air oxidation of chromium(II).

Chromium(II) solutions were stored under a positive pressure of nitrogen in screw-cap bottles equipped with self-sealing Buna-N rubber disks. Aliquots were removed with a nitrogen-flushed hypodermic syringe and needle.

Chromium(II) solutions for tracer studies were prepared in two ways. (1) Chromium-51 in the form of a chromium(III) solution in hydrochloric acid obtained from Nuclear Science Engineering Corporation was added to a chromium(II) solution and allowed to come to exchange equilibrium. The solution was not used until a day after its preparation and exchange equilibrium was assumed. (2) Chromium-51 was added to a solution of chromium(III) perchlorate which was then reduced electrolytically to chromium(II). The concentration of chloride ion added with the chromium-51 was sufficiently low that it could not be detected by silver ion.

Thallium(III) solutions

Cyanide solutions of thallium(III) were prepared by three methods:

(1) A slight excess of $Ba(ClO_4)_2$ was added to a solution of $Tl_2(SO_4)_3$ (~.3M Tl) in ~.25M $HClO_4$. Precipitated $BaSO_4$ was removed by filtration. Sodium cyanide was added as a solid until the pH of the solution was 6-7. Nitrogen gas was

bubbled through the solution to remove dissolved HCN. The C_{CN^-}/[Tl(III)] ratio was probably ≥ 4. Thallium(III) concentration was determined by reaction with excess Cr^{2+}. Excess $Co(NH_3)_5Cl^{2+}$ was added and the Co^{2+} produced was determined spectrophotometrically. The Tl(III) concentration was calculated as one-half the difference between the $[Cr^{2+}]$ added and the $[Co^{2+}]$ measured. Ionic strength was measured by titration of the acid released from ion exchange resin.

(2) A mixture of Tl_2O_3 and NaCN was added to a perchloric acid solution in a sealed flask. The mixture was stirred until all the solid had dissolved. The C_{CN^-}/[Tl(III)] ratio was ~4.

(3) A mixture of $Tl(ClO_4)_3$ (G. F. Smith Chem. Co.) and NaCN was stirred into 0.8 M $HClO_4$ solution in a sealed flask. The C_{CN^-}/[Tl(III)] ratio was ~1.0.

trans-Cyanoaquotetraamminecobalt(III) chloride

Preparation of $[Co(NH_3)_4(H_2O)CN]Cl_2$ was carried out by the method of Siebert (34). The solid was recrystallized several times from conductivity water.

Solutions of this and other cobalt(III) complexes were analyzed for cobalt content by reaction with excess chromium (II) solution. The Co^{2+} produced was analyzed spectrophotometrically as described for the analysis of Cr^{2+}. The purity of the complexes was indicated by quantitative agreement of the visible (and in some cases, infrared) spectra with published values.

Cyanopentaamminecobalt(III) perchlorate

Conversion of $[Co(NH_3)_4(H_2O)CN]Cl_2$ to $[Co(NH_3)_5CN](ClO_4)_2 \cdot \frac{1}{2}H_2O$ was carried out by the method of Siebert (34). The solid was recrystallized from perchloric acid several times.

trans-Cyanoaquobis(ethylenediamine)cobalt(III) chloride

Solutions of $[Co(en)_2(H_2O)CN]^{2+}$ were prepared by dissolution of $[Co(en)_2(OH)CN]Cl \cdot 2H_2O$ in excess perchloric acid. The latter solid was prepared by the method of Chan and Tobe (35) via a series of intermediate trans complexes $[Co(en)_2Cl_2]Cl$ (36), $[Co(en)_2(SO_3)Cl]$, $[Co(en)_2(SO_3)CN]$ and $[Co(en)_2(CN)Cl]Cl$. Difficulties were encountered in the purification of the hydroxocyano complex and the chlorocyano complex is a probable impurity.

cis-Dicyanobis(ethylenediamine)cobalt(III) chloride

The complex $[Co(en)_2(CN)_2]Cl$ was prepared from the thiosulfate salt by the method of Chan and Tobe (35). The latter salt was prepared by the method of Rây and Sarma (37), who incorrectly identified it as a trans complex (35).

Tricyanotriaquochromium(III) perchlorate

The cis complex $Cr(CN)_3$ is produced in the stepwise aquation of $K_3Cr(CN)_6$ (30), which was prepared by the method of Bigelow (38). When $K_3Cr(CN)_6$ was dissolved in 3-4 equivalents of $HClO_4$ of appropriate dilution and allowed to stand 1-2 hours, the resulting solution (generally .01-.15 <u>M</u> Cr(III)) contained mostly $Cr(CN)_3$, along with small amounts of other Cr(III) complexes. Precipitated $KClO_4$ was removed by filtration and the solution was passed through Dowex 50W-X8, 50-100 mesh cation resin in the Li^+ form to remove cationic complexes and then through Dowex 1-X8, 50-100 mesh anion resin in the ClO_4^- form to remove anionic complexes. The absence of anionic complexes was demonstrated by addition of aliquots to solutions of Hg^{2+}, which forms a precipitate with these species. The resulting solution of the neutral species $Cr(CN)_3$(.01-.04M) was flushed with a stream of N_2 gas to remove any dissolved HCN. The chromium content of the solution was determined by oxidation with alkaline peroxide and measurement of the chromate absorbance at 3720Å (32). The Li^+ content of the solution was determined by titration with NaOH of the washings when an aliquot was passed through H^+ resin. The solution was stored at -78°C in a chest filled with Dry Ice.

cis-Dicyanotetraquochromium(III) perchlorate

Solutions of cis-$Cr(CN)_2^+$ were prepared from $K_3Cr(CN)_6$ in the same manner as was $Cr(CN)_3$ (30), using four equivalents of acid and somewhat longer aquation times. After rinsing the last remnants of $Cr(CN)_3$ from the cation resin with water, 0.2 M $LiClO_4$ was used to elute $Cr(CN)_2^+$. The solution was analyzed and stored the same as $Cr(CN)_3$. Concentrations of these solutions were quite low ($4x10^{-4}$-$6x10^{-3}$ M).

cis-Tetracyanodiaquochromium(III) perchlorate

Acidic solutions of $K_3Cr(CN)_6$ were allowed to aquate $\frac{1}{2}$-1 hour (30), then passed through Dowex 1-X8 anion resin in the ClO_4^- form. The complex $Cr(CN)_4^-$ was eluted with 0.2 M $NaClO_4$. The solution was analyzed and stored as described for $Cr(CN)_3$.

Cyanopentaaquochromium(III) perchlorate

Solutions of $CrCN^{2+}$ were prepared in two ways: (1) Excess Cr^{2+} was allowed to react with $Co(NH_3)_5CN^{2+}$ or $Co(NH_3)_4(H_2O)CN^{2+}$ (6). The excess Cr^{2+} was destroyed by reaction with air to produce the Cr(III) dimer, $Cr_2(OH)_2{}^{4+}$ (33). The complex was absorbed onto Dowex 50W-X8, 50-100 mesh cation resin in the Na^+ form, kept at 0°C in a water jacketed column. Separation from other species, including Co^{2+}, was accomplished by slow elution with 0.99 M $NaClO_4$, 0.01 M $HClO_4$. Solutions were analyzed for Cr(III) and stored as described for $Cr(CN)_3$. Cyanide was determined by heating an acidic $CrCN^{2+}$ solution and distilling the liberated HCN into a NaOH solution. The CN^- was titrated with silver nitrate solution to a silver iodide end point. The $[CN^-]/[Cr]$ ratio determined for one preparation was 0.998 ± 0.003.

(2) Chromium(II) catalyzes the aquation of $Cr(CN)_3$ and $Cr(CN)_2^+$, giving $CrCN^{2+}$. The mixture of aquation products of $K_3Cr(CN)_6$ prepared as described for the preparation of $Cr(CN)_3$ (but containing 5 equivalents of acid) was flushed with N_2 gas and a small amount of Cr^{2+} was added. The Cr^{2+} was

destroyed by air oxidation after several minutes and the complex purified as described above. Stock solutions were generally 0.01-0.04 M $CrCN^{2+}$.

Mercury(II) perchlorate

Stock solutions of mercury(II) perchlorate were prepared by dissolving reagent grade mercury(II) oxide in a slight excess of perchloric acid. Solutions were analyzed by the methods described by Espenson and Birk (39).

Ion exchange resin

Dowex 50W-X8 cation resin was cleaned by rinsing with 4-6 M HCl until free of iron(III) (when the resin is new) or until free of most chromium complexes from previous usage. The resin was then rinsed with solutions of sodium hydroxide-hydrogen peroxide and generally allowed to stand overnight in the presence of this solution. The resin was reconverted to the acid form by rinsing with 4-6 M HCl, followed by rinsing with water to remove all excess acid and chloride ion.

Anion resin was generally just rinsed with water or with an acid solution containing the anion in the form of which the resin was desired.

Other reagents

All other reagents were of the best available grade and were used without further purification. Solutions used in volumetric procedures were prepared and analyzed by accepted procedures.

Kinetics Experiments

Reactions with Cr^{2+}

Because Cr^{2+} reacts with oxygen to form $Cr_2(OH)_2^{4+}$(33), reactions involving Cr^{2+} were carried out under an inert nitrogen atmosphere. Oxygen was removed from reaction solutions by bubbling a stream of purified nitrogen gas through the solution for at least 20 minutes. Reaction vessels were capped with rubber serum caps and the nitrogen introduced through a Teflon needle. Generally Cr^{2+} was the last reagent added. A calibrated hypodermic syringe and needle preflushed with purified nitrogen was used to inject the chromium(II) through the rubber serum cap. If Cr^{2+} was not the last reagent added, the other solution was also deoxygenated and added with a preflushed syringe.

Conventional spectrophotometric rate measurements

Most reaction kinetics were studied spectrophotometrically with a Cary Model 14 recording spectrophotometer. Reaction vessels were cylindrical spectrophotometer cells capped with rubber serum caps. Reaction solutions, complete but for the last reagent, and flushed with nitrogen when necessary, were brought to temperature by immersion in a constant temperature water bath for at least 30 minutes prior to injection of the last reagent with a calibrated syringe. Constant temperature was maintained during reaction by circulating constant temperature water through coils surrounding the spectrophotometer cell holder. The cell holder was made water tight by fastening a quartz plate over each end window and was filled with water so that the reaction vessel was immersed in a small constant temperature water bath. Temperature remained constant to within ± 0.01°C except at high temperatures (55-75°C), where ± 0.1°C is probably a better estimate. The absorbance due to water in the light path was small and could be compensated for by adjustment of the base line.

In some studies of the aquation of $CrCN^{2+}$ at high temperatures (55-75°C), where volumes of room temperature $CrCN^{2+}$ solution of 0.5 ml or greater were added, the temperature was measured immediately after reaction was complete, using a thermistor thermometer.

In studies at temperatures below room temperature, a continuous stream of dry air was passed through the cell compartment to prevent condensation of water vapor on surfaces in the light path.

Concentrations of reagents within a series of runs were varied in a random order to minimize the apparent appearance of trends due to systematic errors. The concentration range studied was generally as large as possible.

Method of aliquots

Some studies of the aquation of $CrCN^{2+}$ at 55°C were carried out by an alternate method. Solutions were made up in darkened, 100 ml volumetric flasks, complete but for $CrCN^{2+}$.

After the solutions had come to temperature, the $CrCN^{2+}$ was added and the solutions were mixed well. Aliquots were withdrawn at appropriate intervals with quick draining 10 ml pipets and delivered into test tubes immersed in a dry ice-ethanol bath. The frozen samples were stored for as long as a week at -78°C. After the samples were quickly melted and brought to room temperature, the absorbances were read at an appropriate wavelength.

Stopped-flow experiments

The oxidation-reduction reactions of Cr^{2+} with $Co(NH_3)_4(OH_2)CN^{2+}$ and $Co(en)_2(OH_2)CN^{2+}$ are fairly rapid. Since the concentrations of Cr^{2+} needed to bring the rates into the conventionally observable range (10^{-5} - 10^{-4} M) are difficult to handle without air oxidation, these reactions were also studied with a stopped-flow apparatus.

The apparatus was based on the design of Dulz and Sutin (40) and was purchased from the Atom-Mech Machine Co., Patchogue, New York. A motor-driven block equipped with a slip clutch pushed the reagent syringes, driving reactants through an eight-jet mixing chamber into a 3 mm observation tube. The transmittance of the solution, which remained stationary on filling a stopping syringe, was measured spectrophotometrically with a Beckman Model DU monochromator. The light intensity was measured by connecting the signal from a photomultiplier tube (EMI 6256B), via a filtering and amplifying circuit, to the A input of a Tektronix 535A oscilloscope. The photomultiplier bias voltage was varied between 500 and 600 volts, with the monochromator slit width at 2.0 mm. The B input to the oscilloscope was a constant potential, so that the net input was (A-B), allowing amplification of small changes in A without amplifying the total A input. An oscilloscope trace was initiated electronically shortly before the stopping syringe was filled and was photographed with a Polaroid camera. A second trace was triggered manually.

Absorbance changes were kept less than 0.1 so that absorbance and transmittance were always linearly related, which allowed the ordinate of the trace to be treated as concentration. The abscissa (time) was calibrated with a time-mark generator. Each solution was prepared at the same ionic strength, so that density was about the same in each solution, optimum for best mixing.

Typical oscilloscope traces are shown in Fig. 1.

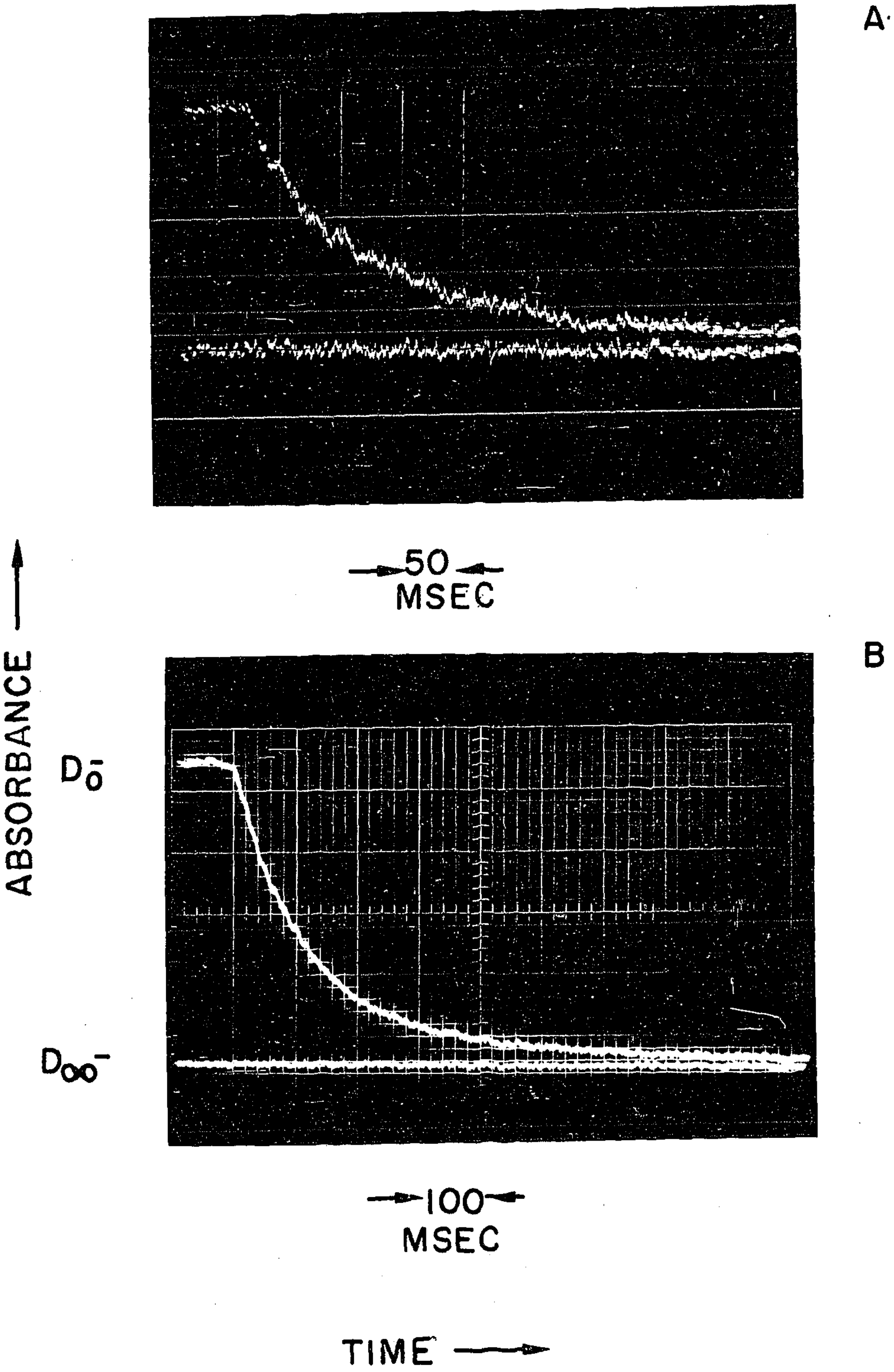
Measurement of H^+ concentration

In most kinetic studies, the H^+ concentration was calculated from the contributions made by the various reagents. In most studies of the $CrCN^{2+}$ aquation, however, the amount of acid added with the $CrCN^{2+}$ solution was known only roughly. In this case, $[H^+]$ was determined by direct titration with NaOH of the spent reaction solutions. The chromium(III) content was usually sufficiently low to cause no interference

Fig. 1. Typical stopped flow oscillograms

A. 4.31×10^{-4} $\underline{M}$ $Co(NH_3)_4(H_2O)CN^{2+}$, 6.11×10^{-3} $\underline{M}$ Cr^{2+}, 0.129 $\underline{M}$ H^+, I = 0.150 $\underline{M}$, 25.0°C; 4550Å, 560 volts bias voltage, 50 msec/cm sweep speed; $k_{ox} = 1500$ $\underline{M}^{-1}sec^{-1}$

B. 1.31×10^{-3} $\underline{M}$ $Co(en)_2(H_2O)CN^{2+}$, 5.04×10^{-3} $\underline{M}$ Cr^{2+}, 0.129 $\underline{M}$ H^+, I = 0.150 $\underline{M}$, 34.2°C; 4450Å, 600 volts bias voltage, 100 msec/cm sweep speed; $k_{ox} = 1710$ $\underline{M}^{-1}sec^{-1}$


A
50
MSEC
B
ABSORBANCE
D₀⁻
D∞⁻
100
MSEC
TIME

with the titration, and was also sufficiently low that $[H^+]$ changed negligibly during the run as CN^- was released.

Data Treatment

With the exception of stopped-flow experiments and some first-order kinetic data, most data were treated with an IBM 7074 or 360 computer. Data were fit to the appropriate equation with a non-linear least squares program[1].

Activation parameters were calculated from the absolute rate theory expression, Eq. 8, assuming $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (κ = 1)

$$k = \kappa(k_BT/h)\exp(\Delta S^\ddagger/R - \Delta H^\ddagger/RT) \qquad (8)$$

are independent of temperature. The subroutine used in these calculations treats all data simultaneously, fitting both temperature dependence and any hydrogen ion dependence associated with the rate constant.

The weighting scheme used in the non-linear least squares calculations depended on the manner in which the uncertainty (Δy) of the dependent variable (y) varied with the magnitude of y. If data are being fit to the relation $y = f(x)$, the function being minimized is:

$$F = \sum_i w_i(y_i - f_i)^2 = \sum_i w_i y_i^2(1 - \frac{f_i}{y_i})^2 \qquad (9)$$

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[1] The author is grateful to Dr. T. W. Newton of Los Alamos Scientific Laboratory for supplying the least squares programs and some of the subroutines used with these programs. The programs are based on a report by Moore and Zeigler (41).

The contribution of each term to the sum is proportional to $w_i y_i^2$ for a given relative approximation of f_i to y_i. The following cases may be distinguished:

1) The relative uncertainty of each data point is the same ($\Delta y/y \backsimeq$ constant). Thus, each term in the summation should count equally, independent of the magnitude of y. This is accomplished by setting $w_i = y_i^{-2}$, giving $w_i y_i^2 (=1)$. Most derived rate data fall in this category.

2) The absolute uncertainty of each data point is approximately constant ($\Delta y \backsimeq$ constant). The precision increases with the magnitude of y and each term in the summation should contribute proportionate to the magnitude of y. With $w_i = y_i^{-1}$, each term is proportional to $w_i y_i^2 (=y_i)$. This weighting scheme was used for the calculation of rate constants from absorbance-time data.

3) If it is desired to make each term depend even more heavily on the magnitude of y_i, the weights used are $w_i = 1$, with $w_i y_i^2 (=y_i^2)$.

4) When neither the absolute nor the relative uncertainty is constant, it may be desirable to take the precision of each data point into account. Each term should count more, the smaller the relative uncertainty. This is accomplished with $w_i = (y_i \Delta y_i)^{-1}$ giving $w_i y_i^2 (=y_i/\Delta y_i)$.

Tracer Experiments

Exchange of $*Cr^{2+}$ with $CrCN^{2+}$

Exchange reactions were initiated by the addition of $*Cr^{2+}$ solution to a nitrogen-flushed solution containing all other reagents and previously brought to constant temperature. The solution was contained in a 150 ml milk dilution bottle capped with a self-sealing Buna N rubber disk. These reactions were followed typically for 30 minutes, but in some cases for as long as 160 minutes. Since repeated puncturing of the rubber disk to withdraw samples could cause oxygen leakage, a further precaution was taken. The neck of the bottle was inserted into a large, one-hole rubber stopper and a glass cylinder was placed over the stopper. The glass cylinder was sealed off except for a nitrogen inlet tube in the side and a small hole in the top, through which samples were withdrawn with syringe and needle. Aliquots of 1-5 ml, depending on the $*Cr^{2+}$ concentration, were withdrawn at appropriate times and quenched by delivery into a small beaker through which a stream of air was bubbled, converting Cr^{2+} to $Cr_2(OH)_2^{4+}$ (33). The volume of the aliquot quenched was not critical since the specific activity rather than the activity of $Cr_2(OH)_2^{4+}$ was measured.

The separation of $Cr_2(OH)_2^{4+}$ from $CrCN^{2+}$ was carried out by an ion exchange procedure. The quenched aliquots were transferred to columns of Dowex 50W-X8, 50-100 mesh cation resin in the H^+ form, contained in a piece of tygon tubing about 12 mm x 8 cm. The resin was then rinsed with about 200 ml of 2 M $HClO_4$. Most of the $CrCN^{2+}$ was eluted by the first 10-20 ml of acid. The length of resin containing the $Cr_2(OH)_2^{4+}$ was treated with sodium hydroxide-hydrogen peroxide solution to remove the chromium.

The specific activity of the chromium(VI) solution resulting from oxidation of $Cr_2(OH)_2^{4+}$ was determined by counting a 5 ml sample in a well-type scintillation counter[1] at the energy maximum of the Cr^{51} γ-radiation and spectrophotometrically analyzing for chromium as chromate (32) after dilution of aliquots and heating in a boiling water bath to destroy excess peroxide. No colored species which might interfere with the chromium analysis could be removed from the resin.

Since Cr^{2+} is air sensitive and there was a possibility of some oxidation during the initial addition of $^*Cr^{2+}$ and during the withdrawal of aliquots, analyses were made twice during a run, at approximately one and four half-lives for exchange. Only runs where there was no appreciable change in Cr^{2+} concentration were retained as valid experiments.

The hydrogen ion concentration range was limited to <0.4M since even at this concentration, aquation is sufficiently rapid to cause changes in $CrCN^{2+}$ concentration during

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[1] The author is grateful to Dr. A. F. Voigt for use of counting facilities.

the time required for an exchange study (ten minutes to three hours). No satisfactory method was found for treatment of data for an exchange accompanied by net reaction.

Exchange of $*Cr^{2+}$ with the intermediate

Tracer experiments were used to determine the role of Cr^{2+} in the catalyzed disappearance of the intermediate (described below). Nonlabelled Cr^{2+} was used to reduce $Co(NH_3)_4(H_2O)CN^{2+}$, rapidly producing the intermediate. Labelled Cr^{2+} was then added and the reaction with intermediate allowed to proceed for 4-5 half-lives before the Cr^{2+} was oxidized in a stream of air. The separation of Cr^{2+} and $CrCN^{2+}$ and measurement of the specific activity of the Cr^{2+} fraction was carried out as described above. The first 15-20 ml of acid eluant was collected as the $CrCN^{2+}$ fraction, and contained most of the $CrCN^{2+}$ and Co^{2+} produced. The specific activity of this fraction was measured by counting a 5 ml sample and analyzing for chromium by the diphenylcarbazide method (42). The alkaline chromate method could not be used because of interference by Co^{2+}. A blank experiment to correct for exchange of Cr^{2+} and $CrCN^{2+}$ consisted of the same procedure, except that the disappearance of intermediate was allowed to go to completion before the tagged Cr^{2+} was added. The blank constitutes an overcorrection, since the concentration of $CrCN^{2+}$ was increasing during the tracer experiment, while it was at the final value throughout the blank experiment. Mathematical difficulties, as well as some zero-time exchange, prevented the calculation of a true blank, so that the results are not expected to be strictly quantitative.

Measurement of Spectra

Visible and ultraviolet spectra of relatively stable species were obtained by scanning the wavelength region of interest with a Cary Model 14 recording spectrophotometer. An appropriate blank was measured in the same cell to account for any effects due to changes in the baseline setting with wavelength. Infrared spectra were measured with a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer[1].

A special procedure was required in the case of the metastable intermediate, which could not be isolated in pure form. Repetitive spectra were taken at constant temperature (2-5°C) of a solution in which intermediate had been produced by reaction of Cr^{2+} with an excess of the appropriate cobalt(III) complex. Spectra were taken every 90 sec until the reaction had gone about 90% to completion, then every 5 min until constant readings were observed. Under these conditions, formation of the intermediate should have always been completed within one minute or less, while disappearance of the intermediate (forming $CrCN^{2+}$) continued for much longer times (30-

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[1] The author is grateful to Dr. V. A. Fassel for use of facilities and to Miss E. E. Conrad for taking I.R. spectral data.

60 min). The decay of the intermediate followed pseudo-first-order kinetics (see below). Linear plots of log $(D_t - D_\infty)$ vs. time (D = absorbance at the indicated time) were extrapolated to zero time to obtain the quantity $(D_o - D_\infty)$ at various wavelengths. The following equations were used to calculate absorbancy indices for the intermediate:

$$D_o - D_\infty = \Delta\epsilon \cdot b \cdot C_{lim} \tag{10}$$

$$\epsilon_{intermediate} = \epsilon_{CrCN^{2+}} + \Delta\epsilon \tag{11}$$

where b is the light-path length and C_{lim} is the concentration of the limiting reagent. Assuming that all $CrCN^{2+}$ is formed via a path involving the intermediate, the initial concentration of intermediate is C_{lim}.

RESULTS AND DISCUSSION

Oxidation-Reduction Reactions

Taube and Myers (43) first studied the reaction of Cr^{2+} with $Co(NH_3)_5X^{+3-n}$, Eq. 12.

$$Cr^{2+} + Co(NH_3)_5X^{+3-n} + 5H^+ = CrX^{+3-n} + Co^{2+} + 5NH_4^+ \qquad (12)$$

The formation of CrX^{+3-n} with many ligands X^{n-} established an inner-sphere bridged mechanism for electron transfer. Rate data for a number of these reactions are presented in Table 1.

Table 1. Rate data for reactions of Cr^{2+} with $Co(NH_3)_5X^{+3-n}$ at 25°C

X^{n-}	I	$k(\underline{M}^{-1}sec^{-1})$	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	Reference
F^-	0.1$\underline{M}$	$(2.5\pm0.5)x10^5$			(44)
	1.0	$(9\pm1)x10^5$			(44)
Cl^-	0.1	$(6\pm1)x10^5$			(44)
	1.0	$(2.6\pm0.5)x10^6$			(44)
Br^-	0.1	$(1.4\pm0.4)x10^6$			(44)
I^-	0.1	$(3\pm1)x10^6$			(44)
NH_3[a]	0.4	$8.9x10^{-5}$	14.7	-30	(45)
H_2O	1.2	0.5	2.9	-52	(46)
N_3^-	1.0	$3x10^5$			(47)
$-NCS^-$	1.0	19	6.9	-29	(47)
SO_4^{2-}	1.0	18	6.2	-32	(47)
OAc^-	1.0	0.18			(48)
NO_3^-	1.0	90			(47)

[a] This reaction is likely outer-sphere, since NH_3 is not transferred.

Reactions with cyanide as the bridging ligand have not previously been studied, although some experiments related to this work have been published (6,49). Particular interest in this ligand arises because it is apparently the first system for which there is direct evidence for remote attack by Cr^{2+} (2).

Although the immediate product of the reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, $Co(NH_3)_4(H_2O)CN^{2+}$, or $Co(en)_2(H_2O)CN^{2+}$ is a metastable intermediate (discussed below), this intermediate decays to form $CrCN^{2+}$. The stoichiometry of these reactions (Eq. 13) was determined by ion exchange and spectrophotometric

$$Cr^{2+} + CoL_5CN^{2+} + 5H^+ = CrCN^{2+} + Co^{2+} + 5HL^+ \qquad (13)$$

techniques. Ion exchange separation of the products of each reaction indicated that the only chromium(III) product was $CrCN^{2+}$.

The addition of various amounts of Cr^{2+} to solutions of Co(III) gave changes in absorbance directly related to the Cr^{2+} concentration when $[Cr^{2+}]_o/[Co(III)]_o$ was ≤ 1.0. The absorbance change was invariant, however, when the ratio $[Cr^{2+}]_o/[Co(III)]_o$ was ≥ 1.0. This is consistent only with the 1:1 stoichiometry indicated in Eq. 13. No attempt was made to verify the stoichiometry with respect to H^+.

Studies of the kinetics of these reactions were carried out by spectrophotometric techniques (conventional and stopped-flow) at wavelengths in the ultraviolet region, where absorbancy indices of each Co(III) complex are large (~20,000 $\underline{M}^{-1}cm^{-1}$ at 2100Å) and at the maxima in the visible spectra of Co(III), shown in Fig. 2. There was little interference from absorbance changes due to decay of the intermediate. Rate studies were carried out at 5-35°C and 0.150$\underline{M}$ ionic strength over the concentration ranges: $Co(NH_3)_5CN^{2+}$:4.5×10^{-5} - 6.5×10^{-3} $\underline{M}$ Cr^{2+}, 2.1×10^{-6} - 6.0×10^{-3} $\underline{M}$ Co(III), 0.03 - 0.150 $\underline{M}$ H^+; $Co(NH_3)_4(H_2O)CN^{2+}$:3.7×10^{-5} - 1.3×10^{-2} $\underline{M}$ Cr^{2+}, 1.5×10^{-6} - 6.1×10^{-4} $\underline{M}$ Co(III), 0.015 - 0.150 $\underline{M}$ H^+; $Co(en)_2(H_2O)CN^{2+}$:1.5×10^{-5} - 1.3×10^{-2} $\underline{M}$ Cr^{2+}, 8.0×10^{-7} - 1.3×10^{-2} $\underline{M}$ Co(III), 0.010 - 0.150 $\underline{M}$ H^+. Experimental results are presented in Tables 2-4. Although the rate constants are not highly precise, particularly in the case of $Co(NH_3)_4(H_2O)CN^{2+}$ and $Co(en)_2(H_2O)CN^{2+}$ experiments, the fair constancy of second-order rate constants for a given complex over the quite large ranges of concentrations studied indicates that the rate law is adequately described by Eq. 14.

$$-d[Co(III)]/dt = k_{ox}[Cr^{2+}][CoL_5CN^{2+}] \qquad (14)$$

This rate law is identical with those found for the related systems listed in Table 1. Rate constants for the aquo complexes were greater than that for the pentaammine complex, as was observed also in work on the reaction of Cr^{2+} with acetatocobalt(III) complexes (50) and with chlorochromium(III) complexes (51).

Data for the three reactions were fit to the Eyring

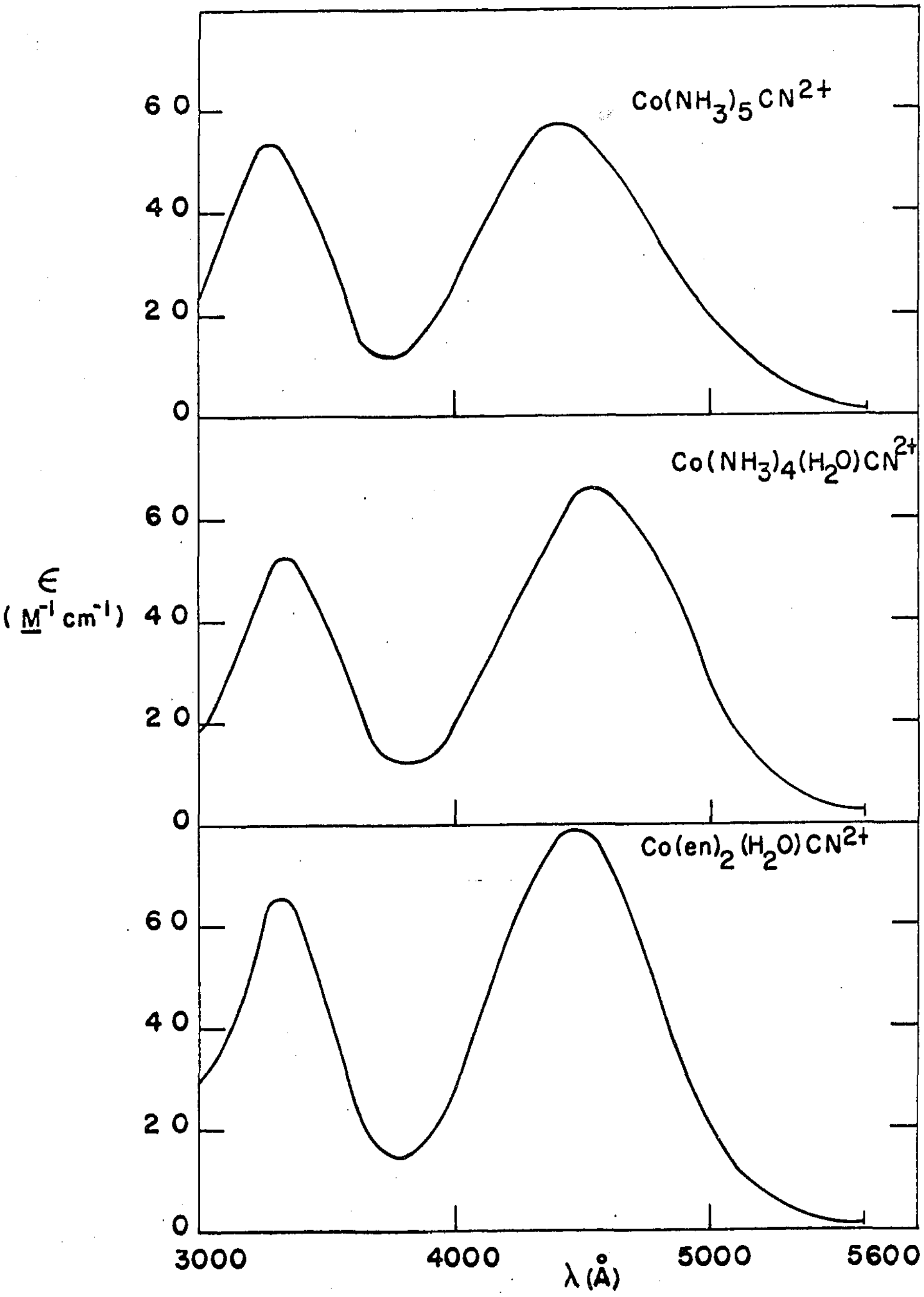

Fig. 2. Spectra of cyanocobalt(III) complexes

Table 2. Rate constants for the oxidation-reduction reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$[a]

$10^4[Cr^{2+}]_o$	$10^5[Co(III)]_o$	$[H^+]_o$	λ(Å)	Temp (°C)	k_{ox} ($\underline{M}^{-1}sec^{-1}$) obsd.[b]	calc[c]
34.5 $\underline{M}$	17.5 $\underline{M}$	.139 $\underline{M}$	2400	5.2	21.3±0.7[d]	14.5
1.11	.495	.150	2100	"	14.0±0.1	"
4.95	2.06	.148	"	"	14.4±0.2	"
1.98	.248	.149	"	5.1	15.7±0.3	14.4
1.98	.495	.149	"	"	15.0±0.2	"
9.08	4.12	.147	2200	"	14.3±0.4	"
13.8	7.10	.146	2400	5.2	21.1±0.7[d]	14.5
1.98	.991	.149	2100	5.0	14.0±0.1	14.3
44.9	255.	.129	4400	15.0	21.6±0.2	22.9
36.4	511.	.124	"	"	17.5±0.1[d]	"
60.0	310.	.123	"	"	22.2±0.2	"
34.7	562.	.123	"	"	23.6±0.2	"
57.7	281.	.124	"	"	21.0±0.3	"
3.37	491.	.134	"	"	33.5±2.3[d]	"
64.9	300.	.113	"	"	20.8±0.3	"

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[a] Determined with a Cary Model 14 spectrophotometer. I = 0.150 $\underline{M}$ with $HClO_4$ and $LiClO_4$, except as noted.

[b] Calculated from absorbance-time data using a computer program for first-order or second-order data. Uncertainties are standard deviations and represent the fit of data to the appropriate equation.

[c] Calculated from the activation parameters given in Table 5.

[d] These data points were not used in the calculation of the activation parameters (Table 5).

Table 2. (Continued)

$10^4[Cr^{2+}]_o$	$10^5[Co(III)]_o$	$[H^+]_o$	λ(Å)	Temp (°C)	$k_{ox}(\underline{M}^{-1}sec^{-1})$	
					obsd.[b]	calc.[c]
64.9	300.	.100	4400	15.0	19.8±0.3	22.9
21.7	599.	.125	"	"	26.9±0.6	"
2.28	1.24	.149	2065	"	25.8±0.2	"
2.28	1.24	.149	2100	"	24.0±0.2	"
3.44	1.90	.149	2200	"	23.7±0.1	"
1.98	.991	.149	2100	"	24.9±0.2	"
.449	.206	.150	"	"	20.3±1.5	"
1.98	.248	.149	"	"	20.1±0.5	"
4.95	2.06	.148	"	"	24.3±0.1	"
1.98	.495	.149	"	"	24.7±0.3	"
9.08	4.12	.147	2200	"	23.0±0.3	"
34.5	17.5	.139	2400	"	26.3±0.5	"
13.8	7.10	.146	"	"	26.6±0.7	"
.449	.206	.150	2100	25.0	28.4±1.5[d]	35.5
1.98	.495	.149	"	"	38.3±0.8	"
4.95	2.06	.148	"	"	35.6±0.2	"
1.11	.495	.150	"	"	33.1±0.6	"
13.8	7.10	.146	2400	"	44.7±1.2[d]	"
1.98	.991	.149	2100	"	35.4±0.2	"
9.08	4.12	.147	2200	"	38.0±0.5	"
1.98	.248	.149	2100	"	36.2±1.1	"
1.98	.991	.149	"	"	35.0±0.2	"

Table 2. (Continued)

$10^4[Cr^{2+}]_o$	$10^5[Co(III)]_o$	$[H^+]_o$	λ(Å)	Temp (°C)	k_{ox} ($\underline{M}^{-1}sec^{-1}$) obsd.[b]	calc.[c]
40.9	409.	.052	4400	15.0	22.8[e]	
40.9	409.	.125	"	"	32.0	
40.9	409.	.475	"	"	54.1[f]	
		1.0	"	"	61±6[g]	
40.9	409.	.035	"	"	51.4[f]	
"	"	.104	"	"	53.0[f]	
"	"	.254	"	"	53.6[f]	
"	"	.354	"	"	52.2[f]	
"	"	.504	"	"	51.2[f]	

[e] $I = 0.077$ $\underline{M}$.

[f] $I = 0.53$ $\underline{M}$.

[g] $I = 1.00$ $\underline{M}$ under a variety of concentration conditions (6).

Table 3. Rate constants for the oxidation-reduction reaction of Cr^{2+} with trans-$Co(NH_3)_4(H_2O)CN^{2+}$[a]

$10^3[Cr^{2+}]_o$	$10^4[Co(III)]_o$	$[H^+]_o$	λ(Å)	Method[b]	Temp (°C)	k_{ox}($\underline{M}^{-1}sec^{-1}$)[c]	
						obsd	calc
.257	.124	.150	2100	C	15.0	1280	1215
.0371	.0150	"	"	"	"	1510	"
.549	.251	"	"	"	"	≥1250[d]	"
.0647	.0312	"	"	"	"	1260	"
.128	.0626	"	"	"	"	1460	"
.667	.302	"	2300	"	"	≥1050[d]	"
.257	.124[e]	"	"	"	"	1170	"
.0371	.0150[e]	"	2100	"	"	1620	"
.549	.251[e]	"	2100	"	"	≥1250[d]	"
.128	.0626[e]	"	"	"	"	1320	"
.667	.302[e]	"	2300	"	"	≥1050[d]	"

[a] I = 0.150 $\underline{M}$ with $HClO_4$ and $LiClO_4$. The Co(III) complex was added as the chloride salt.

[b] Measurements were made with a Cary Model 14 recording spectrophotometer (C) or on a stopped-flow apparatus (SF).

[c] Observed values of k_{ox} were evaluated graphically from plots of $\log(D_t-D_\infty)$ vs. t. Numbers in parentheses are the number of determinations of k_{ox}, using the same solutions. The uncertainties given are average deviations, representing the precision with which experiments could be reproduced. Calculated values of k_{ox} were obtained from the activation parameters given in Table 5.

[d] Reaction was complete on mixing. The limit was placed on k_{ox} by assuming that $t_{\frac{1}{2}} \leq 1$ sec. These values were not used in the calculation of activation parameters.

[e] To show that the rate was independent of $[Cl^-]$, 0.01 $\underline{M}$ Cl^- was added to these solutions.

Table 3. (Continued)

$10^3[Cr^{2+}]_o$	$10^4[Co(III)]_o$	$[H^+]_o$	λ(Å)	Method[b]	Temp (°C)	$k_{ox}(\underline{M}^{-1}sec^{-1})^c$	
						obsd	calc
5.95	4.31	.129	4550	SF	15.8	1290±57(8)	1231
12.5[f]	6.13	.0887	"	"	"	1180±84(11)	"
12.9[f]	6.13	.0156	"	"	"	1217±108(9)	"
6.11	4.31	.129	"	"	25.0	1532±113(8)	1420
10.2[f]	4.09	.101	"	"	"	1547±78(7)	"
13.1[f]	4.90	.0156	4450	"	"	1299±27(8)	"
6.08	4.31	.129	4550	"	34.2	1720±179(8)	1625
10.2[f]	4.09	.101	"	"	"	1594±65(7)	"
13.2[f]	4.90	.0156	4450	"	"	1614±43(7)	"

[f] These solutions contained Zn^{2+} of concentration $\frac{1}{2}[Cr^{2+}]$.

Table 4. Rate constants for the oxidation-reduction reaction of Cr^{2+} with trans-$Co(en)_2(H_2O)CN^{2+}$[a]

$10^3[Cr^{2+}]_o$	$10^4[Co(III)]_o$	$[H^+]_o$	$\lambda(\mathring{A})$	Method[b]	Temp (^oC)	$k_{ox}(\underline{M}^{-1}sec^{-1})$[c] obsd	calc
.0467	.0241	.150	2200	C	15.0	1024	769
.0933	.0482	"	"	"	"	1076	"
.0933	.0482	"	2100	"	"	1031	"
.140	.0724	"	"	"	"	1237	"
.0156	.00804	"	"	"	"	988	"
.0469	.0241	"	"	"	"	966	"
.0234	.0121	"	"	"	"	1160	"
.0467	.0241	"	"	"	"	1024	"
13.1[d]	5.25	.0890	4450	SF	15.8	917±49(8)	791
7.25	3.75	.0100	"	"	"	842±49(8)	"
5.00	13.1	.129	"	"	"	702±33(7)	"
9.66	10.3	.101	"	"	"	641±44(7)	"
1.05	5.15	.144	"	"	"	706±37(5)	"
7.97	5.15	.0199	"	"	"	750±60(5)	"
.375	1.03	.145	"	"	"	1123±81(6)	"

[a] $I = .150\ \underline{M}$ with $HClO_4$ and $LiClO_4$.

[b] Measurements were made with a Cary Model 14 spectrophotometer (C) or with a stopped-flow apparatus (SF).

[c] Observed values of k_{ox} were evaluated graphically. Numbers in parentheses are the number of determinations of k_{ox}, using the same solutions. The uncertainties given are average deviations, representing the precision with which experiments could be reproduced. Calculated values of k_{ox} were obtained from the activation parameters given in Table 5.

[d] These solutions contained Zn^{2+} of concentration $\frac{1}{2}[Cr^{2+}]$.

Table 4. (Continued)

$10^3[Cr^{2+}]_0$	$10^4[Co(III)]_o$	$[H^+]_o$	λ(Å)	Method[b]	Temp (°C)	$k_{ox}(\underline{M}^{-1}sec^{-1})$[c]	
						obsd	calc
13.2[d]	6.56	.0886	4450	SF	25.0	1001±51(7)	1089
7.28	3.75	.0100	"	"	"	1185±56(8)	"
5.13	13.1	.129	"	"	"	1122±23(8)	"
9.77	10.3	.101	"	"	"	1143±8(5)	"
1.08	5.15	.144	"	"	"	983±40(5)	"
8.01	5.15	.0199	"	"	"	1095±53(7)	"
.415	10.3	.145	"	"	"	1340±150(6)	"
13.3[d]	6.56	.0886	"	"	"	1267±49(8)	1472
7.28	3.75	.0100	"	"	"	1751±53(8)	"
5.04	13.1	.129	"	"	"	1560±82(8)	"
9.79	10.3	.101	"	"	"	1515±48(5)	"
1.13	5.15	.144	"	"	"	1250±49(5)	"
8.01	5.15	.0199	"	"	"	1531±85(8)	"
.433	10.3	.145	"	"	"	1732±112(6)	"

equation (Eq. 8) with a non-linear least squares computer program. Activation parameters, as well as observed and calculated rate constants at the temperatures studied, are given in Table 5.

Table 5. Activation parameters for the Cr^{2+}-Co(III) oxidation-reduction reactions[a]

Co(III) complex	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	Temp ($^{\circ}C$)	k_{ox} ($\underline{M}^{-1}sec^{-1}$)[b] obsd	calc
$Co(NH_3)_5CN^{2+}$	6.92±0.35	-28.3±1.2	5.1	14.5±0.5	14.4
			15.0	22.8±2.0	22.9
			25.0	35.8±1.3	35.5
$Co(NH_3)_4(H_2O)CN^{2+}$	2.07±0.26	-37.2±0.9	15.8	1230±80	1231
			25.0	1450±130	1420
			34.2	1670±110	1625
$Co(en)_2(H_2O)CN^{2+}$	5.36±0.30	-26.7±1.0	15.8	770±120	791
			25.0	1120±90	1089
			34.2	1490±160	1472

[a] I = 0.150 $\underline{M}$ with $LiClO_4$ and $HClO_4$. Activation parameters were calculated with a non-linear least squares computer program. Weighting was carried out as k^{-2}.

[b] Observed values of k_{ox} are weighted averages (weight = k^{-2}) and uncertainties are weighted average deviations. Calculated values of k_{ox} were determined from the activation parameters.

Values of k_{ox} at 1.00 $\underline{M}$ ionic strength for $Co(NH_3)_5CN^{2+}$ were determined to be 61 ± 6 $\underline{M}^{-1}sec^{-1}$ at 15°C (6) and 100 ± 20 $\underline{M}^{-1}sec^{-1}$ at 25°C (49). Estimates of the activation parameters based on these values of k_{ox}, $\Delta H^{\ddagger} \sim 9$ kcal/mole and $\Delta S^{\ddagger} \sim -30$ e.u., are similar to those calculated for solutions of 0.150 $\underline{M}$ ionic strength, where k_{ox} = 22.8 ± 2.0

$\underline{M}^{-1}sec^{-1}$ at 15°C and 35.8 ± 1.3 $\underline{M}^{-1}sec^{-1}$ at 25°C, and $\Delta H^{\ddagger}$ = 6.92 ± 0.35 kcal/mole and $\Delta S^{\ddagger}$ = -28.3 ± 1.2 e.u. (see Table 5).

The effect of ionic strength on the values of k_{ox} for the reaction with $Co(NH_3)_5CN^{2+}$ is shown in Table 2. The ionic strength effect is adequately described by an extended Debye-Hückel equation (Eq. 15). In Eq. 15, k_o is the rate constant

$$\log k = \log k_o + \frac{A\Delta(Z^2)^{\ddagger}\sqrt{I}}{1+\sqrt{I}} + BI \qquad (15)$$

at infinite solution, A is a constant which is characteristic of the solvent, $\Delta(Z^2)^{\ddagger}$ is the change in the square of the charges of the species involved in the net activation process, and B is an empirical constant. For the reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, A = 0.50 and $\Delta(Z^2)^{\ddagger}$ = 16-4-4 = 8. The best fit of data to Eq. 15 is obtained with $B \simeq -0.55$, giving $k_o \simeq 6.7$.

Identification and Kinetics of Disappearance of the Intermediate

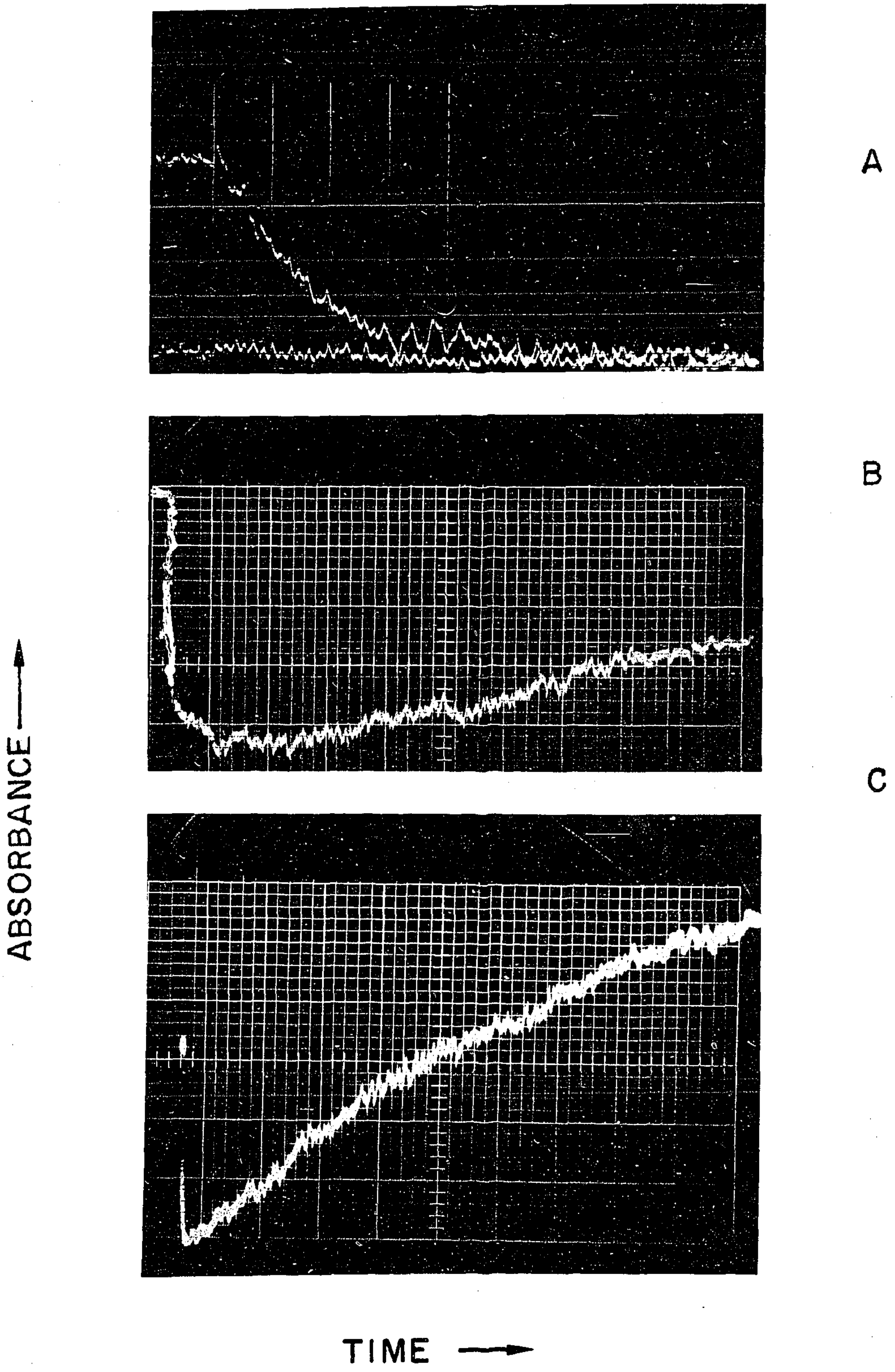
Evidence for an intermediate

Evidence for the existence of an intermediate in the reaction of Cr^{2+} with CoL_5CN^{2+} is as follows. At some wavelengths (e.g., 3270Å for $Co(NH_3)_5CN^{2+}$) the absorbance decreases rapidly with rate constant k_{ox}, reaches a minimum, and then slowly rises to a constant value. At other wavelengths (e.g., 4400Å for $Co(NH_3)_5CN^{2+}$), there is an initial rapid decrease in absorbance with rate constant k_{ox}, with very little change in absorbance after this. At still other wavelengths (e.g., 5200Å for $Co(NH_3)_5CN^{2+}$), the absorbance increases somewhat during the time required for the first stage reaction, then continues to rise considerably to a constant value. Similar observations were made with the other two complexes, $Co(NH_3)_4(H_2O)CN^{2+}$ and $Co(en)_2(H_2O)CN^{2+}$. Absorbance behavior for $Co(NH_3)_4(H_2O)CN^{2+}$ at 5200Å is shown in Fig. 3. These observations are inconsistent with the occurrence of a single reaction. Since the slower reaction occurs subsequent to the initial reaction and with either reactant in excess, it must necessarily be a reaction involving the product(s) of the initial rapid reaction, i.e., a metastable intermediate is formed.

Although there may be other possibilities, two logical choices for an initial product of a reaction between Cr^{2+} and CoL_5CN^{2+}, which reacts further to give $CrCN^{2+}$, are the isocyanide $CrNC^{2+}$ and the binuclear complex $CrNCCoL_5{}^{4+}$. The spectral observations on a given Co(III) complex are consistent with either of these formulations.

The problem remains to distinguish between the two formulations for the intermediates or to uncover any other possibilities. The most convincing evidence for the identification of an intermediate would be its isolation and chemical analysis. An intermediate for which isolation was achieved is $(NC)_5FeCNCo(CN)_5{}^{6-}$, formed in the reaction of $Fe(CN)_6{}^{3-}$ with

Fig. 3. Stopped flow oscillograms showing the presence of an intermediate in the reaction of Cr^{2+} with $Co(NH_3)_4(H_2O)CN^{2+}$; 5.25×10^{-3} $\underline{M}$ Cr^{2+}, 9.65×10^{-4} $\underline{M}$ Co(III), .995 $\underline{M}$ H^+, I = 1.00 $\underline{M}$, 25°C, 5200Å; sweep speed; A = 50 msec/cm, B = 2.0 sec/cm, C = 16.4 sec/cm


A
B
C
ABSORBANCE
TIME

$Co(CN)_5^{3-}$ (52). However, the short lifetime of the intermediate(s) involved here precludes this method of identification. A second technique is the production of the same intermediate by several reactions. As indicated above, the reactions of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, $Co(NH_3)_4(H_2O)CN^{2+}$ and $Co(en)_2(H_2O)CN^{2+}$ each produce an intermediate. A common intermediate, as demonstrated by identical properties, would eliminate the formulation as a binuclear complex, since variation of the non-bridging ligands on Co(III) should cause changes in properties of the intermediates. The properties to be investigated are kinetics of disappearance of the intermediate, reaction of intermediate with tagged Cr^{2+}, and spectra of the intermediate.

Kinetics of decay of the intermediate

The rate of disappearance of the intermediate formed from the three Co(III) complexes was studied at 1.00 M ionic strength (maintained with $LiClO_4$) under the following conditions: 15.0°C, $4x10^{-3}$ M Co(III), 0-.042 M Cr^{2+} (in excess of Co(III)), 0.400 M H^+ (Table 6); 25.0°C, $4x10^{-3}$ M Co(III), $8.1x10^{-4}$ - $4.1x10^{-2}$ M Cr^{2+} (excess), .05-.91 M H^+ (Table 7). More experiments were performed at 15.0°C and 0.40 M H^+, with 0-.056 M Cr^{2+} and .002-.015 M Co(III), but are not reported in Table 6 since the Co(III) solutions used in those experiments probably contained impurities, as indicated by changes in rate after recrystallization. However, data qualitatively con-

Table 6. Rate constants for disappearance of intermediate at 15.0°C[a]

Source[b]	$10^3[Cr^{2+}]_{xs}$	$k_i(sec^{-1})^c$	
		obsd	calc
A	8.15	.0159 ± .0003	.0159
B	8.23	.0167 ± .0003	.0159
C	8.21	.0147 ± .0002	.0159
A	36.96	.0269 ± .0006	.0296
B	37.04	.0341 ± .0002	.0296
C	37.02	.0377 ± .0008	.0296
A	2.41	.0114 ± .0003	.0131
B	2.49	.0117 ± .0003	.0131
C	2.47	.0098 ± .0002	.0131
A	16.61	.0180 ± .0004	.0199
B	16.69	.0182 ± .0004	.0199
C	16.67	.0201 ± .0002	.0199
A	0.0[d]	.0166 ± .0002	.0120
B	0.0[d]	.0176 ± .0001	.0120
C	0.0[d]	.0142 ± .0002	.0120
A	41.54	.0300 ± .0009	.0318
B	41.62	.0306 ± .0010	.0318
C	41.60	.0326 ± .0007	.0318
A	0.83	.0125 ± .0004	.0124
B	0.91	.0132 ± .0004	.0124
C	0.89	.0109 ± .0005	.0124
A	4.01	.0112 ± .0002	.0139
B	4.09	.0121 ± .0003	.0139
C	4.07	.0115 ± .0002	.0139
A	26.91	.0255 ± .0004	.0248
B	26.99	.0263 ± .0005	.0248
C	26.97	.0233 ± .0006	.0248

[a] I = 1.00 M with $LiClO_4$; 0.400 M H^+. Spectrophotometric measurements at 5200Å, using a ten-fold expanded scale slide wire.

[b] A = $Co(NH_3)_5CN^{2+}$ (3.93×10^{-3} M)
B = $Co(NH_3)_4(H_2O)CN^{2+}$ (3.85×10^{-3} M)
C = $Co(en)_2(H_2O)CN^{2+}$ (3.87×10^{-3} M).

[c] Observed values of k_i were obtained from absorbance-time data with a computer program for first-order kinetic data; weighting was carried out as 1/D (D=absorbance). Calculated values were obtained from the best fit of the data to the equation: $k_i = k_o' + k_1' [Cr^{2+}]$ (Table 8).

[d] Cobalt(III) was in excess by .00192, .00184, and .00186M respectively in these three experiments.

Table 7. Rate constants for disappearance of intermediate at 25.0°C[a]

Source[b]	$[H^+]$($\underline{M}$)	$10^3[Cr^{2+}]_{xs}$($\underline{M}$)	$10^2k_i(sec^{-1})$[c] obsd	calc
A	.0493	2.38	5.66 ± .14	5.24
	.0495	3.93	5.47 ± .04	5.46
	.0494	7.78	6.87 ± .20	6.01
	.0499	9.53	8.23 ± .35	6.25
	.0495	12.81	7.61 ± .30	6.72
	.0494	15.96	7.35 ± .12	7.17
	.0498	26.14	8.47 ± .41	8.61
	.0505	29.28	5.28 ± .40	9.06
	.0501	39.97	11.97 ± .61	10.58
	.0999	3.93	4.74 ± .21	5.26
	.1003	9.53	5.50 ± .49	6.03
	.0998	15.96	6.16 ± .47	6.91
	.0998	16.13	8.19 ± .49	6.93
	.0993	29.28	14.46 ± .66	8.74
	.201	3.93	5.65 ± .14	4.90
	.200	9.53	6.22 ± .27	5.62
	.201	15.96	7.13 ± .24	6.44
	.201	16.43	6.85 ± .35	6.46
	.200	29.28	10.25 ± .19	8.14
	.400	.81	5.01 ± .05	3.97
	.400	2.39	4.46 ± .11	4.15
	.401	3.98	3.90 ± .16	4.33
	.400	7.87	4.79 ± .19	4.77
	.399	9.53	4.99 ± .14	4.96
	.400	15.96	5.61 ± .09	5.68
	.400	16.13	5.42 ± .15	5.70
	.399	26.19	8.57 ± .13	6.83
	.400	36.22	8.60 ± .08	7.96
	.400	40.71	8.27 ± .21	8.46

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[a] I = 1.00 $\underline{M}$ with $LiClO_4$; spectrophotometric data taken in 5 cm cells at 5200Å, using a ten-fold expanded scale slidewire.

[b] A = $Co(NH_3)_5CN^{2+}$ ($3.93 \times 10^{-3}\underline{M}$)
B = $Co(NH_3)_4(H_2O)CN^{2+}$ ($3.85 \times 10^{-3}\underline{M}$)
C = $Co(en)_2(H_2O)CN^{2+}$ ($3.87 \times 10^{-3}\underline{M}$).

[c] Observed values of k_i were determined from absorbance-time data using a computer program for first-order kinetic data. Weighting was carried out as 1/absorbance. Calculated values were determined from the best fit of the data with sources A and B to the equation: $k = (k_o + k_1[Cr^{2+}])Q/(Q+[H^+])$ (Table 9).

Table 7. (Continued)

Source[b]	$[H^+]$($\underline{M}$)	$10^3[Cr^{2+}]_{xs}$($\underline{M}$)	10^2k_i(sec^{-1})[c]	
			obsd	calc
A	.601	3.93	4.03 ± .09	3.86
	.600	29.28	6.85 ± .21	6.41
	.800	2.38	3.82 ± .05	3.35
	.801	3.93	3.17 ± .16	3.49
	.800	7.78	3.85 ± .12	3.84
	.799	9.53	3.76 ± .09	4.00
	.800	12.81	4.04 ± .07	4.30
	.800	15.96	4.47 ± .10	4.59
	.800	16.43	4.32 ± .06	4.60
	.799	26.17	5.46 ± .26	5.52
	.800	29.28	4.94 ± .15	5.80
	.800	39.97	5.65 ± .18	6.77
B	.0505	4.01	2.19 ± .14	5.47
	.0504	7.86	7.21 ± .39	6.01
	.0493	9.61	6.90 ± .32	6.27
	.0505	12.89	5.76 ± .46	6.73
	.0504	10.04	8.45 ± .19	7.18
	.0508	26.25	8.95 ± .43	8.62
	.0499	29.36	10.27 ± .76	9.07
	.0992	4.01	10.26 ± .36	5.27
	.0997	9.61	7.11 ± .20	6.04
	.1008	16.04	7.77 ± .87	6.91
	.1008	16.21	7.62 ± .48	6.94
	.200	4.01	5.12 ± .20	4.92
	.200	9.61	5.35 ± .46	5.63
	.200	16.04	6.15 ± .11	6.45
	.200	16.21	7.99 ± .30	6.47
	.199	29.36	9.20 ± .19	8.16
	.400	.89	6.13 ± .18	3.98
	.403	4.06	4.85 ± .24	4.33
	.400	7.95	4.08 ± .25	4.77
	.400	9.61	4.31 ± .19	4.96
	.400	16.04	5.44 ± .16	5.68
	.400	16.21	6.44 ± .13	5.70
	.400	26.27	6.92 ± .27	6.84
	.401	36.30	8.48 ± .13	7.96
	.400	2.47	3.82 ± .08	4.16
	.400	40.79	8.53 ± .23	8.47
	.600	4.01	3.82 ± .11	3.87
	.599	29.36	5.73 ± .14	6.42
	.800	2.46	3.92 ± .10	3.36
	.800	4.01	3.15 ± .10	3.50
	.800	7.86	4.95 ± .15	3.85
	.800	9.61	3.40 ± .15	4.01

Table 7. (Continued)

Source[b]	$[H^+](\underline{M})$	$10^3[Cr^{2+}]_{xs}(\underline{M})$	$10^2k_i(sec^{-1})$[c] obsd	calc
B	.800	12.89	4.41 ± .08	4.31
	.800	16.04	4.48 ± .10	4.59
	.800	16.21	4.48 ± .09	4.61
	.800	26.25	5.17 ± .26	5.52
	.799	29.36	5.39 ± .14	5.81
	.800	40.05	6.31 ± .21	6.78
C	.200	9.59	3.93 ± .15	5.63
	.200	16.02	5.62 ± .12	6.45
	.200	16.02	5.58 ± .09	6.45
	.400	9.59	4.52 ± .23	4.96
	.400	16.02	4.76 ± .06	5.68
	.400	16.02	5.27 ± .05	5.68
	.600	3.99	2.91 ± .07	3.87
	.600	16.02	4.77 ± .04	5.08
	.599	29.34	6.76 ± .14	6.42
	.800	2.44	2.80 ± .02	3.36
	.800	3.99	2.97 ± .03	3.50
	.800	7.84	3.50 ± .09	3.85
	.800	9.59	3.40 ± .12	4.01
	.800	9.59	3.76 ± .08	4.01
	.800	12.87	4.41 ± .05	4.31
	.800	16.02	3.66 ± .06	4.59
	.800	16.02	3.41 ± .10	4.59
	.800	16.02	3.87 ± .06	4.59
	.800	26.23	5.08 ± .14	5.52
	.799	29.34	5.47 ± .17	5.81
	.800	40.03	6.50 ± .08	6.77
	.910	16.02	2.63 ± .16	4.36
	.930	9.59	3.09 ± .13	3.77

formed to the kinetic behavior to be described below throughout the concentration ranges given. All experiments reported here were carried out at 5200Å, but preliminary experiments and data taken in the measurement of spectra (described below) indicate that the rate of disappearance of the intermediate is independent of wavelength.

All kinetic data conformed to the pseudo-first-order rate equation (Eq. 16),

$$-d \ln(D_\infty - D_t)/dt = k_i \qquad (16)$$

where D_t is the absorbance at the indicated time. The observed rate constant k_i was found to increase with increasing concentration of Cr^{2+}. Plots of k_i vs. $[Cr^{2+}]$ (Fig. 4 and Fig. 5) at constant $[H^+]$ are linear with non-zero intercept, indicating the rate law given in Eq. 17.

$$k_i = k_o' + k_1'[Cr^{2+}] \qquad (17)$$

This rate law reveals two parallel paths for decay of the intermediate, one intramolecular and the other catalyzed by Cr^{2+}. Data at 15°C and 0.4 M H^+ were fit to Eq. 17. Results are presented in Table 8.

Table 8. Derived rate constants for disappearance of the intermediate at 15°C[a]

Data used[b]	k_o' (sec^{-1})	k_1' ($M^{-1}sec^{-1}$)
A,B,C	.0120 ± .0007	.478 ± .056
A,B	.0129 ± .0007	.442 ± .055
A	.0121 ± .0014	.411 ± .091
B	.0137 ± .0014	.462 ± .101
C	.0104 ± .0010	.555 ± .089

[a] I = 1.00 M with $LiClO_4$; 0.400 M H^+. Data were fit to the equation: $k_i = k_o' + k_1'[Cr^{2+}]$, where $k_o' = k_oQ/(Q+[H^+])$ and $k_1' = k_1Q/(Q+[H^+])$ according to the complete rate law determined at 25.0°C. Weighting was carried out as $(k\Delta k)^{-1}$.

[b] A = $Co(NH_3)_5CN^{2+}$, B = $Co(NH_3)_4(H_2O)CN^{2+}$, C = $Co(en)_2(H_2O)CN^{2+}$.

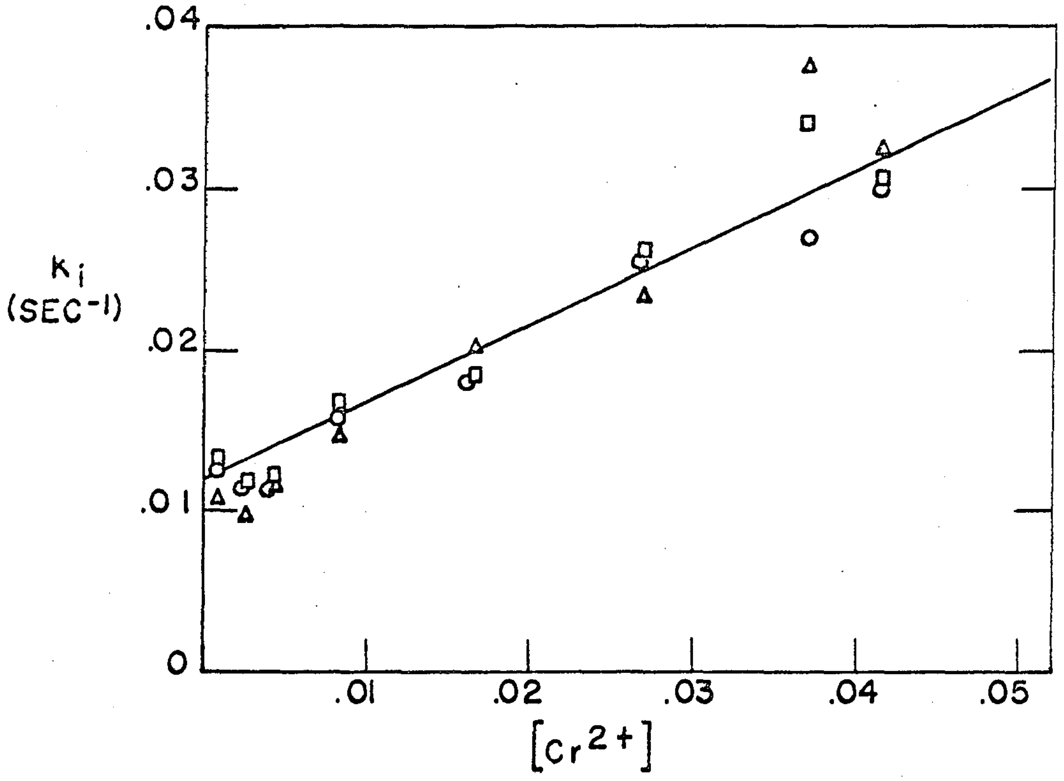


Fig. 4. Plot of k_i vs. $[Cr^{2+}]$ for decay of the intermediate at 15.0°C, 0.40 M H^+, I = 1.00 M

○ $Co(NH_3)_5CN^{2+}$

□ $Co(NH_3)_4(H_2O)CN^{2+}$

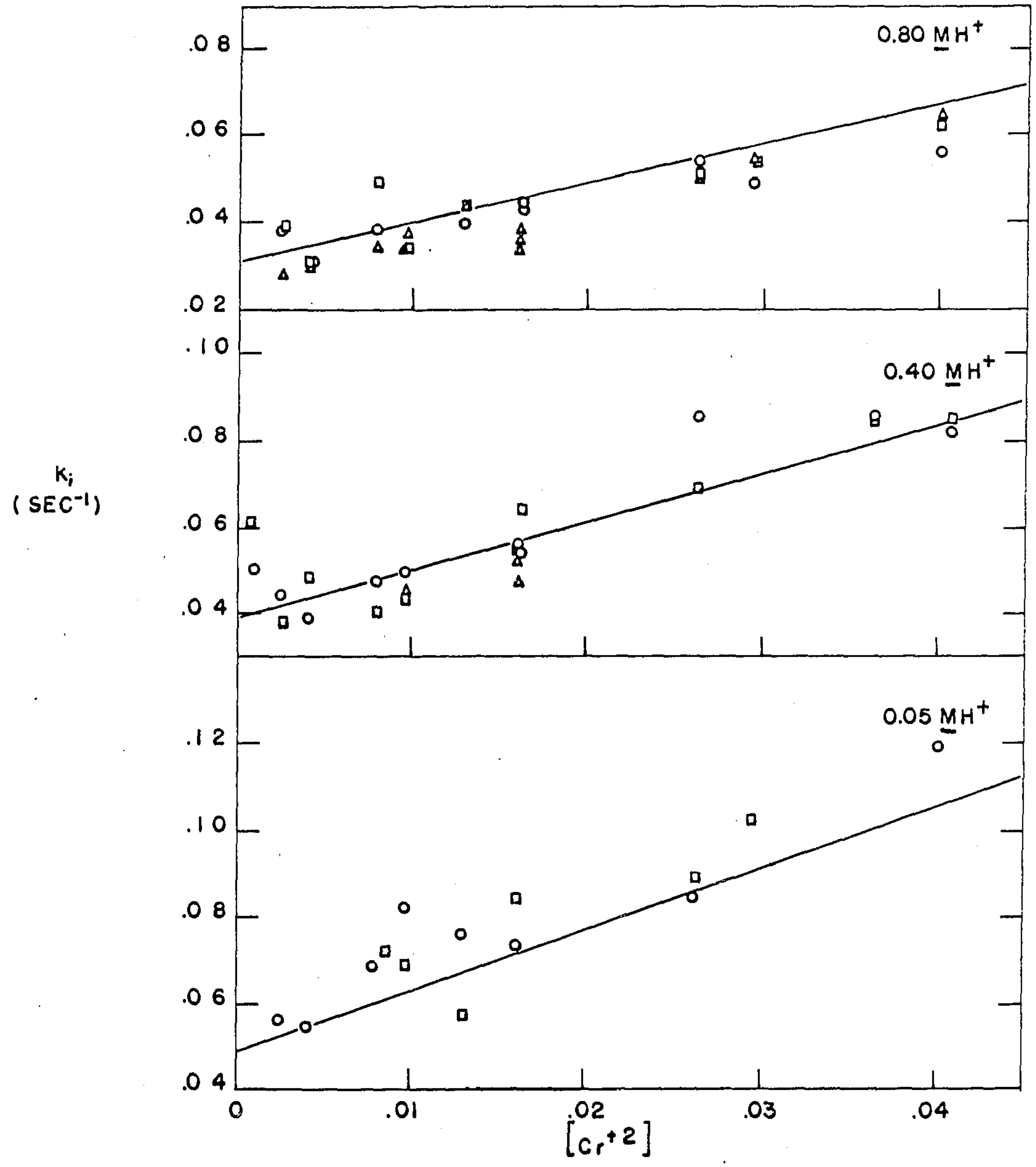
△ $Co(en)_2(H_2O)CN^{2+}$

Fig. 5. Plot of k_i *vs.* $[Cr^{2+}]$ at constant $[H^+]$ for the decay of the intermediate at 25.0°C, $I = 1.00$ *M*; lines were calculated from the best fit of the data to the equation, $k_i = (k_o+k_1[Cr^{2+}])Q(Q+[H^+])^{-1}$

○ $Co(NH_3)_5CN^{2+}$

□ $Co(NH_3)_4(H_2O)CN^{2+}$

△ $Co(en)_2(H_2O)CN^{2+}$


0.80 M H+
.08
.06
.04
.02
0.40 M H+
.10
.08
.06
.04
0.05 M H+
.12
.10
.08
.06
.04
k_i
(SEC^{-1})
0
.01
.02
.03
.04
[Cr+2]

With constant $[Cr^{2+}]$, k_i increases with decreasing $[H^+]$. Plots of log k_i vs. log $[H^+]$ at constant $[Cr^{2+}]$ have slope which decreases with increasing $[H^+]$ (Fig. 6). Such behavior indicates a sum of terms in the denominator of the rate law. In this case, the slope changes from 0 to -1, indicating two terms, one zero-order in $[H^+]$ and the other first-order in $[H^+]$. Since plots at various $[Cr^{2+}]$ are parallel, both reaction paths must have the same $[H^+]$ dependence. A further verification of the $[H^+]$ dependence is provided by plots of k_i^{-1} vs. $[H^+]$ at constant $[Cr^{2+}]$ (Fig. 7), which are linear with non-zero intercept. These observations are consistent with the rate equation (Eq. 18):

$$k_i = \frac{a + b[Cr^{2+}]}{c + [H^+]} \qquad (18)$$

Data at 25.0°C for the three sources of intermediate were fit to this equation separately and in various combinations of source, as shown in Table 9. The terms used in this table correspond to $a = k_0Q$, $b = k_1Q$, and $c = Q$ and arise in connection with the interpretation of these data to be described below.

Data from all three Co(III) complexes fit these equations about equally well. However values of k_i recalculated for $Co(en)_2(H_2O)CN^{2+}$ from the parameters (Table 9) derived with all the data were low more often than they were high. Since the $Co(en)_2(H_2O)CN^{2+}$ solutions used contained at least small

Fig. 6. Logarithmic plot of k_i *vs*. $[H^+]$ at constant $[Cr^{2+}]$ for decay of the intermediate at 25.0°C, $I = 1.00$ *M*; lines were calculated from the best fit of the data to the equation, $k_i = (k_o + k_1[Cr^{2+}])Q(Q+[H^+])^{-1}$

○ $Co(NH_3)_5CN^{2+}$

□ $Co(NH_3)_4(H_2O)CN^{2+}$

△ $Co(en)_2(H_2O)CN^{2+}$

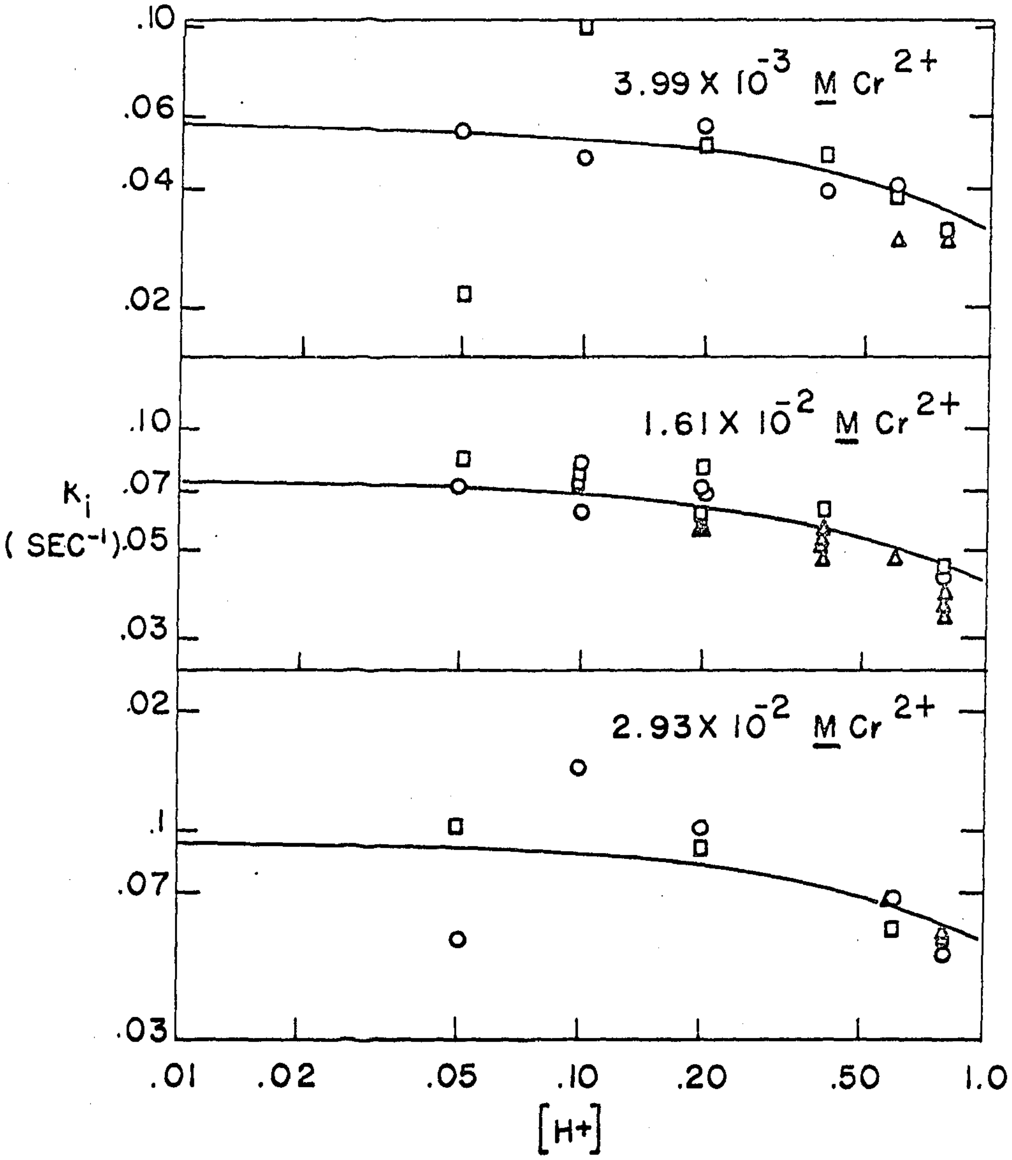

3.99 X 10^{-3} M Cr^{2+}
1.61 X 10^{-2} M Cr^{2+}
2.93 X 10^{-2} M Cr^{2+}
k_i (SEC^{-1})
.10
.06
.04
.02
.10
.07
.05
.03
.02
.1
.07
.03
.01
.02
.05
.10
.20
.50
1.0
[H+]

Fig. 7. Plot of k_i^{-1} *vs.* $[H^+]$ at constant $[Cr^{2+}]$ for decay of the intermediate at 25.0°C, I = 1.00 *M*; lines were calculated from the best fit of the data to the equation, $k_i = (k_0+k_1[Cr^{2+}])Q(Q+[H^+])^{-1}$

○ $Co(NH_3)_5CN^{2+}$

□ $Co(NH_3)_4(H_2O)CN^{2+}$

△ $Co(en)_2(H_2O)CN^{2+}$

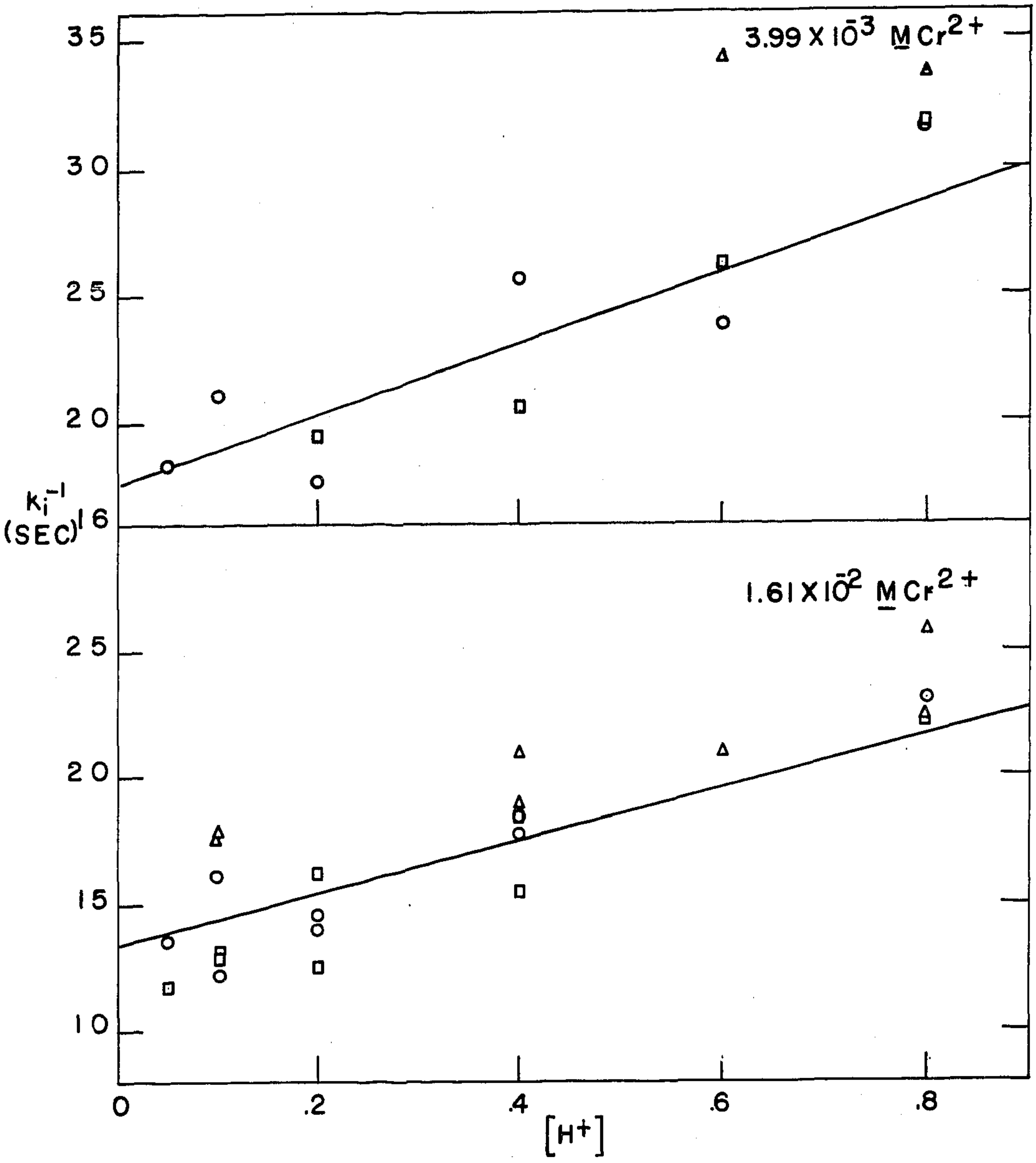

3.99 X 10⁻³ M Cr2+
1.61 X 10⁻² M Cr2+
35
30
25
20
16
25
20
15
10
k_i^-1 (SEC)
0
.2
.4
.6
.8
[H+]

Table 9. Derived rate constants for disappearance of the intermediate at 25.0°C[a]

Data used[b]	k_oQ($\underline{M}$ sec^{-1})	k_1Q(sec^{-1})	Q($\underline{M}$)
A,B,C(102)	.0522 ± .0049	1.69 ± .19	1.06 ± .13
A,B(79)	.0653 ± .0087	1.89 ± .27	1.28 ± .20
A(41)	.0636 ± .0078	1.57 ± .23	1.14 ± .17
B(38)	.0686 ± .0197	2.50 ± .71	1.56 ± .51
C(23)	.0550 ± .0098	2.14 ± .47	1.40 ± .36

[a] I = 1.00 $\underline{M}$ with $LiClO_4$. Data were fit to the equation: $k_i = (k_o + k_1[Cr^{2+}])Q/(Q + [H^+])$. Weighting was carried out as $(k\Delta k)^{-1}$.

[b] A = $Co(NH_3)_5CN^{2+}$, B = $Co(NH_3)_4(H_2O)CN^{2+}$, C = $Co(en)_2(H_2O)CN^{2+}$. Numbers in parentheses are the number of data points used in the calculations.

amounts of $Co(en)_2ClCN^+$, which gives $CrCl^{2+}$ on reaction with Cr^{2+}, the best values of the parameters (Table 9) are probably those derived from data for $Co(NH_3)_5CN^{2+}$ and $Co(NH_3)_4(H_2O)CN^{2+}$. Due to the large number of constants in the rate law and the relatively large amount of scatter observed, a complete study of temperature dependence was not attempted.

Tracer experiments on the intermediate

The role of Cr^{2+} in the catalyzed disappearance of the intermediate was investigated to elucidate further the mechanism and the identity of the intermediate. The Cr^{2+} catalysis is most reasonable if the intermediate is $CrNC^{2+}$, and arguments will be presented here in terms of this formulation. On the basis of this formulation, it is possible to make predictions concerning the exchange of Cr^{2+} with the intermediate. Tracer experiments were carried out in an attempt to verify these predictions, which are presented below.

The exchange of $*Cr^{2+}$ with $CrCN^{2+}$ complicates the tracer experiments, necessitating a blank experiment, described in the experimental section, which only approximately represents the appropriate correction. Correction of measured specific activities, using the blank, should result in a number which is too small for the $CrCN^{2+}$ fraction, and too large for the Cr^{2+} fraction. Results of two experiments, where intermediate was generated by reaction of Cr^{2+} with $Co(NH_3)_4(H_2O)CN^{2+}$, are presented in Table 10. Tagged Cr^{2+} was added at a time when the rapid oxidation-reduction reaction should have been nearly complete and the second-stage reaction should have been barely started. Experiments were not carried out with $Co(NH_3)_5CN^{2+}$, since the first-stage reaction is relatively slow, or with $Co(en)_2(H_2O)CN^{2+}$, due to the probable presence of $Co(en)_2(CN)Cl^{+}$, which produces $CrCl^{2+}$ on reaction with Cr^{2+}. The experiments would be complicated by the rapid exchange of Cr^{2+} with $CrCl^{2+}$ (24,25).

Four models for exchange can be considered. Derivations of the equations used to calculate specific activities are presented in the Appendix. In these equations, a_o is the initial specific activity of $*Cr^{2+}$, $a_{Cr^{2+}}$ is the specific activity of $*Cr^{2+}$ after the intermediate has decayed complete-

Table 10. Exchange of $*Cr^{2+}$ with the intermediate[a]

Expt	$10^3[CrNC^{2+}]_o$[b]	$10^3[CrCN^{2+}]_o$[c]	$[*Cr^{2+}]$	10^{-5}x specific activity[d] (cpm/mmole)	
				Cr^{2+} fraction	$CrCN^{2+}$ fraction
A	9.98	0	.0111[e]	5.46	4.78
A	0	9.98	.0111[e]	6.84	2.55
B	9.98	0	.0204[f]	7.57	6.74
B	0	9.98	.0204[f]	8.83	3.66

[a] I = 1.00 M with $LiClO_4$; 0.400 M H^+; 15.0°C.

[b] Intermediate was generated by the rapid reaction of Cr^{2+} with $Co(NH_3)_4(H_2O)CN^{2+}$.

[c] Generated by allowing the intermediate to decay completely before adding $*Cr^{2+}$.

[d] Specific activity = counts per minute of 5 ml solution in a standard cell/mmoles of Cr in 5 ml solution.

[e] Initial specific activity of $*Cr^{2+}$ was 9.91×10^5 cpm/mmole.

[f] Initial specific activity of $*Cr^{2+}$ was 10.70×10^5 cpm/mmole.

ly, and $a_{CrCN^{2+}}$ is the corresponding quantity for product $CrCN^{2+}$. The latter quantity can be calculated from $a_{Cr^{2+}}$ by the relation given in Eq. 19.

$$a_o[Cr^{2+}]_o = a_{Cr^{2+}}[Cr^{2+}]_{total} + a_{CrCN^{2+}}[CrCN^{2+}]_{total} \qquad (19)$$

Model I: Exchange occurs by the k_o path but not by the k_1 path. A possible mechanism by which this could occur is written in terms of the $CrNC^{2+}$ formulation.

$$CrNC^{2+} \xrightarrow{k_o} \text{"}CrNC^{2+}\text{"} \qquad (20)$$

$$\text{"}CrNC^{2+}\text{"} + {}^*Cr^{2+} = {}^*CrCN^{2+} + Cr^{2+} \text{ (rapid)} \qquad (21)$$

$$\text{"}CrNC^{2+}\text{"} + Cr^{2+} = CrCN^{2+} + Cr^{2+} \text{ (rapid)} \qquad (22)$$

$$CrNC^{2+} + {}^*Cr^{2+}(\text{or } Cr^{2+}) \xrightarrow{k_1} CrCN^{2+} + {}^*Cr^{2+} (\text{or } Cr^{2+}) \qquad (23)$$

$$a_{Cr^{2+}} = a_o \exp(-[CrNC^{2+}]_o/[Cr^{2+}]_{tot}) \qquad (24)$$

In this model "$CrNC^{2+}$" represents some unspecified transformation of $CrNC^{2+}$. This species would be present only in steady state concentrations.

Model II: Exchange occurs by the k_1 path, but not by the k_o path. This model appears to be the most reasonable for the $CrNC^{2+}$ formulation and would have been predicted on the basis of the rate law for decay of intermediate.

$$CrNC^{2+} \xrightarrow{k_o} CrCN^{2+} \qquad (25)$$

$$CrNC^{2+} + {}^*Cr^{2+} \xrightarrow{k_1} {}^*CrCN^{2+} + Cr^{2+} \qquad (26)$$

$$CrNC^{2+} + Cr^{2+} \xrightarrow{k_1} CrCN^{2+} + Cr^{2+} \qquad (27)$$

$$a_{Cr^{2+}} = a_o \exp[-k_1[CrNC^{2+}]_o/(k_o+k_1[Cr^{2+}]_{tot})] \qquad (28)$$

Model III: Exchange occurs by both the k_o and k_1 paths. The mechanism corresponding to this model is given by combination of Eq. 20-22 with Eq. 26 and 27.

$$a_{Cr^{2+}} = a_o \exp[-k_o[CrNC^{2+}]_o/[Cr^{2+}]_{tot}(k_o+k_1[Cr^{2+}]_{tot})] \quad (29)$$

Model IV: Exchange does not occur by either path. In this case, $a_{Cr^{2+}} = a_o$.

Results of these calculations as well as corrected observed values are presented in Table 11. The corrections were made by the relations presented in Eq. 30 and Eq. 31.

$$a_{Cr^{2+}}(\text{corr}) = a_{Cr^{2+}}(\text{obsd}) + a_o - a_{Cr^{2+}}(\text{blank}) \quad (30)$$

$$a_{CrCN^{2+}}(\text{corr}) = a_{CrCN^{2+}}(\text{obsd}) - a_{CrCN^{2+}}(\text{blank}) \quad (31)$$

Table 11. Interpretation of tracer studies on the intermediate

Expt[a]	Model[b]	$a_{Cr^{2+}}$ (10^{-5}cpm/mmole) calc	$a_{Cr^{2+}}$ (10^{-5}cpm/mmole) obsd[c]	$a_{CrCN^{2+}}$ (10^{-5}cpm/mmole) calc	$a_{CrCN^{2+}}$ (10^{-5}cpm/mmole) obsd[c]
A	I	5.15	8.06	5.29	2.23
	II	7.76		2.34	
	III	4.03		6.54	
	IV	9.91		0.0	
B	I	8.29	9.44	5.55	3.08
	II	8.77		3.96	
	III	6.56		8.46	
	IV	10.7		0.0	

[a] These experiments are described in Table 10.

[b] The models are described in the text.

[c] These values of the specific activities are corrections of the values given in Table 10. The corrections are described in the text.

Since [$CrCN^{2+}$] was at its maximum value in the blank experiment, but was increasing throughout the tracer experiment, $a_{Cr^{2+}}$(corr) is expected to be somewhat high and $a_{CrCN^{2+}}$(corr) somewhat low. Within experimental error, the results presented in Table 11 are consistent with Model II, exchange by the k_1 path but not by the k_o path.

Spectrum of the intermediate

It was difficult to measure any of the properties of the intermediate, due to its transitory nature. However, the absorption spectrum was measured by extrapolation of changes in absorbance at a given wavelength to zero time, as described in the experimental section. The spectra were measured at 2-5°C, where the rate of disappearance of intermediate is sufficiently low that measurements could be made on the same solution at all wavelengths by taking repetitive scans, rather than by measuring absorbance changes on a different solution at each wavelength.

These spectra were measured to provide additional information for the identification of the intermediate. The long wavelength maximum in the visible spectrum of Cr(III) and Co(III) complexes provides a measure of the ligand field strength of the ligand, since the wavelength at which this maximum occurs is determined by the difference in energy between the t_{2g} and e_g orbitals. The spectrum of the intermediate should distinguish between Co(III) and Cr(III) and should help establish which end of cyanide is bonded to the metal ion. If the intermediate is a binuclear complex, the spectrum should vary slightly with the Co(III) complex used to produce it.

The wavelengths and absorbancy indices at the maxima in the visible spectra are presented in Table 12. Spectra taken as a function of $[H^+]$ for the intermediate produced by the reaction of Cr^{2+} with $Co(NH_3)_4(H_2O)CN^{2+}$ are shown in Fig. 8. The precision of these data is indicated by the duplicate experiments shown. The spectrum of $CrCN^{2+}$, given in Fig. 9 and Table 13, was used in the calculation of the spectra of the intermediates. Spectra of Cr(III) and Co(III) complexes

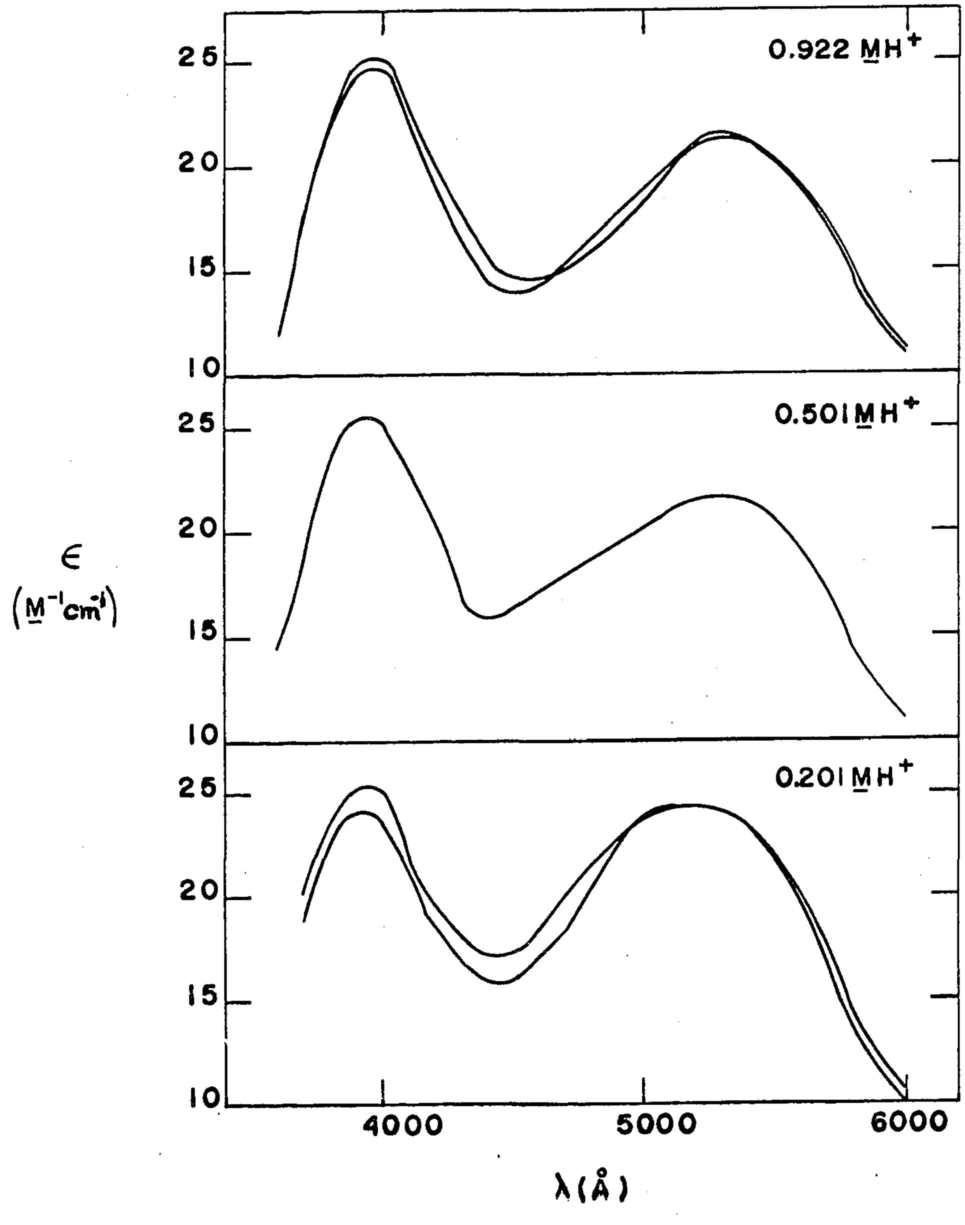
Table 12. Spectra of the intermediate[a]

Source[b]	$[H^+]$	λ_{max} (Å)	ϵ_{max} ($\underline{M}^{-1}cm^{-1}$)	λ_{max}	ϵ_{max}
A	.913	5420	19.8	3920	23.2
	.906	5390	19.6	3950	22.5
	.907	5360	19.4	3960	22.3
	.201	5300	23.0	3930	20.9
B	.922	5300	21.6	3980	25.2
	.923	5310	21.2	3960	24.8
	.501	5300	21.7	3940	25.6
	.201	5170	24.6	3940	24.2
	.201	5200	24.2	3950	25.3
C	.917	5320	22.4	3940	22.5

[a] I = 1.00 $\underline{M}$ with $LiClO_4$, 2-5°C. Measured by extrapolation of $\log(D_t-\bar{D}_\infty)$ vs. t plots to time t = 0.

[b] A = $Co(NH_3)_5CN^{2+}$, B = $Co(NH_3)_4(H_2O)CN^{2+}$, C = $Co(en)_2(H_2O)CN^{2+}$.

Fig. 8. Spectra of the intermediate formed in the reaction of Cr^{2+} with $Co(NH_3)_4(H_2O)CN^{2+}$; precision of the data is indicated by duplicate experiments at 0.922 M and 0.201 M H^+


0.922 MH$^+$
0.501 MH$^+$
0.201 MH$^+$
25
20
15
10
ϵ
($M^{-1}cm^{-1}$)
4000
5000
6000
λ(Å)

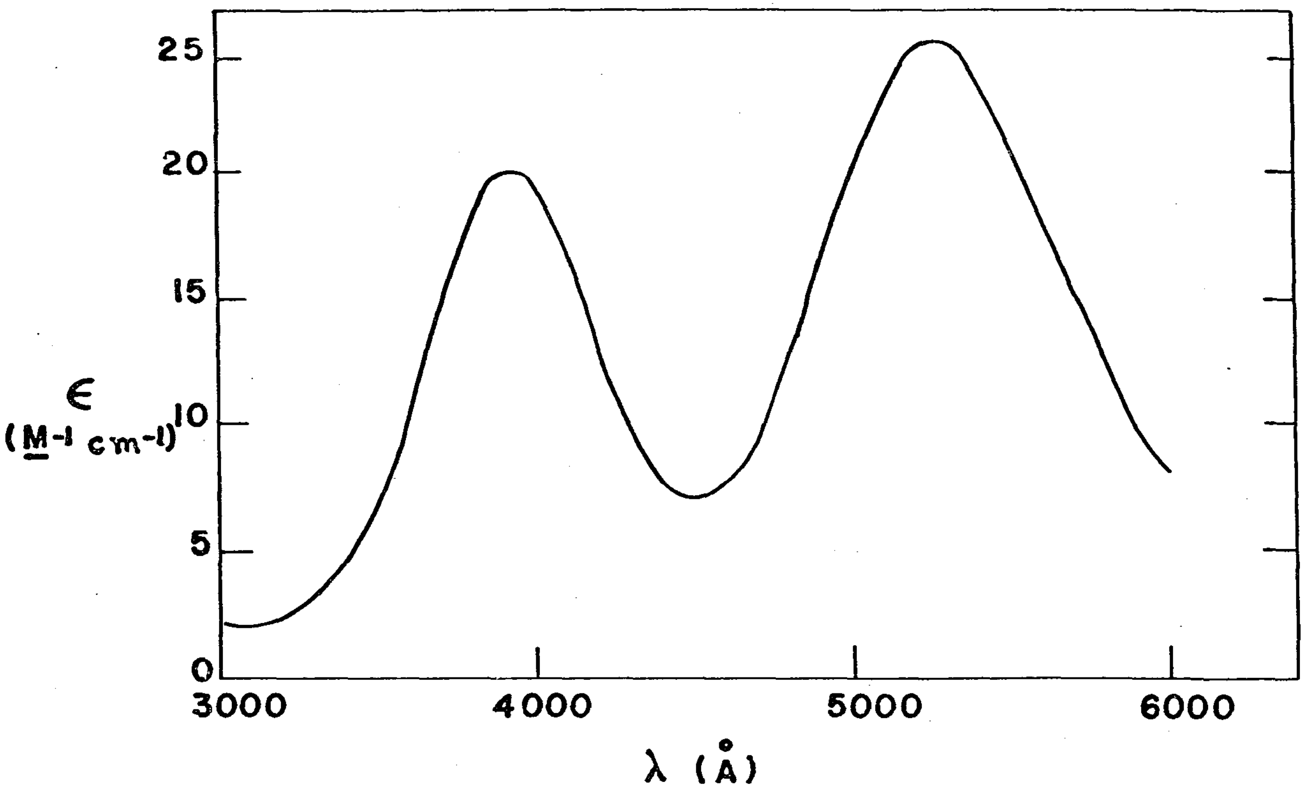


Fig. 9. Spectrum of $CrCN^{2+}$

Table 13. Spectrum of CrCN^{2+}[a]

λ(Å)	$\epsilon(\underline{M}^{-1}\mathrm{cm}^{-1})$	λ(Å)	$\epsilon(\underline{M}^{-1}\mathrm{cm}^{-1})$
7000	0.42 ± .04	4500(min)	6.89 ± .27
	0.69 ± .01		7.51 ± .26
	1.04 ± .01		9.75 ± .36
	1.35 ± .03		13.3 ± .41
	1.69 ± .03		16.89 ± .40
6500	2.16 ± .12	4000	19.43 ± .39
	3.09 ± .04	3930(max)	20.04 ± .40
	4.01 ± .06	3900	19.96 ± .42
	5.19 ± .03		18.07 ± .43
	6.61 ± .07		14.31 ± .45
6000	8.13 ± .33		10.04 ± .49
	9.44 ± .63	3500	6.56 ± .54
	12.36 ± .31		4.27 ± .71
	15.11 ± .39		3.03 ± .75
	18.27 ± .55		2.31 ± .75
5500	21.28 ± .38		2.10 ± .84
	23.76 ± .34	3000	2.24 ± .86
5300	25.07 ± .35		10.2 ± 1.4
5250(max)	25.23 ± .36		10.8 ± 1.4
5200	24.94 ± .33		10.7 ± 1.4
	23.11 ± .30		23.1 ± 4.5
5000	20.02 ± .32	2500	58 ± 7
	16.24 ± .31		189 ± 14
	12.50 ± .23		444 ± 18
	9.41 ± .24		990 ± 30
	7.53 ± .23		2000 ± 65
		2000	3900 ± 80
		1900	4720 ± 320

[a] Unless otherwise noted, each entry is at a wavelength 100Å shorter than the previous entry.

are presented in Table 14 for the purpose of comparison.

Nature of the intermediate

The results presented above have uncovered no additional formulations for the intermediate. The fair quantitative agreement of rates of disappearance of the intermediates prepared by three different reactions indicates that the kinetics are very similar for the second stage of reaction for each of the three cobalt complexes. Within experimental error the kinetic data are consistent with a single common intermediate. It cannot be stated that three distinct cobalt-containing intermediates are not involved, however, since there is no reason to insist that their kinetic behavior would be different, although it seems probable that it would. The reactions of Cr^{2+} with cis-$Co(en)_2(CN)_2^+$, $Cr(CN)_2^+$ and $Cr(CN)_3$ each produced an intermediate, but unfortunately these intermediates did not conform to the kinetic behavior observed for reactions with CoL_5CN^{2+}. Results of the reactions with higher cyano complexes will be presented below. However, in addition to the agreement of rates, it is difficult to postulate a mechanism for the decomposition of a binuclear intermediate which is consistent with the observed rate law without resorting to an extremely complicated series of elementary reactions.

A mechanism consistent with the formulation as $CrNC^{2+}$ is given in Eqs. 32-35.

$$CoL_5CN^{2+} + Cr^{2+} + 5H^+ \quad = \quad Co^{2+} + 5LH^+ + CrNC^{2+} \qquad (32)$$

Table 14. Spectra of some Cr(III) and Co(III) complexes[a]

X^{n-3}	$Cr(H_2O)_5X^{n+}$			$Co(NH_3)_5X^{n+}$			trans-$Co(NH_3)_4$ $(H_2O)X^{n+}$			trans-$Co(en)_2$ $(H_2O)X^{n+}$		
	λ	ε	Ref.	λ	ε	Ref.	λ	ε	Ref.	λ	ε	Ref.
I^-	6500	36	(53)	5800	80	(47)						
Br^-	6220	20	(43)	5500	53	(47)				6130	35	(54)
Cl^-	6090	16	(53)	5330	49	(47)				5900	31	(55)
F^-	5950	12	(53)	5100	44	(47)						
N_3^-	5850	68	(56)	5200	265	(47)				5500	240	(57)
OH_2	5740	13	_b	4900	47	(47)	5120		(58)	5500	32	(59)
NCS^-	5700	32	(60)	4970	192	(47)				5400	190	(61)
NH_3	5470	20	(62)	4750	55	(47)	4900		(47)	4800	48	(63)
CN^-	5250	25	_b	4400	58	_b	4550	66	_b	4450	79	_b

[a] Wavelengths, given in Å, are for the long wavelength maximum in the visible spectrum. Absorbancy indices are given in $\underline{M}^{-1}cm^{-1}$.

[b] This work.

$$CrNCH^{3+} \overset{Q}{\rightleftharpoons} CrNC^{2+} + H^+ \quad \text{(rapid)} \qquad (33)$$

$$CrNC^{2+} \xrightarrow{k_o} CrCN^{2+} \qquad (34)$$

$$CrNC^{2+} + {}^*Cr^{2+} \xrightarrow{k_1} \left\{Cr{-}{-}{-}NC{-}{-}{-}{}^*Cr^{4+}\right\}^{\ddagger} \qquad (35)$$

$$\longrightarrow Cr^{2+} + {}^*CrCN^{2+}$$

The rate law (Eq. 36 and Eq. 37) derived for this mechanism corresponds exactly to the empirical rate law.

$$-d(C_{CrNC^{2+}})/dt = \frac{(k_o+k_1[Cr^{2+}])Q\ C_{CrNC^{2+}}}{Q + [H^+]} \qquad (36)$$

$$C_{CrNC^{2+}} = [CrNC^{2+}] + [CrNCH^{3+}] \qquad (37)$$

Rate constants derived for this mechanism are presented in Table 9. This mechanism is similar to that postulated for the isomerization of $CrSCN^{2+}$ (4,5), where an intramolecular path and a Cr^{2+} catalyzed path were observed.

Results of the Cr^{51} tracer experiments are consistent with identification of the intermediate as $CrNC^{2+}$, but are difficult to explain if the intermediate is a binuclear complex. The appearance of Cr^{2+} catalyst in the $CrCN^{2+}$ product indicates that Cr^{2+} and Cr(III) exchange during the catalytic process and that cyanide in the intermediate must be available to act as a bridging ligand. In addition, the quantitative agreement of observed specific activities with those calculated if exchange occurs by the k_1 path but not the k_o path is consistent with the mechanism proposed. The Cr^{2+} catalysis is then interpreted as a second electron transfer step, Eq. 38.

$$*Cr^{2+} + CrNC^{2+} \xrightarrow{k1} *CrCN^{2+} + Cr^{2+} \qquad (38)$$

Spectra of the intermediate favor the identification as $CrNC^{2+}$. One possible formulation of a binuclear intermediate, a Co(III)-Cr(II) complex, can be ruled out. Such a formulation would require the first-stage reaction to be an association of Cr^{2+} with CoL_5CN^{2+}. Since the formation of an association complex is a substitution on Cr^{2+}, which would be quite rapid due to the substitution lability of Cr^{2+}, the rates (k_{ox}) should be much larger than observed. In addition, the rates would not be expected to vary much with changes in the non-bridging ligands on Co(III), which would correspond to slight structural changes in the ligand CoL_5CN^{2+}. The spectra of such binuclear intermediates should look like those of Co(III) complexes. Addition of Hg^{2+} to solutions of CoL_5CN^{2+}, forming stable complexes CoL_5CNHg^{4+} (34), does not shift the wavelength of maximum absorption, and increases the absorbancy index by only 2-3%. Thus such an intermediate should have a maximum absorbance at 4400-4600Å and absorbancy index 60-80. The observed maxima (Table 12) occur at 5200-5400Å (ϵ = 20-25 $\underline{M}^{-1}cm^{-1}$), depending on acid concentration, and to some extent, on the source of the intermediate. Comparison of spectra of the intermediate with those of Co(III) and Cr(III) complexes (Table 14) indicates that the intermediate probably contains Cr(III).

The other formulation for a binuclear intermediate is a

Co(II)-Cr(III) complex. The decay of the intermediate would be aquation of a Co(II) complex, with $CrCN^{2+}$ or $CrNC^{2+}$ as the ligand displaced by H_2O. In this formulation, if $CrNC^{2+}$ were the displaced ligand, the isomerization would have to occur sufficiently rapidly to prevent the detection of this species. Although no data are available for the aquation of the Co(II) complexes CoL_5X^{+2-n} in acidic solution, changes in the ligands L cause significant differences in the rates of aquation of Co(III) and Cr(III) complexes.

In the reaction of Cr^{2+} with $Co(NH_3)_5X^{+3-n}$, $Co(NH_3)_5{}^{2+}$ has been postulated as an immediate product of transient stability, but it has never been detected and the substitution lability of Co(II) makes it very unlikely that the amine ligands would remain in the first coordination sphere of Co(II) in acidic aqueous solution. It is probably equally unlikely that Co^{2+} would remain bonded to cyanide in a binuclear intermediate $CoCNCr^{4+}$. The effect of $[H^+]$ on the rate of disappearance of intermediate for this formulation would be quite difficult to interpret in terms of currently fashionable ideas in inorganic mechanisms.

The effect of $[H^+]$ on the spectrum of the intermediate (Fig. 8), although not very large or known very precisely, is consistent with an equilibrium between $CrNC^{2+}$ and $CrNCH^{3+}$, in accord with the $[H^+]$ dependence found in the rate law. On the basis of spectral changes with $[H^+]$ (Eq. 39), it should be

$$\epsilon_{\text{obsd}} = \frac{\epsilon_{\text{CrNC}^{2+}}Q + \epsilon_{\text{CrNCH}^{3+}}[\text{H}^+]}{Q + [\text{H}^+]} \tag{39}$$

possible to calculate the acid dissociation constant for $CrNCH^{3+}$ (known independently from kinetic data) and the absorbancy indices for the acidic and basic forms of the intermediate. Although data at many wavelengths were not sufficiently precise to fit Eq. 39 well, at those wavelengths where the fit was reasonable, Q fell in the range 0.02-0.4 M, with most values around 0.2 M at 2-5°C. This is reasonable in comparison with the value of 1.3 M obtained from kinetic data at 25°C. Derived values of the absorbancy indices were not sufficiently complete to calculate spectra of the two forms of intermediate.

An alternative explanation for the spectral changes with $[H^+]$ should be examined. In the reaction of Cr^{2+} with CoL_5NCS^{n+} (5), both $CrNCS^{2+}$ and the intermediate $CrSCN^{2+}$ were formed as immediate products. If $CrCN^{2+}$ as well as $CrNC^{2+}$ were formed directly in the reaction of Cr^{2+} with CoL_5CN^{2+}, the dependence of spectrum on $[H^+]$ could arise from a dependence of $[CrCN^{2+}]_0/[CrNC^{2+}]_0$ on $[H^+]$. This would mean that in the equation used to calculate the absorbancy index of $CrNC^{2+}$ (Eq. 40), $[CrNC^{2+}]_0$ rather than $\Delta\epsilon$ is a function of $[H^+]$.

$$D_0 - D_\infty = b \cdot \Delta\epsilon \cdot [CrNC^{2+}]_0 \tag{40}$$

The ratio of absorbance changes at two different $[H^+]$ should then be independent of wavelength, contrary to observation.

Haim and Sutin (5) were able to determine the amount of $CrNCS^{2+}$ formed directly since Hg^{2+} reacts with $CrNCS^{2+}$ to give $CrNCSHg^{4+}$ but with $CrSCN^{2+}$, the products are Cr^{3+} and $HgNCS^{+}$. Reaction of Hg^{2+} with $CrNC^{2+}$ gives the same product as does reaction with $CrCN^{2+}$. A very stable complex, presumably $CrCNHg^{4+}$ (described below), is formed. No other reaction could be found to distinguish between the two isomers, so it is not known whether any $CrCN^{2+}$ is formed directly. In any event, the reactions of Cr^{2+} with CoL_5CN^{2+} all form quantitative yields of $CrCN^{2+}$ eventually and these yields are not a function of $[H^+]$.

The long wavelength maximum in the absorption spectrum provides a measure of the ligand field strength of a ligand. Shriver, et al. (22) estimated from the spectra of solids containing two different arrangements of bridging cyanide ligands that the nitrogen end of cyanide lies between H_2O and NH_3 in the spectrochemical series. For the complexes $Cr(H_2O)_5X^{3+}$, $\lambda_{max} = 5740\text{Å}$ for $X = H_2O$ and $\lambda_{max} = 5470\text{Å}$ for $X = NH_3$. Thus the spectrum of the intermediate in ~ 1 M H^+ ($\lambda_{max} \sim 5400\text{Å}$), where if Q $\sim .2$M, about 85% of the complex should be in the form $CrNCH^{3+}$, is consistent with that of a nitrogen-bonded bridging cyanide ligand.

Alternate mechanism for isomerization

Another mechanism, also consistent with the empirical rate law, can be proposed for the isomerization of $CrNC^{2+}$

(Eq. 41-44). This mechanism differs from that involving $CrNCH^{3+}$ (Eq. 33-35) only in the way that the acid-base equilibrium is assigned.

$$CrNC^{2+} \overset{Q}{\rightleftharpoons} Cr(OH)NC^{+} + H^{+} \quad \text{(rapid)} \tag{41}$$

$$Cr(OH)NC^{+} \xrightarrow{k_o} Cr(OH)CN^{+} \tag{42}$$

$$Cr(OH)NC^{+} + {}^{*}Cr^{2+} \xrightarrow{k_1} {}^{*}Cr(OH)CN^{2+} + Cr^{2+} \tag{43}$$

$$CrCN^{2+} \rightleftharpoons Cr(OH)CN^{+} + H^{+} \quad \text{(rapid)} \tag{44}$$

With the concentration of the basic form $Cr(OH)NC^{2+}$ given by Eq. 45, the rate law derived for this mechanism (Eq. 46) is

$$[Cr(OH)NC^{+}] = QC_{CrNC^{2+}}/(Q+[H^{+}]) \tag{45}$$

$$k_i = (k_oQ + k_1Q[Cr^{2+}])/(Q+[H^{+}]) \tag{46}$$

exactly the same as the empirical rate law.

This mechanism is inferior to that involving $CrNCH^{3+}$ (Eq. 33-35) for two reasons.

1. While the Cr^{2+} catalyzed isomerization of $Cr(OH)NC^{+}$ but not $CrNC^{2+}$ can be explained by the lower energy of a double-bridged activated complex, it is difficult to explain the uncatalyzed isomerization of $Cr(OH)NC^{+}$ but not $CrNC^{2+}$.

2. The value determined kinetically for Q was 1.3 M at 25°C. The corresponding value for Cr^{3+} is 1.5×10^{-4} M. It is very unlikely that the ligand $-NC^{-}$ would raise the acid dissociation constant by a factor of 10^{4}, since the ligand Cl^{-} lowers Q only by a factor of 20.

Reaction of Cr^{2+} with cyanothallium(III) complexes

The identification of the intermediate as $CrNC^{2+}$ would be firmly established if a completely independent source of intermediate could be found. For this reason, the reaction of Cr^{2+} with cyanothallium(III) complexes was investigated as a possible source of an intermediate which could not contain cobalt.

The product of oxidation of Cr^{2+} depends on the nature of the oxidizing agent. Some one-electron oxidizing agents, which react by a ligand-bridged process (e.g., $Co(NH_3)_5X^{n+}$, CrX^{n+}), produce CrX^{n+}. Other one-electron oxidizing agents (e.g., Fe^{3+}, H_2O_2) produce Cr^{3+}. Many two-electron oxidizing agents (e.g., O_2, Tl^{3+}) produce $Cr_2(OH)_2^{4+}$ (33). The mechanism proposed for the Tl^{3+} oxidation involves a Cr(IV) intermediate:

$$Tl^{3+} + Cr^{2+} = Tl^{+} + Cr(IV) \tag{47}$$

$$Cr(IV) + Cr^{2+} = Cr_2(OH)_2^{4+} + 2H^{+} \tag{48}$$

However, the oxidation of Cr^{2+} by solutions of Tl^{3+} containing CN^- produces no $Cr_2(OH)_2^{4+}$. With $C_{CN^-} \simeq C_{Tl}$, where the major species is probably $TlCN^{2+}$, only Cr^{3+} could be found. With $C_{CN^-} \simeq 4C_{Tl}$, where the major species are probably $Tl(CN)_3$ and $Tl(CN)_4^-$, most of the product is Cr^{3+}, but some $CrCN^{2+}$ ($\leq 10\%$) is also formed.

Spectral behavior is consistent with the formation of an intermediate. At 3500, 3950 and 4400Å, the absorbance rises quickly to a maximum, then decreases more slowly. At 5200Å, the absorbance rises throughout the reaction, with change in slope inconsistent with the occurrence of a single reaction.

These observations are analogous to those made for the systems $Cr^{2+} + CoL_5CN^{2+}$.

Reaction kinetics in solutions with $C_{CN^-}/C_{Tl} \simeq 4$ were investigated at 25.0°C and 1.00 M ionic strength (maintained with $LiClO_4$) over the concentration ranges: 7.7×10^{-3}-2.2×10^{-2} M Tl(III), 0-.028 M Cr^{2+} (in excess of Tl(III)), 0.20-0.82 M H^+. Results for the second reaction (disappearance of intermediate) are presented in Table 15. The observed rate constants increase with increasing $[Cr^{2+}]$, but decrease with increasing $[H^+]$. The rate equation is apparently the same as observed for the disappearance of the intermediate formed in the reactions of Cr^{2+} with CoL_5CN^{2+}, Eq. 49.

$$k = \frac{a+b[Cr^{2+}]}{C+[H^+]} \tag{49}$$

However the rate constants observed for the Cr^{2+}-Tl(III) intermediate are consistently larger, by a factor of 1.3-1.8, than those observed for the Cr^{2+}-CoL_5CN^{2+} intermediates.

The form of the rate law favors the interpretation of a common intermediate ($CrNC^{2+}$), but the lack of agreement of rate constants with those from the cyanocobalt complexes detracts from this interpretation. These experiments have the disadvantage that with the higher cyanothallium(III) complexes, more than one cyanide could be transferred, and that thallium(III) could still be reacting as a two-electron oxidizing agent, even though no $Cr_2(OH)_2^{4+}$ was found. The

Table 15. Rate constants for reaction of Cr^{2+} with Tl(III) at 25.0°C[a]

$[Tl(III)]_o$	$[Cr^{2+}]_o$	$[Cr^{2+}]_{xs}$	$[H^+]$	λ(Å)	k(sec^{-1})[b] obsd	calc for $CrNC^{2+}$
.01105	.02945	.00735	.200	5200	.0972 ± .0037	.0534
.02210	.02363	0.0	.400	"	.0605 ± .0016	.0388
.01105	"	.00153	"	"	.0721 ± .0008	.0405
"	.02945	.00735	"	"	.0840 ± .0015	.0470
"	.05037	.02827	"	"	.1135 ± .0033	.0707
"	.02945	.00735	.800	"	.0554 ± .0013	.0380
"	"	"	.796	"	.0517 ± .0009	.0382
"	"	"	"	4400	.0490 ± .0009	.0382
.00776	"	.01391	.824	5200	.0551 ± .0018	.0435
"	"	"	"	4400	.0573 ± .0064	.0435

[a] I = 1.00 M with $LiClO_4$, $[CN^-]/[Tl(III)] \simeq 4$.

[b] Observed values were calculated with a computer program for first-order kinetics, using absorbance-time data. Calculated values were obtained from the relation $k = (k_oQ + k_1Q[Cr^{2+}])(Q+[H^+])^{-1}$ using the parameters derived for the Cr^{2+} + CoL_5CN^{2+} reactions (Table 9).

reaction of Cr^{2+} with $Pt(NH_3)_5Cl^{3+}$, a two-electron oxidizing agent, gave only Cr^{3+} and $CrCl^{2+}$.[1] The results were interpreted as a two-electron oxidation of Cr^{2+} to a transient Cr(IV) intermediate which reacted with Cr^{2+} to form a Cr(III) dimer. An analogous mechanism for the thallium(III) reaction would be:

$$Tl(CN)_4^- + Cr^{2+} + 3H^+ \longrightarrow Tl^+ + Cr(IV)CN^{3+} + 3HCN \qquad (50)$$

$$Cr(IV)CN^{3+} + Cr^{2+} \longrightarrow \text{"}Cr_2CN^{5+}\text{"} \quad \text{(rapid)} \qquad (51)$$

$$\text{"}Cr_2CN^{5+}\text{"} + H^+ \overset{Q}{\rightleftharpoons} \text{"}Cr_2CNH^{6+}\text{"} \quad \text{(rapid)} \qquad (52)$$

$$\text{"}Cr_2CN^{5+}\text{"} \xrightarrow{k_1} Cr^{3+} + CrCN^{2+} \qquad (53)$$

$$\text{"}Cr_2CN^{5+}\text{"} + Cr^{2+} \xrightarrow{k_2} Cr^{3+} + CrCN^{2+} + Cr^{2+} \qquad (54)$$

The rate law corresponding to this mechanism (Eq. 55), where

$$d[CrCN^{2+}]/dt = (k_1+k_2[Cr^{2+}])C_{int}/(1+Q[H^+]) \qquad (55)$$

C_{int} is the concentration of dimer, is just a rearrangement of the observed rate law. This mechanism does not account for the poor yield of $CrCN^{2+}$, however, but neither does a mechanism consisting of two one-electron oxidations with $CrNC^{2+}$ as an intermediate. In the Cr^{2+}-$Pt(NH_3)_5Cl^{3+}$ reaction at low acidities, the yield of $CrCl^{2+}$ was considerably decreased. This was attributed to a conjugate base form of Cr(IV), which rapidly lost Cl^-.

In view of the fact that Co(III) has always been found to be a one-electron oxidizing agent in reactions with Cr^{2+}, an

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[1] J. K. Beattie and F. Basolo, Evanston, Illinois. The reduction of chloropentaammineplatinum(IV) ion by aquochromium(II) ion. Private communication. 1967.

analogous mechanism for the Cr^{2+}-CoL_5CN^{2+} reactions is highly unlikely.

Aquation of $CrCN^{2+}$

Results

In acidic solution, $CrCN^{2+}$ loses cyanide ion slowly (Eq. 56) relative to the rate of decay of the intermediate. The

$$CrCN^{2+} + H^+ = Cr^{3+} + HCN \tag{56}$$

product of the decomposition of $CrCN^{2+}$ was identified as Cr^{3+} on the basis of its visible spectrum (Fig. 10).

The aquation of $CrCN^{2+}$ was studied at ionic strength 1.00 M under the following conditions:

(1) Ionic strength maintained with $NaClO_4$ (Table 16): 35-75°C, 0.02-1.0 M H^+. The reaction was studied by a variety of techniques as indicated in Table 16. Kinetic results were independent of the method used to follow the progress of the reaction.

(2) Ionic strength maintained with $LiClO_4$ (Table 17): 45-65°C, 8×10^{-4}-1.0 M H^+. All rate studies consisted of continuous absorbance measurements on solutions of purified $CrCN^{2+}$.

At constant hydrogen ion concentration, the rate of aquation follows the pseudo-first-order rate law:

$$-d[CrCN^{2+}]/dt = k_{aq}[CrCN^{2+}] \tag{57}$$

As with previously studied pentaaquochromium(III) complexes, k_{aq} was found to have a hydrogen ion dependence of the form

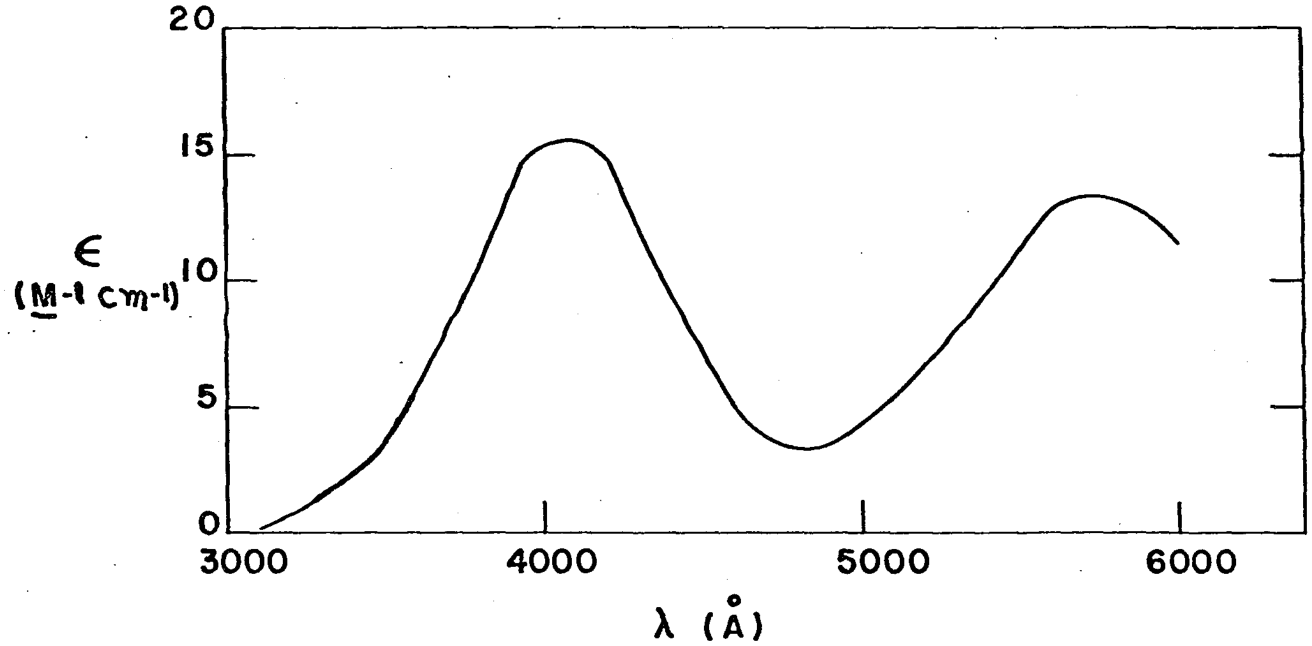


Fig. 10. Spectrum of $Cr(H_2O)_6{}^{3+}$

Table 16. Rate constants for the aquation of $CrCN^{2+}$ in $NaClO_4$ media[a]

$10^3[CrCN^{2+}]_0$	$[H^+]$(M)[b]	Temp (°C)	Wave-length	$10^3 k_{aq}$ (sec^{-1}) obsd	calc
.260[c]	.058$_9$	35.0	2200 Å	.107 ± .002	.120
"	.110	"	"	.156 ± .002	.168
"	.211	"	"	.264 ± .007	.264
"	.289	"	"	.349 ± .011	.338
"	.508	"	"	.550 ± .013	.546
"	.611	"	"	.634 ± .017	.642
.285[d]	.607	34.9	"	.668 ± .010	.631
"	.759	35.0	"	.788 ± .011	.782
"	.857	"	"	.882 ± .025	.874
"	.973	34.9	"	.912 ± .028	.984
.634[e]	.110	34.2	2300	.136 ± .002	.153
.634[f]	.210	34.3	"	.259 ± .004	.242
"	.310	34.4	"	.333 ± .006	.334
"	.510	34.3	"	.497 ± .003	.505
"	.606	34.4	"	.552 ± .006	.596

[a] I = 1.00 M with $NaClO_4$ and $HClO_4$. Observed values of k_{aq} were calculated from absorbance time data with a computer program for first-order data. Calculated values were obtained from the activation parameters given in Table 18.

[b] Determined by direct titration of aliquots of the spent reaction solutions with NaOH.

[c] Aliquots were withdrawn from a darkened vessel and frozen in test tubes immersed in a dry ice-methanol bath. These were later melted and the absorbance measured in a 2 cm cell.

[d] A continuous recording of absorbance was made, with the cell contained in a cell holder modified to operate as a constant temperature bath.

[e] Intermittant readings of absorbance were made. The cell was in the cell holder described in (d).

[f] Intermittant readings of absorbance were made. The cells were kept in a constant temperature air bath between readings. Temperature control is probably not as good as with the other methods.

Table 16. (Continued)

$10^3[CrCN^{2+}]_0$	$[H^+](\underline{M})^b$	Temp (°C)	Wave-length	$10^3k_{aq}(sec^{-1})$	
				obsd	calc
$.672^e$	$.053_9$	45.0	2300Å	.365 ± .007	.393
$.672^d$	.104	"	"	.530 ± .005	.528
"	.204	"	"	.79 ± .01	.797
"	.304	"	"	1.02 ± .01	1.07
"	.502	"	"	1.64 ± .02	1.60
"	.602	"	"	1.92 ± .02	1.87
"	.601	"	"	1.94 ± .04	1.87
"	.750	"	"	2.10 ± .04	2.27
"	.750	"	"	2.37 ± .04	2.27
"	.852	"	"	2.82 ± .05	2.54
"	.967	"	"	3.03 ± .02	2.85
5.36^d	$.073_5$	"	5200	.369 ± .003	.445
"	.419	"	"	1.38 ± .01	1.38
"	.685	"	"	1.92 ± .05	2.09
5.19^g	.050	53.5	5250	1.22 ± .01	1.04
"	.100	53.4	"	1.61 ± .01	1.34
"	.200	53.5	"	2.54 ± .02	1.98
"	.300	"	"	3.29 ± .03	2.60
"	.600	"	"	5.15 ± .12	4.47
"	.940	53.4	"	6.91 ± .06	6.52
"	.940	53.5	"	7.37 ± .05	6.59
"	.940	53.6	"	7.56 ± .04	6.65
$.295^c$	$.021_2$	54.4	2200	0.880 ± .026	.960
"	.110	"	"	1.58 ± .03	1.56
"	.212	"	"	2.34 ± .03	2.26
"	.314	"	"	2.69 ± .14	2.95
"	.314	"	"	2.95 ± .07	2.95
$.261^c$	.609	"	"	5.91 ± .26	4.95
"	.759	"	"	6.20 ± .12	5.97
"	.857	"	"	7.31 ± .21	6.64
$.285^d$	$.021_6$	"	"	.943 ± .021	.963
"	.111	"	"	1.66 ± .06	1.57
"	.211	"	"	2.51 ± .06	2.25

---

[g] $CrCN^{2+}$ was generated in the cell by reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$. Any excess Cr^{2+} was quenched by addition of several ml of air. Continuous absorbance readings were made, with the cells in the cell holder described in (d).

Table 16. (Continued)

$10^3[\mathrm{CrCN}^{2+}]_o$	$[\mathrm{H}^+]$(M)^b	Temp (°C)	Wave-length	10^3k_{aq}(sec^{-1})	
				obsd	calc
.285^d	.311	54.3	2200	3.56 ± .08	2.90
"	.391	54.4	"	4.42 ± .05	3.47
"	.411	"	"	4.26 ± .09	3.61
"	.511	54.5	"	5.01 ± .11	4.33
"	.607	54.4	"	5.83 ± .12	4.94
"	.857	54.3	"	6.04 ± .12	6.57
"	.857	54.4	"	7.05 ± .16	6.64
"	.969	"	"	7.66 ± .20	7.40
.672^d	.025	65.0	2300	3.51 ± .061	3.35
"	$.061_8$	"	"	4.52 ± .09	4.02
"	.113	"	"	5.05 ± .25	4.95
"	.213	"	"	7.25 ± .19	6.76
"	.311	"	"	8.52 ± .19	8.54
"	.510	"	"	12.1 ± .3	12.2
"	.607	"	"	14.6 ± .3	13.9
"	.757	"	"	15.4 ± .4	16.6
"	.857	"	"	17.5 ± .3	18.4
"	.970	"	"	19.4 ± .3	20.5
"	$.028_0$	75.0	"	10.5 ± .2	10.1
"	$.062_4$	"	"	11.8 ± .4	11.6
"	.112	"	"	13.4 ± .7	13.8
"	.212	"	"	16.2 ± .7	18.1
"	.311	"	"	19.3 ± .6	22.4
"	.509	"	"	27.6 ± .9	31.1
"	.606	"	"	32.0 ± 1.7	35.3
"	.759	"	"	38.0 ± 1.2	41.9
"	.857	"	"	39.8 ± 1.1	46.2
"	.968	"	"	45.7 ± .12	51.0

Table 17. Rate constants for the aquation of $CrCN^{2+}$ in $LiClO_4$ media[a]

$10^4[CrCN^{2+}]_o$	$[H^+]$[b]	Temp(°C)	$10^3k_{aq}(sec^{-1})$[c]	
			obsd	calc
1.60	.0503	45.0	.429 ± .009	.422
"	.0967	"	.512 ± .008	.577
"	.204	"	.953 ± .009	.939
"	.286	"	1.50 ± .02	1.21
"	.405	"	1.78 ± .02	1.61
"	.595	"	2.27 ± .03	2.25
"	.793	"	2.52 ± .06	2.91
"	.898	"	3.38 ± .26	3.27
"	.993	"	3.89 ± .08	3.59
"	.995	"	3.28 ± .05	3.60
1.00	.00078	55.0	1.91 ± .02	1.73[d]
"	.00097	"	1.54 ± .01	1.58[d]
"	.00165	"	1.33 ± .02	1.34[d]
"	.00254	"	1.11 ± .01	1.22[d]
"	.00435	"	1.21 ± .02	1.14[d]
"	.00462	"	1.15 ± .01	1.14[d]
"	.00815	"	1.13 ± .02	1.11[d]
2.00	.0101	55.0	.973 ± .013	1.08
"	.0518	"	1.48 ± .02	1.41
"	.0978	"	1.92 ± .03	1.77
"	.201	"	2.93 ± .04	2.59
"	.299	"	3.79 ± .07	3.36
"	.395	"	4.52 ± .08	4.12
"	.401	"	4.56 ± .06	4.16
"	.500	"	5.01 ± .10	4.94
"	.702	"	6.69 ± .06	6.53
"	.799	"	7.33 ± .09	7.30
"	.890	"	8.22 ± .12	8.02

[a] I = 1.00 M with $LiClO_4$ and $HClO_4$; continuous absorbance measurements at ~2100 Å.

[b] Measured by direct titration of aliquots of spent reaction solution with NaOH. Chromium(III) content was ~10^{-4} M, sufficiently low to allow direct titration.

[c] Observed values of k_{aq} were calculated from absorbance-time data with a computer program for first-order data. Calculated values were obtained from the activation parameters given in Table 18.

[d] These data were not used in the calculation of activation parameters. Calculated values of k_{aq} were obtained from the best fit of all 55.0°C data to the equation:

$$k_{aq} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+].$$

Table 17. (Continued)

$10^4[CrCN^{2+}]_o$	$[H^+]^b$	Temp(°C)	$10^3 k_{aq}(sec^{-1})^c$ obsd	calc
2.00	.992	55.0	7.30 ± .14	8.82
"	.996	"	8.76 ± .09	8.85
"	.996	"	8.35 ± .25	8.85
"	.00986	65.0	3.87 ± .06	3.84
"	.0491	"	4.35 ± .09	4.53
"	.0981	"	5.36 ± .11	5.39
"	.204	"	6.89 ± .23	7.24
"	.296	"	9.79 ± .20	8.86
"	.393	"	11.7 ± .2	10.6
"	.593	"	13.4 ± .3	14.1
"	.794	"	16.8 ± .2	17.6
"	.889	"	18.9 ± .2	19.3
"	.992	"	21.0 ± .3	21.1

$k_{aq} = \Sigma k_i[H^+]^i$. A plot of log k_{aq} vs. log $[H^+]$ for the $NaClO_4$ media over the range .02-1.0 M H^+ is shown in Fig. 11. The increase in slope with increasing $[H^+]$ indicated a sum of terms in the numerator of the rate law. In this case, the slope changes from 0 to +1, corresponding to a rate law (Eq. 58):

$$k_{aq} = k_o + k_1 [H^+] \qquad (58)$$

This rate law is further verified by linearity of a plot of k_{aq} vs. $[H^+]$, shown for $LiClO_4$ media in Fig. 12.

Systematic deviations of observed data from the calculated lines in Fig. 11 for $NaClO_4$ media at 54.4°C and 75.0°C arise from the manner in which the data were treated. The calculated lines were determined from the activation parameters which were calculated by simultaneously considering

Fig. 11. Logarithmic plot of k_{aq} vs. $[H^+]$ for the aquation of $CrCN^{2+}$ in $NaClO_4$ media; lines were calculated from the activation parameters

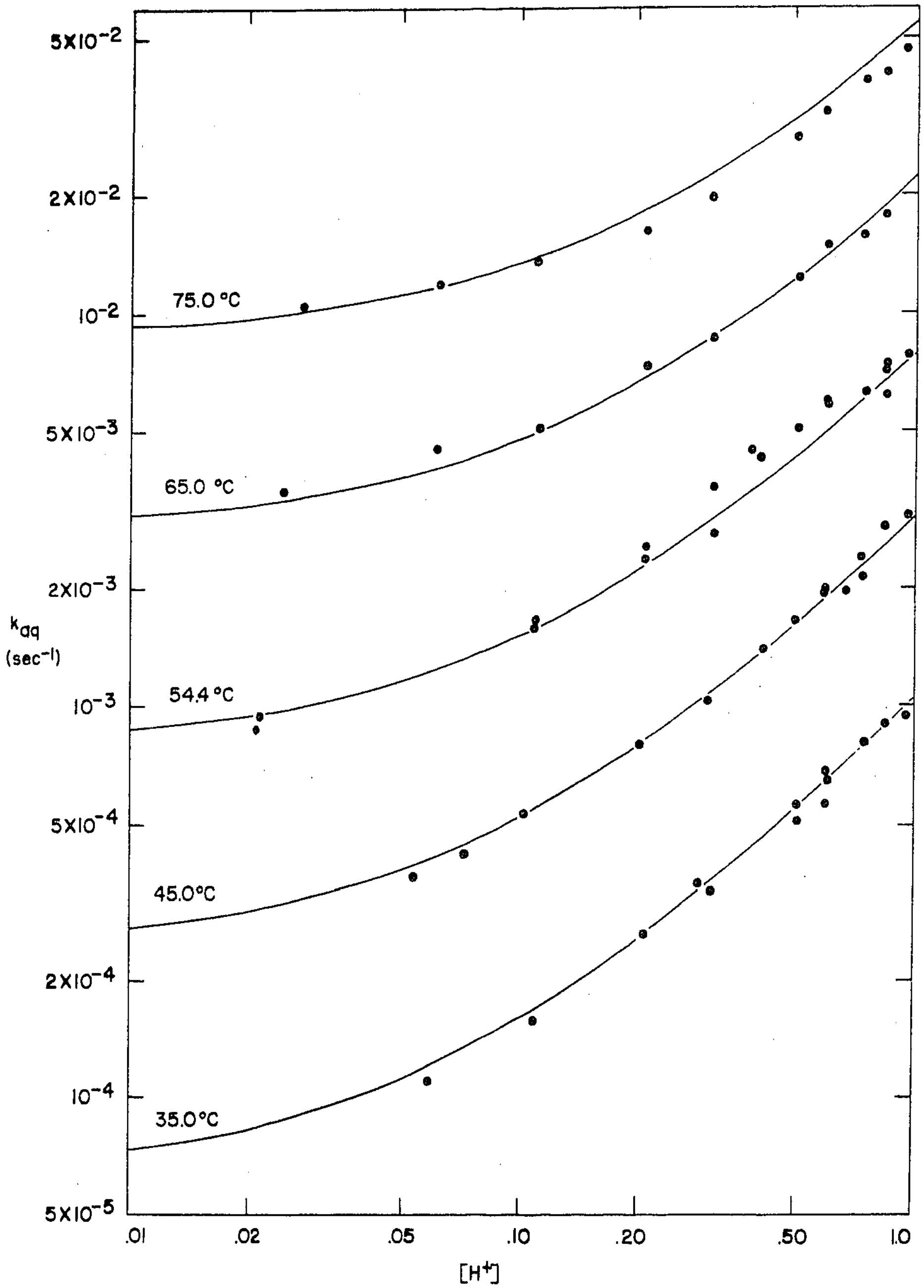
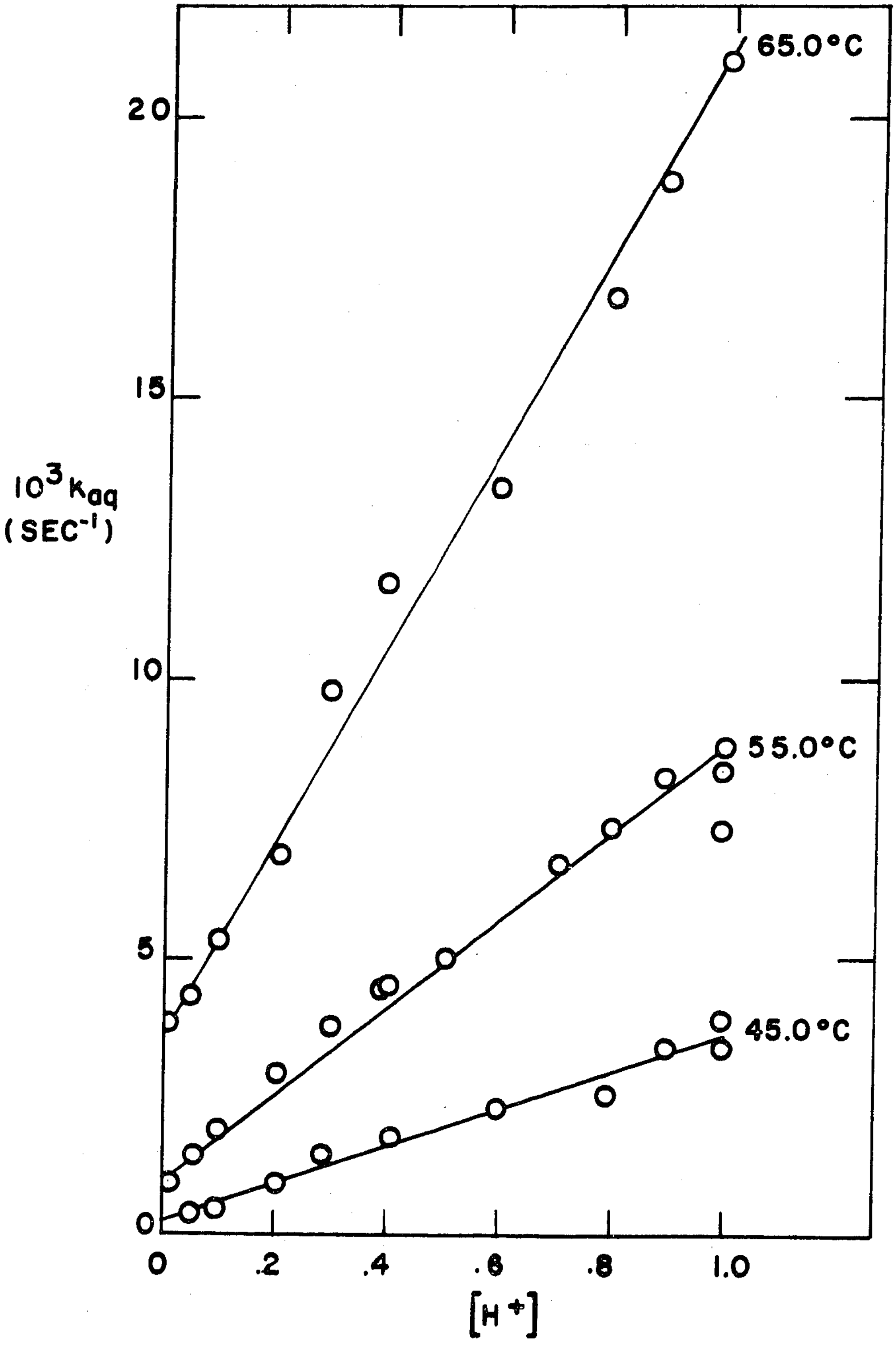

5X10⁻²
2X10⁻²
10⁻²
5X10⁻³
2X10⁻³
10⁻³
5X10⁻⁴
2X10⁻⁴
10⁻⁴
5X10⁻⁵
k_aq
(sec⁻¹)
75.0 °C
65.0 °C
54.4 °C
45.0°C
35.0°C
.01
.02
.05
.10
.20
.50
1.0
[H⁺]

Fig. 12. Plot of k_{aq} vs. $[H^+]$ for the aquation of $CrCN^{2+}$ in $LiClO_4$ media; lines were calculated from the activation parameters


65.0°C
55.0°C
45.0°C
20
15
10
5
0
$10^3 k_{aq}$
(SEC^{-1})
0
.2
.4
.6
.8
1.0
$[H^+]$

data at each $[H^+]$ and temperature. These lines then represent a compromise between fitting the data to the $[H^+]$ dependence exactly at each temperature and fitting the data to the Eyring equation (Eq. 8) exactly at each $[H^+]$.

Activation parameters for the paths corresponding to k_o and k_1 are presented in Table 18 for both the $LiClO_4$ and $NaClO_4$ media.

Table 18. Activation parameters for the aquation of $CrCN^{2+}$[a]

Path	Medium	$\Delta H^{\ddagger}$(kcal/mole)	$\Delta S^{\ddagger}$(e.u.)
k_o	$LiClO_4$	27.9 ± 1.4	12.7 ± 4.2
k_1	$LiClO_4$	$17.0_5 \pm 0.7_3$	-16.4 ± 2.2
k_o	$NaClO_4$	25.6 ± 1.0	5.4 ± 3.1
k_1	$NaClO_4$	$19.7_6 \pm 0.4_8$	-8.3 ± 1.5

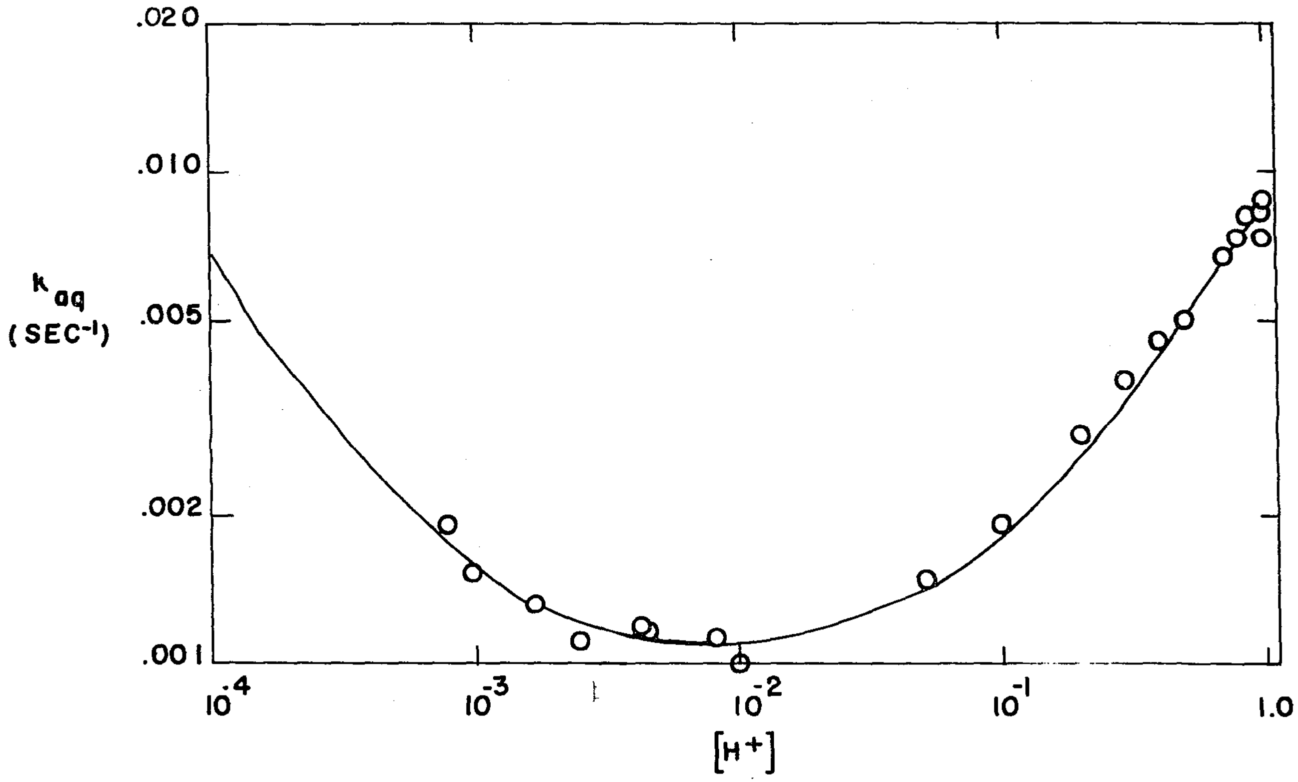
[a] I = 1.00 M maintained with $LiClO_4$ or $NaClO_4$ as indicated. Weighting for the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was carried out as $1/k^2$.

In $LiClO_4$ media at 55°C, the $[H^+]$ range was extended below 0.01 M (Table 17). A plot of log k_{aq} *vs*. log $[H^+]$ (Fig. 13) for all data at 55°C reveals another path for aquation with an inverse $[H^+]$ dependence:

$$k_{aq} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+] \qquad (59)$$

This path was relatively unimportant in studies at other temperatures and in the $NaClO_4$ media, where no experiments were carried out with $[H^+] \leq 0.01$ M. Fit of all the 55°C data

Fig. 13. Logarithmic plot of k_{aq} vs. $[H^+]$ for the aquation of $CrCN^{2+}$ in $LiClO_4$ media at 55.0°C, showing fit of data to the equation $k_{aq} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+]$


.020
.010
.005
.002
.001
k_{aq}
(SEC^{-1})
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1.0
[H$^+$]

from Table 17 to Eq. 59 yielded values of the rate constants: $10^7k_{-1} = 5.8 \pm 1.1$ $\underline{M}$ sec^{-1}, $10^3k_o = 0.972 \pm 0.052$ sec^{-1}, and $10^3k_1 = 7.99 \pm 0.28$ $\underline{M}^{-1}sec^{-1}$. These compare well with the rate constants calculated from the activation parameters (Table 18) for the two paths: $10^3k_o = 1.001$ sec^{-1} and $10^3k_1 = 7.88$ $\underline{M}^{-1}sec^{-1}$.

Discussion of results

In studies of the $[H^+]$ dependence of the rate of a reaction involving ionic species, it is common practice to maintain constant ionic strength with $NaClO_4$ or $LiClO_4$. Since the replacement of H^+ by Na^+ or Li^+ changes the medium, changes in the activity coefficients of H^+ may occur. An indication of the changes to be expected can be obtained from a study of the activity coefficient of HCl in solutions of HCl-MCl at constant ionic strength (64). When M = Li, the activity coefficient of H^+ was found to be relatively independent of $[H^+]$ compared to solutions with M=Na, where the activity coefficient decreased significantly with decreasing $[H^+]$.

In view of these results, it is not surprising that the rate constants for aquation of $CrCN^{2+}$ change on going from $NaClO_4$ to $LiClO_4$ media (Tables 16 and 17). Since the activity coefficient of H^+ probably varies less in the $LiClO_4$ media, the rate constants in these media would seem to provide a better description of the $[H^+]$ dependence.

The rate law for aquation of CrX^{+3-n} complexes has invariably been found to be of the form: $k_{aq} = \sum_i k_i[H^+]^i$, with one or more terms in the sum. Rate laws for all complexes for which data are presently available are summarized in Table 19.

Table 19. Rate laws for aquation of chromium(III) complexes

Ligand	Rate law terms observed (i)^a				Reference
CN^-		-1	0	+1	This work
SCN^-		-1	0		(5)
NCS^-	(-2)	-1	0		(65)
N_3^-	(-2)	-1	0	+1	(56)
F^-		(-1)	0	+1	(53)
Cl^-		-1	0		(53)
Br^-		-1	0		(66)
I^-		-1	0		(53,67)
$H_2PO_2^-$				+1	(68)
H_2O			0		(69)

^{a}Rate laws are of the form $k_{aq} = \sum k_i[H^+]^i$. Terms in parentheses are doubtful.

It has been postulated that in substitution reactions, the partial molar entropies of the entering and leaving groups are relevant in determining the entropy of activation for the reaction, i.e., the partial molar entropy of the activated complex (70). Thus, there should be a linear relationship between $\Delta S_0^{\ddagger}$ and $\bar{S}_0(X^-)$ for the aquation of a series of CrX^{2+} complexes, by a path independent of $[H^+]$, with activated complex $\left\{Cr(H_2O)_{5+n}X^{2+}\right\}^{\ddagger}$. This is expected, since the transition state is intermediate between reactants and immediate products, assuming the partial molar entropies of a series of reactants CrX^{2+} are nearly the same. The presence of such a relationship was previously demonstrated for the halo complexes (53) and is extended here to include all complexes aquating by an acid-independent path (Table 19) for which data are presently available (Fig. 14). Partial molar entropies were obtained from Latimer (71), except for the value for fluoride ion, which came from Stephenson, et al. (72). Using three complexes (Cl^-, Br^-, I^-) to define the linear relationship as before (53), all ligands of appreciable basicity fall above the line, although the value of $\Delta S_0^{\ddagger}$ for CN^- in the $NaClO_4$ medium is not significantly high. This is consistent with an "internal acid catalysis", with activated complex $\{Cr(H_2O)_{4+n}(OH)XH^{2+}\}^{\ddagger}$ having immediate products $CrOH^{2+}$ and HX. A more positive entropy of activation is to be expected for such a transition state than for one in which there is development of more charge separation (products Cr^{3+} and X^-). The negative deviation of $CrNCS^{2+}$ has not been explained, but may indicate a greater value of n, i.e., greater participation of the entering ligand H_2O in the transition state.

A similar correlation between $\Delta S_{-1}^{\ddagger}$ and $\bar{S}_0(X^-)$ should hold, but is not as good (Fig. 15). This has been discussed by Swaddle and King (53), who point out that the values of $\Delta S^{\ddagger}$ depend on the manner in which these values are calculated.

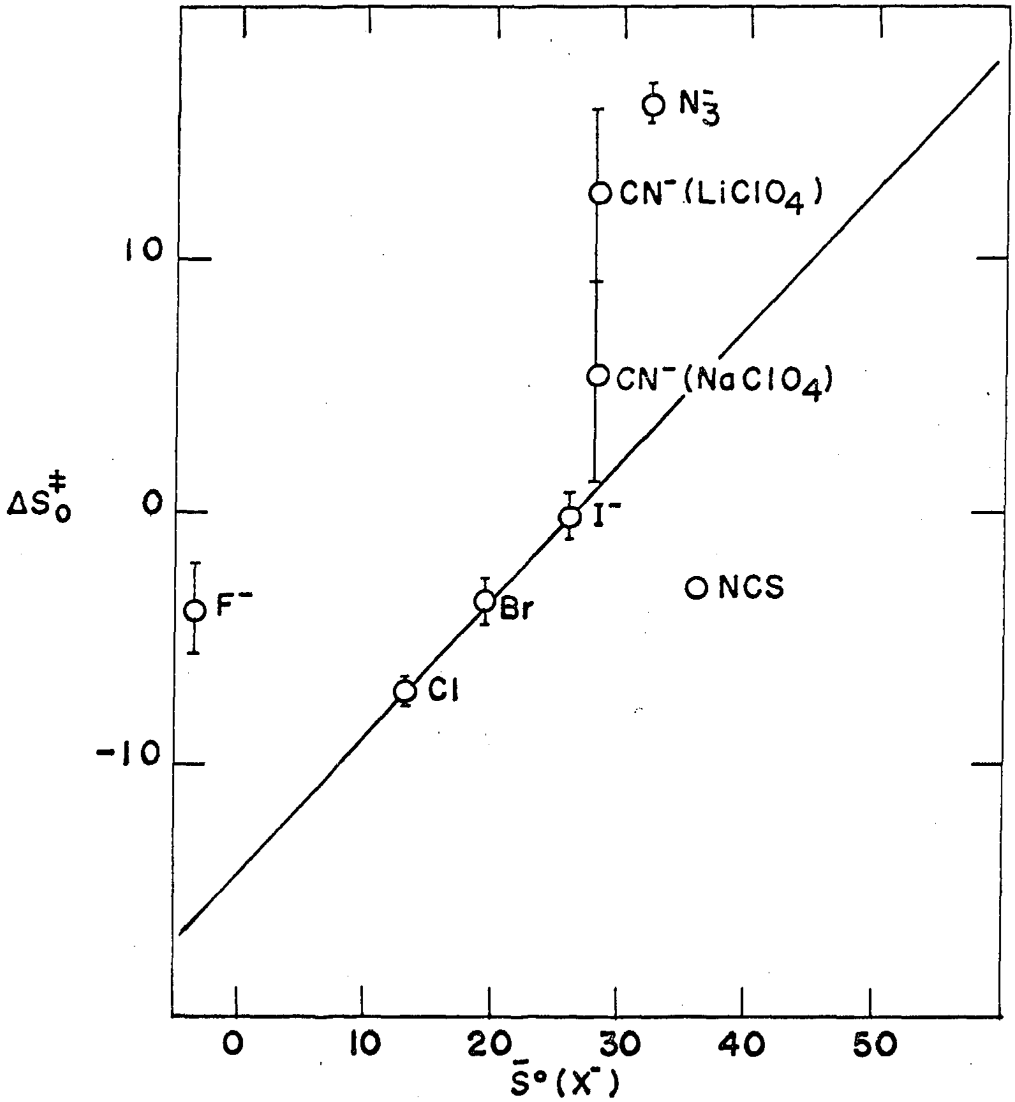


Fig. 14. Plot of $\Delta S_o^{\ddagger}$ vs. $\bar{S}^o(X^-)$ for the complexes CrX^{2+}

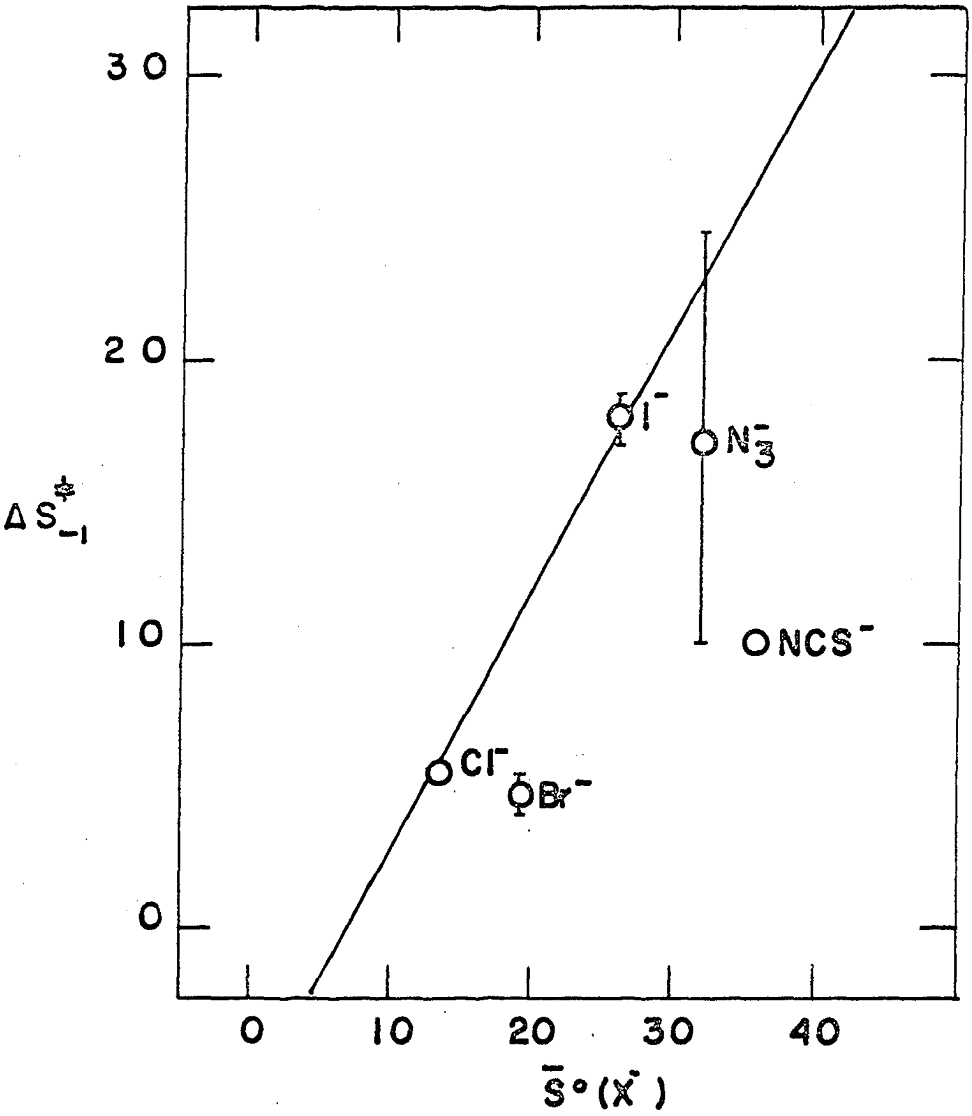


Fig. 15. Plot of $\Delta S^{\ddagger}_{-1}$ vs. $\bar{S}^{o}(X^{-})$ for the complexes CrX^{2+}

For the k_1 path, the distribution of protons in the transition state is probably $\left\{Cr(H_2O)_{5+n}XH^{3+}\right\}^{\ddagger}$ rather than $\left\{Cr(H_2O)_{4+n}(H_3O)X^{3+}\right\}^{\ddagger}$, since there is no apparent advantage to the latter transition state over that of charge +2, and only complexes having a ligand which is appreciably basic (CN^-, N_3^-, F^-, $H_2PO_2^-$) have a term $k_1[H^+]$ associated with them. This is true also for the aquation of the iron(III) complexes, FeX^{+3-n} (27). A correlation of $\Delta S_1^{\ddagger}$ with $\bar{S}_o(HX)$ should hold for this path (Fig. 16). The negative deviation of $CrH_2PO_2^{2+}$ is striking. It has been suggested that one more water molecule may be involved in the transition state for this complex than for the others (68).

An attempt has been made to correlate the relative magnitude of the acid-dependent term (k_1/k_o) with the basicity of the ligand (68), but was not successful.

Based on the above arguments, the mechanism for aquation of $CrCN^{2+}$ would apparently be:

$$CrCN^{2+} \overset{Q}{\rightleftharpoons} Cr(OH)CN^{+} + H^{+} \tag{60}$$

$$Cr(OH)CN^{+} \xrightarrow{k'_{-1}} CrOH^{2+} + CN^{-} \text{ (or } Cr(OH)_2^{+} + HCN) \tag{61}$$

$$CrCN^{2+} \xrightarrow{k_o} CrOH^{2+} + HCN \tag{62}$$

$$CrCN^{2+} + H^{+} \xrightarrow{k_1} Cr^{3+} + HCN \tag{63}$$

The rate equation derived from this mechanism is:

$$-d(\ln[CrCN^{2+}])/dt = k'_{-1}Q[H^{+}]^{-1} + k_o + k_1[H^{+}] \tag{64}$$

Recent results of Wakefield and Schaap (73) on the aquation of $CrCN^{2+}$ are in slight disagreement with the results

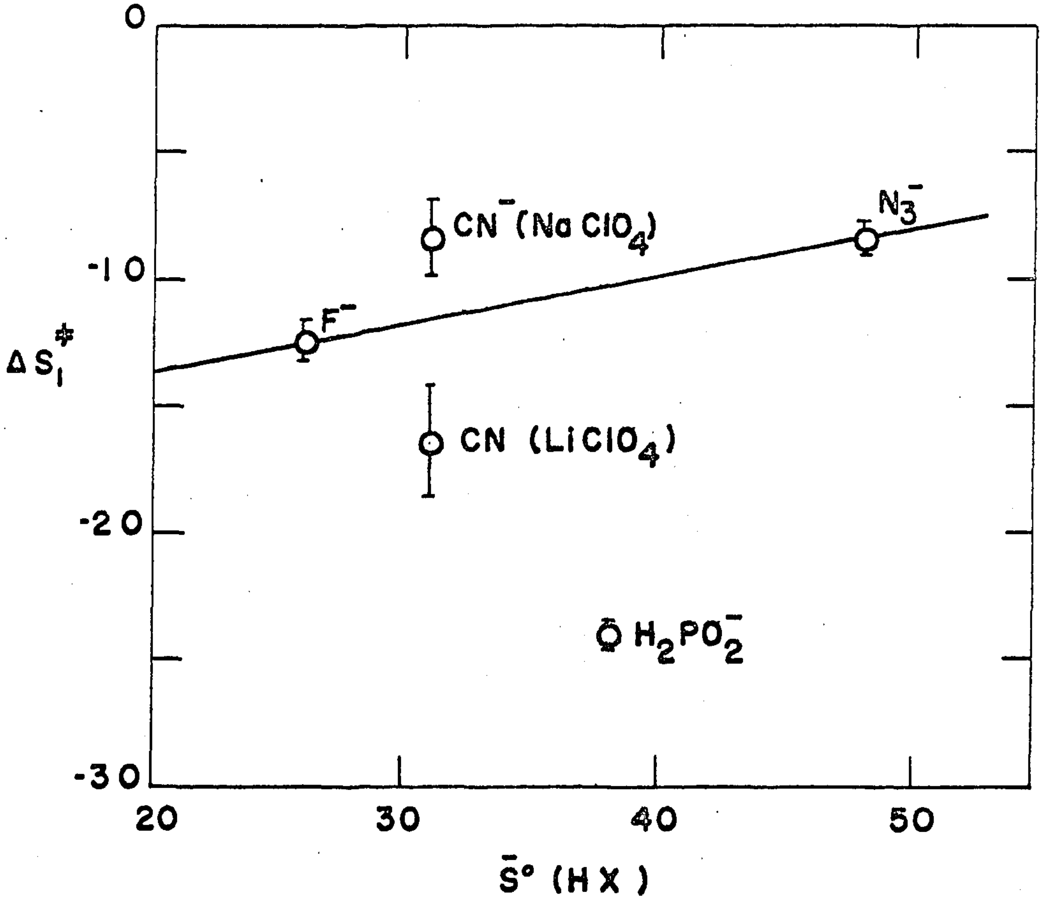


Fig. 16. Plot of $\Delta S_1^{\ddagger}$ *vs*. $\bar{S}^{\circ}$(HX) for the complexes CrX^{2+}

presented above. In solutions of 2.0 M ionic strength maintained with $NaClO_4$, over the temperature range 15-40°C, they found a rate law:

$$-dC_{CrCN^{2+}}/dt = \frac{(k_o' + k_1'K_{eq}[H^+])C_{CrCN^{2+}}}{1 + K_{eq}[H^+]} \qquad (65)$$

The mechanism proposed for this rate law is given in Eq. 66-68.

$$CrCN^{2+} + H^+ \overset{K_{eq}}{\rightleftharpoons} CrCNH^{3+} \quad \text{(rapid)} \qquad (66)$$

$$CrCN^{2+} \xrightarrow{k_o'} Cr^{3+} + CN^- \qquad (67)$$

$$CrCNH^{3+} \xrightarrow{k_1} Cr^{3+} + HCN \qquad (68)$$

Values of the parameters at 25°C were $k_o' = 1.1 \times 10^{-5} sec^{-1}$, $k_1'K_{eq} = 5.9 \times 10^{-4}$ $\underline{M}^{-1}sec^{-1}$ and $K_{eq} = 0.18$ $\underline{M}^{-1}$. These parameters can be compared with those for solutions of 1.0 M ionic strength derived from the activation parameters given in Table 18: $k_o = 1.53 \times 10^{-5} sec^{-1}$ and $k_1 = 3.10 \times 10^{-4}$ $\underline{M}^{-1}sec^{-1}$. Activation parameters derived by Wakefield and Schaap (73) are: k_o', $\Delta H^{\ddagger} = 27$ kcal/mole, $\Delta S^{\ddagger} = 9$ e.u.; $k_1'K_{eq}$, $\Delta H^{\ddagger} =$ 20 kcal/mole, $\Delta S^{\ddagger} = -6$ e.u. These are similar to the values obtained in this work (Table 18): $\Delta H_o^{\ddagger} = 25.6$ kcal/mole, $\Delta S_o^{\ddagger} = 5.4$ e.u.; $\Delta H_1^{\ddagger} = 19.8$ kcal/mole, $\Delta S_1^{\ddagger} = -8.3$ e.u.

Since the experimental data of Wakefield and Schaap are not available, it is difficult to decide whether there is significant disagreement between the two studies. However, several points can be made. The acid association constant

K_{eq} is quite small and would be even smaller in the solutions of 1.00 M ionic strength studied here. The decrease in slope of a plot of k_{aq} vs. $[H^+]$ calculated from the parameters of Wakefield and Schaap is not very large for $[H^+] \leq 1.0$ M, and with a normal amount of experimental scatter, a straight line could probably be drawn through the experimental data. The deviations do become larger at higher $[H^+]$, but as can be seen from the data in Fig. 11, there are no significant deviations for solutions of 1.00 M ionic strength.

A second point is that the activity coefficient of H^+ in solutions of Na^+ at constant ionic strength probably does not remain constant on changing $[H^+]$ (64). The deviations from linearity could possibly be attributed to changes in the activity coefficient of H^+. Data calculated from the empirical rate parameters of Wakefield and Schaap were fit to Eq. 69, where A is an empirical parameter used to account for

$$k_{aq} = k_o + k_1 [H^+]\exp(A[H^+]) \qquad (69)$$

nonlinearity. The calculated data fit this equation quite well, and yielded values of the parameters: $k_o = 1.14\text{x}10^{-5}$ sec^{-1}, $k_1 = 5.77\text{x}10^{-4}\text{sec}^{-1}$, and $A = -0.150$ M^{-1}. This value of A is reasonable in view of the magnitude of changes in the activity coefficient expected in solutions of $NaClO_4$ at constant ionic strength (74). The question of which empirical parameter, K_{eq} or A, should be used to correct for nonlinearity in plots of k_{aq} vs. $[H^+]$ could possibly be answered by studies of the aquation of $CrCN^{2+}$ in solutions of 2.0 M ionic strength maintained with $LiClO_4$, where the activity coefficient of H^+ is expected to vary somewhat less than in solutions of $NaClO_4$ (64).

At any rate, a third parameter is not needed to adequately describe the data presented here in solutions of 1.00 M ionic strength maintained with either $NaClO_4$ or $LiClO_4$.

Catalysis of $CrCN^{2+}$ Aquation by Cr^{2+}

Results

Taube and King (25) first observed the Cr^{2+} catalysis of the aquation of $CrCl^{2+}$, Eq. 70.

$$CrCl^{2+} = Cr^{3+} + Cl^- \qquad (70)$$

This catalysis has now been observed for a number of chromium (III) complexes (Table 20) (23,62,75,76), including $CrCN^{2+}$, which is reported here. Data at 55° are presented in Table 21.

According to the principle of microscopic reversibility (77,78), the reverse of this reaction, the catalysis of the formation of Cr(III) complexes, must also exist. This has been observed for a number of ligands X^{n-} by Hunt and Earley (79), but not for any of the ligands reported in Table 20. They interpreted this effect in terms of a non-bridging ligand effect on the chromium(II)-(III) exchange reaction:

$$Cr^{2+} + X^{n-} \rightleftharpoons CrX^{+2-n} \qquad (71)$$

Table 20. Rate constants for the Cr^{2+} catalyzed aquation of some chromium(III) complexes

Complex	k_2^a (sec^{-1})	k_3^a ($\underline{M}^{-1}sec^{-1}$)	Temp.	Reference
$Cr(H_2O)_6^{3+}$	$10.4x10^{-5}$	$1.94x10^{-5}$	25°	(23)
$CrNH_3^{3+}$	$5.92x10^{-5}$	$2.39x10^{-5}$	25°	(62)
CrI^{2+}	$2.2x10^{-2}$	---	25°	(75)
$CrBr^{2+}$	$2x10^{-3}$	---	25°	(75)
$CrCl^{2+}$	$4x10^{-4}$	---	25°	(75)
	$2.6x10^{-4}$	---	25°	(76)
$CrCN^{2+}$	$2.68x10^{-3}$	---	55°	This work

^{a}Defined by $k_{obs} = k_{spont} + k_2[Cr^{2+}][H^+]^{-1} + k_3[Cr^{2+}]$.

$$CrX^{+2-n} + {}^*Cr^{3+} \longrightarrow CrX^{+3-n} + {}^*Cr^{2+} \qquad (72)$$

The order of increasing rate of catalysis paralleled the apparent order of stabilities of the chromium(III) complexes formed.

The rate equation for the aquation of $CrCN^{2+}$ in solutions of Cr^{2+} is given by Eq. 73 and Eq. 74.

$$-d(\ln[CrCN^{2+}])/dt = k_{spont} + k_2[Cr^{2+}][H^+]^{-1} \qquad (73)$$

$$k_{spont} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+] \qquad (74)$$

The value of k_2 at 55° and 1.0 $\underline{M}$ ionic strength is $(2.68 \pm 0.15)x10^{-3}sec^{-1}$. The data presented in Table 21 are adequately fit by Eq. 73 (Fig. 17), but are not sufficiently

Table 21. Catalysis of $CrCN^{2+}$ aquation by Cr^{2+a}

$10^3[CrCN^{2+}]_o$	$[Cr^{2+}]$	$[H^+]$	$10^3k_{aq}(sec^{-1})^b$	$10^3k_{spont}(sec^{-1})^c$	10^3k_{aq}, calc $(sec^{-1})^d$
3.04	.0324	.0332	3.422 ± 0.075	1.255	3.868
6.08	.0168	.0098	5.233 ± 0.093	1.068	5.685
3.04	.0429	.0480	4.061 ± 0.084	1.368	3.758
3.04	.0168	.0159	3.056 ± 0.043	1.136	3.958
9.14	.0429	.0358	5.231 ± 0.194	1.275	4.479
6.08	.0429	.0419	4.064 ± 0.073	1.321	4.058
3.04	.0429	.0293	5.655 ± 0.156	1.226	5.138
3.04	.0168	.0096	5.925 ± 0.228	1.110	5.795

[a] I = 1.00 $\underline{M}$ with $LiClO_4$; 55.0°C; 5250Å.

[b] Calculated from absorbance-time data by a computer program for first-order kinetic data.

[c] Calculated from the equation for spontaneous aquation: $k_{spont} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+]$.

[d] Calculated from the equation: $k_{aq,calc} = k_{spont} + k_2[Cr^{2+}][H^+]^{-1}$. All data were weighted equally when fit to this equation with a non-linear least squares program to determine k_2.

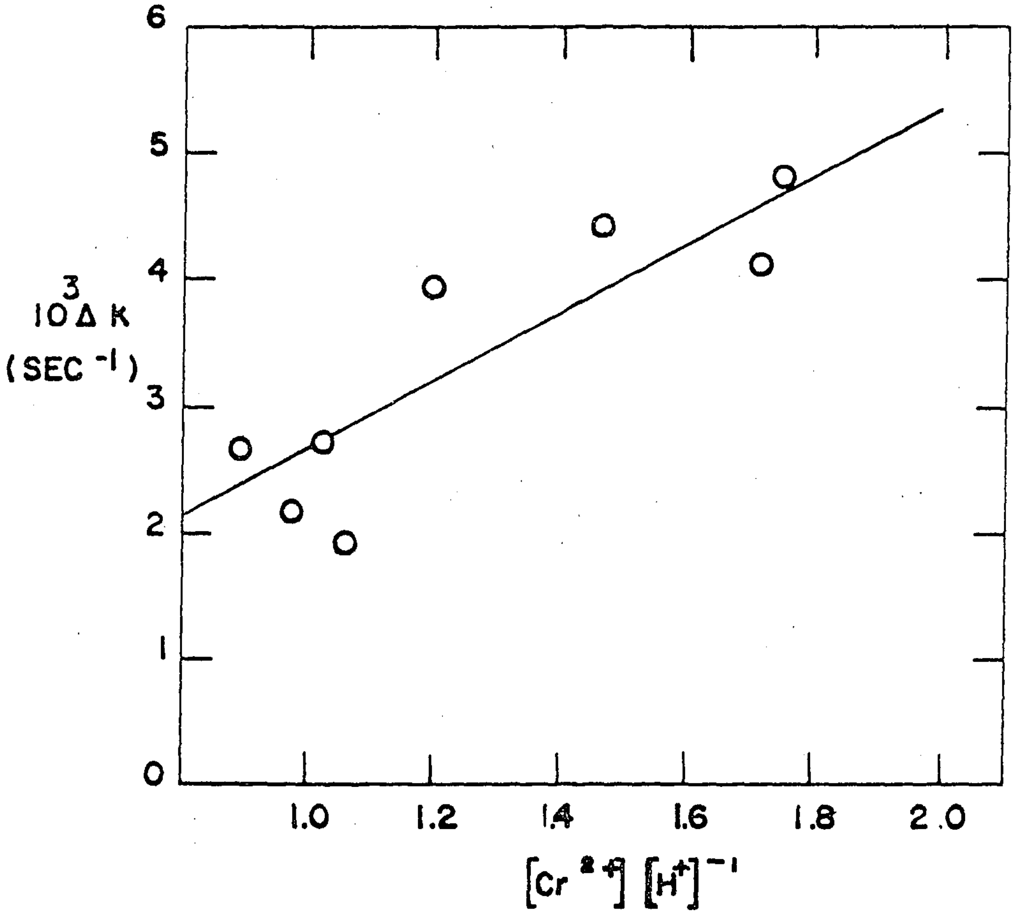


Fig. 17. Plot of Δk vs. $[Cr^{2+}][H^+]^{-1}$ for the Cr^{2+} catalyzed aquation of $CrCN^{2+}$, with $\Delta k = k_{obs} - k_{spont}$

precise to rule out an additional term $k_3[Cr^{2+}]$. All of the reactions listed in Table 20 have obeyed a similar rate equation:

$$k_{cat} = k_2[Cr^{2+}][H^+]^{-1} + k_3[Cr^{2+}] \qquad (75)$$

with the k_2 term much more important than the k_3 term.

Discussion of results

The most reasonable mechanistic interpretation of the catalysis is as an electron transfer reaction between Cr^{2+} and Cr(III), having, for the k_2 path, a transition state $\{NCCr(OH)Cr^{3+}\}^{\ddagger}$. The observed k_2 is then $k_2'Q$, with Q being the equilibrium constant for the acid dissociation:

$$CrCN^{2+} \rightleftharpoons Cr(OH)CN^+ + H^+ \qquad (76)$$

The catalysis observed here, and the similar V^{2+} catalysis of the formation and aquation of $CrCl^{2+}$ (80), can be contrasted with the Hg^{2+} catalysis of the aquation of $CrCl^{2+}$ (39) and $CrCN^{2+}$ (described below). The former reactions are examples of oxidation-reduction catalysis, proceeding by an electron transfer mechanism; the latter are examples of coordination catalysis, where displacement of the aquating ligand is assisted by coordination to the catalyst.

The relative efficiency of nonbridging ligands in promoting electron transfer by a hydroxide bridged path follows the order, $I^- > Br^- > Cl^- > H_2O > NH_3 > CN^-$ (Table 20). The position of cyanide in this series is somewhat uncertain since measurements were made only at 55°C, where

$k_{NH_3} = 1.69x10^{-3}sec^{-1}$ (62) and $k_{CN^-} = 2.68x10^{-3}sec^{-1}$. However, since the $CrNH_3^{3+}$ aquation was studied at higher ionic strength (2.0 M compared to 1.0 M for $CrCN^{2+}$) and the charges of the two complexes are different, CN^- very likely belongs at the end of the series. This series follows the inverse of the spectrochemical series for chromium(III) complexes, suggesting a significant contribution of the crystal field stabilization energy to the energy of activation. A higher field ligand trans to the bridging hydroxide ligand raises the vacant Cr(III) e_g orbitals to a higher energy, resulting in a higher activation energy for electron transfer. This "trans effect" has been used previously to explain rate correlations (51,62,81,82).

Exchange Reaction of Cr^{2+} and $CrCN^{2+}$

Results

An electron exchange reaction may be defined as an oxidation-reduction reaction involving two different oxidation states of the same element, with no net chemical change, so that isotopic tracers must be used to study the reaction. In electron exchange reactions of metal ions proceeding by an inner-sphere mechanism, the bridging ligand, if present in the first coordination sphere of one of the metal ions, must be transferred for the reaction to qualify as an electron exchange reaction.

Data for the exchange reaction of $*Cr^{2+}$ with $CrCN^{2+}$ (specific activity of Cr^{2+} as a function of time, a_t) were fit to the McKay equation (83):

$$-d(\ln[1-f])/dt = -d(\ln[\frac{a_t-a_\infty}{a_o-a_\infty}])/dt = R\frac{[Cr^{2+}]+[CrCN^{2+}]}{[Cr^{2+}][CrCN^{2+}]} \quad (77)$$

where f is the fraction of exchanged atoms and R is the rate of the exchange reaction. An exchange reaction should follow the McKay equation to isotopic equilibrium, regardless of the rate law for exchange (R). The form of R can be determined only by varying the concentrations of the exchanging species.

Except in those experiments where aquation of cyanochromium(III) ion was a competing reaction ($\gtrsim .4$ $\underline{M}$ H^+), McKay plots of log $(a_t-a_\infty/a_o-a_\infty)$ $\underline{vs.}$ t were linear. By varying the concentrations of exchanging species, the exchange rate law at constant hydrogen ion concentration was determined to be:

$$R = \frac{.693}{t_{\frac{1}{2}}(ex)}\frac{[Cr^{2+}][CrCN^{2+}]}{[Cr^{2+}]+[CrCN^{2+}]} = k_{ex}[Cr^{2+}][CrCN^{2+}] \quad (78)$$

where $t_{\frac{1}{2}}(ex)$ is the half-time for exchange. The exchange reaction was studied between 5-35°C over the concentration ranges: $*Cr^{2+}$, 5.17×10^{-3}-5.02×10^{-2} $\underline{M}$; $CrCN^{2+}$, 3.83×10^{-3}-2.65×10^{-2} $\underline{M}$; H^+, 0.01-0.35 $\underline{M}$ (Table 22). The effect of $[H^+]$ on the exchange rate, shown in Fig. 18 and Fig. 19, conforms to the equation:

$$k_{ex} = k_o + k_{-1}[H^+]^{-1} \quad (79)$$

Table 22. Rate constants for exchange of $CrCN^{2+}$ with $*Cr^{2+a}$

$[CrCN^{2+}]$	$[Cr^{2+}]^b$	% Cr^{2+} oxid. initially	$[H^+]$	Temp (^oC)	10^3k_1 (sec^{-1})^c	k_2($\underline{M}^{-1}sec^{-1}$) obsd^d	k_2($\underline{M}^{-1}sec^{-1}$) calc^e
.00800 $\underline{M}$	.01405 $\underline{M}$	13	.0224 $\underline{M}$	5.0	.795±.045	.0361±.0020	.0358
.01333	.02581	18	.0487	"	1.125±.023	.0287±.0006	.0282
.01600	.03334	12	.0997	"	1.092±.069	.0221±.0014	.0249
.01600	.02380	37	.200	"	.862±.059	.0280±.0015	.0233
.00765	.01825	8	.050	15.0	1.84 ±.19	.0710±.0073	.0632
.00452	.01039	5	.050	"	.622±.081	.0417±.0054	.0632
.01037	.01774	15	.050	"	1.78 ± .47	.0633±.0167	.0632
.00689	.01924	8	.050	"	2.41 ±.95	.0922±.0363	.0632
.01145	.01706	5	.050	"	1.64 ±.26	.0575±.0091	.0632
.02648	.01715	4	.050	"	2.39 ±.12	.0548±.0028	.0632
.01630	.01663	6	.050	"	2.05 ±.14	.0623±.0043	.0632
.00815	.01352	24	.050	"	1.48 ±.12	.0683±.0055	.0632
.01177	.00946	12	.100	"	1.52 ±.06	.0716±.0028	.0539
.00516	.00517	3	.0115	"	1.09 ±.05	.1055±.0048	.126
.01290	.03096	40	.100	"	2.52 ±.49	.0575±.0112	.0539
.01290	.02860	3	.100	"	2.27 ±.17	.0547±.0041	.0539

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[a] I = 1.00 $\underline{M}$ with $LiClO_4$ and $NaClO_4$.

[b] Analyses were made at approximately one and four half-lives. Invariably any Cr^{2+} oxidation occurred early in the experiment, probably on mixing.

[c] Evaluated by a computer program; $k_1 = .693/t_{\frac{1}{2}}$.

[d] $k_2(obsd) = k_1/([CrCN^{2+}]+[*Cr^{2+}])$.

[e] Calculated from the activation parameters given in Table 23.

Table 22. (Continued)

$[CrCN^{2+}]^a$	$[Cr^{2+}]^b$	% Cr^{2+} oxid. initially	$[H^+]$	Temp (^oC)	10^3k_1 (sec^{-1})^c	k_2($\underline{M}^{-1}sec^{-1}$) obsd^d	calc^e
.01290	.05016	2	.200	15.0	4.24 ±.78	.0672±.0124	.0492
.01290	.02436	17	.200	"	2.02 ±.23	.0542±.0062	.0492
.00516	.00521	3	.0115	"	1.32 ±.05	.127 ±.005	.126
.00674	.01520	1	.050	"	1.62 ±.09	.0738±.0041	.0632
.00571	.00712	4	.0157	"	1.62 ±.08	.126 ±.006	.104
.00732	.00882	6	.0199	"	1.73 ±.12	.107 ±.007	.0915
.00999	.02394	3	.0997	25.0	3.90 ±.34	.115 ±.010	.113
.00713	.01041	1	.0498	"	3.85 ±.37	.219 ±.021	.139
.01427	.01394	6	.1995	"	3.19 ±.17	.113 ±.006	.100
.00459	.00936	4	.0200	"	3.66 ±.33	.262 ±.027	.216
.00698	.01358	8	.0499	"	3.41 ±.29	.166 ±.014	.139
.01552	.01975	52	.349	"	2.85 ±.96	.081 ±.027	.0948
.00383	.00358	10	.0198	35.0	3.36 ±.27	.453 ±.036	.499
.00582	.00691	19	.0496	"	4.11 ±.20	.323 ±.016	.298
.01019	.00717	24	.0996	"	3.60 ±.21	.207 ±.012	.231
.00919	.00691	31	.212	"	2.64 ±.19	.164 ±.012	.195

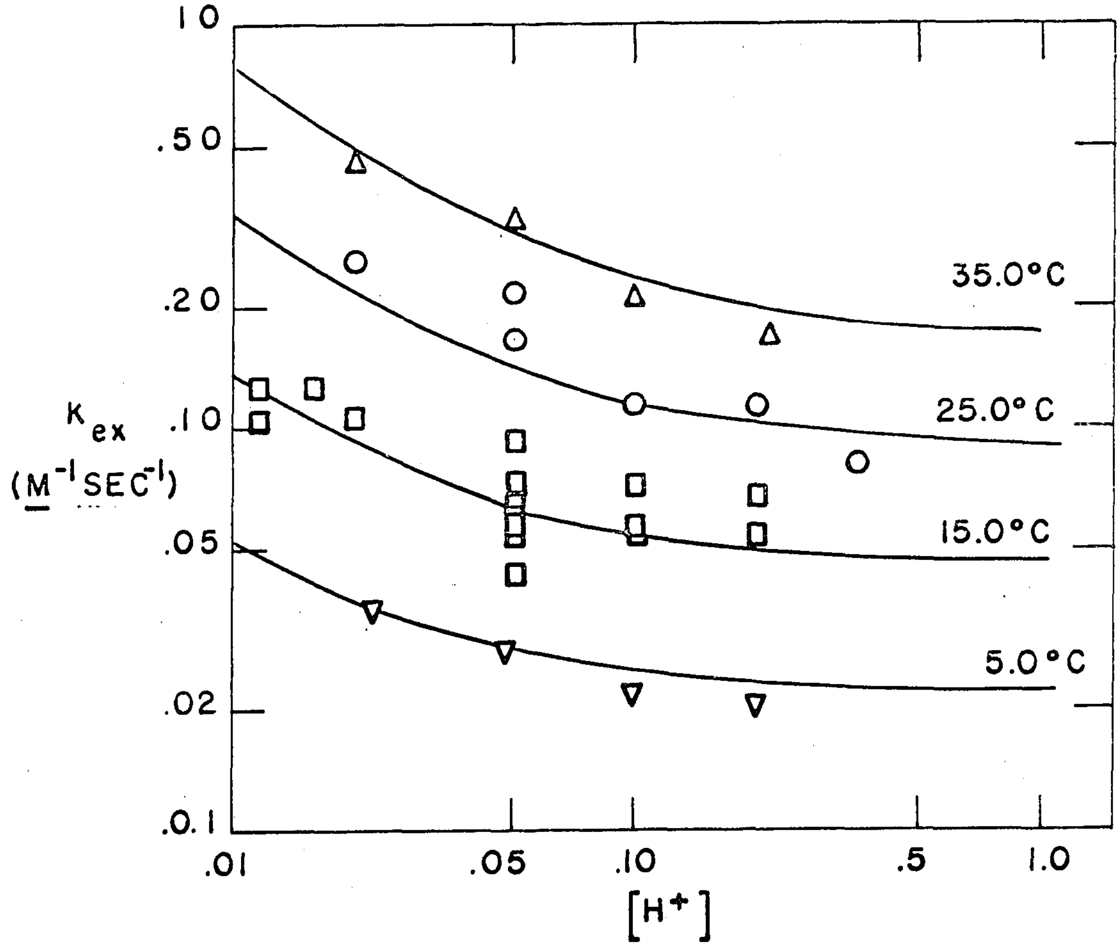

Fig. 18. Logarithmic plot of k_{ex} vs. [H$^+$] for the exchange reaction of Cr^{2+} with $Cr\overline{CN}^{2+}$, I = 1.00 $\underline{M}$, showing fit of data to the equation $k_{ex} = k_o + k_{-1}[H^+]^{-1}$

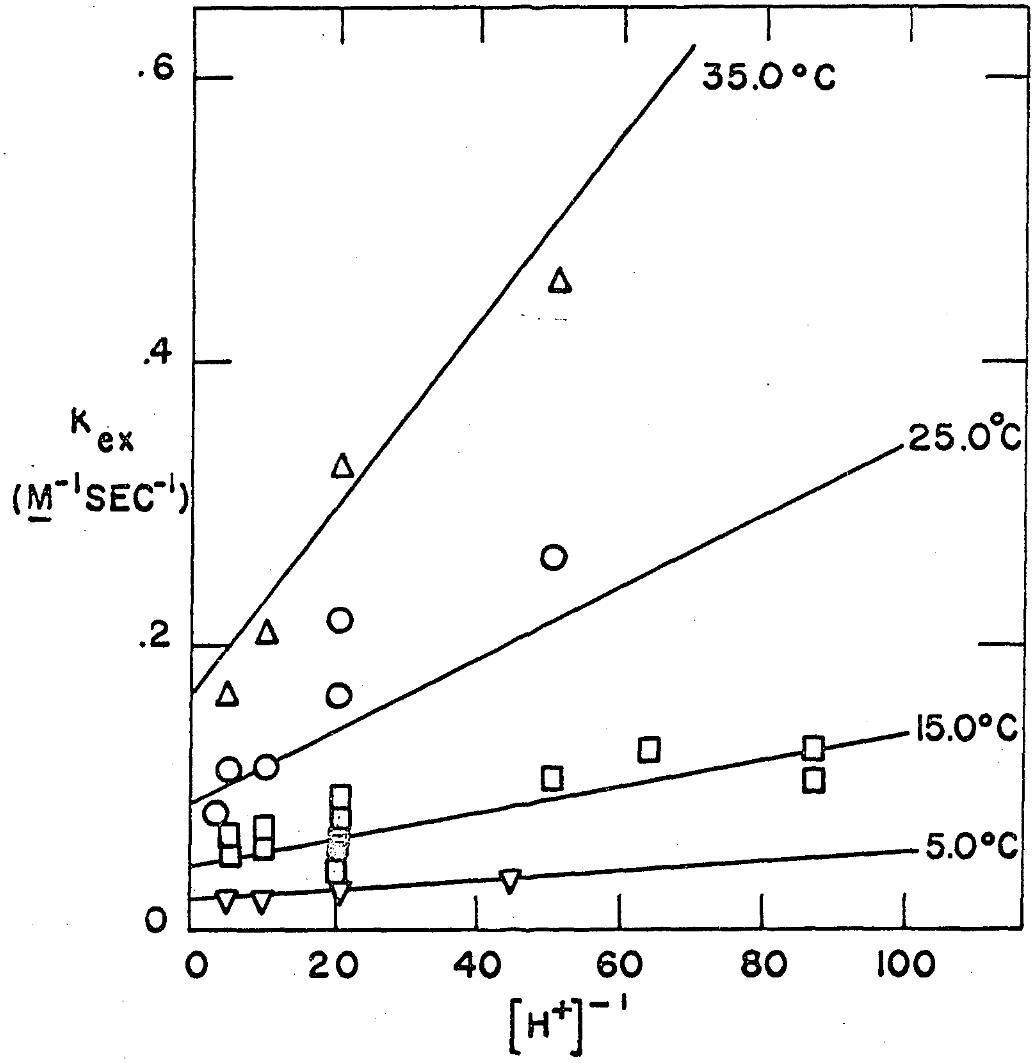

Fig. 19. Plot of k_{ex} vs. $[H^+]^{-1}$ for the exchange reaction of Cr^{2+} with $CrCN^{2+}$, showing fit of data to the equation $k_{ex} = k_o + k_{-1}[H^+]^{-1}$

Activation parameters calculated for the two paths are given in Table 23.

Table 23. Activation parameters for the exchange of $^*Cr^{2+}$ with $CrCN^{2+}$ [a]

Path	$\Delta H^{\ddagger}$(kcal/mole)	$\Delta S^{\ddagger}$(e.u.)	Temp (°C)	k^b
k_o	10.9 ± 1.0	-26.8 ± 3.6	5	$.0220\ \underline{M}^{-1}sec^{-1}$
			15	.0452
			25	.0886
			35	.1663
k_{-1}	16.7 ± 2.2	-14.4 ± 7.5	5	$3.132 \times 10^{-4} sec^{-1}$
			15	9.255×10^{-4}
			25	2.547×10^{-3}
			35	6.570×10^{-3}

[a] I = 1.00 $\underline{M}$ with $LiClO_4$ and $NaClO_4$. Weighting was carried out as $1/k^2 \cdot k/\Delta k$, where Δk is the standard deviation of the rate constant.

[b] These rate constants are calculated from the appropriate activation parameters.

While $LiClO_4$ was added to maintain constant ionic strength, $NaClO_4$ (in concentrations of 0-0.9 $\underline{M}$, usually < 0.3 $\underline{M}$) was also added with the stock solution of $CrCN^{2+}$. Since the activity coefficient of H^+ is probably more constant in solutions of $LiClO_4$ than in solutions of $NaClO_4$ (64), and since there was considerable scatter of data at constant $[H^+]$, it was necessary to determine whether the rate constant for exchange depended on the concentrations of Li^+ or Na^+. Data at 15°C and 0.05 $\underline{M}$ H^+ were treated according to Harned's Rule:

$$k_{obs} = k_o \exp(A[M^+]) \qquad (80)$$

When $M^+ = Li^+$, $A = -0.017 \pm 0.25\ \underline{M}^{-1}$ and when $M^+ = Na^+$, $A = 0.034 \pm 0.22\ \underline{M}^{-1}$, indicating that such medium effects were not of importance.

<u>Discussion of results</u>

For all chromium(II)-(III) exchange reactions

$$*Cr^{2+} + CrX^{+3-n} = *CrX^{+3-n} + Cr^{2+} \qquad (81)$$

which have been studied (Table 24), the rate law has been of the form:

$$R = k_{ex}[Cr^{2+}][CrX^{+3-n}] \qquad (82)$$

For all complexes CrX^{+3-n}, k_{ex} was found to be independent of $[H^+]$, except for $CrH_2PO_2^{2+}$[1], with $k_{ex} = k_{-1}[H^+]^{-1}$, and $Cr(H_2O)_6^{3+}$ (23), with $k_{ex} = k_o + k_{-1}[H^+]^{-1}$. The inverse $[H^+]$ dependence in the $CrH_2PO_2^{2+}$ exchange was explained in terms of (1) a structural isomerism of ligand $H_2PO_2^-$, necessitating acid dissociation previous to formation of a bridged activated complex; or (2) acid dissociation of a water molecule in the first coordination sphere of chromium(III), giving a double-bridged activated complex, involving $H_2PO_2^-$ and a cis OH^- as bridging ligands. The double-bridged activated complex was invoked to maintain a symmetrical activated complex, requiring less expenditure of energy to equalize the electronic energies of the two metal ions so that electron exchange may

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[1] K. A. Schroeder and J. H. Espenson, Ames, Iowa. Kinetics and mechanism of the inner-sphere electron exchange reaction of hypophosphitochromium(III) and chromium(II) ions in acidic solution. Private communication. 1966.

Table 24. Rate data for exchange reactions of Cr^{2+} with CrX^{+3-n}

X^{n-}	k_1($\underline{M}^{-1}$sec^{-1})	$\Delta H^{\ddagger}_{o}$ (kcal/ mole)	$\Delta S^{\ddagger}_{o}$ (e.u.)	k_{-1}(sec^{-1})	$\Delta H^{\ddagger}_{-1}$	$\Delta S^{\ddagger}_{-1}$	Reference
Cl^-	9.1(0°C)						(24)
Br^-	60(0°)						(24)
F^-	$2.6x10^{-3}$(0°) $2.6x10^{-2}$(27°)	13.7	-20				(24)
$-NCS^-$	$1.2x10^{-4}$(24°)						(24)
$-SCN^-$[a]	40(25°)			2(25°)			(4,5)
N_3^-	1.27(0°) 4.68(20°)	9.6	-22.8				(24)
H_2O	$1.94x10^{-5}$(24.5°)	21	-8	$10.4x10^{-5}$(24.5°)			(23)
OH^-	0.66(24.5°)	21	12				(23)
$H_2PO_2^-$				$6.11x10^{-4}$(25°)	19.7	-7.2	-[b]
$-CN^-$	.0886(25°)	10.9	-26.8	$2.55x10^{-3}$(25°)	16.7	-14.4	This work
$-NC^-$[a]	1.5(25°)						This work

[a] These are not strictly exchange reactions since net reaction (isomerization) occurs.

[b] K. A. Schroeder and J. H. Espenson, Ames, Iowa. Kinetics and mechanism of the inner-sphere electron exchange reaction of hypophosphitochromium(III) and chromium(II) ions in acidic solution. Private communication. 1966.

occur (84). Although an unsymmetrical activated complex might require greater adjustments of bond lengths in the first coordination sphere, it cannot be ruled out. The principle of microscopic reversibility does not exclude mechanisms which lack a symmetric activated complex, but requires only that the activated complex for the reverse reaction be a mirror image of that in the forward reaction, i.e., the energy <u>vs</u>. reaction coordinate diagrams must be mirror images (77).

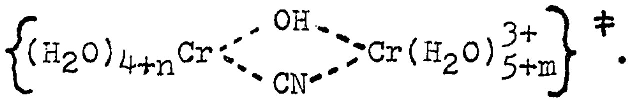
An acid dependence formally like that of the $CrCN^{2+}$ exchange was observed for the $Cr(H_2O)_6{}^{3+}$ (23) and $CrSCN^{2+}$ (5) exchanges. However reaction of Cr^{2+} with $CrSCN^{2+}$ is not strictly an electron exchange reaction, since a net chemical change, isomerization, occurs.

The Cr^{2+}-Cr^{3+} exchange differs from that of $CrCN^{2+}$ in that the ligand OH^- produced by the acid dissociation process presumably acts as the bridging ligand.

The two term rate equation for the $CrCN^{2+}$ exchange indicates activated complexes with probable structures:

$$\left\{(H_2O)_{5+n}Cr\text{---}CN\text{---}Cr(H_2O)^{4+}_{5+m}\right\}^{\ddagger} \quad \text{and}$$

$$\left\{(H_2O)_{4+n}(OH)Cr\text{---}CN\text{---}Cr(H_2O)^{3+}_{5+m}\right\}^{\ddagger} \quad \text{or}$$



$$\left\{(H_2O)_{4+n}Cr\overset{OH}{\underset{CN}{\lessgtr}}Cr(H_2O)^{3+}_{5+m}\right\}^{\ddagger}.$$

The latter two activated complexes cannot, of course, be distinguished, and the configuration of cyanide ion in the activated complex cannot be determined. The path inverse in acid concentration presumably becomes operative either because of decreased repulsive forces with a decrease in charge, or because of a lowering in the activation energy by double bridging.

Because of the absence of an acid dependent term in previous studies of chromium(II)-(III) exchange reactions (24,26), the acid dependence observed for $CrCN^{2+}$ was not expected. That the acid dependence was not due to separation-induced exchange at low acid concentrations was demonstrated by quenching aliquots of exchange solutions into acid through which air was bubbled. No effect was observed. The absence of an acid dependent term in previous studies may be due to conditions of $[H^+]$ and temperature unfavorable to its detection. Under most conditions for other studies, the term would not have been observed for $CrCN^{2+}$. The exchange of $CrCl^{2+}$ was studied with $[H^+]$ as low as 0.05 $\underline{M}$, while the lowest $[H^+]$ studied in the $CrCN^{2+}$ exchange was 0.01 $\underline{M}$. However, no other exchange reactions were studied with $[H^+] < 0.10$ $\underline{M}$ and most studies were at $[H^+] = 0.5\text{-}1.0$ $\underline{M}$. Alternatively the lack of a $[H^+]$ dependence in other exchange reactions could be real and the exchange of $CrCN^{2+}$ by the path inverse in $[H^+]$ may be a special case, i.e., double bridging in the activated complex.

Using data from Table 24, it is possible to compare the rates of Cr^{2+}-CrX^{+3-n} exchange reactions by the acid independent path over the temperature range 0-25°C. The exchange rates follow the order:

$$Br^- > (-SCN^-) > Cl^- > N_3^- > (-NC^-) > OH^- > -CN^- > F^- > -NCS^- > H_2O \qquad (83)$$

The ligands SCN^- and NC^- do not properly belong in this series inasmuch as they are not strictly exchange reactions, since a net chemical change (isomerization) occurs. If k_{-1}, the acid dependent term of the $CrCN^{2+}$ exchange, is identified as $k'_{-1}Q_a$, where Q_a is the equilibrium constant for the acid dissociation (Eq. 84),

$$CrCN^{2+} \rightleftharpoons Cr(OH)CN^+ + H^+ \qquad (84)$$

then the exchange of $Cr(OH)CN^+$ occurs at a rate slightly lower than does CrN_3^{2+} (assuming $Q_a = 1.5 \times 10^{-4}$ $\underline{M}$, the value for $Cr(H_2O)_6^{3+}$).

The above series roughly parallels the spectrochemical series:

$$Br^- < -SCN^- < Cl^- < F^- < N_3^- < OH^- < H_2O < -NCS^- < (-NC^-) < -CN^- \qquad (85)$$

The major deviations from the spectrochemical series are those ligands which contain multiple bonds and should therefore be relatively good ligands for electron transfer. This suggests that both the crystal field stabilization energy and the ability of the ligand to act as an electron conductor are influential in determining the activation energy for electron transfer. This ligand-field correlation differs from that made previously for the Cr^{2+} catalyzed aquation of Cr(III) complexes in that different bridging ligands on each complex are involved here while the same ligand (OH^-) was involved in the catalyzed aquation.

Although an additional path involving adjacent attack may exist, the reaction of Cr^{2+} with CoL_5CN^{2+} must occur at least partially by remote attack since $CrNC^{2+}$ is formed. The exchange reaction of Cr^{2+} with $CrCN^{2+}$ may occur by remote attack or adjacent attack or both. Since the isomerization of $CrNC^{2+}$ proceeds more rapidly than the exchange reaction, any $CrNC^{2+}$ formed would be present only in very low, probably steady-state, concentrations, so no direct evidence (e.g., detection of $CrNC^{2+}$) for remote attack is available. However, it may be constructive to examine the kinetic data more closely to see if a detailed mechanism for exchange can be deduced.

The first possibility to be examined is that only remote attack occurs. The exchange rate law then requires that the reactions given in Eq. 86-88 occur.

$$CrCN^{2+} + {*Cr^{2+}} \xrightarrow{1} {*CrNC^{2+}} + Cr^{2+} \qquad (86)$$

$$CrCN^{2+} \xrightleftharpoons{Q_1} Cr(OH)CN^{+} + H^{+} \text{ (rapid, } Q_1 \ll 1) \qquad (87)$$

$$Cr(OH)CN^{+} + {*Cr^{2+}} \xrightarrow{2} {*Cr(OH)NC^{+}} + Cr^{2+} \qquad (88)$$

These reactions are followed by the isomerization of $CrNC^{2+}$, Eq. 89-91.

$$CrNCH^{3+} \xrightleftharpoons{Q_2} CrNC^{2+} + H^{+} \text{ (rapid, } Q_2 \simeq 1.3) \qquad (89)$$

$$CrNC^{2+} \xrightarrow{3} CrCN^{2+} \qquad (90)$$

$$CrNC^{2+} + Cr^{2+} \xrightarrow{4} CrCN^{2+} + Cr^{2+} \qquad (91)$$

Application of the principle of microscopic reversibility to the reaction given in Eq. 88 indicates that another path for isomerization must exist (Eq. 92 and Eq. 93).

$$CrNC^{2+} \overset{Q_3}{\rightleftharpoons} Cr(OH)NC^{+} + H^{+} \text{ (rapid,} Q_3 \ll 1) \qquad (92)$$

$$Cr(OH)NC^{+} + Cr^{2+} \xrightarrow{5} Cr(OH)CN^{+} + Cr^{2+} \qquad (93)$$

The rate law derived for this mechanism for the isomerization is:

$$\frac{-dC_{CrNC^{2+}}}{dt} = \frac{\left\{k_3Q_2+(k_4Q_2+k_5Q_3Q_2[H^+]^{-1})[Cr^{2+}]\right\}C_{CrNC^{2+}}}{Q_2 + [H^+]} \qquad (94)$$

Microscopic reversibility makes the further demand that $k_5/k_2 = k_4/k_1$. At 25°C, $k_1 = 0.0886$ $\underline{M}^{-1}sec^{-1}$ (Table 23), $k_2Q_1 = 2.55x10^{-3}sec^{-1}$ (Table 23) and $k_4 = 1.48$ $\underline{M}^{-1}sec^{-1}$ (Table 9). Assuming that $Q_3 \simeq Q_1$, $k_5Q_3Q_2 \simeq k_2Q_1k_4Q_2/k_1 = (2.55x10^{-3})(1.48)(1.3)/(.0886) \simeq .055$. Data for the isomerization reaction were fit to the above Eq. 94, as well as to Eq. 95, which lacks the term $k_5Q_3Q_2[H^+]^{-1}$.

$$\frac{-dC_{CrNC^{2+}}}{dt} = \frac{(k_3Q_2 + k_4Q_2[Cr^{2+}])C_{CrNC^{2+}}}{Q_2 + [H^+]} \qquad (95)$$

Values of the derived constants, using various portions of the data, are given in Table 25.

Table 25. Rate constants for two possible mechanisms for the isomerization of $CrNC^{2+}$

Data used[a]	k_3Q_2		k_4Q_2		$k_5Q_3Q_2$	Q_2	
	Eq. 94	Eq. 95	Eq. 94	Eq. 95	Eq. 94	Eq. 94	Eq. 95
A, B, C	.0497±.0063	.0522±.0049	1.66±.19	1.69±.19	-.012±.020	.98±.17	1.06±.13
A,B	.0616±.0097	.0653±.0087	1.85±.24	1.89±.27	-.012±.022	1.19±.24	1.28±.20
A	.0525±.0077	.0636±.0078	1.51±.19	1.57±.23	-.034±.016	.88±.17	1.14±.17
B	.0891±.0479	.0686±.0197	2.94±1.35	2.50±.71	.077±.136	2.16±1.38	1.56±.51
C	.0469±.0199	.0550±.0098	1.97±.57	2.14±.47	-.104±.226	1.08±.78	1.40±.36

[a] A = $Co(NH_3)_5CN^{2+}$, B = $Co(NH_3)_4(H_2O)CN^{2+}$, C = $Co(en)_2(H_2O)CN^{2+}$.

Within experimental error, $k_5Q_3Q_2 \simeq 0$, rather than 0.055 as required by the postulated mechanism (Eq. 89-93). This indicates that the reactions given in Eq. 92 and Eq. 93 do not contribute significantly to the isomerization of $CrNC^{2+}$. Microscopic reversibility then requires that the exchange of Cr^{2+} with $Cr(OH)CN^{+}$ must occur predominantly by adjacent attack, Eq. 96.

$$*Cr^{2+} + Cr(OH)CN^{+} \xrightarrow{2} *Cr(OH)CN^{+} + Cr^{2+} \qquad (96)$$

These arguments do not exclude the possibility that the acid-independent exchange of Cr^{2+} with $CrCN^{2+}$ proceeds by remote attack however. The principle of microscopic reversibility, applied to the Cr^{2+} catalyzed path for isomerization (Eq. 91), requires that at least part of the exchange of Cr^{2+} with $CrCN^{2+}$ must occur by remote attack (Eq. 86). Exchange by adjacent attack (Eq. 97) may also occur, but the above

$$*Cr^{2+} + CrCN^{2+} \xrightarrow{1} *CrCN^{2+} + Cr^{2+} \qquad (97)$$

arguments provide no information regarding the existence of this pathway. Adjacent attack could be the predominant path for exchange, since microscopic reversibility requires only that an exchange path involving remote attack must exist, but not that it be predominant. On the other hand, no evidence is available to indicate that adjacent attack must occur, even as a minor pathway.

Reactions of Cr^{2+} with $Cr(CN)_2^+$ and $Cr(CN)_3$

Aquation of the cyanochromium(III) complexes cis-$Cr(CN)_2^+$ and 1,2,3-$Cr(CN)_3$ is catalyzed by Cr^{2+}:

$$Cr(CN)_2^+ + H^+ = CrCN^{2+} + HCN \tag{98}$$

$$Cr(CN)_3 + 2H^+ = CrCN^{2+} + 2HCN \tag{99}$$

This catalysis is not observed with the other known cyanochromium(III) complexes, $Cr(CN)_4^-$ and $Cr(CN)_6^{3-}$, where a precipitate forms on addition of Cr^{2+}.

These reactions were of interest to the present study because they were possible sources of the intermediate $CrNC^{2+}$, and because they presumably represent a case of a cyanide-bridged electron transfer between Cr^{2+} and Cr(III). Qualitative observations on the kinetics of the catalyzed aquations are as follows. First-order kinetics was followed at some wavelengths, especially at wavelengths in the vicinity of the long-wavelength maximum of the reactant complex. At most wavelengths there was a fairly rapid change in absorbance, followed by a slower change. It was generally possible to draw straight lines through the initial and final portions of a plot of log $(D_t - D_\infty)$ _vs_. t, but the slopes of these lines were quite dependent on wavelength. The initial slopes were similar to those observed at wavelengths where first-order kinetics was followed throughout the reaction. These observations are consistent with the production of an intermediate (or intermediates), but the secondary reaction proceeds too slowly to be the isomerization of $CrNC^{2+}$.

Experiments carried out at wavelengths where first-order kinetics was observed (4600Å for $Cr(CN)_2^+$ and 4400Å for $Cr(CN)_3$), are summarized in Tables 26 and 27.

Table 26. Rate constants for the Cr^{2+} catalyzed aquation of $Cr(CN)_2^+$ at 25°C[a]

$10^3[Cr^{2+}]$	$[H^+]_o$	$k_{obs}(sec^{-1})$[b]	$k_{calc}(sec^{-1})$[c]
8.35 M	.399 M	.0416 ± .0005	.0375
1.99	.401	.01033± .00009	.01086
3.92	.400	.0205 ± .0001	.0189
21.39	.399	.0907 ± .0039	.0921
21.39	.100	.0851 ± .0020	.0921

[a] I = 1.00 M with $LiClO_4$. $[Cr(CN)_2^+] = 9.6 \times 10^{-4}$ M. Spectrophotometric observations at 4600Å.

[b] Calculated from absorbance-time data by a non-linear least squares computer program. All data points were weighted equally.

[c] Calculated from the best least squares fit of the observed rate constants to the equation: $k = k_o + k_1[Cr^{2+}]$. Weighting was carried out as $1/k^2$.

The $Cr(CN)_2^+$ aquation was studied at 25°C over the concentration ranges: 9.6×10^{-4} M $Cr(CN)_2^+$, 2×10^{-3}-2×10^{-2} M Cr^{2+}, 0.10-0.40 M H^+. The corresponding ranges for the $Cr(CN)_3$ aquation at 25°C were: 1.3×10^{-3}-2.2×10^{-3} M $Cr(CN)_3$, 4.7×10^{-4}-5.0×10^{-2} M Cr^{2+}, 0.05-0.40 M H^+. The rate equation is apparently adequately described in both reactions by Eq. 100.

Table 27. Rate constants for the Cr^{2+} catalyzed aquation of $Cr(CN)_3$ at 25°C[a]

$10^3[Cr(CN)_3]_o$	$10^3[Cr^{2+}]$	$[H^+]_o$	k_{obs}[b](sec^{-1})	k_{calc}[c] (sec^{-1})
1.33M	4.25M	.100M	.0234 ±.0005	.0230
"	1.00	.100	.00859±.00029	.00819
"	16.24	.100	.0807 ±.0020	.0777
"	7.59	.0996	.0411 ±.0008	.0382
"	2.07	.0997	.0132 ±.0002	.0131
"	4.25	.395	.0269 ±.0007	.0230
"	11.65	.0966	.0425 ±.0012	.0567
"	30.5	.100	.145 ±.007	.143
"	16.24	.100	.0679 ±.0027	.0777
"	.466	.100	.00530±.00018	.00575
"	20.4	.100	.120 ±.009	.0966
"	4.36	.200	.0255 ±.0005	.0235
"	4.36	.0505	.0270 ±.0009	.0235
2.22	25.5	.0997	.130 ±.003	.120
"	30.5	.100	.116 ±.005	.143
"	50.8	.100	.208 ±.009	.285
"	25.5	.0997	.133 ±.003	.120
"	40.7	.0998	.186 ±.010	.189
"	30.5	.100	.140 ±.006	.143
"	25.5	.0997	.122 ±.005	.120
"	30.5	.100	.138 ±.004	.143
"	25.5	.0997	.133 ±.003	.120
"	30.5	.100	.174 ±.010	.143
"	50.8	.100	.229 ±.014	.235
"	40.7	.0998	.192 ±.007	.189
"	20.4	.100	.117 ±.003	.0966

[a] I = 1.00 M with $LiClO_4$. Spectrophotometric observations at 4400 Å.

[b] Calculated from absorbance-time data by a non-linear least squares computer program. Weighting of these data was carried out as 1/D (D = absorbance).

[c] Calculated from the best least squares fit of the observed rate constants to the equation: $k = k_o + k_1[Cr^{2+}]$. Weighting was carried out as $1/k^2$.

$$-d(\ln[Cr(CN)_n^{+3-n}])/dt = k_o + k_1[Cr^{2+}] \qquad (100)$$

This rate law was established by plots of k_{obsd} vs. $[Cr^{2+}]$ (Fig. 20 and Fig. 21), which are linear with non-zero intercept. The concentration of Cr^{2+} is constant throughout an experiment, so the reactions followed pseudo-first-order kinetics. Values observed for the rate constants are: $Cr(CN)_2^+$, k_o = .0025 ± .0012 sec^{-1}, k_1 = 4.19 ± .27 $\underline{M}^{-1}sec^{-1}$; $Cr(CN)_3$, k_o = .0036 ± .0005 sec^{-1}, k_1 = 4.56 ± .15 $\underline{M}^{-1}sec^{-1}$. The similarity of rate constants for the two reactions is striking. The k_o paths probably arise from absorbance changes due to spontaneous aquation of $Cr(CN)_2^+$ to $CrCN^{2+}$ or $Cr(CN)_3$ to $Cr(CN)_2^+$.

Attempts to fit data at other wavelengths to equations for consecutive first-order reactions were not successful, suggesting that the mechanism may be more complex, perhaps involving double bridged activated complexes, with the production of $Cr(NC)_2^+$ or other intermediates.

Direct evidence for double bridged activated complexes has been found only for reaction of Cr^{2+} with the complexes cis-$Cr(N_3)_2^+$ (85) and cis-$Co(NH_3)_4(N_3)_2^+$ (86). There is also a strong indication of this phenomenon in the Cr^{2+}-cis-Cr$(H_2PO_2)_2^+$ exchange reaction[1].

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[1] K. A. Schroeder and J. H. Espenson, Ames, Iowa. Electron exchange reaction of Cr^{2+} and $Cr(H_2PO_2)_2^+$ in acidic solution. Private communication. 1966.

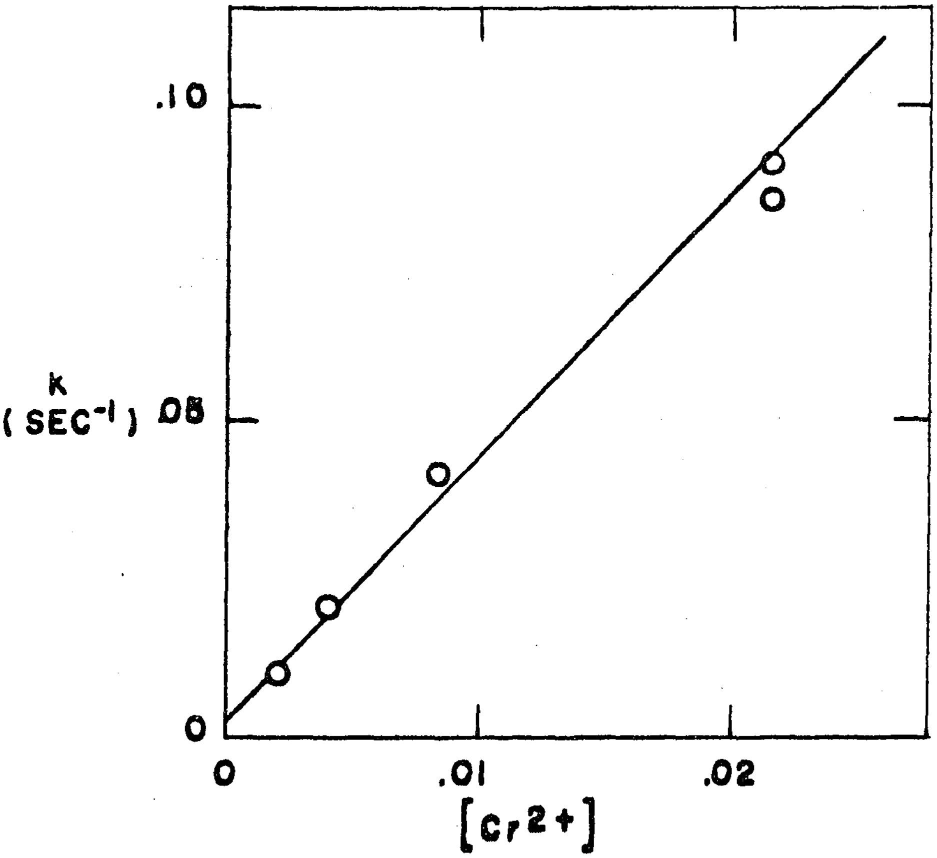

Fig. 20. Plot of k *vs.* [Cr^{2+}] for the reaction of Cr^{2+} with Cr(CN)$_2^+$ at 25.0°C, I = 1.00 *M*, 4600 Å

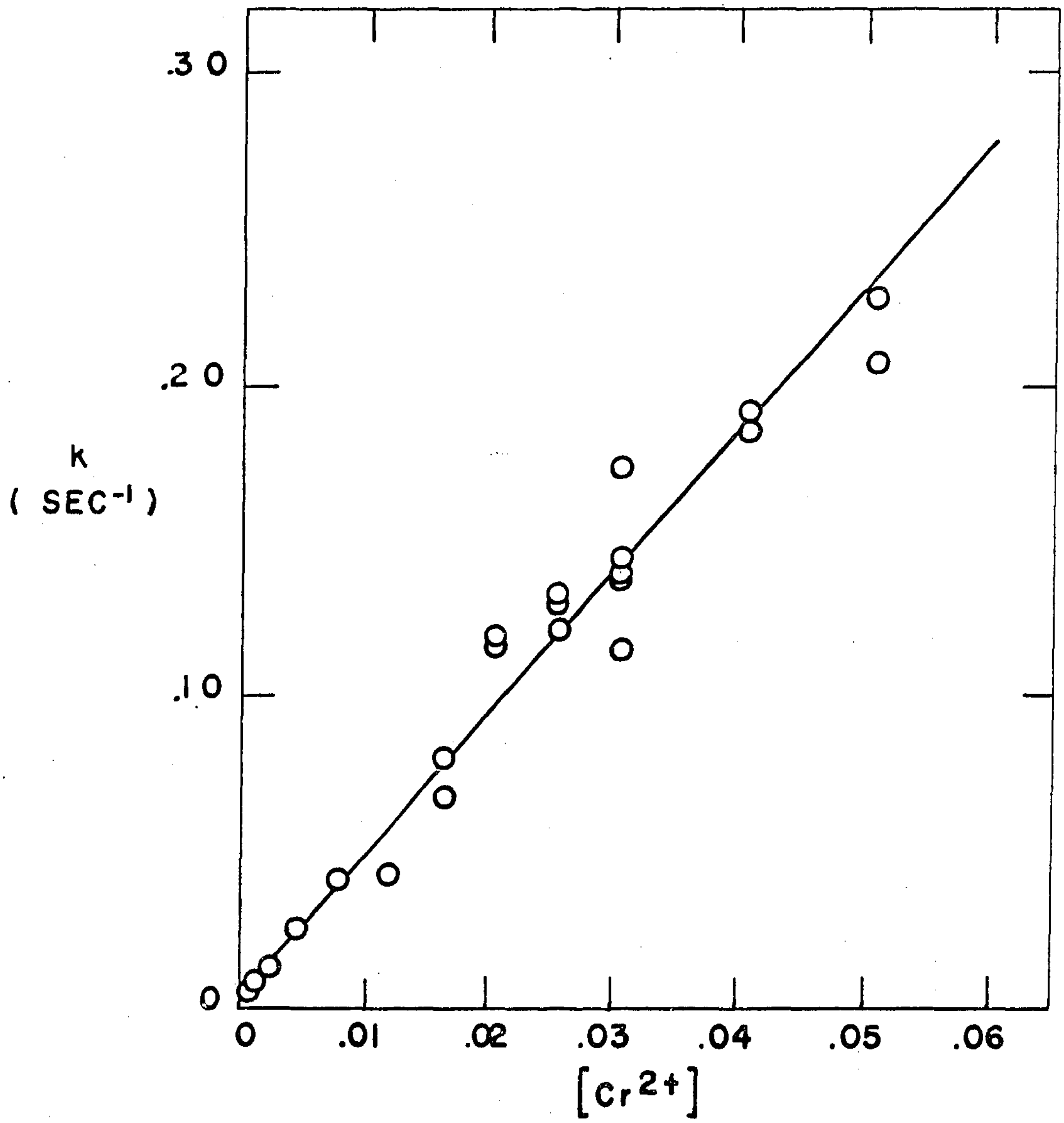

Fig. 21. Plot of k vs. [Cr^{2+}] for the reaction of Cr^{2+} with $Cr(CN)_3$ at 25.0°C, I = 1.00 M, 4400Å

Reaction of Cr^{2+} with cis-$Co(en)_2(CN)_2^+$

The reaction of Cr^{2+} with cis-$Co(en)_2(CN)_2^+$ produces $CrCN^{2+}$ and was also of interest as a possible source of $CrNC^{2+}$. The reaction was investigated under pseudo-first-order conditions in the spectral range 2100-3000Å, over the concentration ranges, $2x10^{-4}$-$2x10^{-2}$ M Cr^{2+} and $5x10^{-6}$-$1x10^{-3}$ M Co(III) (Table 28).

Table 28. Rate constants for reaction of Cr^{2+} with cis-$Co(en)_2(CN)_2^+$ at 15°C[a]

$10^3[Cr^{2+}]_o$	$10^4[Co(III)]_o$	λ(Å)	$k_{ox}(M^{-1}sec^{-1})$[b]
.867	.948	2400	3.98
2.02	.948	2500	2.07
.338	.119	2300	4.67
.203	.0499	2100	5.35
4.84	2.37	2500	6.38
20.1[c]	10.3	3000	.110
20.1[c]	9.76	2800	.064

[a] I = .150 M with $HClO_4$.

[b] Since $[Cr^{2+}] \geq 20[Co(III)]$, pseudo-first-order conditions were observed and k_{ox} was calculated from the slope of a plot of log (D_t-D_∞) *vs.* t; $k_{ox} = .693/t_{\frac{1}{2}}[Cr^{2+}]$.

[c] The absorbance quickly rose to 3.5-4 in these experiments, then dropped slowly at the indicated rate.

Except at 2800-3000Å, the reaction followed pseudo-first-order kinetics, with average second-order rate constant at 15°C, $k_{ox} = 4.5 \pm 1.2$ $M^{-1}sec^{-1}$. At 2800-3000Å, the absorbance quickly rose to very high values, then dropped slowly. This is consistent with formation and disappearance of an intermediate, but the rate of its disappearance is far too low for this intermediate to be $CrNC^{2+}$. The existence of double-bridged activated complexes is also possible here.

No $Cr(CN)_2^+$ could be separated from quenched reaction solutions by ion exchange but since the rate of the Cr^{2+} catalyzed aquation of $Cr(CN)_2^+$ is about the same as the rate of the Cr^{2+} reduction of $Co(en)_2(CN)_2^+$, it is possible that the suspected intermediate never builds up to detectable concentrations.

This system appears deceptively simple, but its study in detail would be complicated by a multitude of possible Cr(III) species (dicyano and monocyano, both N- and C-bonded and mixed) and by the subsequent reactions of each (isomerization and catalyzed aquation).

Reactions of Hg^{2+} with Cyanochromium(III) Complexes

Mercury(II) forms an extremely stable complex with $CrCN^{2+}$. Addition of Hg^{2+} to solutions of $CrCN^{2+}$ causes spectral shifts to longer wavelengths. With $[CrCN^{2+}] = 0.02$ *M* in these experiments, spectral shifts were observed until $[Hg^{2+}]/[CrCN^{2+}] = 1.0$. The complex is very likely $CrCNHg^{4+}$ (or $CrNCHg^{4+}$) with spectrum, $\lambda_{max} = 5650\text{Å}$ ($\epsilon_{max} = 17.9$ $\underline{M}^{-1}cm^{-1}$) and 4010Å (22.6). This can be compared with the spectra of $CrCN^{2+}$ (5250Å (25.2) and 3930Å (20.0)) and Cr^{3+} (5740Å (13.3) and 4080Å (15.8)). The formation of a stable $MCNHg^{4+}$ complex has been reported for $M = Co(NH_3)_5$ by Siebert (34).

A lower limit was set on the value of the association constant for the reaction:

$$Hg^{2+} + CrCN^{2+} = CrCNHg^{4+} \tag{101}$$

$$Q_a = [CrCNHg^{4+}][Hg^{2+}]^{-1}[CrCN^{2+}]^{-1} \tag{102}$$

A solution 0.017 $\underline{M}$ in each reactant was diluted appropriately so that spectra taken in cells of various path lengths should have been identical if no dissociation had taken place. For solutions as dilute as 0.0033 $\underline{M}$ Cr(III) at 25°C, differences in spectra were within experimental error. Assuming conservatively that the equilibrium (Eq. 101) lies $\geq 95\%$ toward the right even at the lowest concentration studied (0.0033 $\underline{M}$), a lower limit on the association constant is $Q_a \geq 10^5 \underline{M}^{-1}$.

Ion exchange behavior of solutions of Hg^{2+} and $CrCN^{2+}$ confirms the 4+ charge assumed for the complex. The complex was not moved by acid at concentrations which will slowly spread a band of Cr^{3+}.

Solutions of $CrCN^{2+}$ and Hg^{2+} are not stable indefinitely however, and chromium(III) aquation occurs.

Kinetic behavior for the Hg^{2+}-$CrCN^{2+}$ system at 55°C can be described by three types of absorbance change.

(1) A very fast change to give a spectrum like that found for $CrCNHg^{4+}$. Since this process presumably represents

substitution on Hg^{2+}, it is expected to be very rapid.

(2) A slower change to give a spectrum much like that of Cr^{3+}. Ion exchange behavior of rapidly cooled solutions indicated substantial conversion to Cr^{3+}.

(3) A very slow change (at 5250Å) of unexplained origin. The magnitude of the change was much less than that of (1) and (2).

Data for change (2) were taken at 55°C and 5250Å and are presented in Table 29.

Table 29. Rate constants for the reaction of Hg^{2+} with $CrCN^{2+}$[a]

$[Hg^{2+}]$	$[H^+]$	$10^3k_{aq}(sec^{-1})$[b] obsd	uncatalyzed
.0967	.043	6.3	1.33
.0504	.042	8.7	1.32
.0252	.041	7.7	1.31
.0126	.040	6.9	1.31
.0504	.482	5.7	4.82
"	.242	4.8	2.91
"	.122	7.4	1.94
"	.482	5.9	4.82

[a] I = 1.00 M with $LiClO_4$; 55.0°C; 0.0010 M $CrCN^{2+}$; spectrophotometric data were taken at 5250Å.

[b] Observed values of k_{aq} were determined from absorbance-time data by the Guggenheim method. Calculated values were obtained from the best fit of the data for the uncatalyzed aquation of $CrCN^{2+}$ (Table 17) to the equation $k_{aq} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+]$.

Data obey first-order kinetics, with the rate constants in these experiments evaluated by the Guggenheim method (87). Although there is considerable scatter, the rate constant is apparently independent of $[Hg^{2+}]$ over the range 0.012-0.097 M and $[H^+]$ over the range 0.04-0.48 M, with an average value of $k_{cat} = 0.0066 \pm 0.0009\ sec^{-1}$. Some small trends observed are easily within the medium effects expected to result from concentration variations in which a +1 ion (H^+) replaces a +2 ion (Hg^{2+}) (39). Since the first rapid change in absorbance is probably the formation of $CrCNHg^{4+}$, a mechanism consistent with the $[Hg^{2+}]$ dependence is:

$$CrCN^{2+} + Hg^{2+} \overset{Q_a}{\rightleftharpoons} CrCNHg^{4+} \text{ (rapid, } Q_a \geq 10^5 \text{ at } 25^\circ C) \tag{103}$$

$$CrCNHg^{4+} \xrightarrow{k_{cat}} Cr^{3+} + HgCN^+ \tag{104}$$

The rate law derived for this mechanism is:

$$d[Cr^{3+}]/dt = k_{cat}[CrCNHg^{4+}] \tag{105}$$

$$= \frac{k_{cat}Q_a[Hg^{2+}]C_{CrCN^{2+}}}{1 + Q_a[Hg^{2+}]} \tag{106}$$

$$C_{CrCN^{2+}} = [CrCN^{2+}] + [CrCNHg^{4+}] \tag{107}$$

In these experiments, $[Hg^{2+}] \geq 10^{-2}$ and $Q_a \geq 10^5$ (at 25°) so that $Q_a[Hg^{2+}] \geq 10^3 \gg 1$. The rate law then becomes:

$$d[Cr^{3+}]/dt = k_{cat}C_{CrCN^{2+}} \tag{108}$$

Although the equilibrium constant Q_a probably is not as large at 55° as at 25°C, the estimate of $Q_a \geq 10^5$ at 25° was conservative and Q_a is almost surely large enough at 55° so that $Q_a[Hg^{2+}] \gg 1$ should still be a good assumption.

It is interesting to note that even though the transition state associated with the postulated mechanism is $\{CrCNHg^{4+}\}^{\ddagger}$, the concentration of Hg^{2+} does not appear in the rate law. This situation arises because the rate law is written in terms of stoichiometric concentrations of reagents, rather than concentrations of predominant species. In the reaction of Hg^{2+} with $CrCN^{2+}$, presumably $C_{CrCN^{2+}} \simeq [CrCNHg^{4+}]$, so the rate law (Eq. 105) written in terms of the predominant species $CrCNHg^{4+}$ does predict the correct composition of the transition state.

According to this interpretation, Hg^{2+} acts as a "catalyst" for the aquation of $CrCN^{2+}$. It should be noted though that since the "catalysis" is independent of $[H^+]$, Hg^{2+} acts as an inhibitor for $[H^+] \gtrsim 0.71$ M. This system can be contrasted to the Hg^{2+} "catalysis" of the aquation of $CrCl^{2+}$ (39), where the rate was not independent of $[Hg^{2+}]$:

$$-d[CrCl^{2+}]/dt = (k_o+k_{-1}[H^+]^{-1})[Hg^{2+}][CrCl^{2+}] \qquad (109)$$

There was no evidence for the formation of a stable complex $CrClHg^{4+}$, and the rate law dictates that if such were the case, $1 \gg Q[Hg^{2+}]$, or $Q \ll 10\ \underline{M}^{-1}$ at the concentrations of Hg^{2+} studied in the $CrCl^{2+}$ aquation.

Qualitative observations were made on the reaction of Hg^{2+} with $Cr(CN)_2^+$ and with $Cr(CN)_3$. When Hg^{2+} was added to solutions of either of the cyanochromium(III) complexes at room temperature, the spectrum changed at measurable rates to that of $CrCNHg^{4+}$, and then slowly changed in a manner consistent with conversion to Cr^{3+}.

A precipitate was formed on addition of Hg^{2+} to solutions of $Cr(CN)_4^-$ and $Cr(CN)_6^{3-}$.

SUMMARY

The reactions of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, trans-$Co(NH_3)_4(H_2O)CN^{2+}$ and trans-$Co(en)_2(H_2O)CN^{2+}$ were studied in acidic solution. The immediate product of the reaction (Eq. 110) is

$$Cr^{2+} + CoL_5CN^{2+} + 5H^+ = CrNC^{2+} + Co^{2+} + 5LH^+ \qquad (110)$$

a metastable intermediate, postulated to be the isocyano complex $CrNC^{2+}$, which decays to form $CrCN^{2+}$. The oxidation-reduction reaction of Cr^{2+} with CoL_5CN^{2+} followed a second order rate law, Eq. 111, with k_{ox} much larger for $Co(NH_3)_4$

$$-d[Co(III)]/dt = k_{ox}[Cr^{2+}][CoL_5CN^{2+}] \qquad (111)$$

$(H_2O)CN^{2+}$ and $Co(en)_2(H_2O)CN^{2+}$ than for $Co(NH_3)_5CN^{2+}$.

The decay of the intermediate produced in each of the above reactions followed the rate law given in Eq. 112.

$$d[CrCN^{2+}]/dt = \frac{(k_0Q+k_1Q[Cr^{2+}])}{Q+[H^+]}[\text{intermediate}] \qquad (112)$$

The values of the parameters were independent of the source of intermediate, indicating that the intermediate is the same in each reaction. On the basis of this agreement of rates, of spectra of the intermediate, and of quantitative transfer of Cr^{51} tag in the Cr^{2+} catalyzed path for decay of the intermediate, the intermediate was identified as $CrNC^{2+}$ in rapid equilibrium with $CrNCH^{3+}$. The mechanism proposed for the isomerization of $CrNC^{2+}$ is given in Eq. 113-115.

$$\mathrm{CrNCH^{3+}} \overset{Q}{\rightleftharpoons} \mathrm{CrNC^{2+}} + \mathrm{H^+} \quad \text{(rapid)} \tag{113}$$

$$\mathrm{CrNC^{2+}} \xrightarrow{k_o} \mathrm{CrCN^{2+}} \tag{114}$$

$$\mathrm{{*}Cr^{2+}} + \mathrm{CrNC^{2+}} \xrightarrow{k_1} \mathrm{{*}CrCN^{2+}} + \mathrm{Cr^{2+}} \tag{115}$$

The electron exchange reaction of Cr^{2+} with $CrCN^{2+}$ (Eq. 116) was investigated. Contrary to studies of most other

$$\mathrm{{*}Cr^{2+}} + \mathrm{CrCN^{2+}} = \mathrm{Cr^{2+}} + \mathrm{{*}CrCN^{2+}} \tag{116}$$

Cr^{2+}-Cr(III) exchange reactions, the rate of exchange was dependent on $[H^+]$ (Eq. 117).

$$\text{Exchange rate} = (k_o + k_{-1}Q[\mathrm{H^+}]^{-1})[\mathrm{Cr^{2+}}][\mathrm{CrCN^{2+}}] \tag{117}$$

It was postulated that exchange by the acid dependent path proceeds predominantly by adjacent attack (Eq. 118 and Eq. 119),

$$\mathrm{CrCN^{2+}} \overset{Q}{\rightleftharpoons} \mathrm{Cr(OH)CN^+} + \mathrm{H^+} \quad (\text{rapid, } Q<<1) \tag{118}$$

$$\mathrm{{*}Cr^{2+}} + \mathrm{Cr(OH)CN^+} \xrightarrow{k_{-1}} \mathrm{{*}Cr(OH)CN^+} + \mathrm{Cr^{2+}} \tag{119}$$

while exchange by the acid independent path proceeds at least partially by remote attack (Eq. 120), followed by isomerization of the $CrNC^{2+}$ formed (Eq. 121), but may also proceed by adjacent attack (Eq. 122).

$$\mathrm{{*}Cr^{2+}} + \mathrm{CrCN^{2+}} \xrightarrow{k_{or}} \mathrm{Cr^{2+}} + \mathrm{CrNC^{2+}} \tag{120}$$

$$\mathrm{CrNC^{2+}} = \mathrm{CrCN^{2+}} \tag{121}$$

$$\mathrm{{*}Cr^{2+}} + \mathrm{CrCN^{2+}} \xrightarrow{k_{oa}} \mathrm{Cr^{2+}} + \mathrm{{*}CrCN^{2+}} \tag{122}$$

The aquation of $CrCN^{2+}$ (Eq. 123) followed pseudo-first-

$$CrCN^{2+} + H^+ = Cr^{3+} + HCN \qquad (123)$$

order kinetics, with the rate constant having the $[H^+]$ dependence given in Eq. 124.

$$k_{aq} = k_{-1}[H^+]^{-1} + k_o + k_1[H^+] \qquad (124)$$

On the basis of entropy correlations, the mechanism for aquation was postulated to be:

$$CrCN^{2+} \xrightleftharpoons{Q} Cr(OH)CN^+ + H^+ \text{ (rapid,} Q<<1) \qquad (125)$$

$$Cr(OH)CN^+ \xrightarrow{k'_{-1}} CrOH^{2+} + CN^- \text{ (or } Cr(OH)_2^+ + HCN) \qquad (126)$$

$$CrCN^{2+} \xrightarrow{k_o} CrOH^{2+} + HCN \qquad (127)$$

$$CrCN^{2+} + H^+ \xrightarrow{k_1} Cr^{3+} + HCN \qquad (128)$$

In this mechanism k'_{-1} is identified as k_{-1}/Q.

In solutions of low $[H^+]$, the aquation of $CrCN^{2+}$ was catalyzed by Cr^{2+}. The rate law, Eq. 129, indicates that the

$$-d(\ln[CrCN^{2+}])/dt=k'_{-1}Q[H^+]^{-1}+k_o+k_1[H^+]+k_2Q[Cr^{2+}][H^+]^{-1} \qquad (129)$$

catalysis probably occurs by a hydroxide-bridged electron transfer mechanism, Eq. 130 and Eq. 131.

$$CrCN^{2+} \xrightleftharpoons{Q} Cr(OH)CN^+ + H^+ \text{ (rapid,} Q<<1) \qquad (130)$$

$$*Cr^{2+} + Cr(OH)CN^{2+} \xrightarrow{k_2} Cr^{2+}+CrOH^{2+}+CN^- \qquad (131)$$

Mercury(II) forms an extremely stable complex with $CrCN^{2+}$, presumably $CrCNHg^{4+}$. The aquation of this complex follows the rate law given in Eq. 132.

$$-dC_{CrCN^{2+}}/dt = k_{cat}C_{CrCN^{2+}} \qquad (132)$$

Since $C_{CrCN^{2+}} \simeq [CrCNHg^{4+}]$, the mechanism was postulated to be:

$$CrCN^{2+} + Hg^{2+} \rightleftharpoons CrCNHg^{4+} \text{ (rapid, } Q \geq 10^5) \qquad (133)$$

$$CrCNHg^{4+} \xrightarrow{k_{cat}} Cr^{3+} + HgCN^{+} \qquad (134)$$

Chromium(II) catalyzed the aquation of cis-$Cr(CN)_2^+$ (Eq. 135) and 1,2,3-$Cr(CN)_3$ (Eq. 136).

$$Cr(CN)_2^{+} + H^{+} = CrCN^{2+} + HCN \qquad (135)$$

$$Cr(CN)_3 + 2H^{+} = CrCN^{2+} + 2HCN \qquad (136)$$

An intermediate was formed in each of these reactions, but the decay of this intermediate was too slow to be the isomerization of $CrNC^{2+}$. The formation of intermediate in each reaction followed the rate law:

$$-d[Cr(CN)_n^{+3-n}]/dt = (k_0+k_1[Cr^{2+}])[Cr(CN)_n^{+3-n}] \qquad (137)$$

The decay of the intermediate was not investigated in detail. The reaction of Cr^{2+} with cis-$Co(en)_2(CN)_2^+$ (Eq. 138) also

$$Cr^{2+} + Co(en)_2(CN)_2^{+} + H^{+} = CrCN^{2+} + Co^{2+} + HCN + 2en \qquad (138)$$

produced an intermediate which decayed to form $CrCN^{2+}$. The decay of this intermediate, not investigated in detail, was too slow to be the isomerization of $CrNC^{2+}$.

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APPENDIX

Derivations will be presented for the equations used for calculation of specific activities in the tracer experiments on the Cr^{2+} catalyzed isomerization of $CrNC^{2+}$. For simplification in writing expressions, species and their concentrations will be indicated by:

$$A = CrNC^{2+}$$
$$B = Cr^{2+}$$
$$\text{and} \quad C = CrCN^{2+}.$$

Unless otherwise noted, a subscript will indicate time and a superscript * will indicate a tagged Cr atom.

Model I: The k_o path, but not the k_1 path leads to transfer of activity.

$$A \xrightarrow{k_o} C^* \qquad (139)$$

$$A + B^* \xrightarrow{k_1} C + B^* \qquad (140)$$

$$A + B \xrightarrow{k_1} C + B \qquad (141)$$

The pertinent differential equations are:

$$-dA/dt = (k_o+k_1B_T)A \qquad (142)$$

$$B_T = B^* + B \qquad (143)$$

$$dC^*/dt = -dB^*/dt = k_oA(B^*/B_T) \qquad (144)$$

Solution of Eq. 142 gives A as a function of time:

$$A = A_o \exp[-(k_o+k_1B_T)t] \qquad (145)$$

Substitution into Eq. 144 gives:

$$-dB^*/dt = k_oA_o \exp[-(k_o+k_1B_T)t](B^*/B_T) \qquad (146)$$

Integration of Eq. 146 gives the concentration of B* as a function of time:

$$\ln(B^*/B_0^*)=[k_oA_o/B_T(k_o+k_1B_T)][\exp(-[k_o+k_1B_T]t)-1] \qquad (147)$$

At the end of the tracer experiment ($t = \infty$), the concentration of B* is given by Eq. 148.

$$B_\infty^* = B_o^* \exp[-k_oA_o/B_T(k_o+k_1B_T)] \qquad (148)$$

Using the symbols a_o = initial specific activity of B, a_B = final specific activity of B, and a_C = final specific activity of C, the specific activity of B at $t = \infty$ is related to B* by Eq. 149. Note that $B_o^* = B_T$ in these experiments.

$$a_B = B_\infty^* a_o/B_T = a_o\exp[-k_oA_o/B_T(k_o+k_1B_T)] \qquad (149)$$

Conservation of activity leads to Eq. 150, from which a_C can be calculated.

$$a_oB_T = a_BB_T + a_CA_o \qquad (150)$$

Model II: The k_1 path, but not the k_o path leads to transfer of activity.

$$A \xrightarrow{k_o} C \qquad (151)$$

$$A + B^* \xrightarrow{k_1} C^* + B \qquad (152)$$

$$A + B \xrightarrow{k_1} C + B \qquad (153)$$

An analogous derivation can be applied here:

$$-dA/dt = (k_o+k_1B_T)A \qquad (154)$$

$$dC^*/dt = -dB^*/dt = k_1AB^* \qquad (155)$$

$$A = A_o \exp[-(k_o+k_1B_T)t] \qquad (156)$$

$$-dB^*/dt = k_1A_oB^* \exp[-(k_o+k_1B_T)t] \tag{157}$$

$$\ln(B^*/B_o^*) = [k_1A_o/(k_o+k_1B_T)][\exp(-[k_o+k_1B_T]t)-1] \tag{158}$$

$$B_\infty^* = B_o \exp[-k_1A_o/(k_o+k_1B_T)] \tag{159}$$

$$a_B = B_\infty^* a_o/B_T = a_o \exp[-k_1A_o/(k_o+k_1B_T)] \tag{160}$$

$$a_C = (a_o-a_B)B_T/A_o \tag{161}$$

Model III: Activity is transferred by both the k_o and the k_1 paths.

$$A \xrightarrow{k_o} C^* \tag{162}$$

$$A \xrightarrow{k_o} C \tag{163}$$

$$A + B^* \xrightarrow{k_1} C^* + B \tag{164}$$

$$A + B \xrightarrow{k_1} C + B \tag{165}$$

The derivation is analogous to those given above.

$$-dA/dt = (k_o+k_1B_T)A \tag{166}$$

$$dC^*/dt = -dB^*/dt = k_oA(B^*/B_T) + k_1AB^* \tag{167}$$

$$A = A_o \exp[-(k_o+k_1B_T)t] \tag{168}$$

$$-dB^*/dt = (k_1+k_o/B_T)A_oB^* \exp[-(k_o+k_1B_T)t] \tag{169}$$

$$\ln(B^*/B_o^*) = [(k_1+k_o/B_T)A_o/(k_o+k_1B_T)] [\exp(-[k_o+k_1B_T]t)-1] \tag{170}$$

$$B_\infty^* = B_o^* \exp[-A_o(k_1+k_o/B_T)/(k_o+k_1B_T)] \tag{171}$$

$$B_\infty^* = B_o^* \exp(-A_o/B_T) \tag{172}$$

$$a_B = B_\infty^* a_o/B_T = a_o\exp(-A_o/B_T) \tag{173}$$

$$a_C = (a_o-a_B)B_T/A_o \tag{174}$$

Model IV: No exchange occurs. The results are obvious.

$$a_B = a_o \tag{175}$$

$$a_C = 0 \tag{176}$$